INFLUENCE OF INTERMOLECULAR FORCES ON THE MAGNETIC BIREFRINGENCE OF IMPERFECT GASES AND THEIR MIXTURES

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The molecular Cotton-Mouton constant C_m for imperfect gases and their mixtures is represented in the form of a series: $C_m = A_C + B_C \varrho + \ldots$ The first virial coefficient A_C of this series describes the magnetic birefringence of perfect gases. The second virial coefficient B_C takes account of the influence of intermolecular two-molecule interactions upon the C_m constant. It is calculated for some molecular models. In these calculations, besides the usual central forces, also anisotropic dispersion forces and various tensorial intermolecular forces arising from interaction between dipole or quadrupole gas molecules have been taken into consideration. Also, additional contributions to B_C resulting from the existence of molecular electric or magnetic fields in real gases are computed. Numerical estimations are given, which reveal the rôle of the individual molecular factors in the magnetic birefringence of real gases. Finally, general formulas for the electrostatic interaction energy of two arbitrary charge distributions, and for inductive interaction of such systems are derived.

1. Introduction

One can calculate the molecular Cotton-Mouton constant C_m from experimental data on the basis of the following formula:

$$C_m = \frac{6n^2}{(n^2 + 2)^2} \, V \, C, \tag{1.1}$$

where V denotes the molar volume of the diamagnetic medium with the refractive index n, and C is the experimental Cotton-Mouton constant. On the other hand, the classical theory of magnetic birefringence based on statistical mechanics gives the following formula for the constant C_m of a diamagnetic medium (Kielich 1962):

$$C_m = \frac{\pi}{45} \, \varepsilon_{\sigma\tau:\nu\varrho} \left\langle \sum_{p=1}^{N} \frac{\cdot \partial^3 m_\sigma^{e(p)}}{\partial E_\tau \, \partial H_\nu \, \partial H_\varrho} + \frac{1}{kT} \sum_{p=1}^{N} \sum_{q=1}^{N} \frac{\partial m_\sigma^{e(p)}}{\partial E_\tau} \frac{\partial m_\nu^{m(q)}}{\partial H_\varrho} \right\rangle, \tag{1.2}$$

wherein we have used the notation:

$$\varepsilon_{\sigma\tau:\nu\varrho} = -2\delta_{\sigma\tau} \delta_{\nu\varrho} + 3\delta_{\sigma\nu} \delta_{\tau\varrho} + 3\delta_{\sigma\varrho} \delta_{\tau\nu}.$$

Here, $m_\sigma^{e(p)}$ is the σ-component of the electric dipole moment of the p-th molecule of the medium acted on by the electric field $\boldsymbol{E}$ of the incident light wave and the magnetic field $\boldsymbol{H}$ causing birefringence of the medium. $m_\nu^{m(q)}$ is the ν-component of the magnetic dipole moment of the q-th molecule of the medium in the presence of the fields $\boldsymbol{E}$ and $\boldsymbol{H}$. The symbol $\langle\dots\rangle$ denotes the mean statistical value when external fields are absent ($\boldsymbol{E} = \boldsymbol{H} = 0$), whereas $\delta_{\sigma\tau}$ is the unit tensor.

In a preceding paper (Kielich 1962) the equation (1.2) was discussed for liquids and their solutions. Also, a short review of diverse present theories of magnetic birefringence for gases and liquids is given there.

In the present paper we shall apply Eq. (1.2) to real gases. It will be shown that the constant C_m can be represented in the form of a power series in the density ϱ:

$$C_m = A_C + B_C \varrho + C_C \varrho^2 + \dots, \tag{1.3}$$

where the successive coefficients of our expansion: A_C, B_C, C_C, and so on are termed the first, second, third $etc.$ Cotton-Mouton constant virial coefficients.

According to classical statistical mechanics, the first virial coefficient A_C describes a system of noninteracting molecules, $i.\ e.$, the Cotton-Mouton effect in a perfect gas. The second virial coefficient B_C characterizes the two-body interactions of the molecules of the system, the third virial coefficient C_C — three-body interactions, $etc.$ In the case when the gas is subjected to not too high pressure, the second virial coefficient B_C defines the main deviation of the molecular constant C_m from its value for a perfect gas ($i.\ e.$ from A_C). This deviation is due to mutual interaction between pairs of molecules and, consequently, the value of this departure gives us information about the type of intermolecular forces and their rôle in the phenomenon of magnetic birefringence. Further corrections to the constant C_m, defined by means of higher virial coefficients, will not be discussed in this paper. We shall take up only the calculation of the second virial coefficient for several molecular models of non-dipolar, quadrupolar and dipolar gases.

Similarly, we shall calculate the influence of various types of intermolecular interactions on the constant C_m in the case of polar gas mixtures.

2. Non-dipolar gases

Spherical molecules. In the case of isolated spherical molecules, we have the following expressions when external fields are absent ($E = H = 0$):

$$\left(\frac{\partial m_\sigma^{e(p)}}{\partial E_\tau}\right)_0 = \alpha\delta_{\sigma\tau}\ , \qquad \left(\frac{\partial m_\nu^{m(q)}}{\partial H_\varrho}\right)_0 = \chi\delta_{\nu\varrho}\ ,$$

$$\left(\frac{\partial^3 m_\sigma^{e(p)}}{\partial E_\tau\,\partial H_\nu\,\partial H_\varrho}\right)_0 = \eta_\perp\,\delta_{\sigma\tau}\,\delta_{\nu\varrho} + \frac{1}{2}\,(\eta_{||} - \eta_\perp)\,(\delta_{\sigma\nu}\,\delta_{\tau\varrho} + \delta_{\sigma\varrho}\,\delta_{\tau\nu}). \tag{2.1}$$

Here, α and χ denote the optical and magnetic mean polarizabilities, respectively; the coefficients $\eta_{||}$ and $\eta_\perp$ determine the changes in the optical polarizability of the molecule due to the magnetic field, in the direction parallel and perpendicular to this field, respectively.

By substitution of the expression (2.1) into the general Eq. (1.2) we obtain

$$C_m = \frac{2\pi}{3} N (\eta_{||} - \eta_\perp). \tag{2.2}$$

This result means that in the approximation considered the constant C_m depends neither on the temperature nor on the density of the gas (see Buckingham and Pople·1956).

If we take into consideration the fact that in a sufficiently condensed gas there exist molecular fields (electric field $\boldsymbol{F}$ and magnetic field $\boldsymbol{G}$), the expressions (2.1) should be replaced by the following ones:

$$\left(\frac{\partial m_\sigma^{e(p)}}{\partial E_\tau}\right)_0 = \alpha \left(\delta_{\sigma\tau} + \frac{\partial F_\sigma^{(p)}}{\partial E_\tau}\right)_0,$$

$$\left(\frac{\partial m_\nu^{m(q)}}{\partial H_\varrho}\right)_0 = \chi \left(\delta_{\nu\varrho} + \frac{\partial G_\nu^{(q)}}{\partial H_\varrho}\right)_0,$$

$$\left(\frac{\partial^3 m_\sigma^{e(p)}}{\partial E_\tau \partial H_\nu \partial H_\varrho}\right)_0 = \left\{\eta_\perp \delta_{\sigma\chi}\delta_{\lambda\mu} + \frac{1}{2}(\eta_{||} - \eta_\perp)(\delta_{\sigma\lambda}\delta_{\chi\mu} + \delta_{\sigma\mu}\delta_{\chi\lambda})\right\} \times$$

$$\times \left(\delta_{\chi\tau} + \frac{\partial F_\chi^{(p)}}{\partial E_\tau}\right)\left(\delta_{\lambda\nu} + \frac{\partial G_\lambda^{(p)}}{\partial H_\nu}\right)\left(\delta_{\mu\varrho} + \frac{\partial G_\mu^{(p)}}{\partial H_\varrho}\right)_0, \tag{2.3}$$

where we have approximately (Kielich, 1962):

$$\frac{\partial F_\sigma^{(p)}}{\partial E_\chi} = -\alpha \sum_{\substack{r=1 \\ r \neq p}}^{N} T_{\sigma\chi}^{(pr)} + \alpha^2 \sum_{\substack{r=1 \\ r \neq p}}^{N}\sum_{\substack{s=1 \\ s \neq r}}^{N} T_{\sigma\tau}^{(pr)} T_{\tau\chi}^{(rs)} - \ldots,$$

$$\frac{\partial G_\sigma^{(q)}}{\partial H_\chi} = -\chi \sum_{\substack{r=1 \\ r \neq q}}^{N} T_{\sigma\chi}^{(qr)} + \chi^2 \sum_{\substack{r=1 \\ r \neq q}}^{N}\sum_{\substack{s=1 \\ s \neq r}}^{N} T_{\sigma\tau}^{(qr)} T_{\tau\chi}^{(rs)} - \ldots. \tag{2.4}$$

The tensor $T_{\sigma\tau}^{(pq)}$ characterizing the dipole-dipole interactions has the following form:

$$T_{\sigma\tau}^{(pq)} = -r_{pq}^{-5}(3 r_{pq\sigma} r_{pq\tau} - r_{pq}^2 \delta_{\sigma\tau}) \tag{2.5}$$

where the vector $\boldsymbol{r}_{pq}$ connects the centres of the p-th and q-th molecules.

On substituting the expressions (2.3) and (2.4) into the general equation (1.2), we obtain in the same approximation:

$$C_m = \frac{2\pi}{15} \left\{ 5(\eta_{||} - \eta_\perp) \left\langle \sum_{p=1}^{N}\left(1 + \frac{\alpha^2}{3}\sum_{\substack{r=1 \\ r \neq p}}^{N}\sum_{\substack{s=1 \\ s \neq r}}^{\mathring{N}} T_{\sigma\tau}^{(pr)} T_{\sigma\tau}^{(sr)} + \ldots\right)\right\rangle + \right.$$

$$\left. + \frac{\alpha^2\chi^2}{kT}\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\sum_{\substack{r=1 \\ r \neq p}}^{N}\sum_{\substack{s=1 \\ s \neq q}}^{N} T_{\sigma\tau}^{(pr)} T_{\sigma\tau}^{(qs)} + \ldots\right\rangle\right\}. \tag{2.6}$$

In the following discussion of this equation we shall make use of a method similar to that applied by De Boer, Van der Maesen and Ten Seldam (1953) in the theory of molecular polarization of non-polar gases.

If $\Phi(\boldsymbol{r}_1...\boldsymbol{r}_N, \omega_1...\omega_N)$ denotes an arbitrary function of the variables $\boldsymbol{r}_1...,\boldsymbol{r}_N$ determining the position of the molecules, and of the variables $\omega_1, ... \omega_N$ determining their orientation, we have from classical statistical mechanics:

$$\left\langle \sum_{p=1}^{N} \Phi(\boldsymbol{r}_p, \omega_p) \right\rangle = \varrho \int\int \Phi(\boldsymbol{r}_1, \omega_1) g^{(1)}(\boldsymbol{r}_1, \omega_1) d\boldsymbol{r}_1 d\omega_1, \quad \left\langle \sum_{p=1}^{N} \sum_{\substack{q=1 \\ q \neq p}}^{N} \zeta(\boldsymbol{r}_p, \boldsymbol{r}_q, \omega_p, \omega_q) \right\rangle =$$

$$= \varrho^2 \int\int\int\int \Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \omega_1, \omega_2) g^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \omega_1, \omega_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\omega_1 d\omega_2, ... \quad (2.7)$$

Here, $g^{(1)}$ and $g^{(2)}$ are molecular distribution functions and $\varrho = N/V$ is the number density of molecules.

By making use of definition (2.7) we can represent Eq. (2.6) in the following form:

$$C_m = \frac{2\pi\varrho}{15} \left\{ 5(\eta_{||} - \eta_{\perp}) \left[\int\int g^{(1)}(\boldsymbol{r}_1, \omega_1) d\boldsymbol{r}_1 d\omega_1 + \right. \right.$$

$$+ \frac{\alpha^2}{3} \varrho \int\int\int\int T_{\sigma\tau}^{(12)} T_{\sigma\tau}^{(12)} g^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \omega_1, \omega_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\omega_1 d\omega_2 + ... \bigg] +$$

$$+ 2 \frac{\alpha^2 \chi^2}{kT} \varrho \int\int\int\int T_{\sigma\tau}^{(12)} T_{\sigma\tau}^{(12)} g^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \omega_1, \omega_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\omega_1 d\omega_2 + ... \bigg\}. \quad (2.8)$$

In the case of moderately compressed gases the molecular functions $g^{(1)}$ and $g^{(2)}$ are given by the following expressions:

$$g^{(1)}(\boldsymbol{r}_1, \omega_1) = \frac{1}{\Omega}; \qquad \Omega = \int d\boldsymbol{\omega}_1 = \int d\omega_2,$$

$$g^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \omega_1, \omega_2) = \frac{e^{-\frac{u_{12}}{kT}}}{\Omega^2} \{1 + O(\varrho)\}, \quad (2.9)$$

where u_{12} is the total potential energy of the interaction of two gas molecules.

Let us take into account the definitions of the first and second virial coefficient of the molecular Cotton-Mouton constant

$$A_C = \lim_{\varrho \to 0} C_m, \qquad B_C = \lim_{\varrho \to 0} \left\{ [C_m - A_C] \frac{1}{\varrho} \right\}. \quad (2.10)$$

By also making use of (2.9), we can represent Eq. (2.8) in the form of the series (1.3), where A_C and B_C are of the form:

$$A_C = \frac{2\pi}{3} N(\eta_{||} - \eta_{\perp}), \quad (2.11)$$

$$B_C = \frac{4\pi}{15} N\alpha^2 \left\{ 5(\eta_{||} - \eta_{\perp}) + 6 \frac{\chi^2}{kT} \right\} \int r^{-6} e^{-\frac{u(r)}{kT}} dr. \quad (2.12)$$

Here, $u(r)$ denotes the potential energy of the central interaction of two molecules; hence, this energy depends only on $\boldsymbol{r}_{12} = \boldsymbol{r}$.

Thus we have shown that if a gas consisting of spherical molecules is suitably condensed, C_m is a function of the density ϱ and temperature T. By introducing the abbreviation

$$\langle r^{-n} \rangle = \int r^{-n} e^{-\frac{u(r)}{kT}} d\boldsymbol{r} = 4\pi \int_0^\infty r^{2-n} e^{-\frac{u(r)}{kT}} \, dr, \tag{2.13}$$

we can write down the formula (2.12) for the second virial coefficient in the following form:

$$B_C = \frac{4\pi}{15} N\alpha^2 \left\{ 5(\eta_{||} - \eta_\perp) + 6\frac{\chi^2}{kT} \right\} \langle r^{-6} \rangle. \tag{2.14}$$

Anisotropic molecules. If the gas molecules are anisotropically polarizable, then we have in the first approximation under omission of the molecular fields $\boldsymbol{F}$ and $\boldsymbol{G}$:

$$\frac{\partial m_\sigma^{e(p)}}{\partial E_\tau} = \alpha_{\sigma\tau}^{(p)} + \frac{1}{2} \eta_{\sigma\tau:\nu\varrho}^{(p)} H_\nu H_\varrho + \ldots,$$

$$\frac{\partial m_\nu^{m(q)}}{\partial H_\varrho} = \chi_{\nu\varrho}^{(q)} + \ldots, \tag{2.15}$$

where $\alpha_{\sigma\tau}$ and $\chi_{\sigma\tau}$ are respectively the optical and magnetic polarizability tensors for the molecule and $\eta_{\sigma\tau:\nu\varrho}$ is its magnetic hyperpolarizability tensor. All the tensors mentioned refer to the p-th or the q-th isolated molecule, respectively.

