

# The Role of Two-Particle Effects in the Behavior of Refraction of Single-Component Liquids and Two-Component Solutions

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**Abstract**—The role of irreducible two-particle contributions to the refraction properties of liquids and solutions has been studied. Two-particle contributions to the polarization vector of the system are calculated by electrostatics methods, which can be explained by weak deformations and overlaps of the electron shells of atoms and molecules. It is shown that, when the two-particle effects are taken into account, the constant of molecular refraction for binary solutions becomes a weakly nonadditive function of the constant of refraction of the components. It is shown by the example of aqueous solutions of ethanol and methanol that our values of the refractive indices and constants of refraction of the solutions are in good agreement with the experimental data.

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## 1. INTRODUCTION

It is generally assumed [1] that permittivity  $\varepsilon$ , refractive index  $n_r$ , and molecular polarizability  $\alpha$  are interrelated in the visible range by the expressions

$$n_r^2 = \varepsilon, \quad \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} n \alpha, \quad (1)$$

where  $n$  is the density of the system. For a binary solution, the second of the above formulas is naturally generalized [1, 2]:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} (n_1 \alpha_1 + n_2 \alpha_2) \quad \text{or} \quad (2)$$
$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} n(x) [(1 - x) \alpha_1 + x \alpha_2],$$

where  $n(x) = n_1 + n_2$  is the molecular solution density and  $x = \frac{n_2}{n_1 + n_2}$  is the molar alcohol fraction in the solution.

Formulas (1) and (2) describe adequately the properties of liquids and solutions on the whole [1, 2]. For solutions, this is especially true when using the constant of molecular refraction  $R(x) = \frac{1}{n(x)} \frac{\varepsilon - 1}{\varepsilon + 2}$ .

Then, Eqs. (2) can be written as

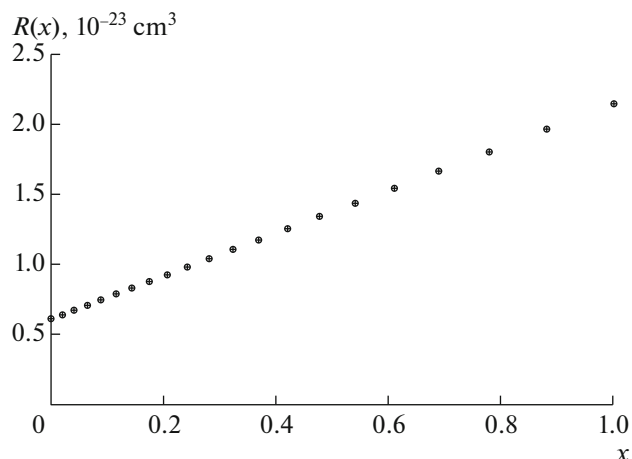
$$R_a(x) = (1 - x)R_w + xR_a, \quad (3)$$

where  $R_a(x)$  is the constant of refraction of solution with a concentration  $x$  within its additivity approximation and  $R_w$  and  $R_a$  are the constants of refraction of water and alcohol, respectively. The linear depen-

dence of  $R_s(x)$  on the molar fraction for aqueous solution of ethanol in Fig. 1 is deceptive all the same. This can clearly be seen in Fig. 2 where the concentration dependence of the refractive index of aqueous solution of ethanol is shown. A deviation of the refractive indices calculated from formulas (1) and (2) from the experimental values reaches 4–5%. The same situation was described in the Feynman Lectures on Physics for water solution of sugar [3]. It was shown in [5, 6] that the polarizability of molecules in liquids begins to change only under very high pressures ( $\sim 10^3$  atm) when their electron shells begin to overlap.

Note that the effects under consideration make contributions no larger than 1–3% of the studied values: refractive index or constant of molecular refraction. Unfortunately, the error in determining the molecular polarizability is on the same order of magnitude. This circumstance is illustrated in Table. 1, where the values of water molecular polarizability, determined in the liquid and vapor phases from the refractive indices or permittivity, are presented.

