

## MOLECULAR REFRACTION OF DENSE MIXTURES

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### Synopsis

A statistical theory of the molecular refraction  $R_m$  of dense mixtures is proposed.  $R_m$  is a strictly additive quantity only in the case of a mixture of perfect gases. In dense mixtures (imperfect gases or liquids), as a result of correlations between the molecules of a single component and between those of various components, the molecular refraction  $R_m$  does not satisfy the rule of additivity. Deviations from this rule are discussed for non-dipolar mixtures composed of isotropic or of anisotropic polarizable molecules, and also for dipolar mixtures consisting of molecules generally assumed to be hyperpolarizable in the dipole field of the other molecules of the mixture. The theory is applied to the case of two component mixtures.

§ 1. *Introduction.* The theory of the molecular refraction of dense mixtures is developed on the bases of the statistical theory of molecular polarization of non-dipolar fluids initiated by Kirkwood<sup>1</sup>). The theory of Kirkwood was discussed and modified by Brown<sup>2</sup>), De Boer *e.a.*<sup>3</sup>), and others\*). For simplicity, we shall not consider here the effect of molecular interaction on the polarizability of the molecules as discussed by Jansen and Mazur<sup>4</sup>) and by Mazur and Mandel<sup>5</sup>).

We consider a large spherical specimen of volume  $V$  (the molar volume), in a vacuum, containing  $N = \sum_i N_i$  unlike molecules;  $N_i$  is the number of molecules of species  $i$  and the summation extends over all the components of the system. The classical theory yields for the molecular refraction (or Lorentz-Lorenz function)

$$R_m = \frac{n^2 - 1}{n^2 + 2} V, \quad (1)$$

the following general expression:

$$R_m = \frac{4\pi}{9} \sum_i \left\langle \sum_{p=1}^{N_i} \frac{\partial m_\alpha^{(p,i)}}{\partial E_\alpha} \right\rangle, \quad (2)$$

where  $m_\alpha^{(p,i)}$  is the  $\alpha$ -component of the dipole moment induced by the total electric field of the light wave in the  $p$ -th molecule of species  $i$ . The brackets

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\*) The original of Yvon's paper (1937) is not available to us in Poznań.

$\langle \rangle$  symbolize the statistical average in the absence of an external electric field ( $E = 0$ ):

$$\langle \Phi \rangle = \frac{\int \Phi(\tau) e^{-\frac{U(\tau)}{kT}} d\tau}{\int e^{-\frac{U(\tau)}{kT}} d\tau}; \quad (3)$$

$U(\tau)$  is the total potential energy of the system when its molecules are in the configuration  $\tau$ . In the classical treatment, the configurational variables  $\tau = (\mathbf{r}, \omega)$  are continuous and account for the positions ( $\mathbf{r}$ ) and orientations ( $\omega$ ) of all molecules in the system.

In a preceding paper<sup>6</sup>) the general equation (2) was discussed for quadrupolar and dipolar liquid mixtures on the basis of Onsager's model<sup>7</sup>).

In the present paper it will be shown that the molecular refraction of a multi-component system can be represented in the form

$$R_m = \sum_i x_i R_m^{(i)} + \sum_{ij} x_i x_j R_m^{(ij)} + \sum_{ijk} x_i x_j x_k R_m^{(ijk)} + \dots, \quad (4)$$

where  $x_i = N_i/N$  is the mole fraction of the  $i$ -th component of the mixture. The first term in (4) expressing additivity of  $R_m$  was already derived by Lorentz<sup>8</sup>). The second, third and further terms define deviations from the rule of additivity of  $R_m$  resulting from interaction both between molecules of the same species and between those of the various components in condensed systems. In the subsequent sections, the quantities  $R_m^{(ij)}$  and  $R_m^{(ijk)}$  will be discussed for interacting anisotropic non-dipolar and dipolar unlike molecules.