By substitution of (2.15) into (1.2) and making use of the definition (2.7) we obtain

$$C_m = \frac{\pi\varrho}{45} \varepsilon_{\sigma\tau:\nu\varrho} \left\{ \int\int \left(\eta_{\sigma\tau:\nu\varrho}^{(1)} + \frac{1}{kT} \alpha_{\sigma\tau}^{(1)} \chi_{\nu\varrho}^{(1)} \right) g^{(1)}(\boldsymbol{r}_1, \omega_1) \, d\boldsymbol{r}_1 \, d\omega_1 + \right.$$

$$\left. + \frac{\varrho}{kT} \int\int\int\int \alpha_{\sigma\tau}^{(1)} \chi_{\nu\varrho}^{(2)} g^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \omega_1, \omega_2) \, d\boldsymbol{r}_1 \, d\boldsymbol{r}_2 \, d\omega_1 \, d\omega_2 \right\}. \tag{2.16}$$

On the basis of the formulae (2.9) and the definitions (2.10) we can represent the above equation also in the form of (1.3), where the virial coefficients A_C and B_C are defined by the following expressions:

$$A_C = \frac{\pi N}{45\Omega} \int \varepsilon_{\sigma\tau:\nu\varrho} \left(\eta_{\sigma\tau:\nu\varrho}^{(1)} + \frac{1}{kT} \alpha_{\sigma\tau}^{(1)} \chi_{\nu\varrho}^{(1)} \right) d\omega_1, \tag{2.17}$$

$$B_C = \frac{\pi N}{45kT\Omega^2} \int\int\int \varepsilon_{\sigma\tau:\nu\varrho} \alpha_{\sigma\tau}^{(1)} \chi_{\nu\varrho}^{(2)} e^{-\frac{u_{12}}{kT}} d\boldsymbol{r} \, d\omega_1 \, d\omega_2. \tag{2.18}$$

In the expression (2.18) the potential energy u_{12} includes not only the central force potential $u(r)$ but also an additional energy resulting from tensorial intermolecular forces. Further calculation of the formula (2.17) and (2.18) is easily performed with the help of the transformations:

$$\alpha_{\sigma\tau}^{(1)} = \omega_{\sigma\alpha}^{(1)} \omega_{\tau\beta}^{(1)} \alpha_{\alpha\beta}, \quad \chi_{\nu\varrho}^{(2)} = \omega_{\nu\gamma}^{(2)} \omega_{\varrho\delta}^{(2)} \chi_{\gamma\delta}, \quad \eta_{\sigma\tau:\nu\varrho}^{(1)} = \omega_{\sigma\alpha}^{(1)} \omega_{\tau\beta}^{(1)} \omega_{\nu\gamma}^{(1)} \omega_{\varrho\delta}^{(1)} \eta_{\alpha\beta:\gamma\delta}, \tag{2.19}$$

which transform the components of the tensors $\alpha_{\sigma\tau}$, $\chi_{\nu\varrho}$ and $\eta_{\sigma\tau:\nu\varrho}$ of the 1-st or 2-nd molecule from the fixed coordinate system (X_σ) to one of the molecular systems rigidly connected

with the individual molecules. The transformation coefficients $\omega_{\sigma\alpha}^{(1)}, \ldots$ or $\omega_{\sigma\alpha}^{(2)}, \ldots$ are the cosines of the angles subtended by the axes of the fixed system with the axes of the respective molecular systems.

By assuming that the tensors $\alpha_{\alpha\beta}$ and $\chi_{\gamma\delta}$ given in the molecular systems are fully symmetric, and that the tensor $\eta_{\alpha\beta:\gamma\delta}$ is symmetric in the pairs of indices $\alpha\beta$ and $\gamma\delta$, we may write Eq. (2.17) in the following form (after applying the transformation (2.19)):

$$A_C = \frac{2\pi}{45} N \left\{ 3\eta_{\alpha\beta:\alpha\beta} - \eta_{\alpha\alpha:\beta\beta} + \frac{1}{kT} (3\alpha_{\alpha\beta}\chi_{\alpha\beta} - \alpha_{\alpha\alpha}\chi_{\beta\beta}) \right\}. \tag{2.20}$$

The expression (2.18) will be discussed first for the case of non-polar molecules. Besides the central interaction energy $u(r)$, we shall take into account the additional energy v_{12}^{disp} resulting from London's anisotropic dispersion forces (1942). In this case the total potential has the following form (see Appendix A):

$$u_{12} = u(r) - \tfrac{1}{8} h\nu \left(a_{\sigma\tau}^{(1)} a_{\nu\varrho}^{(2)} - a^2 \delta_{\sigma\tau}\delta_{\nu\varrho} \right) T_{\sigma\nu}^{(12)} T_{\tau\varrho}^{(12)}, \tag{2.21}$$

where $a_{\sigma\tau}$ is the electric polarizability tensor of an isolated molecule, a — the mean polarizability of this molecule, ν — the mean frequency of electron oscillations, h — Planck's constant.

On substituting (2.21) into (2.18) and using the transformation (2.19), we obtain (see Appendix B)

$$B_C = \frac{\pi h\nu N}{13500\, k^2 T^2} \left\{ (3\alpha_{\alpha\beta}a_{\alpha\beta} - \alpha_{\alpha\alpha}a_{\beta\beta})(3\chi_{\gamma\delta}a_{\gamma\delta} - \chi_{\gamma\gamma}a_{\delta\delta}) \left(\langle r^{-6} \rangle + \right. \right.$$

$$+ \frac{3h\nu a^2}{4kT} \langle r^{-12} \rangle + \ldots \bigg) - \frac{h\nu}{294\, kT} \left[7 \left(9\alpha_{\alpha\beta}a_{\alpha\gamma}a_{\beta\gamma} - 6\alpha_{\alpha\beta}a_{\alpha\beta}a_{\gamma\gamma} - \right.\right.$$

$$- 3\alpha_{\alpha\alpha}a_{\beta\gamma}a_{\beta\gamma} + 2\alpha_{\alpha\alpha}a_{\beta\beta}a_{\gamma\gamma})(3\chi_{\delta\varepsilon}a_{\delta\varepsilon} - \chi_{\delta\delta}a_{\varepsilon\varepsilon})\,a_{\eta\eta} - 19\,(9\alpha_{\alpha\beta}a_{\alpha\gamma}a_{\beta\gamma} - 6\alpha_{\alpha\beta}a_{\alpha\beta}a_{\gamma\gamma} -$$

$$- 3\alpha_{\alpha\alpha}a_{\beta\gamma}a_{\beta\gamma} + 2\alpha_{\alpha\alpha}a_{\beta\beta}a_{\gamma\gamma})(9\chi_{\delta\varepsilon}a_{\delta\eta}a_{\varepsilon\eta} - 6\chi_{\delta\varepsilon}a_{\delta\varepsilon}a_{\eta\eta} - 3\chi_{\delta\delta}a_{\varepsilon\eta}a_{\varepsilon\eta} + 2\chi_{\delta\delta}a_{\varepsilon\varepsilon}a_{\eta\eta}) +$$

$$+ 7(9\chi_{\alpha\beta}a_{\alpha\gamma}a_{\beta\gamma} - 6\chi_{\alpha\beta}a_{\alpha\beta}a_{\gamma\gamma} - 3\chi_{\alpha\alpha}a_{\beta\gamma}a_{\beta\gamma} + 2\chi_{\alpha\alpha}a_{\beta\beta}a_{\gamma\gamma}) \times$$

$$\times (3\alpha_{\delta\varepsilon}a_{\delta\varepsilon} - \alpha_{\delta\delta}a_{\varepsilon\varepsilon})\,a_{\eta\eta}]\, \langle r^{-12} \rangle + \ldots \bigg\}. \tag{2.22}$$

When the molecules possess symmetry with respect to the 3-rd axis of the molecular system, the following tensor components differ from zero:

$$\alpha_{11} = \alpha_{22} = \alpha_1, \qquad \chi_{11} = \chi_{22} = \chi_2, \qquad a_{11} = a_{22} = a_1,$$

$$\alpha_{33} = \alpha_3, \qquad\qquad \chi_{33} = \chi_3, \qquad\qquad a_{33} = a_3, \tag{2.23}$$

so that the expressions (2.20) and (2.22) are now obtained in the following simplified form (under the assumption $\eta_{\alpha\beta:\gamma\delta} = 0$):

$$A_C = \frac{4\pi N}{5kT} \alpha\delta_\alpha \chi\delta_\chi, \tag{2.24}$$

$$B_C = \frac{3\pi h\nu N}{125\, k^2 T^2} \alpha\delta_\alpha \chi\delta_\chi a^2\delta_a^2 \left\{ \langle r^{-6} \rangle + \frac{3h\nu a^2}{4kT} \left(1 - \frac{4}{7}\,\delta_a + \frac{38}{49}\,\delta_a^2 \right) \langle r^{-12} \rangle + \ldots \right\}. \tag{2.25}$$

Following Langevin (1910), we have introduced the dimensionless quantities

$$\delta_\alpha = \frac{\alpha_3 - \alpha_1}{3\alpha}, \qquad \delta_\chi = \frac{\chi_3 - \chi_1}{3\chi}, \qquad \delta_a = \frac{a_3 - a_1}{3a} \qquad (2.26)$$

which determine the degree of anisotropy of the optical, magnetic and electric polarizabilities of an isolated axial symmetric molecule. Here, the quantities

$$\alpha = \tfrac{1}{3}(\alpha_3 + 2\alpha_1), \quad \chi = \tfrac{1}{3}(\chi_3 + 2\chi_1), \quad a = \tfrac{1}{3}(a_3 + 2a_1) \qquad (2.27)$$

denote the respective mean polarizabilities.

Quadrupole molecules. Let us now calculate B_C for the case of gas molecules having a permanent quadrupole moment defined by the tensor $\Theta_{\sigma\tau}$ (see Appendix A). The potential energy of mutual interaction of two anisotropically polarizable quadrupole molecules is given by the general equation (Kielich, 1960)

$$u_{12} = u(r) - \tfrac{1}{9}\Theta_{\sigma\tau}^{(1)}\Theta_{\nu\varrho}^{(2)} T_{\sigma\tau\nu\varrho}^{(12)} - \tfrac{1}{18}(a_{\sigma\tau}^{(1)}\Theta_{\nu\varrho}^{(2)}\Theta_{\lambda\mu}^{(2)} + a_{\sigma\tau}^{(2)}\Theta_{\nu\varrho}^{(1)}\Theta_{\lambda\mu}^{(1)}) T_{\sigma\nu\varrho}^{(12)} T_{\tau\lambda\mu}^{(12)}. \qquad (2.28)$$

In this equation, the second term determines the quadrupole-quadrupole interaction energy, and the third — the quadrupole-induced dipole interaction energy. The tensors $T_{\sigma\tau\nu}$ and $T_{\sigma\tau\nu\varrho}$ characterizing these interactions are defined in Appendix A.

We apply (2.28) to (2.18) and obtain, on integration over all possible orientations of the molecules

$$B_C = \frac{4\pi N}{4725\,k^2 T^2} \left\{ [(3\alpha_{\alpha\beta}a_{\alpha\beta} - \alpha_{\alpha\alpha}a_{\beta\beta})(3\chi_{\gamma\delta}\Theta_{\gamma\varepsilon}\Theta_{\delta\varepsilon} - \chi_{\gamma\gamma}\Theta_{\delta\varepsilon}\Theta_{\delta\varepsilon}) + \right.$$
$$+ (3\chi_{\alpha\beta}a_{\alpha\beta} - \chi_{\alpha\alpha}a_{\beta\beta})(3\alpha_{\gamma\delta}\Theta_{\gamma\varepsilon}\Theta_{\delta\varepsilon} - \alpha_{\gamma\gamma}\Theta_{\delta\varepsilon}\Theta_{\delta\varepsilon})]\langle r^{-8}\rangle +$$
$$\left. + \frac{16}{3kT}(3\alpha_{\alpha\beta}\Theta_{\alpha\gamma}\Theta_{\beta\gamma} - \alpha_{\alpha\alpha}\Theta_{\beta\gamma}\Theta_{\beta\gamma})(3\chi_{\delta\varepsilon}\Theta_{\delta\eta}\Theta_{\varepsilon\eta} - \chi_{\delta\delta}\Theta_{\varepsilon\eta}\Theta_{\varepsilon\eta})\langle r^{-10}\rangle + ... \right\}. \qquad (2.29)$$

In this expression, the first term multiplied by $\langle r^{-8}\rangle$ results from inductive interaction between the quadrupole and induced dipole, whereas the term multiplied by $\langle r^{-10}\rangle$ results from interaction of the permanent molecular quadrupoles. For axially symmetric molecules we have (2.23) and $\Theta_{33} = -2\Theta_{11} = -2\Theta_{22} = \Theta$. Hence, we obtain from (2.29)

$$B_C = \frac{8\pi\alpha\delta_\alpha\chi\delta_\chi\Theta^2 N}{175\,k^2 T^2} \left\{ 3a\delta_a\langle r^{-8}\rangle + 2\frac{\Theta^2}{kT}\langle r^{-10}\rangle \right\}. \qquad (2.30)$$

3. Dipole gases

Dipole molecules. The total potential energy of mutual interaction between two dipole molecules is given by the following equation (*cf.* Barker 1953, Kielich 1960):

$$u_{12} = u(r) + \mu_\sigma^{(1)}\mu_\tau^{(2)} T_{\sigma\tau}^{(12)} - \tfrac{1}{2}(a_{\sigma\tau}^{(1)}\mu_\nu^{(2)}\mu_\varrho^{(2)} + a_{\sigma\tau}^{(2)}\mu_\nu^{(1)}\mu_\varrho^{(1)}) T_{\sigma\nu}^{(12)} T_{\tau\varrho}^{(12)} - ... \qquad (3.1)$$

Besides $u(r)$, herein are included terms representing dipole-dipole and dipole-induced dipole interactions; μ_σ is the σ-component of the permanent dipole moment of the isolated molecule. In the case considered we can apply in the first approximation the expression (2.18)

for B_C. Thus we obtain by inserting (3.1) into that formula

$$B_C = \frac{\pi N}{3375\, k^2 T^2} \left\{ [(3\alpha_{\alpha\beta}\, a_{\alpha\beta} - \alpha_{\alpha\alpha}\, a_{\beta\beta})\,(3\chi_{\gamma\delta}\mu_\gamma\mu_\delta - \chi_{\gamma\gamma}\mu_\delta^2) + \right.$$
$$+ (3\chi_{\alpha\beta}\, a_{\alpha\beta} - \chi_{\alpha\alpha}\, a_{\beta\beta})\,(3\alpha_{\gamma\delta}\mu_\gamma\mu_\delta - \alpha_{\gamma\gamma}\mu_\delta^2)]\,\langle r^{-6}\rangle + \ldots$$
$$\left. + \frac{1}{kT}\,(3\alpha_{\alpha\beta}\mu_\alpha\mu_\beta - \alpha_{\alpha\alpha}\mu_\beta^2)\,(3\chi_{\gamma\delta}\mu_\gamma\mu_\delta - \chi_{\gamma\gamma}\mu_\delta^2)\left(\langle r^{-6}\rangle + \frac{12\mu^4}{49\,k^2T^2}\langle r^{-12}\rangle + \ldots\right)\right\}.$$
$$(3.2)$$

For axially symmetrical dipolar molecules, the above expression becomes

$$B_C = \frac{4\pi a\delta_a^{\ddot{}}\chi\delta_\chi\mu^2 N}{375\,k^2 T^2}\left\{6a\delta_a\,\langle r^{-6}\rangle + \ldots + \frac{\mu^2}{kT}\left(\langle r^{-6}\rangle + \frac{12\mu^4}{49\,k^2T^2}\langle r^{-12}\rangle + \ldots\right)\right\}. \quad (3.3)$$

Dipole molecules with hyperpolarizability. Let us now consider the situation when the molecular electric field in the gas is so strong that the dipole molecules undergo nonlinear deformation. In this case we have at $E = H = 0$ (Kielich 1962)

$$\left(\frac{\partial m_\sigma^{e(p)}}{\partial E_\chi}\right)_0 = \left\{\alpha_{\sigma\tau}^{(p)} + \beta_{\sigma\tau:\nu}^{(p)}F_{0\nu}^{(p)} + \frac{1}{2}\,\gamma_{\sigma\tau:\nu\varrho}^{(p)}F_{0\nu}^{(p)}F_{0\varrho}^{(p)} + \ldots\right\}\left\{\delta_{\tau\chi} + \frac{\partial F_\tau^{(p)}}{\partial E_\chi}\right|_0\right\}, \quad (3.4)$$

$$\left(\frac{\partial m_\sigma^{m(q)}}{\partial H_\chi}\right)_0 = \left\{\chi_{\sigma\tau}^{(q)} + \xi_{\nu:\sigma\tau}^{(q)}F_{0\nu}^{(q)} + \frac{1}{2}\,\eta_{\nu\varrho:\sigma\tau}^{(q)}F_{0\nu}^{(q)}F_{0\varrho}^{(q)} + \ldots\right\}\left\{\delta_{\tau\chi} + \frac{\partial G_\tau^{(q)}}{\partial H_\chi}\right|_0\right\}, \quad (3.5)$$

where $\boldsymbol{F}^{(p)}$ is the molecular electric field inducing the hyperpolarizability of molecules, defined by the tensors $\beta_{\sigma\tau:\nu}$, $\gamma_{\sigma\tau:\nu\varrho}$, $\xi_{\nu:\sigma\tau}$ and $\eta_{\nu\varrho:\sigma\tau}$.