It follows from Table 1 that the polarizability was determined in both phases only in [4, 7]. However, the obtained results are opposite: the polarizability of a water molecule in the gas phase is larger than that in the liquid phase in [4] and vice versa in [8]. Below, we will give preference to the suggestion that the molecular polarizability in the vapor phase is 1–3% lower than that in the liquid phase. This choice is substantiated by the fact that the polarizability in the vapor phase obtained in [7, 8] based on more recent (in comparison with [4]) data is much smaller than the corre-



**Fig. 1.** Dependence of  $R_s(x) = \frac{1}{n(x)} \frac{n_r^2 - 1}{n_r^2 + 2}$  on the alcohol molar fraction  $x$  for the aqueous solution of ethanol: (crosses) experimental data and (circles) calculation from (3).

sponding value in [4]. The same conclusion can be drawn from [5, 6] where the dependence of the water molecular polarizability on pressure was investigated.

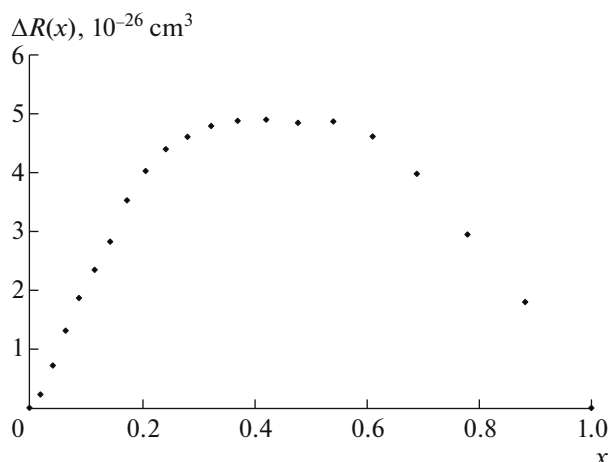
In single-component liquids, the refractive index values calculated from formulas (1) with the electron polarizability corresponding to the vapor phase and found experimentally are also not in good agreement. For example, in the case of liquid water, the value  $\alpha^{(ef)} = 1.47 \times 10^{-24} \text{ cm}^3$  must be used to obtain tabular refractive index  $n_r = 1.333$  at  $20^\circ\text{C}$  instead of polarizability  $\alpha = 1.45 \times 10^{-24} \text{ cm}^3$  [10, 11] determined in the gas phase. As can be seen, the difference between these parameters is about 1.5% of the  $\alpha$  value. The same situation occurs for one-atomic alcohols.

These facts indicate that the permittivity and refractive index of liquids and solutions are formed by the effective polarizability rather than the polarizability of isolated atoms or molecules; the effective polarizability includes two-particle effects and also, perhaps, higher-order effects.

In this context, we will calculate the contributions to the effective polarizability, which are made by two-

**Table 1.** Polarizabilities of water molecules in liquid ( $L$ ) and vapor ( $V$ ) phases

Compound	$\alpha_{ef}(L), \text{\AA}^3$	$\alpha(V), \text{\AA}^3$
[7]		1.4654
[8]	1.444, 1.45, 1.58	1.431–1.456
[9]	1.457	
[4]	1.471	1.542



**Fig. 2.** Concentration dependence of  $\Delta R_s(x) = (1-x)R_w + xR_a - R_s(x)$  for the aqueous solution of ethanol corresponding to the reference data [10–12].

particle interactions in (i) single-component low-molecular liquids and (ii) their binary solutions. Since the electron shells of neighboring atoms are overlapped only slightly, we can restrict ourselves to the electrostatic approximation. It will be shown that the thus-determined small additives, although being no higher than several percent, completely eliminate the aforementioned contradictions.

## 2. REFRACTIVE INDEX OF WATER–ALCOHOL SOLUTIONS

In this section, we successively (i) consider the general theory of refractive index in single-component liquids and binary solutions and (ii) describe the method of calculating the irreducible components of binary polarizability.

### a) A General Form of the Refractive Index in Single-Component Liquids

Permittivity  $\varepsilon$  of a homogeneous and isotropic system is determined by the following general expression:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \frac{P}{E_0}, \quad (4)$$

where  $P$  is a component of polarization vector  $\mathbf{P}$  directed along strength  $\mathbf{E}_0$  of a uniform external field. This formula can be most easily derived for a sphere-shaped system placed in a uniform electric field [13]. In this case,  $\mathbf{P} \parallel \mathbf{E}_0$ . The system polarization vector can be written as

$$\mathbf{P} = \frac{1}{V} \left( \langle \alpha_N \rangle + \frac{\beta}{3} \langle \mathbf{D}_N^2 \rangle \right) \mathbf{E}_0, \quad (5)$$

where  $\alpha_N$  and  $\mathbf{D}_N$  are, respectively, the polarizability and dipole moment of the  $N$ -particle system;  $V$  is the volume of this system;  $\beta = 1/k_B T$ ;  $\mathbf{I}$  is the isotropic tensor; and  $\langle \dots \rangle$  indicates averaging over the molecular positions and orientations.