§ 2. *Systems of non-dipolar molecules.* The dipole moment induced in the  $p$ -th anisotropic molecule of species  $i$  is given by

$$m_\alpha^{(p,i)} = \alpha_{\alpha\beta}^{(p,i)} (E_\beta + F_\beta^{(p,i)}), \quad \alpha, \beta = 1, 2, 3, \quad (5)$$

where  $\alpha_{\alpha\beta}^{(p,i)}$  is the optical polarizability tensor of the  $p$ -th isolated molecule of species  $i$  and  $F_\beta^{(p,i)}$  the electric field at its center due to the induced dipoles of all the other molecules of the system, in the presence of the external electric field  $E$ . The molecular field  $F_\alpha^{(p,i)}$  is given as follows

$$F_\alpha^{(p,i)} = - \sum_{j \substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} m_\beta^{(q,j)}, \quad (6)$$

wherein

$$T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5} (3r_{pq\alpha} r_{pq\beta} - r_{pq}^2 \delta_{\alpha\beta}) \quad (7)$$

is the tensor of dipole-dipole interaction;  $\mathbf{r}_{pq} = \mathbf{r}_q - \mathbf{r}_p$  is the vector connecting the centers of molecules  $p$  and  $q$  ( $\mathbf{r}_p$  and  $\mathbf{r}_q$  being their position vectors), and  $\delta_{\alpha\beta}$  is the substitution tensor (unity if  $\alpha = \beta$  and zero when  $\alpha \neq \beta$ ).

From eqs. (5) and (6) we obtain in good approximation (for comparison see refs. 1 and 9):

$$m_{\alpha}^{(p,i)} = \alpha_{\alpha\beta}^{(p,i)} E_{\beta} - \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\delta}^{(q,j)} E_{\delta} e^{i\mathbf{k} \cdot \mathbf{r}_{pq}} + \\ + \sum_{jk} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{s=1 \\ s \neq q}}^{N_k} \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\delta}^{(q,j)} T_{\delta\epsilon}^{(qs)} \alpha_{\epsilon\eta}^{(s,k)} E_{\eta} e^{i\mathbf{k} \cdot \mathbf{r}_{ps}} - \dots, \quad (8)$$

where  $\mathbf{k}$  is the wave vector of the incident light.

With respect to the foregoing expression the following result is obtained from the general equation (2):

$$R_m = \frac{4\pi}{9} \left\{ \sum_i \langle \sum_{p=1}^{N_i} \alpha_{\alpha\alpha}^{(p,i)} \rangle - \sum_{ij} \langle \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\alpha}^{(q,j)} e^{i\mathbf{k} \cdot \mathbf{r}_{pq}} \rangle + \right. \\ \left. + \sum_{ijk} \langle \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{s=1 \\ s \neq q}}^{N_k} \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\delta}^{(q,j)} T_{\delta\epsilon}^{(qs)} \alpha_{\epsilon\alpha}^{(s,k)} e^{i\mathbf{k} \cdot \mathbf{r}_{ps}} \rangle - \dots \right\}. \quad (9)$$

Assuming that the wave length is large with respect to the intermolecular distance and using the method of classical statistical mechanics, we can represent the successive terms of eq. (9) as follows:

$$\sum_i \langle \sum_{p=1}^{N_i} \alpha_{\alpha\alpha}^{(p,i)} \rangle = \rho \sum_i x_i \int \alpha_{\alpha\alpha}^{(p,i)} g_i^{(1)}(\tau_p) d\tau_p, \\ \sum_{ij} \langle \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\alpha}^{(q,j)} \rangle = \rho^2 \sum_{ij} x_i x_j \iint \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\alpha}^{(q,j)} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \\ \sum_{ijk} \langle \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{s=1 \\ s \neq q}}^{N_k} \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\delta}^{(q,j)} T_{\delta\epsilon}^{(qs)} \alpha_{\epsilon\alpha}^{(s,k)} \rangle = \\ = \rho^2 \sum_{ij} x_i x_j \iint \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\delta}^{(q,j)} T_{\delta\epsilon}^{(pq)} \alpha_{\epsilon\alpha}^{(p,i)} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q + \\ + \rho^3 \sum_{ijk} x_i x_j x_k \iiint \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\delta}^{(q,j)} T_{\delta\epsilon}^{(qs)} \alpha_{\epsilon\alpha}^{(s,k)} g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_s) d\tau_p d\tau_q d\tau_s, \dots, \quad (10)$$