From the general formula (1.2) we now obtain (the temperature-independent part of C_m is neglected)

$$C_m = \frac{\pi}{45\,kT}\,\varepsilon_{\sigma\tau:\nu\varrho}\left\langle \sum_{p=1}^{N}\sum_{q=1}^{N}\,(\alpha_{\sigma\tau}^{(p)}\chi_{\nu\varrho}^{(q)} + \alpha_{\sigma\tau}^{(p)}\xi_{\lambda:\nu\varrho}^{(q)}F_{0\lambda}^{(q)} + \right.$$
$$+ \chi_{\nu\varrho}^{(q)}\beta_{\sigma\tau:\lambda}^{(p)}F_{0\lambda}^{(p)} + \beta_{\sigma\tau:\lambda}^{(p)}\xi_{\mu:\nu\varrho}^{(q)}F_{0\lambda}^{(p)}F_{0\mu}^{(q)} +$$
$$\left. + \tfrac{1}{2}\,\alpha_{\sigma\tau}^{(p)}\eta_{\lambda\mu:\nu\varrho}^{(q)}F_{0\lambda}^{(q)}F_{0\mu}^{(q)} + \tfrac{1}{2}\,\chi_{\nu\varrho}^{(q)}\gamma_{\sigma\tau:\lambda\mu}^{(p)}F_{0\lambda}^{(p)}F_{0\mu}^{(p)} + \ldots\right)\right\rangle. \quad (3.6)$$

The molecular field $\boldsymbol{F}_0^{(p)}$ produced at the centre of the p-th molecule by neighbouring dipole molecules is given in the first approximation by the formula

$$F_{0\sigma}^{(p)} = -\sum_{\substack{r=1\\ r\neq p}}^{N} T_{\sigma\tau}^{(pr)}\mu_\tau^{(r)}. \quad (3.7)$$

By inserting into (3.6) and neglecting higher order terms we have

$$C_m = \frac{\pi}{45kT}\,\varepsilon_{\sigma\tau:\nu\varrho}\left\langle \sum_{p=1}^{N}\sum_{q=1}^{N}\left(\alpha_{\sigma\tau}^{(p)}\chi_{\nu\varrho}^{(q)} - \right.\right.$$
$$\left.\left. - \sum_{\substack{r=1\\ r\neq q}}^{N}\alpha_{\sigma\tau}^{(p)}\xi_{\lambda:\nu\varrho}^{(q)}T_{\lambda\mu}^{(qr)}\mu_\mu^{(r)} - \sum_{\substack{r=1\\ r\neq p}}^{N}\chi_{\nu\varrho}^{(q)}\beta_{\sigma\tau:\lambda}^{(p)}T_{\lambda\mu}^{(pr)}\mu_\mu^{(r)} + \ldots\right)\right\rangle. \quad (3.8)$$

By making use of the definition (2.7), we reduce (3.8) to

$$C_m = \frac{\pi\varrho}{45\,kT}\,\varepsilon_{\sigma\tau:\nu\varrho}\left\{\iint \alpha^{(1)}_{\sigma\tau}\chi^{(1)}_{\nu\varrho}\,g^{(1)}(\boldsymbol{r}_1,\omega_1)\,d\boldsymbol{r}_1\,d\omega_1 +\right.$$

$$+\varrho\iiiint[\alpha^{(1)}_{\sigma\tau}\chi^{(2)}_{\nu\varrho} - \alpha^{(1)}_{\sigma\tau}(\xi^{(1)}_{\lambda:\nu\varrho}\mu^{(2)}_{\mu} + \xi^{(2)}_{\lambda:\nu\varrho}\mu^{(1)}_{\mu})\,T^{(12)}_{\lambda\mu} - \chi^{(2)}_{\nu\varrho}(\beta^{(2)}_{\nu\varrho:\lambda}\mu^{(1)}_{\mu} + \beta^{(1)}_{\nu\varrho:\lambda}\mu^{(2)}_{\mu})\,T^{(12)}_{\lambda\mu} + ...] \times$$

$$\left. \times\,g^{(2)}(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega_1,\omega_2)\,d\boldsymbol{r}_1\,d\boldsymbol{r}_2\,d\omega_1\,d\omega_2 + ... \right\}. \tag{3.9}$$

Hence we obtain with (2.9) and (2.10) the formula for the second virial coefficient

$$B_C = \frac{\pi N}{45\,kT\Omega^2}\iiint \varepsilon_{\sigma\tau:\nu\varrho}\left\{\alpha^{(1)}_{\sigma\tau}\chi^{(2)}_{\nu\varrho} - \alpha^{(1)}_{\sigma\tau}(\xi^{(1)}_{\lambda:\nu\varrho}\mu^{(2)}_{\mu} + \xi^{(2)}_{\lambda:\nu\varrho}\mu^{(1)}_{\mu})\,T^{(12)}_{\lambda\mu} - \chi^{(2)}_{\nu\varrho}(\beta^{(2)}_{\nu\varrho:\lambda}\mu^{(1)}_{\mu} +\right.$$

$$\left. + \beta^{(1)}_{\nu\varrho:\lambda}\mu^{(2)}_{\mu})\,T^{(12)}_{\lambda\mu} + ...\right\}e^{-\frac{u_{12}}{kT}}\,d\boldsymbol{r}\,d\omega_1\,d\omega_2. \tag{3.10}$$

We substitute herein the energy u_{12} in the form given by expression (3.1), obtaining

$$B_C^{\mathrm{hyp}} = B_C + \frac{2\pi N}{3375\,k^2T^2}\left\{50\,(3\alpha_{\alpha\beta}\,\xi_{\gamma:\alpha\beta}\,\mu_\gamma + \alpha_{\alpha\alpha}\,\xi_{\gamma:\beta\beta}\,\mu_\gamma)\,\mu^2 +\right.$$

$$+ (3\alpha_{\alpha\beta}\mu_\alpha\mu_\beta - \alpha_{\alpha\alpha}\mu_\beta^2)\,(3\xi_{\gamma:\delta\gamma}\mu_\delta - \xi_{\gamma:\delta\delta}\mu_\gamma) +$$

$$(3\chi_{\alpha\beta}\mu_\alpha\mu_\beta - \chi_{\alpha\alpha}\mu_\beta^2)\,(3\beta_{\gamma\delta:\gamma}\mu_\delta - \beta_{\gamma\gamma:\delta}\mu_\delta) + 50\,(3\chi_{\alpha\beta}\beta_{\alpha\beta:\gamma}\mu_\gamma - \chi_{\alpha\alpha}\beta_{\beta\beta:\gamma}\mu_\gamma)\,\mu^2\left.\right\}\langle r^{-6}\rangle + ...,$$
$$\tag{3.11}$$

where B_C is defined by formula (3.2).

For axially symmetrical dipole molecules, Eq. (3.11) reduces to

$$B_C^{\mathrm{hyp}} = B_C + \frac{208\pi\mu^3 N}{375k^2T^2}\,\{\alpha\delta_\alpha\xi\delta_\xi + \chi\delta_\chi\beta\delta_\beta^{\cdot}\}\,\langle r^{-6}\rangle, \tag{3.12}$$

where B_C is given by Eq. (3.3). The quantities

$$\delta_\beta^{\cdot} = \frac{\beta_3 - \beta_1}{3\beta}\,, \qquad [\delta_\xi = \frac{\xi_3 - \xi_1}{3\xi} \tag{3.13}$$

determine, respectively, the degree of electric and magnetic hyperpolarizability of the isolated dipole molecule, whereas

$$\beta = \tfrac{1}{3}\,(\beta_3 + 2\beta_1), \qquad \xi = \tfrac{1}{3}\,(\xi_3 + 2\xi_1) \tag{3.14}$$

are its mean hyperpolarizabilities. In these expressions we used the abbreviations:

$$\beta_{11:3} = \beta_{22:3} = \beta_1, \qquad \xi_{3:11} = \xi_{3:22} = \xi_1,$$

$$\beta_{33:3} = \beta_3, \qquad\qquad \xi_{3:33} = \xi_3.$$

Eqs. (3.11) and (3.12) express the influence of the hyperpolarizability of the dipole molecules on the second Cotton-Mouton constant virial coefficient for dipolar gases.

4. Polar gas mixtures

For a multi-component system we have the following form of the molecular Cotton-Mouton constant (Kielich 1962):

$$C_m = \frac{\pi N}{45}\, \varepsilon_{\sigma\tau:\nu\varrho} \left\{ \sum_{i=1}^{s} x_i \left(\eta_{\sigma\tau:\nu\varrho}^{(i)} + \frac{1}{kT}\, \alpha_{\sigma\tau}^{(i)} \chi_{\nu\varrho}^{(i)} \right) + \right.$$

$$\left. + \frac{\varrho}{kT} \sum_{i=1}^{s} \sum_{j=1}^{s} x_i x_j \iiint \alpha_{\sigma\tau}^{(1,i)} \chi_{\nu\varrho}^{(2,j)} g_{ij}^{(2)} (\mathbf{r}_{ij}, \omega_i, \omega_j)\, d\mathbf{r}_{ij}\, d\omega_i\, d\omega_j \right\}, \qquad (4.1)$$

where x_i is the mole fraction of the i-th component and s is the number of components of the system. The tensors $\alpha_{\sigma\tau}^{(i)}$, $\chi_{\nu\varrho}^{(j)}$ and $\eta_{\sigma\tau:\nu\varrho}^{(i)}$ retain their previous physical meaning with the additional remark that they now refer to an isolated molecule of species i or j.

In analogy to (2.9) we have now

$$g_{ij}^{(2)} (\mathbf{r}_{ij}, \omega_i, \omega_j) = \frac{e^{-\frac{u_{12}^{(ij)}}{kT}}}{\varOmega^2} \{1 + O(\varrho)\}. \qquad (4.2)$$

Hence we can represent Eq. (4.1) in the form of the virial expansion

$$C_m = \sum_{i=1}^{s} x_i A_C^{(i)} + \varrho \sum_{i=1}^{s} \sum_{j=1}^{s} x_i x_j B_C^{(ij)} + \ldots, \qquad (4.3)$$

where

$$A_C^{(i)} = \frac{2\pi}{45}\, N \left\{ 3\eta_{\alpha\beta:\alpha\beta}^{(i)} - \eta_{\alpha\alpha:\beta\beta}^{(i)} + \frac{1}{kT} (3\alpha_{\alpha\beta}^{(i)} \chi_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)} \chi_{\beta\beta}^{(i)}) \right\}. \qquad (4.4)$$

$$B_C = \frac{\pi N}{90\, kT \varOmega^2} \iiint \varepsilon_{\sigma\tau:\nu\varrho} (\alpha_{\sigma\tau}^{(1,i)} \chi_{\nu\varrho}^{(2,j)} + \chi_{\sigma\tau}^{(1,i)} \alpha_{\nu\varrho}^{(2,j)})\, e^{-\frac{u_{12}^{(ij)}}{kT}}\, d\mathbf{r}_{ij}\, d\omega_i\, d\omega_j. \qquad (4.5)$$

Here $u_{12}^{(ij)}$ denotes the total potential energy of mutual interaction of molecule "1" of species i with molecule "2" of species j.

The expression (4.5) can be calculated successively for molecular models analogous to those discussed in sections 2 and 3. Let us, however, begin with the case of a polar gas mixture. For simplicity let us assume that the molecules of all components possess the axial symmetry. In this case, with the transformation formulae (2.19) we obtain

$$\alpha_{\sigma\tau}^{(1,i)} = \alpha_i \delta_{\sigma\tau} + \alpha_i \delta_{\alpha,i} (3\omega_{\sigma3}^{(1,i)} \omega_{\tau3}^{(1,i)} - \delta_{\sigma\tau}), \qquad \chi_{\nu\varrho}^{(2,j)} = \chi_j \delta_{\nu\varrho} + \chi_j \delta_{\chi,j} (3\omega_{\nu3}^{(2,j)} \omega_{\varrho3}^{(2,j)} - \delta_{\nu\varrho}). \quad (4.6)$$

Hence, the second virial coefficient (4.5) reduces to

$$B_C^{(ij)} = \frac{\pi N}{5\, kT \varOmega^2} (\alpha_i \delta_{\alpha,i} \chi_j \delta_{\chi,j} + \chi_i \delta_{\chi,i} \alpha_j \delta_{\alpha,j}) \iiint (3\cos^2 \theta_{12}^{(ij)} - 1)\, e^{-\frac{u_{12}^{(ij)}}{kT}}\, d\mathbf{r}_{ij}\, d\omega_i\, d\omega_j \quad (4.7)$$

where $\theta_{12}^{(ij)}$ is the angle between the symmetry axis of molecule "1" of species i and that of molecule "2" of species j.