Within the two-particle approximation, the system polarizability is determined by the expression

$$\alpha_N = \sum_{i=1}^N \alpha_i^{(1)} + \sum_{1 \leq i < j \leq N} \alpha_{ij}^{(2)} + \dots,$$

where the superscripts indicate the order of polarizability (single-particle, irreducible two-particle, etc.). Note that expansion of the system polarizability in partial irreducible contributions was performed for the first time by Prof. I.Z. Fisher in one of his lectures for postgraduates (which, unfortunately, has not been published).

The average values of single-particle contributions are identical and well known:

$$\langle \alpha_i^{(1)} \rangle \Rightarrow \alpha^{(1)} I, \quad \alpha^{(1)} = \frac{1}{3} \text{Sp} \alpha_i^{(1)}, \quad (6)$$

where Sp is the symbol of calculating the spur of matrix.

The behavior of two-particle contributions has hardly been discussed in the literature. Here, we will dwell on only the structure of average values of two-particle contributions for a uniform and isotropic system. It is assumed that the spatial orientations of molecules are described by an isotropic distribution and the positions of the molecular centers of mass are determined by a binary distribution function  $g(r_{12})$ . Then,

$$\begin{aligned} \langle \alpha_2(r_{ij}) \rangle &= \langle \alpha_2(r_{12}) \rangle = \frac{\gamma^{(2)}}{V} I, \\ \gamma^{(2)} &= \frac{1}{3} \int_V \text{Sp} \alpha_{12}^{(2)}(r_{12}) g(r_{12}) dr_2, \end{aligned} \quad (7)$$

and expression (1) for the system permittivity can be written as

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} n \left( \alpha^{(1)} + \frac{1}{2} n \gamma^{(2)} + \dots \right), \quad (8)$$

where  $n$  is the molecular density of the system. We will show below that  $n\gamma^{(2)} \Rightarrow z\alpha^{(2)}(\zeta)$ , where  $Z$  is the number of nearest neighbors and  $\alpha^{(2)}(\zeta)$  is the averaged binary polarizability at point  $\zeta$  corresponding to the position of the maximum of binary distribution function (approximately  $\zeta \approx n^{-1/3}$ ). Therefore,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} n \alpha_{ef}, \quad \alpha_{ef} = \alpha^{(1)} + \frac{1}{2} Z \alpha^{(2)}(\zeta) + \dots \quad (9)$$

Note that it is correct to use the concept of the number of nearest neighbors only for the condensed

phase. For the gas phase, it should be assumed that  $Z = 0$ .

Thus, a difference from the classical Lorenz–Lorentz formula is the addition of contribution related to the irreducible two-particle polarizability at point  $\zeta \approx n^{-1/3}$  to the single-particle polarizability.

### b) A General Form of the Refractive Index in Two-Component Liquids

For a microhomogeneous mixture of molecules of two types, there is an expression similar to the following one:

$$\begin{aligned} \frac{n_r^2 - 1}{n_r^2 + 2} &= \frac{4\pi}{3} \left[ n_1 \alpha_1^{(1)} + n_2 \alpha_2^{(1)} \right. \\ &\left. + \frac{1}{2} n_1^2 \alpha_{11}^{(2)} + 2n_1 n_2 \alpha_{12}^{(2)} + n_2^2 \alpha_{22}^{(2)} + \dots \right] \end{aligned} \quad (10)$$

or

$$\begin{aligned} \frac{n_r^2 - 1}{n_r^2 + 2} &= \frac{4\pi}{3} n(x) \left[ (1-x) \alpha_1^{(1)} \right. \\ &+ x \alpha_2^{(1)} + \frac{1}{2} n(x) ((1-x)^2 \alpha_{11}^{(2)} \\ &\left. + 2(1-x)x \alpha_{12}^{(2)} + x^2 \alpha_{22}^{(2)}) + \dots \right], \end{aligned}$$