where  $\rho = N/V$  is the number density of molecules of the medium. In the foregoing expressions  $g_i^{(1)}$  is the ordinary correlation function for the molecules of species  $i$ ,  $g_{ij}^{(2)}$  is the binary correlation function for pairs of molecules of species  $i$  and  $j$ ,  $g_{ijk}^{(3)}$  is the ternary correlation function for triples of molecules of species  $i$ ,  $j$  and  $k$ , etc. The configurational variable  $\tau_p$  consists of the variables  $\mathbf{r}_p$  and  $\omega_p$  determining the position and orientation of the  $p$ -th molecule, respectively. Thus

$$\int d\tau_p = \int_V d\mathbf{r}_p \int_{\Omega} d\omega_p = V\Omega$$

is an integral over all configurations of the  $p$ -th molecule.

By expressions (10) we can represent eq. (9) in the form of (4), where  $R_m^{(i)}$ ,  $R_m^{(ij)}$  and  $R_m^{(ijk)}$  are given as follows:

$$R_m^{(i)} = \frac{4\pi}{9} \rho \int \alpha_{\alpha\alpha}^{(p,i)} g_i^{(1)}(\tau_p) d\tau_p, \tag{11}$$

$$R_m^{(ij)} = \frac{4\pi}{9} \rho^2 \iint \left\{ -\alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\alpha}^{(q,j)} + \frac{1}{2} (\alpha_{\alpha\beta}^{(p,i)} \alpha_{\gamma\delta}^{(q,j)} \alpha_{\epsilon\alpha}^{(p,i)} + \alpha_{\alpha\beta}^{(q,j)} \alpha_{\gamma\delta}^{(p,i)} \alpha_{\epsilon\alpha}^{(q,j)}) T_{\beta\gamma}^{(pq)} T_{\delta\epsilon}^{(pq)} + \dots \right\} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \tag{12}$$

$$R_m^{(ijk)} = \frac{4\pi}{9} \rho^3 \iiint \alpha_{\alpha\beta}^{(p,i)} T_{\beta\gamma}^{(pq)} \alpha_{\gamma\delta}^{(q,j)} T_{\delta\epsilon}^{(qs)} \alpha_{\epsilon\alpha}^{(s,k)} g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_s) d\tau_p d\tau_q d\tau_s + \dots \tag{13}$$

§ 3. *Special cases.* If the system presents no molecular interaction, we have

$$\Omega g_i^{(1)} = \Omega^2 g_{ij}^{(2)} = \Omega^3 g_{ijk}^{(3)} = \dots = 1,$$

hence  $R_m^{(ij)} = R_m^{(ijk)} = \dots = 0$ ; and eq. (4) becomes the well-known Lorentz result<sup>8)</sup>,

$$R_m = \sum_i x_i R_m^{(i)} \tag{14}$$

expressing additivity of the molecular refraction

$$R_m^{(i)} = \frac{4\pi}{3} N \alpha_i \tag{15}$$

of the individual components, whose molecules possess the scalar and constant polarizability  $\alpha_i = \frac{1}{3} \alpha_{\alpha\alpha}^{(i)}$ .

For isotropically polarizable molecules,  $\alpha_{\alpha\beta}^{(p,i)} = \alpha_i \delta_{\alpha\beta}$ , eqs. (12) and (13) reduce to

$$R_m^{(ij)} = \frac{4\pi}{3} \alpha_i \alpha_j (\alpha_i + \alpha_j) \rho^2 \iint r_{pq}^{-6} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q + \dots, \tag{16}$$

$$R_m^{(ijk)} = \frac{4\pi}{3} \alpha_i \alpha_j \alpha_k \rho^3 \iiint \{ 3(\mathbf{r}_{pq} \cdot \mathbf{r}_{qs})^2 - r_{pq}^2 r_{qs}^2 \} \times r_{pq}^{-5} r_{qs}^{-5} g_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_s) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_s + \dots \tag{17}$$

Restricting ourselves to pairwise correlations, we obtain from the foregoing expressions

$$R_m^{(ij)} = \frac{4\pi}{3} N \alpha_i \alpha_j (\alpha_i + \alpha_j) \rho \int r_{pq}^{-6} g_{ij}(\mathbf{r}_{pq}) d\mathbf{r}_{pq}, \tag{18}$$

where  $g_{ij}(\mathbf{r}_{pq})$  is the well-known radial correlation function.