We substitute herein the energy in the form

$$u_{12}^{(ij)} = u\,(r_{ij}) + v_{12}^{(ij)}, \tag{4.8}$$

where $v_{12}^{(ij)}$ denotes the energy of noncentral interaction of the polar molecules, defined in Appendix A as the sum of expressions (A. 11) and (A. 16), and we obtain (see Appendix B)

$$
B_C^{(ij)} = \frac{2\pi N}{125\,k^2 T^2}\,(\alpha_i\,\delta_{\alpha,i}\,\chi_j\,\delta_{\chi,j} + \chi_i\,\delta_{\chi,i}\,\alpha_j\,\delta_{\alpha,j})\Bigg\{\big(a_i\,\delta_{a,i}\,\mu_j^2 + \mu_i^2\,a_j\,\delta_{a,j}\big)\,\langle r_{ij}^{-6}\rangle +
$$

$$
+ \frac{4\mu_i^2\,\mu_j^2}{49\,k^2 T^2}\,[7\,(a_i\,\mu_j^2 + \mu_i^2\,a_j) + 11\,(a_i\,\delta_{a,i}\,\mu_j^2 + \mu_i^2\,a_j\,\delta_{a,j})]\,\langle r_{ij}^{-12}\rangle + \dots
$$

$$
+ \frac{\mu_i^2\,\mu_j^2}{3\,kT}\left(\langle r_{ij}^{-6}\rangle + \frac{12\,\mu_i^2\,\mu_j^2}{49\,k^2 T^2}\,\langle r_{ij}^{-12}\rangle + \dots\right) +
$$

$$
+ \frac{5}{7}\left[3(a_i\,\delta_{a,i}\,\Theta_j^2 + \Theta_i^2\,a_j\,\delta_{a,j})\,\langle r_{ij}^{-8}\rangle + \frac{4}{kT}\,\Theta_i^2\,\Theta_j^2\,\langle r_{ij}^{-10}\rangle + \dots\right] +
$$

$$
+ \frac{5}{7kT}\left[(\mu_i^2\,\Theta_j^2 + \Theta_i^2\,\mu_j^2)\,\langle r_{ij}^{-8}\rangle - \frac{4}{kT}\,\mu_i^2\,\Theta_i\,\Theta_j\,\mu_j^2\,\langle r_{ij}^{-11}\rangle + \dots\right]\Bigg\}. \tag{4.9}
$$

In the parenthesis {...} there appear successively terms resulting from the following interactions: dipole-induced dipole, dipole-dipole, quadrupole-induced dipole, quadrupole-quadrupole and dipole-quadrupole.

In the above calculations let us moreover take into consideration the anisotropic dispersive forces, which give the following expression for their energy $v_{12}^{(ij)}$ (see Appendix A):

$$
v_{12}^{(ij)} = \frac{3}{4}\,h\,\frac{\nu_i\,\nu_j}{\nu_i + \nu_j}\,\frac{a_i\,a_j}{r_{ij}^6}\Bigg\{\delta_{a,i} + \delta_{a,j} - 3\,(1 - \delta_{a,j})\,\delta_{a,i}\cos^2\theta_i -
$$

$$
- 3(1 - \delta_{a,i})\,\delta_{a,j}\cos^2\theta_j - 3\delta_{a,i}\delta_{a,j}(\cos\theta_{ij} - 3\cos\theta_i\cos\theta_j)^2\Bigg\}. \tag{4.10}
$$

On substituting this expression in Eq. (4.7), we obtain the following contributions to B_C resulting from anisotropic dispersive forces (see Appendix B):

$$
B_C^{(ij)} = \frac{3\pi h N}{125\,k^2 T^2}\,\frac{\nu_i\,\nu_j}{\nu_i + \nu_j}\,a_i\,\delta_{a,i}\,a_j\,\delta_{a,j}(\alpha_i\,\delta_{\alpha,i}\,\chi_j\,\delta_{\chi,j} +
$$

$$
+ \chi_i\,\delta_{\chi,i}\,\alpha_j\,\delta_{\alpha,j})\Bigg\{\langle r_{ij}^{-6}\rangle + \frac{3h}{98kT}\,\frac{\nu_i\,\nu_j}{\nu_i + \nu_j}\,a_i\,a_j\,[49 -
$$

$$
- 14\,(\delta_{a,i} + \delta_{a,j}) + 38\,\delta_{a,i}\delta_{a,j}]\,\langle r_{ij}^{-12}\rangle + \dots\Bigg\}. \tag{4.11}
$$

For a one-component gas we obtain from (4.9) the previously proved formulae (2.30) and (3.3), while (4.11) reduces to (2.25).

5. *Discussion and conclusions*

Let us estimate numerically the second virial coefficient B_C for the Lennard-Jones (6:12) potential (1924)

$$u(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\}, \tag{5.1}$$

which allows us to express (2.13) in a simple way by means of the functions $H_n(y)$, which were tabulated by Buckingham and Pople (1955). We have namely

$$\langle r^{-n} \rangle = \frac{\pi}{3} \left(\sigma^6 y\right)^{\frac{3-n}{6}} \sum_{m=1}^{\infty} \Gamma\left(\frac{6m+n-3}{12}\right) \frac{y^m}{m!} = \frac{\pi\sigma^{3-n}}{3y^4} H_n(y), \tag{5.2}$$

where $y = 2\,(\varepsilon/kT)^{\frac{1}{2}}$, and σ and ε are well-known central force parameters of the dimensions of a length and energy, respectively.

With the help of (5.2) we represent the expression (2.14) in a form suitable for direct numerical estimation:

$$B_C = \frac{4\pi^2\alpha^2 N}{45\sigma^3 y^4} \left\{ 5(\eta_{||} - \eta_{\perp}) + \frac{3\chi^2 y^2}{2\varepsilon} \right\} H_6(y). \tag{5.3}$$

We have the following data for methane[1]: $\sigma = 3.882$ Å, $\varepsilon/k = 137°$K, $\alpha = 2.6 \times \times 10^{-24}$ cm^3, $\chi = -20.3 \times 10^{-30}$ cm^3, and $\eta_{||} = -212 \times 10^{-44}$ e. m. u., $\eta_{\perp} = -356 \times 10^{-44}$ e. m. u. (these valeus of $\eta_{||}$ and $\eta_{\perp}$ are four times larger than the appropriate values calculated by Buckingham and Pople (1956) for atomic hydrogen). Thus we obtain on the basis of Eqs. (2.11) and (5.3) for $T = 280°$K

$$A_C = 1.8 \times 10^{-18},$$

$$B_C = (244.8 + 2.2) \times 10^{-44} = 2.47 \times 10^{-42}.$$

Let us represent Eq. (1.3) in the following form:

$$C_m = A_C \left(1 + B_C^* \varrho + C_C \varrho^2 + ...\right), \tag{5.4}$$

where

$$B_C^* = B_C/A_C, \qquad C_C^* = C_C/A_C, \, ...$$

By (5.4), we obtain for CH$_4$:

$$C_m = 1.8 \times 10^{-18} \left(1 + 1.4 \times 10^{-24}\, \varrho\; \text{cm}^3 + ...\right).$$

From this we see that there is only a slight influence of central interactions on the constant C_m of methane under not too high pressure.

---

[1] In the present paper we draw all data for σ and ε from the monograph of Hirschfelder, Cuitiss and Bird *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), and all values of α and χ from the well-known Landolt-Börnstein Tables, Vol. I, Part 3, 1951 (J. Springer).

For quadrupole gases we obtain, on the basis of (2.24), (2.30) and (5.2),

$$B_C^* = \frac{\pi \Theta^2}{420 \, \varepsilon \sigma^2} \left\{ \frac{6a \, \delta_a}{\sigma^3 \, y^2} H_8 \, (y) + \frac{\Theta^2}{\varepsilon \sigma^5} H_{10} \, (y) \right\}. \tag{5.5}$$

Let us take into consideration carbon dioxide with the following data: $\sigma = 3.996$ Å, $\varepsilon/k = 190°K$, $3\alpha\delta_\alpha = 2.11 \times 10^{-24}$ cm³, $3a\delta_a = 2.35 \times 10^{-24}$ cm³, $\Theta = 5 \times 10^{-26}$ e. s. u. Formula (5.5) yields in this case for $T = 300°K$

$$B_C^* = (0.4 + 9) \times 10^{-24} \text{ cm}^3 = 9.4 \times 10^{-24} \text{ cm}^3.$$

It results from this formula that the contribution to B_C^* due to quadrupole-induced dipole interaction amounting to 0.4×10^{-24} cm³ is much smaller than the contribution 9×10^{-24} cm³ from quadrupole-quadrupole interaction.

In the case of dipole gases the second virial coefficient B_C (3.3) reduces to the following form when (5.2) is used:

$$B_C^* = \frac{\pi \mu^2}{900 \varepsilon} \left\{ \frac{6a \delta_a}{\sigma^3 \, y^2} \left[H_6(y) + \frac{\mu^4 y^4}{196 \, \varepsilon^2 \sigma^6} \left(\frac{7 + 11 \, \delta_a}{\delta_a} \right) H_{12} \, (y) + \ldots \right] + \right.$$
$$\left. + \frac{\mu^2}{4 \, \varepsilon \sigma^3} \left[H_6 \, (y) + \frac{3 \, \mu^4 y^4}{196 \, \varepsilon^2 \sigma^6} H_{12} \, (y) + \ldots \right] \right\}. \tag{5.6}$$

We have the following data for chloroform: $\sigma = 5.43$ Å, $\varepsilon/k = 327°K$, $3\alpha\delta_\alpha = -2.33 \times 10^{-24}$ cm³, $\mu = 1.05 \times 10^{-18}$ e. s. u. Hence, we obtain from formula (5.6) for $T = 375°K$

$$B_C^* = (-0.8 + 3.9) \times 10^{-24} \text{cm}^3 = 3.1 \times 10^{-24} \text{ cm}^3.$$

The contribution to B_C^* from dipole-induced dipole interaction is negative and five times smaller than from dipole-dipole interaction.

From Eqs. (3.3), (3.12) and (5.2), we obtain for hyperpolarizable dipolar molecules

$$B_C^{*\text{hyp}} = B_C^* + \frac{13 \, \pi \mu^3}{225 \, \varepsilon \sigma^3 y^2} \left\{ \frac{\beta \delta_\beta}{\alpha \delta_\alpha} + \frac{\xi \delta_\xi}{\chi \delta_\chi} \right\} H_6(y), \tag{5.7}$$

where B_C^* is defined by Eq. (5.6).

The electrical hyperpolarizability anisotropy for the $CHCl_3$ molecule is $3\beta\delta_\beta = \beta_3 - \beta_1 = -2.5 \times 10^{-29}$ e.s. u. (Kielich, 1962); hence, we obtain from Eq. (5.7)

$$B_C^{*\text{hyp}} = B_C^* + \left(9.3 + 8.7 \, \frac{\xi \delta_\xi}{\chi \delta_\chi} \times 10^5 \right) \times 10^{-24} \text{cm}^3.$$

We see that the influence of the electrical hyperpolarizability alone on the second virial coefficient B_C is considerable and that this contribution amounts to three times the value of $B_C^* = 3.1 \times 10^{-24}$ cm³ calculated above.

Let us finally consider the influence of London's anisotropic dispersive forces (1942) upon B_C. For this case we have the following formula:

$$B_C^* = \frac{\pi\sigma^3\,\delta_a^2}{75\,y^2}\left\{H_6(y) + y^2\left(1 - \frac{4}{7}\,\delta_a + \frac{38}{49}\,\delta_a^2\right)H_{12}(y) + \ldots\right\}, \qquad (5.8)$$

which can be derived from (2.25).

On the basis of this formula and the numerical data given above we obtain for CO_2

$$B_C^* = 6.3 \times 10^{-24}\ \text{cm}^3$$

and for $CHCl_3$

$$B_C^* = 5.2 \times 10^{-24}\ \text{cm}^3.$$

On comparing these values with the contributions calculated above we see that, in the case of such gases as carbonic dioxide or chloroform, there is a notable contribution from anisotropic dispersive forces to the value of B_C. The total value of B_C for CO_2 is thus

$$B_C^* = (9.4 + 6.3) \times 10^{-24}\ \text{cm}^3 = 15.7 \times 10^{-24}\ \text{cm}^3$$

Hence we have, on the basis of Eq. (5.4),

$$C_m = 25.5\chi\delta_\chi \times 10^{12}\,(1 + 15.7\varrho \times 10^{-24}\ \text{cm}^3).$$

From this we see that for CO_2 under a pressure of p atmospheres and at $T = 300°K$ the influence of intermolecular interactions on the constant C_m can be given approximately by the dependence $B_C^*\varrho = 4\,p \times 10^{-4}\ \text{atm}^{-1}$. Since $\chi = -34.5 \times 10^{-30}\ \text{cm}^3$ and it can be assumed that $|\delta_\chi| = 0.1$, it is evident that the value of the constant C_m for CO_2 is of the order of 10^{-16}, which should be experimentally measurable.

We may call attention to the fact that for anisotropic axially symmetrical molecules we have the following relations:

$$\frac{A_S^{\text{anis}}}{A_C} = \frac{B_S^{\text{anis}}}{B_C} = \frac{26\,\pi^3 kT}{\lambda^4}\,\frac{\alpha\delta_\alpha}{\chi\delta_\chi} \qquad (5.9)$$

between our virial coefficients A_C and B_C and the virial coefficients A_S^{anis} and B_S^{anis} which were calculated in a preceding paper (Kielich 1960) for anisotropic light scattering in imperfect gases; here, λ denotes the light wavelength.

By making use of expressions (4.9) and (4.11), we obtain for a polar gas mixture

$$B_C^{(ij)} = \frac{\pi^2\sigma_{ij}^3 N}{750kT}\,(\alpha_i\delta_{\alpha,i}\chi_j\delta_{\chi,j} + \chi_i\delta_{\chi,i}\alpha_j\delta_{\alpha,j})\left\{4\delta_{a,i}\delta_{a,j}\,[y_{ij}^{-2}H_6(y_{ij}) + H_{12}(y_{ij}) + \ldots] + \right.$$

$$+ \frac{1}{28}\left[(a_i\mu_j^2 + \mu_i^2 a_j)\,y_{ij}^2\,\frac{\mu_i^2\mu_j^2}{\varepsilon_{ij}^3\sigma_{ij}^{12}} - 32\,\delta_{a,i}\delta_{a,j}\left(\delta_{a,i} + \delta_{a,j} - \frac{19}{7}\,\delta_{a,i}\delta_{a,j}\right)\right]H_{12}(y_{ij}) +$$

$$\left. + \frac{1}{\varepsilon_{ij}\sigma_{ij}^6 y_{ij}^2}\,(a_i\delta_{a,i}\mu_j^2 + \mu_i^2 a_j\delta_{a,j})\left[H_6(y_{ij}) + \frac{11\mu_i^2\mu_j^2 y_{ij}^4}{196\varepsilon_{ij}^2\sigma_{ij}^6}\,H_{12}(y_{ij}) + \ldots\right] + \right.$$

$$+ \frac{\mu_i^2 \mu_j^2}{12\,\varepsilon_{ij}^2 \sigma_{ij}^6}\left[H_6(y_{ij}) + \frac{3\,\mu_i^2 \mu_j^2 y_{ij}^4}{196\,\varepsilon_{ij}^2 \sigma_{ij}^6}\,H_{12}(y_{ij}) + \ldots\right] +$$

$$+ \frac{15}{7\varepsilon_{ij}\sigma_{ij}^8 y_{ij}^2}\left[(a_i \delta_{a,i}\,\Theta_j^2 + \Theta_i^2\,a_j\,\delta_{a,j})\,H_8(y_{ij}) + \frac{\Theta_i^2\,\Theta_j^2\,y_{ij}^2}{3\,\varepsilon_{ij}\sigma_{ij}^2}\,H_{10}(y_{ij}) + \ldots\right] +$$

$$+ \frac{5}{28\,\varepsilon_{ij}^2 \sigma_{ij}^8}\left[(\mu_i^2\,\Theta_j^2 + \Theta_i^2\,\mu_j^2)\,H_8(y_{ij}) - \frac{y_{ij}^2}{\varepsilon_{ij}\sigma_{ij}^3}\,\mu_i^2\,\Theta_i\,\Theta_j\,\mu_j^2\,H_{11}(y_{ij}) + \ldots\right] + \ldots\Bigg\}. \tag{5.10}$$

In the case of a two-component gas mixture and by Eq. (4.3), the molecular Cotton-Mouton constant is given by the following series:

$$C_m = x_1 A_C^{(1)} + x_2 A_C^{(2)} + (x_1^2 B_C^{(11)} + 2x_1 x_2 B_C^{(12)} + x_2^2 B_C^{(22)})\,\varrho + \ldots, \tag{5.11}$$

where $x_1 + x_2 = 1$.