where  $x$  is the molar fraction of the second component. At arbitrary concentrations, the refractive index can be rewritten as follows:

$$\begin{aligned} \frac{n_r^2 - 1}{n_r^2 + 2} &= (1-x) \frac{n(x) n_r^2(w) - 1}{n_w n_r^2(w) + 2} + x \frac{n(x) n_r^2(a) - 1}{n_a n_r^2(a) + 2} \\ &- \frac{2\pi}{3} x(1-x) n(x) Z(x) (\alpha_w^{(2)} - 2\alpha_{wa}^{(2)} + \alpha_a^{(2)}) + \dots, \end{aligned} \quad (11)$$

where  $\alpha_w^{(2)}$ ,  $\alpha_a^{(2)}$ , and  $\alpha_{wa}^{(2)}$  are the averaged two-particle polarizabilities of water molecules, alcohol molecules, and a complex of water and alcohol molecules at the points of their direct contact. It is assumed that the average number of nearest neighbors depends on the concentration and formulas in the form (9) are satisfied for one-component systems:

$$\begin{aligned} \frac{n_r^2(k) - 1}{n_r^2(k) + 2} &= \frac{4\pi}{3} n_k \left[ \alpha_k^{(1)} + \frac{1}{2} Z_k \alpha_k^{(2)} + \dots \right], \\ k &= w, a. \end{aligned} \quad (12)$$

The concentration dependence of the molecular solution density is given by the expression

$$n(x) = \frac{\rho(x)}{m_w + x(m_a - m_w)}, \quad (13)$$

where  $\rho(x)$  is the mass solution density. Using the constant of molecular refraction, formula (11) can be rewritten in the form

$$R_s(x) = (1-x)R_w + xR_a - \frac{2\pi}{3}x(1-x)Z(x)\Delta^{(2)}, \quad (14)$$

where  $R_s(x) = \frac{1}{n(x)} \frac{n_r^2 - 1}{n_r^2 + 2}$ ,  $R_w = \frac{1}{n_w} \frac{n_r^2(w) - 1}{n_r^2(w) + 2}$ , and

$R_a = \frac{1}{n_a} \frac{n_r^2(a) - 1}{n_r^2(a) + 2}$  are the constants of refraction for the solution, water, and alcohol, respectively, and

$$\Delta^{(2)} = \alpha_w^{(2)} - 2\alpha_{wa}^{(2)} + \alpha_a^{(2)} + \dots \quad (15)$$

One difference between (14) and standard formula (3) for the constant of solution refraction is the addition of the term proportional to  $\Delta^{(2)}$ .

### c) Longitudinal and Transverse Polarizabilities of Two Identical Spherical Molecules

The form of the tensor of two-particle polarizability is especially simple for noble gases. We will first consider two characteristic cases: a pair of spherical molecules is arranged (i) along the field and (ii) perpendicular to field.

Let two spherical particles with the same polarizability  $\alpha$  be introduced into external dc field  $\mathbf{E}_0$ . The positions of the particles are set by radius vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , and their dipole moments are determined by the equations

$$\begin{aligned} \mathbf{d}_1 &= \alpha(\mathbf{E}_0 + \mathbf{E}_2) \\ \mathbf{d}_2 &= \alpha(\mathbf{E}_0 + \mathbf{E}_1) \end{aligned} \quad (16)$$

where  $\mathbf{E}_1$  is the strength of field exerted on the second particle from the first one (and vice versa for  $\mathbf{E}_2$ ). Since fields  $\mathbf{E}_1$  and  $\mathbf{E}_2$  are mainly formed by dipoles  $\mathbf{d}_1$  and  $\mathbf{d}_2$ , respectively, their explicit expressions can be written as

$$\begin{aligned} \mathbf{E}_1 &= \frac{1}{r_{12}^3} [3(\mathbf{d}_1 \mathbf{e}) \mathbf{e} - \mathbf{d}_1], \\ \mathbf{E}_2 &= \frac{1}{r_{12}^3} [3(\mathbf{d}_2 \mathbf{e}) \mathbf{e} - \mathbf{d}_2], \end{aligned} \quad (17)$$

where  $\mathbf{e} = \frac{\mathbf{r}_2 - \mathbf{r}_1}{|\mathbf{r}_2 - \mathbf{r}_1|}$  is a unit vector.