In the case of one-component systems, the expressions (16)–(18) are identical with the one derived by De Boer *e.a.*<sup>3)</sup> for the molecular polarization of compressed non-polar gases.

If the molecules possess the axial symmetry (the axis of symmetry being the 3-axis), we can express the polarizability tensor  $\alpha_{\alpha\beta}^{(p,i)}$  as follows

$$\alpha_{\alpha\beta}^{(p,i)} = \alpha_i \delta_{\alpha\beta} + \alpha_i \kappa_i (3s_\alpha^{(p)} s_\beta^{(p)} - \delta_{\alpha\beta}), \quad (19)$$

wherein the quantities

$$\kappa_i = \frac{\alpha_{33}^{(i)} - \alpha_{11}^{(i)}}{3\alpha_i}$$

define the anisotropy of polarizability of the molecules of species  $i$ , and  $\mathbf{s}^{(p)} = (s_1^{(p)}, s_2^{(p)}, s_3^{(p)})$  is a unit vector along the axis of symmetry of the  $p$ -th molecule.

By (19), eq. (12) can be written in the form:

$$\begin{aligned} R_m^{(ij)} = & \frac{4\pi}{3} \alpha_i \alpha_j \rho^2 \iint \{ [\kappa_i (1 - \kappa_j) (3 \cos^2 \theta_p - 1) + \\ & + 3\kappa_i \kappa_j (3 \cos \theta_p \cos \theta_q - \cos \theta_{pq}) \cos \theta_{pq} + \kappa_j (1 - \kappa_i) (3 \cos^2 \theta_q - 1)] r_{pq}^{-3} + \\ & + \frac{1}{2} [2(\alpha_i + \alpha_j - \alpha_i \kappa_i - \alpha_j \kappa_j) (1 - \kappa_i) (1 - \kappa_j) + \\ & + \kappa_i (1 - \kappa_j) (2\alpha_i + \alpha_j + \alpha_i \kappa_i - \alpha_j \kappa_j) (3 \cos^2 \theta_p + 1) + \\ & + 3\kappa_i \kappa_j (2\alpha_i + 2\alpha_j + \alpha_i \kappa_i + \alpha_j \kappa_j) (3 \cos \theta_p \cos \theta_q - \cos \theta_{pq})^2 + \\ & + \kappa_j (1 - \kappa_i) (2\alpha_j + \alpha_i + \alpha_j \kappa_j - \alpha_i \kappa_i) (3 \cos^2 \theta_q + 1)] r_{pq}^{-6} + \dots \} \cdot \\ & \cdot g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (20) \end{aligned}$$

where

$$s_\alpha^{(p)} s_\alpha^{(q)} = \cos \theta_{pq} = \cos \theta_p \cos \theta_q + \sin \theta_p \sin \theta_q \cos(\varphi_q - \varphi_p),$$

and  $\theta_{pq}$  is the angle between the symmetry axes of molecules  $p$  and  $q$ ,  $\theta_p$  and  $\theta_q$  are the angles formed by the respective axis and the vector  $\mathbf{r}_{pq}$ , while  $\varphi_p$  and  $\varphi_q$  are the azimuthal angles.

If, in particular, the correlation function  $g_{ij}^{(2)}$  is independent of orientation, we obtain from (20), by averaging over all possible orientations of the molecules:

$$R_m^{(ij)} = \frac{4\pi}{3} N \rho \alpha_i \alpha_j \{ \alpha_i (1 + 2\kappa_i^2) + \alpha_j (1 + 2\kappa_j^2) \} \int r_{pq}^{-6} g_{ij}(\mathbf{r}_{pq}) d\mathbf{r}_{pq}. \quad (21)$$

For molecules of one kind ( $\alpha_i = \alpha_j = \alpha$ ) this expression becomes identical with the one derived by Mazur and Postma<sup>10</sup>.