For the mixture of a quadrupole gas ($\mu_1 = 0$, $\Theta_1 \neq 0$) and a dipole gas ($\mu_2 \neq 0$, $\Theta_2 = 0$), we obtain from (5.10)

$$B_C^{(11)} = \frac{2\pi^2\sigma_1^3 N}{375kT}\,\alpha_1 \delta_{\alpha,1}\,\chi_1 \delta_{\chi,1}\left\{2\delta_{a,1}^2\left[y_1^{-2}H_6(y_1) + \left(1 - \frac{4}{7}\delta_{a,1} + \frac{38}{49}\delta_{a,1}^2\right)H_{12}(y_1) + \ldots\right] + \right.$$

$$\left. + \frac{15\,\Theta_1^2}{7\varepsilon_1\sigma_1^8 y_1^2}\left[a_1 \delta_{a,1}H_8(y_1) + \frac{\Theta_1^2 y_1^2}{6\varepsilon_1 \sigma_1^2}H_{10}(y_1) + \ldots\right]\right\}, \tag{5.12}$$

$$B_C^{(12)} = \frac{\pi^2\sigma_{12}^3 N}{750\,kT}\,(\alpha_1 \delta_{\alpha,1}\chi_2 \delta_{\chi,2} + \chi_1 \delta_{\chi,1}\alpha_2 \delta_{\alpha,2})\left\{4\delta_{a,1}\delta_{a,2}y_{12}^{-2}H_6(y_{12}) + \right.$$

$$+ 4\delta_{a,1}\delta_{a,2}\left[1 - \frac{2}{7}(\delta_{a,1} + \delta_{a,2}) + \frac{38}{49}\delta_{a,1}\delta_{a,2}\right]H_{12}(y_{12}) + \ldots$$

$$\left. + \frac{a_1 \delta_{a,1}\mu_2^2}{\varepsilon_{12}\sigma_{12}^6 y_{12}^2}H_6(y_{12}) + \frac{15\Theta_1^2}{7\varepsilon_{12}\sigma_{12}^8 y_{12}^2}\left(a_2 \delta_{a,2} + \frac{\mu_2^2 y_{12}^2}{12\varepsilon_{12}}\right)H_8(y_{12}) + \ldots\right\}, \tag{5.13}$$

$$B_C^{(22)} = \frac{2\pi^2 \sigma_2^3 N}{375kT}\,\alpha_2 \delta_{\alpha,2}\chi_2 \delta_{\chi,2}\left\{2\delta_{a,2}^2\left[y_2^{-2}H_6(y_2) + \right.\right.$$

$$+ \left(1 - \frac{4}{7}\delta_{a,2} + \frac{38}{49}\delta_{a,2}^2\right)H_{12}(y_2) + \ldots\right] +$$

$$+ \frac{a_2 \delta_{a,2}\mu_2^2}{\varepsilon_2 \sigma_2^6 y_2^2}\left[H_6(y_2) + \frac{\mu_2^4 y_2^4}{196\,\varepsilon_2^2 \sigma_2^6}\left(\frac{7 + 11\delta_{a,2}}{\delta_{a,2}}\right)H_{12}(y_2) + \ldots\right] +$$

$$\left. + \frac{\mu_2^4}{24\varepsilon_2^2 \sigma_2^6}\left[H_6(y_2) + \frac{3\mu_2^4 y_2^4}{196\,\varepsilon_2^2 \sigma_2^6}H_{12}(y_2) + \ldots\right] + \ldots\right\}. \tag{5.14}$$

The above expressions are suitable for direct numerical estimations if we know the molecular parameters appearing therein.

Similarly, one can apply Eq. (5.10) to more complicated gas mixtures.

From the numerical estimations carried out above it follows, first, that whereas the inductive interactions of the molecules play no rôle in some cases (e. g. CO_2), in others

(*e. g.* CHCl$_3$) they may give such great contributions to the constant C_m' that one cannot neglect them in comparison with the contributions resulting from the quadrupole-quadrupole or dipole-dipole interactions. It is obvious that the latter interaction types will prevail if the molecules present a very great dipole or quadrupole moment. It also appears that the nonlinear effect causing hyperpolarizability of dipolar gas molecules exerts an outweighing influence on the constant C_m.

In the case of gases consisting of nonspherical molecules the total numerical value of the second virial coefficient B_C depends in a high degree on the anisotropic dispersive forces.

It thus appears that systematical investigation of magnetic birefringence in imperfect gases, though experimentally difficult, will contribute valuable data relating to the electric and magnetic properties of isolated molecules, the nature and type of the various intermolecular forces, and their rôle in the microscopic mechanism of magnetic birefringence of diamagnetic fluids.

APPENDIX A

Potential energy for the tensorial interaction of polar molecules. The potential energy of interaction between two arbitrary charge distributions (*e. g.* molecules) i and j can be represented by the following expansion:

$$v_{ij} \equiv v_{ji} = e_j \varphi_j - \mu_\sigma^{(j)} F_\sigma^{(j)} - \tfrac{1}{3} \Theta_{\sigma\tau}^{(j)} F_{\sigma\tau}^{(j)} -$$

$$- \tfrac{1}{15} \Omega_{\sigma\tau\nu}^{(j)} F_{\sigma\tau\nu}^{(j)} - \tfrac{1}{105} \Phi_{\sigma\tau\nu\varrho}^{(j)} F_{\sigma\tau\nu\varrho}^{(j)} - \dots, \tag{A. 1}$$

where

$$e_j = \sum_n e_j^{(n)},$$

$$\mu_\sigma^{(j)} = \sum_n e_j^{(n)} r_{j\sigma}^{(n)},$$

$$\Theta_{\sigma\tau}^{(j)} = \tfrac{1}{2} \sum_n e_j^{(n)} (3 r_{j\sigma}^{(n)} r_{j\tau}^{(n)} - r_{jn}^2 \delta_{\sigma\tau}),$$

$$\Omega_{\sigma\tau\nu}^{(j)} = \tfrac{1}{2} \sum_n e_j^{(n)} \{5 r_{j\sigma}^{(n)} r_{j\tau}^{(n)} r_{j\nu}^{(n)} - r_{jn}^2 (r_{j\sigma}^{(n)} \delta_{\tau\nu} + r_{j\tau}^{(n)} \delta_{\nu\sigma} + r_{j\nu}^{(n)} \delta_{\sigma\tau})\},$$

$$\Phi_{\sigma\tau\nu\varrho}^{(j)} = \tfrac{1}{8} \sum_n e_j^{(n)} \{35\, r_{j\sigma}^{(n)} r_{j\tau}^{(n)} r_{j\nu}^{(n)} r_{j\varrho}^{(n)} - 5 r_{jn}^2\, (r_{j\sigma}^{(n)} r_{j\tau}^{(n)} \delta_{\nu\varrho} +$$

$$+ r_{j\tau}^{(n)} r_{j\nu}^{(n)} \delta_{\varrho\sigma} + r_{j\nu}^{(n)} r_{j\varrho}^{(n)} \delta_{\sigma\tau} + r_{j\varrho}^{(n)} r_{j\sigma}^{(n)} \delta_{\tau\nu} + r_{j\sigma}^{(n)} r_{j\nu}^{(n)} \delta_{\tau\varrho} +$$

$$+ r_{j\tau}^{(n)} r_{j\varrho}^{(n)} \delta_{\sigma\nu}) + r_{jn}^4 (\delta_{\sigma\tau} \delta_{\nu\varrho} + \delta_{\sigma\nu} \delta_{\tau\varrho} + \delta_{\sigma\varrho} \delta_{\nu\tau})\}, \dots, \tag{A. 2}$$

denote the electrical multipole moments (unipole, dipole, quadrupole, octopole, hexadecapole, ... 2^n-pole) of the charge distribution j; $e_j^{(n)}$ is the n-th electric charge of the j-th charge distribution and $\boldsymbol{r}_j^{(n)}$ — its radius vector.

The potential and the electric field at the centre of the j-th charge distribution due to the electric charge of the i-th distribution are given by

$$\varphi_j = \frac{e_i}{r_{ij}} + \mu_\sigma^{(i)} T_\sigma^{(ij)} - \frac{1}{3} \Theta_{\sigma\tau}^{(i)} T_{\sigma\tau}^{(ij)} + \frac{1}{15} \Omega_{\sigma\tau\nu}^{(i)} T_{\sigma\tau\nu}^{(ij)} - \frac{1}{105} \Phi_{\sigma\tau\nu\varrho}^{(i)} T_{\sigma\tau\nu\varrho}^{(ij)} + \dots, \tag{A.3}$$

$$F_\sigma^{(j)} = - V_\sigma \varphi_j = T_\sigma^{(ij)} e_i - T_{\sigma\tau}^{(ij)} \mu_\tau^{(i)} + \frac{1}{3} T_{\sigma\tau\nu}^{(ij)} \Theta_{\tau\nu}^{(i)} - \frac{1}{15} T_{\sigma\tau\nu\varrho}^{(ij)} \Omega_{\tau\nu\varrho}^{(i)} + \dots, \tag{A.4}$$

wherein the tensors

$$T_\sigma^{(ij)} = - V_\sigma \left(\frac{1}{r_{ij}} \right) = \frac{r_{ij\sigma}}{r_{ij}^3} = r_{ij}^{-2} \lambda_\sigma,$$

$$T_{\sigma\tau}^{(ij)} = - V_\sigma V_\tau \left(\frac{1}{r_{ij}} \right) = - r_{ij}^{-3} (3\lambda_\sigma \lambda_\tau - \delta_{\sigma\tau}),$$

$$T_{\sigma\tau\nu}^{(ij)} = - V_\sigma V_\tau V_\nu \left(\frac{1}{r_{ij}} \right) = 3 r_{ij}^{-4} \{ 5\lambda_\sigma \lambda_\tau \lambda_\nu - (\lambda_\sigma \delta_{\tau\nu} + \lambda_\tau \delta_{\nu\sigma} + \lambda_\nu \delta_{\sigma\tau}) \},$$

$$T_{\sigma\tau\nu\varrho}^{(ij)} = - V_\sigma V_\tau V_\nu V_\varrho \left(\frac{1}{r_{ij}} \right) = - 3 r_{ij}^{-5} \{ 35 \lambda_\sigma \lambda_\tau \lambda_\nu \lambda_\varrho - 5(\lambda_\sigma \lambda_\tau \delta_{\nu\varrho} + \lambda_\tau \lambda_\nu \delta_{\varrho\sigma} + \lambda_\nu \lambda_\varrho \delta_{\sigma\tau} +$$
$$+ \lambda_\varrho \lambda_\sigma \delta_{\tau\nu} + \lambda_\sigma \lambda_\nu \delta_{\tau\varrho} + \lambda_\tau \lambda_\varrho \delta_{\sigma\nu}) + \delta_{\sigma\tau} \delta_{\nu\varrho} + \delta_{\sigma\nu} \delta_{\tau\varrho} + \delta_{\sigma\varrho} \delta_{\nu\tau} \}, \tag{A.5}$$

characterize respectively the unipole-dipole, dipole-dipole, dipole-quadrupole, quadrupole-quadrupole *etc.* interactions; $\boldsymbol{\lambda} = (\lambda_1, \lambda_2, \lambda_3)$ is the unit vector in the direction of the vector $\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i = \boldsymbol{\lambda} \, r_{ij}$ connecting the centres of the interacting charge distributions, and V_σ is Hamilton's differential operator.

By the expansion of Eq. (A. 3), the electric field gradient, gradient of the field-gradient *etc.* due to the i-th charge distribution at the centre of the j-th charge distribution are

$$F_{\sigma\tau}^{(j)} = - V_\sigma V_\tau \varphi_j = T_{\sigma\tau}^{(ij)} e_i - T_{\sigma\tau\nu}^{(ij)} \mu_\nu^{(i)} + \frac{1}{3} T_{\sigma\tau\nu\varrho}^{(ij)} \Theta_{\nu\varrho}^{(i)} - \dots,$$

$$F_{\sigma\tau\nu}^{(j)} = - V_\sigma V_\tau V_\nu \varphi_j = T_{\sigma\tau\nu}^{(ij)} e_i - T_{\sigma\tau\nu\varrho}^{(ij)} \mu_\varrho^{(i)} + \dots,$$

$$F_{\sigma\tau\nu\varrho}^{(j)} = - V_\sigma V_\tau V_\nu V_\varrho \varphi_j = T_{\sigma\tau\nu\varrho}^{(ij)} e_i - \dots, \dots \tag{A.6}$$

Substituting (A. 3), (A. 4) and (A. 5) in Eq. (A. 1), we obtain the general formula for the tensorial interaction energy of two charge distributions:

$$v_{ij} = \frac{e_i e_j}{r_{ij}} - (e_i \mu_\sigma^{(j)} - \mu_\sigma^{(i)} e_j) T_\sigma^{(ij)} + \mu_\sigma^{(i)} \mu_\tau^{(j)} T_{\sigma\tau}^{(ij)} - \frac{1}{3} (e_i \Theta_{\sigma\tau}^{(j)} + \Theta_{\sigma\tau}^{(i)} e_j) T_{\sigma\tau}^{(ij)} +$$

$$+ \frac{1}{3} (\mu_\sigma^{(i)} \Theta_{\tau\nu}^{(j)} - \Theta_{\sigma\tau}^{(i)} \mu_\nu^{(j)}) T_{\sigma\tau\nu}^{(ij)} - \frac{1}{15} (e_i \Omega_{\sigma\tau\nu}^{(j)} - \Omega_{\sigma\tau\nu}^{(i)} e_j) T_{\sigma\tau\nu}^{(ij)} + \frac{1}{15} (\mu_\sigma^{(i)} \Omega_{\tau\nu\varrho}^{(j)} + \Omega_{\sigma\tau\nu}^{(i)} \mu_\varrho^{(j)}) T_{\sigma\tau\nu\varrho}^{(ij)} -$$

$$- \frac{1}{315} (3 e_i \Phi_{\sigma\tau\nu\varrho}^{(j)} + 35 \Theta_{\sigma\tau}^{(i)} \Theta_{\nu\varrho}^{(j)} + 3 \Phi_{\sigma\tau\nu\varrho}^{(i)} e_j) T_{\sigma\tau\nu\varrho}^{(ij)} + \dots \tag{A.7}$$

For a charge distribution axially symmetric about the 3-axis, each multipole moment is completely specified by a single scalar quantity:

$$\mu \equiv \mu_3, \qquad \Theta \equiv \Theta_{33} = - 2\Theta_{11} = - 2\Theta_{22},$$

$$\Omega \equiv \Omega_{333} = - 2\Omega_{113} = - 2\Omega_{131} = - 2\Omega_{311} = \dots = - 2\Omega_{223},$$

$$\Phi \equiv \Phi_{3333} = - 2\Phi_{1133} = - 2\Phi_{1331} = - 2\Phi_{3311} = \dots = - 2\Phi_{2233} = \frac{8}{3} \Phi_{1111} = \frac{8}{3} \Phi_{2222} = 8\Phi_{1122} =$$

$$= 8\Phi_{1221} = 8\Phi_{2211} = \dots = 8\Phi_{1221}. \tag{A.8}$$

By (A. 8), the multipole moment tensors for axially symmetric systems are:

$$\mu_\sigma^{(i)} = \mu_i s^{(i)},$$

$$\Theta_{\sigma\tau}^{(i)} = \tfrac{1}{2}\,\Theta_i\,(3 s_\sigma^{(i)} s_\tau^{(i)} - \delta_{\sigma\tau}),$$

$$\Omega_{\sigma\tau\nu}^{(i)} = \tfrac{1}{2}\,\Omega_i\,\{5 s_\sigma^{(i)} s_\tau^{(i)} s_\nu^{(i)} - (s_\sigma^{(i)}\,\delta_{\tau\nu} + s_\tau^{(i)}\,\delta_{\nu\sigma} + s_\nu^{(i)}\,\delta_{\sigma\tau})\},$$

$$\Phi_{\sigma\tau\nu\varrho}^{(i)} = \tfrac{1}{8}\,\Phi_i\,\{35 s_\sigma^{(i)} s_\tau^{(i)} s_\nu^{(i)} s_\varrho^{(i)} - 5(s_\sigma^{(i)} s_\tau^{(i)}\,\delta_{\nu\varrho} + s_\tau^{(i)} s_\nu^{(i)}\,\delta_{\varrho\sigma} + s_\nu^{(i)} s_\varrho^{(i)}\,\delta_{\sigma\tau} +$$

$$+ s_\varrho^{(i)} s_\sigma^{(i)}\delta_{\tau\nu} + s_\tau^{(i)} s_\nu^{(i)}\,\delta_{\tau\varrho} + s_\tau^{(i)} s_\varrho^{(i)}\,\delta_{\sigma\nu}) + \delta_{\sigma\tau}\,\delta_{\nu\varrho} + \delta_{\sigma\nu}\,\delta_{\tau\varrho} + \delta_{\sigma\varrho}\,\delta_{\nu\tau}\}, \qquad \text{(A. 9)}$$

where $\boldsymbol{s} = (s_1, s_2, s_3)$ is the unit vector along the axis of symmetry.