If unit vector  $\mathbf{e}$  is oriented parallel to external-field vector  $\mathbf{E}_0$ , it follows from (16) and (17) that vectors  $\mathbf{d}_1$  and  $\mathbf{d}_2$  are determined by the expression

$$\mathbf{d}_1 = \mathbf{d}_2 = \alpha \mathbf{E}_0 \frac{1}{1 - \frac{\alpha}{r_{12}^3}}. \quad (18)$$

By definition, irreducible component  $\alpha_l$  of two-particle polarizability corresponding to the longitudinal arrangement of particles along the field ( $\mathbf{e} \parallel \mathbf{E}_0$ ) is set by the equation

$$\mathbf{d}_1 + \mathbf{d}_2 = (2\alpha + \alpha_l) \mathbf{E}_0. \quad (19)$$

Having combined it with Eq. (18), we find that

$$\alpha_l = \frac{4\alpha^2}{r_{12}^3} \frac{1}{1 - \frac{2\alpha}{r_{12}^3}}. \quad (20)$$

If unit vector  $\mathbf{e}$  is oriented perpendicular to  $\mathbf{E}_0$ , the dipole moments are determined by the equations

$$\mathbf{d}_1 + \frac{\alpha}{r_{12}^3} \mathbf{d}_2 = \alpha \mathbf{E}_0,$$

$$\mathbf{d}_2 + \frac{\alpha}{r_{12}^3} \mathbf{d}_1 = \alpha \mathbf{E}_0.$$

It should be noted that, at this arrangement of particles, their dipole moments  $\mathbf{d}_1$  and  $\mathbf{d}_2$  are also oriented parallel to  $\mathbf{E}_0$  because the strengths of fields formed by the dipoles in their equatorial planes are oriented parallel to their dipole moments. Having found  $\mathbf{d}_1$  and  $\mathbf{d}_2$ , we confirm that the transverse component of the irreducible two-particle polarizability determined similarly to (20) is equal to

$$\alpha_t = -\frac{2\alpha^2}{r_{12}^3} \frac{1}{1 + \frac{\alpha}{r_{12}^3}}. \quad (21)$$

As a result, we obtain the following spur of two-particle polarizability:

$$\frac{1}{3} \text{Sp} \alpha_2(r_{12}) \approx 4 \frac{\alpha^3}{r_{12}^6} \frac{1}{1 - \frac{\alpha}{r_{12}^3} - \frac{2\alpha^2}{r_{12}^6}}, \quad (22)$$

where  $\alpha$  is the single-particle polarizability. The applicability of formula (22) is violated if its denominator turns to zero. This occurs at  $r_{12} \Rightarrow r_* = (2\alpha)^{1/3}$ . One can easily make sure that  $r_*/\sigma \leq 0.75$  for water and alcohols of methanol homologous series ( $\sigma$  is the solid-sphere diameter of water or alcohol molecules). Therefore, the correction terms in denominator of (22) can be neglected, providing satisfactory accuracy even at the point of direct contact of two molecules.

Hence, the expression for  $\frac{1}{3} \text{Sp} \alpha_2(r_{12})$  (i.e., for the two-particle polarizability averaged over angles) obtained using the methods of classical electrostatics is applicable for both gas and liquid phases of the system existence.

In the case of water, at a distance of the direct contact between two molecules approximately equal to their solid-sphere diameter  $\sigma \approx 3 \text{ \AA}$ , we obtain

$$\frac{1}{3} \frac{\text{Sp } \alpha_2(\sigma)}{\alpha} \equiv \frac{\alpha^{(2)}(\sigma)}{\alpha} \approx 0.01. \quad (23)$$

A similar estimate can be obtained for alcohols.