§ 4. *Systems of dipolar molecules.* In certain cases, eqs. (9), (12), (13) or (20) can also be applied to multi-component systems consisting of anisotropic molecules with permanent dipole moments. However, in dipolar systems whose molecules possess large dipolar moments, a strong molecular electric field  $\mathbf{F}_0$  generally exists, which causes a direct (nonlinear) deformation of the molecules. In this case, instead of (5), we have the following expansion:

$$m_\alpha^{(p,i)} = \{ \alpha_{\alpha\beta}^{(p,i)} + \beta_{\alpha\beta:\gamma}^{(p,i)} F_{0\gamma}^{(p,i)} + \frac{1}{2} \gamma_{\alpha\beta:\gamma\delta}^{(p,i)} F_{0\gamma}^{(p,i)} F_{0\delta}^{(p,i)} + \dots \} \{ E_\beta + F_\beta^{(p,i)} \}, \quad (22)$$

where  $\beta_{\alpha\beta:\gamma}^{(p,i)}$  and  $\gamma_{\alpha\beta:\gamma\delta}^{(p,i)}$  are the deformability or hyperpolarizability tensors of the  $p$ -th isolated molecule of species  $i$ .

The molecular electric field  $F_{0\alpha}^{(p,i)}$ , existing at the centre of the  $p$ -th molecule of species  $i$  when an external electric field  $E$  is absent, is given in the first approximation as follows:

$$F_{0\alpha}^{(p,i)} = - \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} T_{\alpha\beta}^{(pq)} \mu_{\beta}^{(q,j)} + \dots, \quad (23)$$

where  $\mu_{\beta}^{(q,j)}$  is the  $\beta$ -component of the permanent dipole moment of the  $q$ -th molecule of species  $j$ .

By (22) and (23), the total polarizability tensor of the  $p$ -th molecule of species  $i$  is given by (terms of order  $\alpha\beta$  and  $\alpha\gamma$  are omitted):

$$\begin{aligned} \frac{\partial m_{\alpha}^{(p,i)}}{\partial E_{\chi}} &= \alpha_{\alpha\chi}^{(p,i)} + \alpha_{\alpha\beta}^{(p,i)} \frac{\partial F_{\beta}^{(p,i)}}{\partial E_{\chi}} - \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \beta_{\alpha\chi:\gamma}^{(p,i)} T_{\gamma\delta}^{(pq)} \mu_{\delta}^{(q,j)} + \\ &+ \frac{1}{2} \sum_{\substack{j,k \\ q \neq p}}^{N_j} \sum_{\substack{s=1 \\ s \neq p}}^{N_k} \gamma_{\alpha\chi:\gamma\delta}^{(p,i)} T_{\gamma\epsilon}^{(pq)} \mu_{\epsilon}^{(q,j)} T_{\delta\eta}^{(ps)} \mu_{\eta}^{(s,k)} + \dots \end{aligned} \quad (24)$$

With the help of (2) and (24) the quantities  $R_m^{(ij)}$  can now be written as

$$\begin{aligned} R_m^{(ij)} &= \frac{4\pi}{9} \rho^2 \iint \left\{ - (\alpha_{\alpha\beta}^{(p,i)} \alpha_{\gamma\alpha}^{(q,j)} + \frac{1}{2} \beta_{\alpha\alpha:\beta}^{(p,i)} \mu_{\gamma}^{(q,j)} + \right. \\ &+ \frac{1}{2} \beta_{\alpha\alpha:\beta}^{(q,j)} \mu_{\gamma}^{(p,i)}) T_{\beta\gamma}^{(pq)} + \frac{1}{2} (\alpha_{\alpha\beta}^{(p,i)} \alpha_{\gamma\delta}^{(q,j)} \alpha_{\epsilon\alpha}^{(p,i)} + \\ &+ \alpha_{\alpha\beta}^{(q,j)} \alpha_{\gamma\delta}^{(p,i)} \alpha_{\epsilon\alpha}^{(q,j)} + \frac{1}{2} \gamma_{\alpha\alpha:\beta\delta}^{(p,i)} \mu_{\epsilon}^{(q,j)} \mu_{\epsilon}^{(p,i)} + \\ &+ \left. \frac{1}{2} \gamma_{\alpha\alpha:\beta\delta}^{(q,j)} \mu_{\gamma}^{(p,i)} \mu_{\epsilon}^{(p,i)}) T_{\beta\gamma}^{(pq)} T_{\delta\epsilon}^{(pq)} + \dots \right\} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q. \end{aligned} \quad (25)$$