Taking into account expressions (A. 5) and (A. 9) and keeping in mind that

$$s_\sigma^{(i)} s_\sigma^{(i)} = s_\tau^{(j)} s_\tau^{(j)} = 1, \quad s_\sigma^{(i)} s_\sigma^{(j)} = \cos\theta_{ij},$$

$$\lambda_\sigma \lambda_\sigma = 1, \quad s_\sigma^{(i)} \lambda_\sigma = \cos\theta_i, \quad s_\tau^{(j)} \lambda_\tau = \cos\theta_j, \qquad \text{(A. 10)}$$

we reduce expression (A. 7) to the form (for comparison, see Margenau 1939, Buckingham 1959)

$$v_{ij} = e_i e_j r_{ij}^{-1} - (e_i \mu_j \cos\theta_j + e_j \mu_i \cos\theta_i)\, r_{ij}^{-2} - \mu_i \mu_j (3\cos\theta_i \cos\theta_j -$$

$$- \cos\theta_{ij})\, r_{ij}^{-3} + \tfrac{1}{2}\{e_i\,\Theta_j\,(3\cos^2\theta_j - 1) + e_j\,\Theta_i\,(3\cos^2\theta_i - 1)\}\, r_{ij}^{-3} +$$

$$+ \tfrac{3}{2}\{\mu_i\,\Theta_j\,(5\cos\theta_i \cos^2\theta_j - 2\cos\theta_{ij} \cos\theta_j - \cos\theta_i) -$$

$$- \mu_j\,\Theta_i\,(5\cos^2\theta_i \cos\theta_j - 2\cos\theta_{ij} \cos\theta_i - \cos\theta_j)\}\, r_{ij}^{-4} -$$

$$- \tfrac{1}{2}\{e_i\,\Omega_j\,(5\cos^2\theta_j - 3)\cos\theta_j + e_j\,\Omega_i\,(5\cos^2\theta_i - 3)\cos\theta_i\}\, r_{ij}^{-4} +$$

$$+ \tfrac{3}{4}\,\Theta_i\,\Theta_j\{1 - 5(\cos^2\theta_i + 3\cos^2\theta_i \cos^2\theta_j + \cos^2\theta_j) + 2(5\cos\theta_i \cos\theta_j -$$

$$- \cos\theta_{ij})^2\}\, r_{ij}^{-5} - \tfrac{1}{2}\{\mu_i\,\Omega_j\,(35\cos\theta_i \cos^3\theta_j - 15\cos\theta_{ij} \cos^2\theta_j -$$

$$- 15\cos\theta_i \cos\theta_j + 3\cos\theta_{ij}) + \mu_j\,\Omega_i\,(35\cos^3\theta_i \cos\theta_j - 15\cos\theta_{ij} \cos^2\theta_i -$$

$$- 15\cos\theta_i \cos\theta_j + 3\cos\theta_{ij})\}\, r_{ij}^{-5} + \tfrac{1}{8}\{e_i\,\Phi_j\,(35\cos^4\theta_j - 30\cos^2\theta_j + 3) +$$

$$+ e_j\,\Phi_i\,(35\cos^4\theta_i - 30\cos^2\theta_i + 3)\}\, r_{ij}^{-5} - \ldots, \qquad \text{(A.11)}$$

where

$$\cos\theta_{ij} = \cos\theta_i \cos\theta_j + \sin\theta_i \sin\theta_j \cos(\varphi_j - \varphi_i), \qquad \text{(A. 12)}$$

and θ_{ij} is the angle between the symmetry axes of the i-th and j-th charge distributions; θ_i and θ_j are the angles between these symmetry axis and the unit vector $\boldsymbol{\lambda}$, while φ_i and φ_j are the azimuth angles.

Generally, one should also consider the additional potential energy arising from the inductive interaction of the charge distributions, $i.\ e.$ from the interactions between the permanent charge distribution of one system and the moments induced in the other system. For anisotropically polarizable systems this is given by

$$v_{ij}^{\text{ind}} = -\tfrac{1}{2}\,(a_{\sigma\tau}^{(i)} F_\sigma^{(i)} F_\tau^{(i)} + a_{\sigma\tau}^{(j)} F_\sigma^{(j)} F_\tau^{(j)}), \qquad \text{(A. 13)}$$

and hence, by (A. 4), we have

$$
\begin{aligned}
v_{ij}^{\text{ind}} = & -\tfrac{1}{2}(a_{\sigma\tau}^{(i)} e_j e_j + a_{\sigma\tau}^{(j)} e_i e_i)\, T_\sigma^{(ij)} T_\tau^{(ij)} + \\
& + (a_{\sigma\tau}^{(i)} e_j \mu_\nu^{(j)} + a_{\sigma\tau}^{(j)} e_i \mu_\nu^{(i)})\, T_\sigma^{(ij)} T_{\tau\nu}^{(ij)} - \\
& - \tfrac{1}{2}(a_{\sigma\tau}^{(i)} \mu_\nu^{(j)} \mu_\varrho^{(j)} + a_{\sigma\tau}^{(j)} \mu_\nu^{(i)} \mu_\varrho^{(i)})\, T_{\sigma\nu}^{(ij)} T_{\tau\varrho}^{(ij)} - \\
& - \tfrac{1}{3}(a_{\sigma\tau}^{(i)} e_j \Theta_{\nu\varrho}^{(j)} + a_{\sigma\tau}^{(j)} e_i \Theta_{\nu\varrho}^{(i)})\, T_\sigma^{(ij)} T_{\tau\nu\varrho}^{(ij)} + \\
& + \tfrac{1}{3}(a_{\sigma\tau}^{(i)} \mu_\nu^{(j)} \Theta_{\varrho\lambda}^{(j)} + a_{\sigma\tau}^{(j)} \mu_\nu^{(i)} \Theta_{\varrho\lambda}^{(i)})\, T_{\sigma\nu}^{(ij)} T_{\tau\varrho\lambda}^{(ij)} + \\
& + \tfrac{1}{15}(a_{\sigma\tau}^{(i)} e_j \Omega_{\nu\varrho\lambda}^{(j)} + a_{\sigma\tau}^{(j)} e_i \Omega_{\nu\varrho\lambda}^{(i)})\, T_\sigma^{(ij)} T_{\tau\nu\varrho\lambda}^{(ij)} - \\
& - \tfrac{1}{15}(a_{\sigma\tau}^{(i)} \mu_\nu^{(j)} \Omega_{\varrho\lambda\mu}^{(j)} + a_{\sigma\tau}^{(j)} \mu_\nu^{(i)} \Omega_{\varrho\lambda\mu}^{(i)})\, T_{\sigma\nu}^{(ij)} T_{\tau\varrho\lambda\mu}^{(ij)} - \\
& - \tfrac{1}{18}(a_{\sigma\tau}^{(i)} \Theta_{\nu\varrho}^{(j)} \Theta_{\lambda\mu}^{(j)} + a_{\sigma\tau}^{(j)} \Theta_{\nu\varrho}^{(i)} \Theta_{\lambda\mu}^{(i)})\, T_{\sigma\nu\varrho}^{(ij)} T_{\tau\lambda\mu}^{(ij)} + \\
& + \tfrac{1}{45}(a_{\sigma\tau}^{(i)} \Theta_{\nu\varrho}^{(j)} \Omega_{\lambda\mu\varphi}^{(j)} + a_{\sigma\tau}^{(j)} \Theta_{\nu\varrho}^{(i)} \Omega_{\lambda\mu\varphi}^{(i)})\, T_{\sigma\nu\varrho}^{(ij)} T_{\tau\lambda\mu\varphi}^{(ij)} - \\
& - \tfrac{1}{450}(a_{\sigma\tau}^{(i)} \Omega_{\nu\varrho\lambda}^{(j)} \Omega_{\mu\varphi\chi}^{(j)} + a_{\sigma\tau}^{(j)} \Omega_{\nu\varrho\lambda}^{(i)} \Omega_{\mu\varphi\chi}^{(i)})\, T_{\sigma\nu\varrho\lambda}^{(ij)} T_{\tau\mu\varphi\chi}^{(ij)} + \ldots
\end{aligned}
\tag{A. 14}
$$

In dealing with axially symmetrical systems, we can express the tensor $a_{\sigma\tau}^{(i)}$ in the following form:

$$
a_{\sigma\tau}^{(i)} = a_i \delta_{\sigma\tau} + a_i \delta_{a,i}(3 s_\sigma^{(i)} s_\tau^{(i)} - \delta_{\sigma\tau}).
\tag{A. 15}
$$

Taking into account this formula and the expressions (A. 5), (A. 9) and (A. 10), we obtain from (A. 14) (the terms with octopole moment have been omitted)

$$
\begin{aligned}
v_{ij}^{\text{ind}} = & -\tfrac{1}{2}\{a_i e_j^2 + e_i^2 a_j + a_i \delta_{a,i} e_j^2 (3\cos^2\theta_i - 1) + a_j \delta_{a,j} e_i^2 (3\cos^2\theta_j - 1)\} r_{ij}^{-4} - \\
& - \{2a_i(1-\delta_{a,i}) e_j \mu_j \cos\theta_j + 2a_j(1-\delta_{a,j}) e_i \mu_i \cos\theta_i + 3(a_i \delta_{a,i} e_j \mu_j \cos\theta_i + \\
& + a_j \delta_{a,j} e_i \mu_i \cos\theta_j)(3\cos\theta_i \cos\theta_j - \cos\theta_{ij})\} r_{ij}^{-5} - \tfrac{1}{2}\{a_i(1-\delta_{a,i}) \mu_j^2 (3\cos^2\theta_j + 1) + \\
& + a_j(1-\delta_{a,j}) \mu_i^2 (3\cos^2\theta_i + 1) + 3(a_i \delta_{a,i} \mu_j^2 + \mu_i^2 a_j \delta_{a,j})(3\cos\theta_i \cos\theta_j - \cos\theta_{ij})^2\} r_{ij}^{-6} - \\
& - \tfrac{3}{2}\{a_i(1-\delta_{a,i}) e_j \Theta_j (3\cos^2\theta_j - 1) + a_j(1-\delta_{a,j}) e_i \Theta_i (3\cos^2\theta_i - 1) + \\
& + 3a_i \delta_{a,i} e_j \Theta_j (5\cos\theta_i \cos^2\theta_j - 2\cos\theta_{ij} \cos\theta_j - \cos\theta_i)\cos\theta_i + \\
& + 3a_j \delta_{a,j} e_i \Theta_i (5\cos^2\theta_i \cos\theta_j - 2\cos\theta_{ij} \cos\theta_i - \cos\theta_j)\cos\theta_j\} r_{ij}^{-6} - \\
& - \tfrac{3}{2}\{4a_i(1-\delta_{a,i}) \mu_j \Theta_j \cos^3\theta_j + 4a_j(1-\delta_{a,j}) \mu_i \Theta_i \cos^3\theta_i + \\
& + 3[a_i \delta_{a,i} \mu_j \Theta_j (5\cos\theta_i \cos^2\theta_j - 2\cos\theta_{ij} \cos\theta_j - \cos\theta_i) + \\
& + a_j \delta_{a,j} \mu_i \Theta_i (5\cos^2\theta_i \cos\theta_j - 2\cos\theta_{ij} \cos\theta_i - \cos\theta_j)](3\cos\theta_i \cos\theta_j - \\
& - \cos\theta_{ij})\} r_{ij}^{-7} - \tfrac{9}{8}\{a_i(1-\delta_{a,i}) \Theta_j^2 (1 - 2\cos^2\theta_j + 5\cos^4\theta_j) + \\
& + a_j(1-\delta_{a,j}) \Theta_i^2 (1 - 2\cos^2\theta_i + 5\cos^4\theta_i) + 3a_i \delta_{a,i} \Theta_j^2 (5\cos\theta_i \cos^2\theta_j - \\
& - 2\cos\theta_{ij} \cos\theta_j - \cos\theta_i)^2 + 3a_j \delta_{a,j} \Theta_i^2 (5\cos^2\theta_i \cos\theta_j - \\
& - 2\cos\theta_{ij} \cos\theta_i - \cos\theta_j)^2\} r_{ij}^{-8} - \ldots
\end{aligned}
\tag{A. 16}
$$

In the first approximation, we can neglect the electric anisotropy of polarizability, $\delta_a = 0$, and Eq. (A. 16) now reduces to the simpler form derived by Hirschfelder, Curtiss and Bird (1954):

$$
\begin{aligned}
v_{ij}^{\text{ind}} = {}& -\tfrac{1}{2}(a_i e_j^2 + e_i^2 a_j)\, r_{ij}^{-4} - \\
& - 2(a_i e_j \mu_j \cos\theta_j + a_j e_i \mu_i \cos\theta_i)\, r_{ij}^{-5} - \\
& - \tfrac{1}{2}\{a_i \mu_j^2 (3\cos^2\theta_j + 1) + a_j \mu_i^2 (3\cos^2\theta_i + 1)\}\, r_{ij}^{-6} - \\
& - \tfrac{3}{2}\{a_i e_j \Theta_j (3\cos^2\theta_j - 1) + a_j e_i \Theta_i (3\cos^2\theta_i - 1)\}\, r_{ij}^{-6} - \\
& - 6(a_i \mu_j \Theta_j \cos^3\theta_j + a_j \mu_i \Theta_i \cos^3\theta_i)\, r_{ij}^{-7} - \\
& - \tfrac{9}{8}\{a_i \Theta_j^2 (1 - 2\cos^2\theta_j + 5\cos^4\theta_j) + \\
& + a_j \Theta_i^2 (1 - 2\cos^2\theta_i + 5\cos^4\theta_i)\}\, r_{ij}^{-8} - \dots
\end{aligned}
\tag{A. 17}
$$