It can easily be seen that, according to (19),

$$\frac{1}{3} \text{Sp } \alpha_{12}^{(2)}(r_{12}) g(r_{12}) \approx \begin{cases} 0, & r_{12} < \zeta, \\ K/r_{12}^6, & r_{12} > \zeta, \end{cases} \quad K = 4\alpha^3;$$

therefore,

$$\gamma^{(2)} \approx \frac{4\pi}{3} \zeta^3 \alpha^{(2)}(\zeta)$$

and the combination  $n\gamma^{(2)}$  can be written as

$$n\gamma^{(2)} \approx Z\alpha^{(2)}(\zeta),$$

where

$$Z = \frac{4\pi}{3} \zeta^3 n$$

is the number of molecules in the first coordination sphere (i.e., the number of nearest neighbors). Hence, within the two-particle approximation, we obtain

$$\langle \alpha_N \rangle = \mathbf{I} V n \left[ \alpha^{(1)} + \frac{1}{2} Z \alpha^{(2)}(\zeta) + \dots \right].$$

#### d) Longitudinal and Transverse Polarizabilities of Two Different Spherical Molecules

In this case, the character of calculations remains the same as in the previous section. In particular, it follows from equations in the form (17) and (18) that the dipole moment of one of two particles, at an arbitrary mutual orientation of the external-field strength and the axis passing through the particle centers, satisfies the equation

$$\begin{aligned} \mathbf{d}_1(r) &= \alpha_1 \mathbf{E}_0 - \frac{\alpha_1 \alpha_2}{r^3} \mathbf{E}_0 \\ &+ 3 \frac{\alpha_1 \alpha_2}{r^3} (\mathbf{E}_0 \mathbf{e}) \mathbf{e} + \frac{\alpha_1 \alpha_2}{r^6} \mathbf{d}_1 + 3 \frac{\alpha_1 \alpha_2}{r^6} (\mathbf{d}_1 \mathbf{n}) \mathbf{n} \mathbf{e}. \end{aligned}$$

Having determined the  $\mathbf{d}_1(r)$  and, similarly,  $\mathbf{d}_2(r)$  values from this equation and then following the above-described algorithm, we find for the longitudinal and transverse components of two-particle polarizability that

$$\alpha_i^{(2)}(r) = 4 \frac{\alpha_1 \alpha_2}{r^3} \frac{1 + \frac{\alpha_1 + \alpha_2}{r^3}}{1 - 4 \frac{\alpha_1 \alpha_2}{r^6}}, \quad (24)$$

$$\alpha_i^{(2)}(r) = -2 \frac{\alpha_1 \alpha_2}{r^3} \frac{1 - \frac{\alpha_1 + \alpha_2}{2r^3}}{1 - \frac{\alpha_1 \alpha_2}{r^6}}. \quad (25)$$

$$\text{Since } \frac{1}{3} \text{Sp } \alpha_2(r_{12}) = \frac{1}{3} (\alpha_i^{(2)}(r) + 2\alpha_i^{(2)}(r)),$$

$$\begin{aligned} &\frac{1}{3} \text{Sp } \alpha_2(r) \\ &= 4 \frac{\alpha_1 \alpha_2}{r^6} \left[ \frac{\frac{1}{2} (\alpha_1 + \alpha_2) + \frac{\alpha_1 \alpha_2}{r^3} - \frac{\alpha_1 \alpha_2 (\alpha_1 + \alpha_2)}{r^6}}{1 - 5 \frac{\alpha_1 \alpha_2}{r^6} + 4 \frac{\alpha_1^2 \alpha_2^2}{r^{12}}} \right]. \end{aligned} \quad (26)$$

It can be assumed with satisfactory accuracy that

$$\frac{1}{3} \text{Sp } \alpha_2(r) \approx 2 \frac{\alpha_1 \alpha_2}{r^6} (\alpha_1 + \alpha_2). \quad (27)$$

In a similar way, one can represent the contribution made by fluctuations of the dipole moments of water and alcohol molecules. However, in the visible range this contribution can be neglected ensuring an acceptable accuracy. Therefore, the refractive indices of pure water and alcohols are described by formulas in the form (12).

### 3. MANIFESTATION OF TWO-PARTICLE CONTRIBUTIONS IN THE CONSTANT OF REFRACTION

The role of two-particle contributions in the formation of the effective polarizability of atoms or molecules is much less important than is that of single-particle contributions, although it is not negligible. For example, in the case of water, for reproduction of the experimental values of the refractive index, it should be assumed that  $\frac{1}{2} Z \alpha^{(2)}(\zeta) = 0.021 \text{ \AA}^3$ , which at  $Z = 4$  yields the estimate  $\frac{\alpha^{(2)}(\zeta)}{\alpha^{(1)}} \approx 0.01$  consistent with (23) at  $\alpha^{(1)} = 1.45 \text{ \AA}^3$ .