In the first approximation, the anisotropy of polarizability and hyperpolarizability of the molecules can be neglected, and the foregoing expressions yield:

$$\begin{aligned} R_m^{(ij)} &= \frac{4\pi}{3} \rho^2 \iint \left\{ \alpha_i \alpha_j (\alpha_i + \alpha_j) r_{pq}^{-6} + \right. \\ &+ \frac{1}{2} (\beta_i \mu_j + \mu_i \beta_j) (3 \cos \theta_p \cos \theta_q - \cos \theta_{pq}) r_{pq}^{-3} + \\ &+ \left. \frac{5}{8} [\gamma_i \mu_j^2 (3 \cos^2 \theta_q + 1) + \gamma_j \mu_i^2 (3 \cos^2 \theta_p + 1)] r_{pq}^{-6} + \dots \right\} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \end{aligned} \quad (26)$$

where  $\beta_i$  and  $\gamma_i$  are the scalar hyperpolarizabilities of the isolated molecule of species  $i$ .

§ 5. *Imperfect gas mixtures.* In the case of moderately compressed gases, classical statistics yields for the pair correlation function<sup>3)</sup>

$$\Omega^2 g_{ij}^{(2)}(\tau_p, \tau_q) = e^{-\frac{u_{ij}(\tau_{pq}, \omega_p, \omega_q)}{kT}} \{1 + O(\rho)\}, \quad (27)$$

where  $u_{ij}$  is the total interaction potential energy of a pair of molecules of species  $i$  and  $j$ .

With the help of this expression the quantity  $R_m^{(ij)}$  can be written as

$$R_m^{(ij)} = \rho \{B_R^{(ij)} + O(\rho)\}, \quad (28)$$

where  $B_R^{(ij)}$  is the second refractivity virial coefficient for two molecules of species  $i$  and  $j$ .

For anisotropic molecules with permanent dipole moments and hyperpolarizabilities we obtain by (25) and (27):

$$\begin{aligned} B_R^{(ij)} = & \frac{4\pi N}{9Q^2} \iint \{ -(\alpha_{\alpha\beta}^{(p,i)} \alpha_{\gamma\alpha}^{(q,j)} + \frac{1}{2} \beta_{\alpha\alpha:\beta\delta}^{(p,i)} \mu_\gamma^{(q,j)} + \\ & + \frac{1}{2} \beta_{\alpha\alpha:\beta\delta}^{(q,j)} \mu_\gamma^{(p,i)}) T_{\beta\gamma}^{(pq)} + \frac{1}{2} (\alpha_{\alpha\beta}^{(p,i)} \alpha_{\gamma\delta}^{(q,j)} \alpha_{\varepsilon\alpha}^{(p,i)} + \\ & + \alpha_{\alpha\beta}^{(q,j)} \alpha_{\gamma\delta}^{(p,i)} \alpha_{\varepsilon\alpha}^{(q,j)} + \frac{1}{2} \gamma_{\alpha\alpha:\beta\delta}^{(p,i)} \mu_\gamma^{(q,j)} \mu_\varepsilon^{(q,j)} + \\ & + \frac{1}{2} \gamma_{\alpha\alpha:\beta\delta}^{(q,j)} \mu_\gamma^{(p,i)} \mu_\varepsilon^{(p,i)}) T_{\beta\gamma}^{(pq)} T_{\delta\varepsilon}^{(pq)} + \dots \} e^{-\frac{u_{ij}(\mathbf{r}_{pq}, \omega_p, \omega_q)}{kT}} d\mathbf{r}_{pq} d\omega_p d\omega_q. \end{aligned} \quad (29)$$

The foregoing expression for  $B_R^{(ij)}$  can be calculated in general for various molecular models by the method used in the previous papers<sup>11</sup>). For unlike molecules possessing the axial symmetry these calculations of  $B_R^{(ij)}$  are performed in ref. 12.