London (1942) obtained the following expression for anisotropic nonpolar molecules with axial symmetry:

$$
\begin{aligned}
u_{ij}^{\text{disp}} = {}& -\{(A - B_1 - B_2 + C)(\cos\theta_{ij} - 3\cos\theta_i \cos\theta_j)^2 + 3(B_1 - C)\cos^2\theta_i + \\
& + 3(B_2 - C)\cos^2\theta_j + B_1 + B_2 + 4C\}\, r_{ij}^{-6},
\end{aligned}
\tag{A. 18}
$$

where

$$
A = \frac{h}{4}\, a_{\parallel}^{(i)} a_{\parallel}^{(j)}\, \frac{\nu_{\parallel}^{(i)} \nu_{\parallel}^{(j)}}{\nu_{\parallel}^{(i)} + \nu_{\parallel}^{(j)}}, \qquad
B_1 = \frac{h}{4}\, a_{\parallel}^{(i)} a_{\perp}^{(j)}\, \frac{\nu_{\parallel}^{(i)} \nu_{\perp}^{(j)}}{\nu_{\parallel}^{(i)} + \nu_{\perp}^{(j)}},
$$

$$
B_2 = \frac{h}{4}\, a_{\perp}^{(i)} a_{\parallel}^{(j)}\, \frac{\nu_{\perp}^{(i)} \nu_{\parallel}^{(j)}}{\nu_{\perp}^{(i)} + \nu_{\parallel}^{(j)}}, \qquad
C = \frac{h}{4}\, a_{\perp}^{(i)} a_{\perp}^{(j)}\, \frac{\nu_{\perp}^{(i)} \nu_{\perp}^{(j)}}{\nu_{\perp}^{(i)} + \nu_{\perp}^{(j)}}.
\tag{A. 19}
$$

Herein, $\nu_{\parallel}^{(i)}$ and $\nu_{\perp}^{(i)}$ denote the frequencies of anisotropic oscillators for vibrations in the directions parallel and perpendicular to the symmetry axis of the i-th molecule; h is the Planck constant.

On taking $\nu_{\parallel} = \nu_{\perp} = \nu$, we can represent Eq. (A. 18) in the following form:

$$
\begin{aligned}
u_{ij}^{\text{disp}} = {}& -\frac{3}{4}\, h\, \frac{\nu_i \nu_j}{\nu_i + \nu_j}\, \frac{a_i a_j}{r_{ij}^6}\, \{2 - \delta_{a,i} - \delta_{a,j} + 3(1 - \delta_{a,j})\, \delta_{a,i} \cos^2\theta_i + \\
& + 3(1 - \delta_{a,i})\, \delta_{a,j} \cos^2\theta_j + 3\delta_{a,i}\, \delta_{a,j} (3\cos\theta_i \cos\theta_j - \cos\theta_{ij})^2\}.
\end{aligned}
\tag{A. 20}
$$

For two like molecules, this expression becomes identical with the one given by De Boer (1942).

On separating the expression (A. 20) into a contribution from central dispersive forces

$$
-\frac{3}{2}\, h\, \frac{\nu_i \nu_j}{\nu_i + \nu_j}\, \frac{a_i a_j}{r_{ij}^6} = -4\varepsilon_{ij} \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6,
\tag{A. 21}
$$

and a contribution from noncentral dispersive interactions

$$
\begin{aligned}
v_{ij}^{\text{disp}} = {}& 2\varepsilon_{ij} \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 \{\delta_{a,i} + \delta_{a,j} - 3(1 - \delta_{a,j})\, \delta_{a,i} \cos^2\theta_i - 3(1 - \delta_{a,i})\, \delta_{a,j} \cos^2\theta_j - \\
& - 3\delta_{a,i}\, \delta_{a,j} (3\cos\theta_i \cos\theta_j - \cos\theta_{ij})^2\},
\end{aligned}
\tag{A. 22}
$$

and on taking into account central repulsive forces, we obtain the total potential

$$u_{ij} = 4\varepsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\} + v_{ij}^{\mathrm{disp}}. \qquad (A.\,23)$$

In the case of molecules of one type, the expressions (A. 22) and (A. 23) become identical with the potential used by Pople (1954) and Buckingham (1955).

In the case of nonpolar molecules of arbitrary symmetry, we obtain instead of (A. 20)

$$u_{ij}^{\mathrm{disp}} = -\frac{h}{4}\frac{\nu_i \nu_j}{\nu_i + \nu_j}\, a_{\sigma\tau}^{(i)} a_{\nu\varrho}^{(j)}\, T_{\sigma\nu}^{(ij)}\, T_{\tau\varrho}^{(ij)}. \qquad (A.\,24)$$

For isotropically polarizable molecules we have $a_{\sigma\tau} = a\,\delta_{\sigma\tau}$; hence, we obtain from (A. 24) London's original expression (1937)

$$u_{ij}^{\mathrm{disp}} = -\frac{h}{4}\frac{\nu_i \nu_j}{\nu_i + \nu_j}\, a_i a_j\, T_{\sigma\tau}^{(ij)}\, T_{\sigma\tau}^{(ij)} = -\frac{3}{2}\,h\,\frac{\nu_i \nu_j}{\nu_i + \nu_j}\,\frac{a_i a_j}{r_{ij}^6}. \qquad (A.25)$$

Obviously one could also obtain (A. 25) by averaging the expression (A. 24) over all possible orientations of the two anisotropic molecules. After subtracting (A. 25) from (A. 24), we obtain the energy resulting from the anisotropy of dispersive forces alone:

$$v_{ij}^{\mathrm{disp}} = -\frac{h}{4}\frac{\nu_i \nu_j}{\nu_i + \nu_j}\, (a_{\sigma\tau}^{(i)} a_{\nu\varrho}^{(j)} - a_i a_j \delta_{\sigma\tau}\delta_{\nu\varrho})\, T_{\sigma\nu}^{(ij)}\, T_{\tau\varrho}^{(ij)}. \qquad (A.\,26)$$

With (A. 21), we can put expression (A. 26) in the following form:

$$v_{ij}^{\mathrm{disp}} = -\frac{2}{3}\frac{\varepsilon_{ij}\sigma_{ij}^{6}}{a_i a_j}\, (a_{\sigma\tau}^{(i)} a_{\nu\varrho}^{(j)} - a_i a_j \delta_{\sigma\tau}\delta_{\nu\varrho})\, T_{\sigma\nu}^{(ij)}\, T_{\tau\varrho}^{(ij)}. \qquad (A.\,27)$$

From this expression and from (A.15), we once more obtain Eq. (A. 22) in the case of axially symmetrical molecules.

APPENDIX B

Method of calculating contributions to B_C resulting from tensorial intermolecular forces. The total potential energy of mutual interaction of two molecules can be represented in the form

$$u_{ij} = u(r_{ij}) + v_{ij}, \qquad (B.\,1)$$

where $u(r_{ij})$ is the central interaction potential energy and v_{ij} is the tensorial interaction energy of molecules discussed in Appendix A. If we consider the energy v_{ij} in Eq. (B. 1) as a perturbation to $u(r_{ij})$, we can rewrite the second virial coefficient $B_C^{(ij)}$ defined by (4.5) as follows:

$$B_C^{(ij)} = \frac{\pi N}{90\,kT}\sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{1}{kT}\right)^n \int J_n^{(ij)}\, e^{-\frac{u(r_{ij})}{kT}}\, d\boldsymbol{r}_{ij}\,, \qquad (B.\,2)$$

where the quantity

$$J_n^{(ij)} = \frac{1}{\Omega^2}\iint \varepsilon_{\sigma\tau\,:\,\sigma'\tau'}\,(\alpha_{\sigma\tau}^{(i)}\chi_{\sigma'\tau'}^{(j)} + \chi_{\sigma\tau}^{(i)}\alpha_{\sigma'\tau'}^{(j)})\, v_{ij}^n\, d\omega_i\, d\omega_j \qquad (B.\,3)$$

determines the successive contributions to $B_C^{(ij)}$ resulting from the tensorial intermolecular forces v_{ij}.

At first we shall show that $J_0^{(ij)} = 0$. On applying transformation formulae analogous to (2.19), we write

$$\frac{1}{\Omega^2} \int\int \alpha_{\sigma\tau}^{(i)} \chi_{\sigma'\tau'}^{(j)} \, d\omega_i \, d\omega_j = \alpha_{\alpha\beta}^{(i)} \chi_{\alpha'\beta'}^{(j)} \, \overline{\omega_{\sigma\alpha}^{(i)} \omega_{\tau\beta}^{(i)}} \, \overline{\omega_{\sigma'\alpha'}^{(j)} \omega_{\tau'\beta'}^{(j)}}. \tag{B. 4}$$

Since

$$\overline{\omega_{\sigma\alpha}^{(i)} \omega_{\tau\beta}^{(i)}} = \frac{1}{\Omega} \int \omega_{\sigma\alpha}^{(i)} \omega_{\tau\beta}^{(i)} \, d\omega_i = \frac{1}{3} \, \delta_{\alpha\beta} \, \delta_{\sigma\tau}, \tag{B. 5}$$

we obtain from (B. 3) for $n = 0$

$$J_0^{(ij)} = \frac{1}{9} \, \varepsilon_{\sigma\tau\,:\,\sigma'\tau'} \, \delta_{\sigma\tau} \, \delta_{\sigma'\tau'} (\alpha_{\alpha\beta}^{(i)} \chi_{\alpha'\beta'}^{(j)} + \chi_{\alpha\beta}^{(i)} \alpha_{\alpha'\beta'}^{(j)}) \, \delta_{\alpha\beta} \, \delta_{\alpha'\beta'}$$

$$= \varepsilon_{\sigma\sigma\,:\,\sigma'\sigma'} (\alpha_i \chi_j + \chi_i \alpha_j) = 0, \quad \text{as} \quad \varepsilon_{\sigma\sigma\,:\,\sigma'\sigma'} = 0, \tag{B. 6}$$

which is just the result we should obtain.

Let us now calculate the quantities $J_1^{(ij)}$, $J_2^{(ij)}$, ..., for the case of nonpolar molecules between which anisotropic dispersive forces act. Taking into account Eq. (A. 26) and the transformation formulae (2.19) we obtain

$$\frac{1}{\Omega^2} \int\int \alpha_{\sigma\tau}^{(i)} \chi_{\sigma'\tau'}^{(j)} v_{ij} \, d\omega_i \, d\omega_j = - \frac{h}{4} \, \frac{\nu_i \nu_j}{\nu_i + \nu_j} \, \{\alpha_{\alpha\beta}^{(i)} a_{\gamma\delta}^{(i)} \chi_{\alpha'\beta'}^{(j)} a_{\gamma'\delta'}^{(j)} \times$$

$$\times \overline{\omega_{\sigma\alpha}^{(i)} \omega_{\tau\beta}^{(i)} \omega_{\nu\gamma}^{(i)} \omega_{\varrho\delta}^{(i)}} \cdot \overline{\omega_{\sigma'\alpha'}^{(j)} \omega_{\tau'\beta'}^{(j)} \omega_{\nu'\gamma'}^{(j)} \omega_{\varrho'\delta'}^{(j)}} - \alpha_{\alpha\beta}^{(i)} a_i \chi_{\alpha'\beta'}^{(j)} a_j \delta_{\nu\varrho} \delta_{\nu'\varrho'} \overline{\omega_{\sigma\alpha}^{(i)} \omega_{\tau\beta}^{(i)}} \, \overline{\omega_{\sigma\alpha}^{(j)} \omega_{\tau\beta}^{(j)}}\} \, T_{\nu\nu'}^{(ij)} T_{\varrho\varrho'}^{(ij)}. \tag{B. 7}$$

We now substitute herein Eq. (B. 5) and the following expression (see Kielich 1961):

$$\overline{\omega_{\sigma\alpha}^{(i)} \omega_{\tau\beta}^{(i)} \omega_{\nu\gamma}^{(i)} \omega_{\varrho\delta}^{(i)}} = \frac{1}{30} \{(4\delta_{\alpha\beta} \delta_{\gamma\delta} - \delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\delta} \delta_{\beta\gamma}) \, \delta_{\sigma\tau} \delta_{\nu\varrho} +$$

$$+ (4\delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\delta} \delta_{\beta\gamma} - \delta_{\alpha\beta} \delta_{\gamma\delta}) \, \delta_{\sigma\nu} \delta_{\tau\varrho} + (4\delta_{\alpha\delta} \delta_{\beta\gamma} - \delta_{\alpha\beta} \delta_{\gamma\delta} - \delta_{\alpha\gamma} \delta_{\beta\delta}) \, \delta_{\sigma\varrho} \delta_{\tau\nu}\}. \tag{B. 8}$$

Hence we obtain:

$$\frac{1}{\Omega^2} \int\int \alpha_{\sigma\tau}^{(i)} \chi_{\sigma'\tau'}^{(j)} v_{ij} \, d\omega_i \, d\omega_j = - \frac{h}{16\,200} \, \frac{\nu_i \nu_j}{\nu_i + \nu_j} \, \{10\alpha_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)} (3\chi_{\gamma\delta}^{(j)} a_{\gamma\delta}^{(j)} -$$

$$- \chi_{\gamma\gamma}^{(j)} a_{\delta\delta}^{(j)}) (3T_{\nu\sigma'}^{(ij)} T_{\nu\tau}^{(ij)} - \delta_{\sigma'\tau'} \, T_{\nu\nu'}^{(ij)} T_{\nu\nu'}^{(ij)}) \, \delta_{\sigma\tau} + 10(3\alpha_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)}) \chi_{\gamma\gamma}^{(j)} a_{\delta\delta}^{(j)} (3T_{\sigma\nu}^{(ij)} T_{\tau\nu'}^{(ij)} -$$

$$- \delta_{\sigma\tau} \, T_{\nu\nu'}^{(ij)} T_{\nu\nu'}^{(ij)}) \, \delta_{\sigma'\tau'} + (3\alpha_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)}) (3\chi_{\gamma\delta}^{(j)} a_{\gamma\delta}^{(j)} - \chi_{\gamma\gamma}^{(j)} a_{\delta\delta}^{(j)}) (9T_{\sigma\sigma'}^{(ij)} T_{\tau\tau'}^{(ij)} +$$

$$+ 9T_{\sigma\tau'}^{(ij)} T_{\sigma'\tau}^{(ij)} - 6\delta_{\sigma'\tau'} \, T_{\sigma\nu}^{(ij)} T_{\tau\nu'}^{(ij)} - 6\delta_{\sigma\tau} \, T_{\sigma'\nu}^{(ij)} T_{\tau'\nu}^{(ij)} + 2\delta_{\sigma\tau} \delta_{\sigma'\tau'} \, T_{\nu\nu'}^{(ij)} T_{\nu\nu'}^{(ij)})\}. \tag{B. 9}$$

With respect to (B. 9), we obtain from (B. 3) for $n = 1$

$$J_1^{(ij)} = - \frac{h}{900} \, \frac{\nu_i \nu_j}{\nu_i + \nu_j} \, \{(3\alpha_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)}) (3\chi_{\gamma\delta}^{(j)} a_{\gamma\delta}^{(j)} - \chi_{\gamma\gamma}^{(j)} a_{\delta\delta}^{(j)}) +$$

$$+ (3\chi_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(i)} - \chi_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)}) (3\alpha_{\gamma\delta}^{(j)} a_{\gamma\delta}^{(j)} - \alpha_{\gamma\gamma}^{(j)} a_{\delta\delta}^{(j)})\} \, T_{\nu\nu'}^{(ij)} T_{\nu\nu'}^{(ij)}. \tag{B. 10}$$

Analogously, we calculate further contributions $J_n^{(ij)}$; the most important of these, $J_2^{(ij)}$, has the following form:

$$J_2^{(ij)} = \frac{h^2}{396\,900} \left(\frac{\nu_i \nu_j}{\nu_i + \nu_j}\right)^2 \{7[2\,(A_\alpha^{(i)} B_\chi^{(j)} + B_\chi^{(i)} A_\alpha^{(j)}) - 7(A_\alpha^{(i)} A_\chi^{(j)} + A_\chi^{(i)} A_\alpha^{(j)}) +$$

$$+ 2(A_\chi^{(i)} B_\alpha^{(j)} + B_\alpha^{(i)} A_\chi^{(j)})](T_{\nu\nu'}^{(ij)} T_{\nu\nu'}^{(ij)} T_{\varrho\varrho'}^{(ij)} T_{\varrho\varrho'}^{(ij)} - 3T_{\nu\nu'}^{(ij)} T_{\nu'\varrho}^{(ij)} T_{\varrho\varrho'}^{(ij)} T_{\varrho'\nu}^{(ij)}) +$$

$$+ (B_\alpha^{(i)} B_\chi^{(j)} + B_\chi^{(i)} B_\alpha^{(j)})\,(72 T_{\nu\nu'}^{(ij)} T_{\nu'\varrho}^{(ij)} T_{\varrho\varrho'}^{(ij)} T_{\varrho'\nu}^{(ij)} - 17 T_{\nu\nu'}^{(ij)} T_{\nu\nu'}^{(ij)} T_{\varrho\varrho'}^{(ij)} T_{\varrho\varrho'}^{(ij)})\}, \tag{B.11}$$

where we have used the notation

$$A_\alpha^{(i)} = (3\alpha_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(i)} - \alpha_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)}) a_{\gamma\gamma}^{(i)}, \qquad A_\chi^{(i)} = (3\chi_{\alpha\beta}^{(i)} a_{\alpha\beta}^{(i)} - \chi_{\alpha\alpha}^{(i)} a_{\beta\beta}^{(i)}) a_{\gamma\gamma}^{(i)},$$

$$B_\alpha^{(i)} = 3(3\alpha_{\alpha\beta}^{(i)} a_{\alpha\gamma}^{(i)} a_{\beta\gamma}^{(i)} - \alpha_{\alpha\alpha}^{(i)} a_{\beta\gamma}^{(i)} a_{\beta\gamma}^{(i)}) - 2A_\alpha^{(i)}, \qquad B_\chi^{(i)} = 3(3\chi_{\alpha\beta}^{(i)} a_{\alpha\gamma}^{(i)} a_{\beta\gamma}^{(i)} - \chi_{\alpha\alpha}^{(i)} a_{\beta\gamma}^{(i)} a_{\beta\gamma}^{(i)}) - 2A_\chi^{(i)}. \tag{B.12}$$

On substituting (B. 6), (B. 10) and (B. 11) into Eq. (B. 2) and on taking into account that, by the definition of Eq. (2.5),

$$T_{\nu\nu'}^{(ij)} T_{\nu\nu'}^{(ij)} = 6r_{ij}^{-6}, \qquad T_{\nu\nu'}^{(ij)} T_{\nu'\varrho}^{(ij)} T_{\varrho\varrho'}^{(ij)} T_{\varrho'\nu}^{(ij)} = 18r_{ij}^{-12}, \tag{B. 13}$$

we finally obtain:

$$B_C^{(ij)} = \frac{\pi h N}{121\,500\,k^2 T^2} \frac{\nu_i \nu_j}{\nu_i + \nu_j} \left\{ \frac{1}{a_i a_j} (A_\alpha^{(i)} A_\chi^{(j)} + A_\chi^{(i)} A_\alpha^{(j)}) \langle r_{ij}^{-6} \rangle + \right.$$

$$+ \frac{3h}{98\,kT} \frac{\nu_i \nu_j}{\nu_i + \nu_j} [49(A_\alpha^{(i)} A_\chi^{(j)} + A_\chi^{(i)} A_\alpha^{(j)}) - 14(A_\alpha^{(i)} B_\chi^{(j)} + B_\chi^{(i)} A_\alpha^{(j)} +$$

$$\left. + A_\chi^{(i)} B_\alpha^{(j)} + B_\alpha^{(i)} A_\chi^{(j)}) + 38(B_\alpha^{(i)} B_\chi^{(j)} + B_\chi^{(i)} B_\alpha^{(j)})] \langle r_{ij}^{-12} \rangle + \ldots \right\}. \tag{B. 14}$$

For axially symmetrical molecules we have, from (B. 12),

$$A_\alpha^{(i)} = 54\alpha_i \delta_{\alpha, i} a_i^2 \delta_{a, i}, \qquad B_\alpha^{(i)} = A_\alpha^{(i)} \delta_{a, i},$$

$$A_\chi^{(i)} = 54\chi_i \delta_{\chi, i} a_i^2 \delta_{a, i}, \qquad B_\chi^{(i)} = A_\chi^{(i)} \delta_{a, i}. \tag{B. 15}$$

With regard to this the expression (B. 14) reduces to the form

$$B_C^{(ij)} = \frac{3\pi h N}{125\,k^2 T^2} \frac{\nu_i \nu_j}{\nu_i + \nu_j}\, a_i \delta_{a, i} a_j \delta_{a, j}(\alpha_i \delta_{\alpha, i}\chi_j \delta_{\chi, j} + \chi_i \delta_{\chi, i} \alpha_j \delta_{\alpha, j}) \left\{ \langle r_{ij}^{-6} \rangle + \right.$$

$$\left. + \frac{3h a_i a_j}{98\,kT} \frac{\nu_i \nu_j}{\nu_i + \nu_j} [49 - 14(\delta_{a, i} + \delta_{a, j}) + 38\delta_{a, i}\delta_{a, j}] \langle r_{ij}^{-12} \rangle + \ldots \right\}. \tag{B.16}$$

For chemically identical molecules we obtain from (B. 14) and (B. 16) the expressions (2.22) and (2.25).

If the molecules possess the axial symmetry, we consider (4.6), and the quantities (B. 3) go over into

$$J_n^{(ij)} = 18(\alpha_i \delta_{\alpha, i} \chi_j \delta_{\chi, j} + \chi_i \delta_{\chi, i} \alpha_j \delta_{\alpha, j})\, Q_n^{(ij)}, \tag{B. 17}$$

where

$$Q_n^{(ij)} = \frac{1}{\Omega^2} \int \int (3\cos^2 \theta_{ij} - 1) \, v_j^{\,n} d\omega_i d\omega_j$$

$$= \frac{1}{16\pi^2} \int_0^\pi \sin \theta_i d\theta_i \int_0^{2\pi} d\varphi_i \int_0^\pi \sin \theta_j d\theta_j \int_0^{2\pi} d\varphi_j (3 \cos^2 \theta_{ij} - 1) \, v_{ij}^n. \qquad (B.18)$$

Let us calculate the quantities $Q_n^{(ij)}$ for polar molecules of different kinds. We take into account the following integrals:

$$\frac{1}{2} \int_0^\pi \cos^n \theta_i \sin \theta_i d\theta_i = \begin{cases} \dfrac{1}{2k+1} & \text{for } n = 2k, \\[2ex] 0 & \text{for } n = 2k+1, \end{cases} \qquad (B.19)$$

$$\frac{1}{2\pi} \int_0^{2\pi} \cos^n \varphi_i d\varphi_i = \begin{cases} \dfrac{(2k-1)!!}{2^k \cdot k!} & \text{for } n = 2k, \\[2ex] 0 & \text{for } n = 2k+1, \end{cases} \qquad (B.20)$$

where $k = 0, 1, 2, 3, \ldots$ Thus we obtain the following non-zero average isotropic values of trigonometrical functions:

$$\overline{\cos^2 \theta_{ij}} = \tfrac{1}{3}, \qquad\qquad \overline{\cos \theta_{ij} \cos \theta_i \cos \theta_j} = \tfrac{1}{9},$$

$$\overline{\cos^4 \theta_{ij}} = \tfrac{1}{5}, \qquad\qquad \overline{\cos \theta_{ij} \cos^3 \theta_i \cos \theta_j} = \tfrac{1}{15},$$

$$\overline{\cos^6 \theta_{ij}} = \tfrac{1}{7}, \qquad\qquad \overline{\cos \theta_{ij} \cos^3 \theta_i \cos^3 \theta_j} = \tfrac{1}{25},$$

$$\overline{\cos^2 \theta_{ij} \cos^2 \theta_i} = \tfrac{1}{9}, \qquad\qquad \overline{\cos \theta_{ij} \cos^5 \theta_i \cos \theta_j} = \tfrac{1}{21},$$

$$\overline{\cos^2 \theta_{ij} \cos^4 \theta_i} = \tfrac{1}{15}, \qquad\qquad \overline{\cos \theta_{ij} \cos^5 \theta_i \cos^3 \theta_j} = \tfrac{1}{35},$$

$$\overline{\cos^4 \theta_{ij} \cos^2 \theta_i} = \tfrac{1}{15}, \qquad\qquad \overline{\cos \theta_{ij} \cos^5 \theta_i \cos^5 \theta_j} = \tfrac{1}{49},$$

$$\overline{\cos^2 \theta_{ij} \cos^2 \theta_i \cos^2 \theta_j} = \tfrac{11}{225}, \qquad\qquad \overline{\cos^3 \theta_{ij} \cos \theta_i \cos \theta_j} = \tfrac{1}{15},$$

$$\overline{\cos^2 \theta_{ij} \cos^4 \theta_i \cos^2 \theta_j} = \tfrac{17}{525}, \qquad\qquad \overline{\cos^3 \theta_{ij} \cos^3 \theta_i \cos \theta_j} = \tfrac{1}{25},$$

$$\overline{\cos^2 \theta_{ij} \cos^4 \theta_i \cos^4 \theta_j} = \tfrac{27}{1225}, \qquad\qquad \overline{\cos^3 \theta_{ij} \cos^3 \theta_i \cos^3 \theta_j} = \tfrac{31}{1225},$$

$$\overline{\cos^4 \theta_{ij} \cos^2 \theta_i \cos^2 \theta_j} = \tfrac{17}{525}, \qquad\qquad \overline{\cos^5 \theta_{ij} \cos \theta_i \cos \theta_j} = \tfrac{1}{21}, \ldots \qquad (B.\,21)$$

On taking the sum of the expressions (A.11) and (A. 16) for the energy v_{ij}, and by Eq. (B. 21), we obtain

$$\overline{v_{ij}} = - (a_i \mu_j^2 + \mu_i^2 a_j) r_{ij}^{-6} - \tfrac{3}{2} (a_i \Theta_j^2 + \Theta_i^2 a_j) r_{ij}^{-8},$$

$$\overline{v_{ij}^2} = \tfrac{2}{3} \mu_i^2 \mu_j^2 r_{ij}^{-6} + (\mu_i^2 \Theta_j^2 + \Theta_i^2 \mu_j^2) r_{ij}^{-8} + \tfrac{14}{5} \Theta_i^2 \Theta_j^2 r_{ij}^{-10},$$

$$\overline{v_{ij}^3} = \tfrac{24}{5} \mu_i^2 \mu_j^2 \Theta_i \Theta_j r_{ij}^{-11} - \tfrac{12}{25} \mu_i^2 \mu_j^2 \{5(a_i \mu_j^2 + \mu_i^2 a_j) +$$

$$+ 4(a_i \delta_{a,i} \mu_j^2 + \mu_i^2 a_j \delta_{a,j})\} r_{ij}^{-12},$$

$$\overline{v_{ij}^4} = \tfrac{24}{25} \mu_i^4 \mu_j^4 r_{ij}^{-12} + \ldots, \qquad (B.\,22)$$

$$\overline{\cos^2\theta_{ij}v_{ij}} = -\tfrac{1}{75}\{25(a_i\mu_j^2 + \mu_i^2 a_j) + 16(a_i\delta_{a,i}\mu_j^2 + \mu_i^2 a_j\delta_{a,j})\}r_{ij}^{-6} -$$
$$-\tfrac{1}{70}\{35(a_i\Theta_j^2 + \Theta_i^2 a_j) + 4(a_i\delta_{a,i}\Theta_j^2 + \Theta_i^2 a_j\delta_{a,j})\}r_{ij}^{-8},$$

$$\overline{\cos^2\theta_{ij}v_{ij}^2} = \tfrac{6}{25}\mu_i^2\mu_j^2 r_{ij}^{-6} + \tfrac{13}{35}(\mu_i^2\Theta_j^2 + \Theta_i^2\mu_j^2)r_{ij}^{-8} + \tfrac{38}{35}\Theta_i^2\Theta_j^2 r_{ij}^{-10},$$

$$\overline{\cos^2\theta_{ij}v_{ij}^3} = \frac{72}{35}\mu_i^2\mu_j^2\Theta_i\Theta_j r_{ij}^{-11} - \frac{12\mu_i^2\mu_j^2}{1225}\{91(a_i\mu_j^2 + \mu_i^2 a_j) +$$
$$+ 80(a_i\delta_{a,i}\mu_j^2 + \mu_i^2 a_j\delta_{a,j})\}r_{ij}^{-12},$$

$$\overline{\cos^2\theta_{ij}v_{ij}^4} = \tfrac{456}{1225}\mu_i^4\mu_j^4 r_{ij}^{-12} + \dots, \dots \tag{B. 23}$$

With Eqs. (B. 22) and (B. 23), we obtain from (B. 18)

$$Q_1^{(ij)} = -\tfrac{2}{25}(a_i\delta_{a,i}\mu_j^2 + \mu_i^2 a_j\delta_{a,j})r_{ij}^{-6} - \tfrac{6}{35}(a_i\delta_{a,i}\Theta_j^2 + \Theta_i^2 a_j\delta_{a,j})r_{ij}^{-8},$$

$$Q_2^{(ij)} = \tfrac{4}{75}\mu_i^2\mu_j^2 r_{ij}^{-6} + \tfrac{4}{35}(\mu_i^2\Theta_j^2 + \Theta_i^2\mu_j^2)r_{ij}^{-8} + \tfrac{16}{35}\Theta_i^2\Theta_j^2 r_{ij}^{-10},$$

$$Q_3^{(ij)} = \tfrac{48}{35}\mu_i^2\mu_j^2\Theta_i\Theta_j r_{ij}^{-11} - \tfrac{48}{1225}\mu_i^2\mu_j^2\{7(a_i\mu_j^2 + \mu_i^2 a_j) +$$
$$+ 11(a_i\delta_{a,i}\mu_j^2 + \mu_i^2 a_j\delta_{a,j})\}r_{ij}^{-12},$$

$$Q_4^{(ij)} = \tfrac{192}{1225}\mu_i^4\mu_j^4 r_{ij}^{-12}, \dots \tag{B. 24}$$

On substituting these expressions into (B. 17) and (B. 2), we obtain the second virial coefficient $B_C^{(ij)}$ defined by Eq. (4.9).

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