§ 6. *Applications to two-component systems.* In the case of a two component system, eq. (4) assumes the form

$$R_m = x_1 R_m^{(1)} + x_2 R_m^{(2)} + x_1^2 R_m^{(11)} + 2x_1 x_2 R_m^{(12)} + x_2^2 R_m^{(22)} + \dots \quad (30)$$

If, in particular, the molecules of component 1 of the mixture are spherical and those of component 2 non-dipolar presenting the axial symmetry, we obtain by expressions (15), (18) and (20):

$$R_m^{(1)} = \frac{4\pi}{3} N \alpha_1, \quad R_m^{(2)} = \frac{4\pi}{3} N \alpha_2, \quad (31)$$

$$R_m^{(11)} = \frac{8\pi}{3} N \alpha_1^3 \rho \int r_{pq}^{-6} g_{11}^{(2)}(\mathbf{r}_{pq}) d\mathbf{r}_{pq}, \quad (32)$$

$$\begin{aligned} R_m^{(12)} = & \frac{4\pi}{3} \alpha_1 \alpha_2 \rho^2 \iint \{ \kappa_2 (3 \cos^2 \theta_q - 1) r_{pq}^{-3} + \\ & + \frac{1}{2} [2(\alpha_1 + \alpha_2 - \alpha_2 \kappa_2)(1 - \kappa_2) + \kappa_2(\alpha_1 + 2\alpha_2 + \alpha_2 \kappa_2)] \times \\ & \times (3 \cos^2 \theta_q + 1) \} r_{pq}^{-6} + \dots \} g_{12}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \end{aligned} \quad (33)$$

$$\begin{aligned} R_m^{(22)} = & \frac{4\pi}{3} \alpha_2^2 \rho^2 \iint \{ \kappa_2 [(1 - \kappa_2)(3 \cos^2 \theta_p + 3 \cos^2 \theta_q - 2) + \\ & + 3\kappa_2(3 \cos \theta_p \cos \theta_q - \cos \theta_{pq}) \cos \theta_{pq}] r_{pq}^{-3} + \\ & + \frac{1}{2} \alpha_2 [4(1 - \kappa_2)^3 + 3\kappa_2(1 - \kappa_2)(3 \cos^2 \theta_p + 3 \cos^2 \theta_q + 2) + \\ & + 6(2 + \kappa_2) \kappa_2^2 (3 \cos \theta_p \cos \theta_q - \cos \theta_{pq})^2] r_{pq}^{-6} + \dots \} g_{22}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q. \end{aligned} \quad (34)$$

We now assume that the molecules of component 1 are again spherical, whilst those of component 2 are dipolar and, for simplicity, isotropically polarizable. In this case  $B_R^{(1)}$ ,  $B_R^{(2)}$  and  $B_R^{(11)}$  are again given by (31) and (32), whilst by (26)  $R_m^{(12)}$  and  $R_m^{(22)}$  are of the form:

$$R_m^{(12)} = \frac{4\pi}{3} \rho^2 \iint \{ \alpha_1 \alpha_2 (\alpha_1 + \alpha_2) + \frac{5}{36} \gamma_1 \mu_2^2 (3 \cos^2 \theta_q + 1) \} r_{pq}^{-6} g_{12}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (35)$$

$$R_m^{(22)} = \frac{4\pi}{3} \rho^2 \iint \{ 2\alpha_2^3 r_{pq}^{-6} + \beta_2 \mu_2 (3 \cos \theta_p \cos \theta_q - \cos \theta_{pq}) r_{pq}^{-3} + \frac{5}{36} \gamma_2 \mu_2^2 (3 \cos^2 \theta_p + 3 \cos^2 \theta_q + 2) r_{pq}^{-6} + \dots \} g_{22}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q. \quad (36)$$

Similarly, eq. (4) can be easily applied to more complex mixtures.

The foregoing theory of molecular refraction proves that investigation of  $R_m$  in multi-component systems can provide new and interesting information on the forces acting between molecules of various species.

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