The single-particle and two-particle contributions to the effective polarizability of water, methanol, and ethanol molecules are compared in Table. 2.

Note that the  $\alpha^{(2)}$  and  $\alpha_{wa}^{(2)}$  values are estimated from the formulas  $\alpha^{(2)} \approx 4 \frac{\alpha^3}{\zeta^6}$  and  $\alpha_{wa}^{(2)} \approx 2^7 \frac{\alpha_w \alpha_a}{(\zeta_w + \zeta_a)^6} (\alpha_w + \alpha_a)$  and  $\Delta^{(2)} = \alpha_w^{(2)}(\zeta_w) - 2\alpha_{wa}^{(2)}((\zeta_w + \zeta_a)/2) + \alpha_a^{(2)}(\zeta_a)$ . The  $\zeta_k$ ,  $k = w, a$  values entering these formulas are determined from the density values. In this case, temperature dependence  $\zeta(T) = n^{-1/3}(T)$  must be taken into account in the coexistence curve. In particular, we find for water that  $\zeta_w = 3.1 \text{ \AA}$ . As can be seen, the

**Table 2.** Single- and two-particle contributions to the effective molecular polarizability ( $\tilde{\alpha}^{(k)} = 10^{24} \alpha^{(k)} \text{ \AA}^3$ )

Compound	$\tilde{\alpha}^{(1)}$	$\tilde{\alpha}^{(2)}$	$\tilde{\alpha}_{wa}^{(2)}$	$\Delta^{(2)}$	$Z$	$\tilde{\delta}^{(2)} = \frac{2}{z} (\tilde{\alpha}^{(ef)} - \tilde{\alpha}^{(1)})$
Water	1.45	0.014			4	0.011
Methanol	3.2	0.029	0.0204	0.0020	4–6	0.02–0.032
Ethanol	4.9	0.05	0.0279	0.0082	8–10	0.04–0.06

calculated ( $\tilde{\alpha}^{(2)}$ ) and experimental ( $\tilde{\delta}^{(2)}$ ) values for water, ethanol, and methanol almost coincide. Note that the number of nearest neighbors of molecules in liquid methanol should be close to that in water because of proximity of the sizes of their molecules, whereas for ethanol this value should be larger by a factor of 2–3 (see an additional argumentation in [15]).

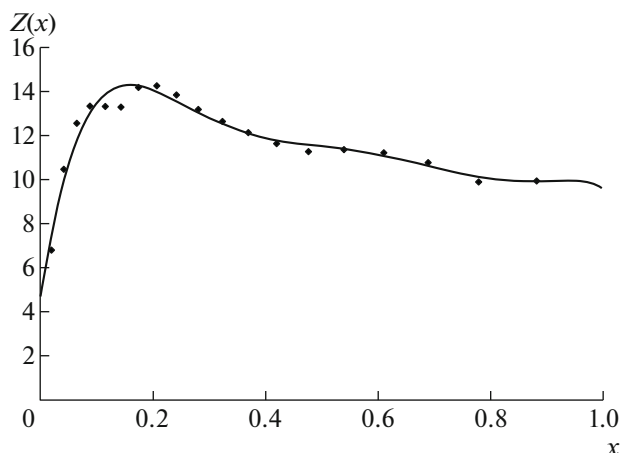
Formula (14) can also be used for determining the concentration dependence of the number of nearest neighbors:

$$Z(x) = \frac{3(1-x)R_w + xR_a - R_s(x)}{2\pi x(1-x)\Delta^{(2)}}. \quad (28)$$

The corresponding character of the dependence is shown in Fig. 3.

The following main properties of the average coordination number of molecules in the aqueous solution of ethanol should be noted:

- (i)  $z(x)$  is close to 4 at  $x \rightarrow 0$ , which is in agreement with the well-known properties of water;
- (ii) in the vicinity of the solution singular point ( $x_p = 0.077$  [14, 15]), the curve  $Z(x)$  ceases to monotonically increase; then there is a short portion of growth again; and then a smooth monotonic decay is observed;



**Fig. 3.** Dependence of coordination number  $Z(x)$  on the molar fraction in the aqueous solution of ethanol determined according to (28).

(iii) at  $x \rightarrow 1$ , the average coordination number tends to 10, which should be considered as its average value in pure ethanol;

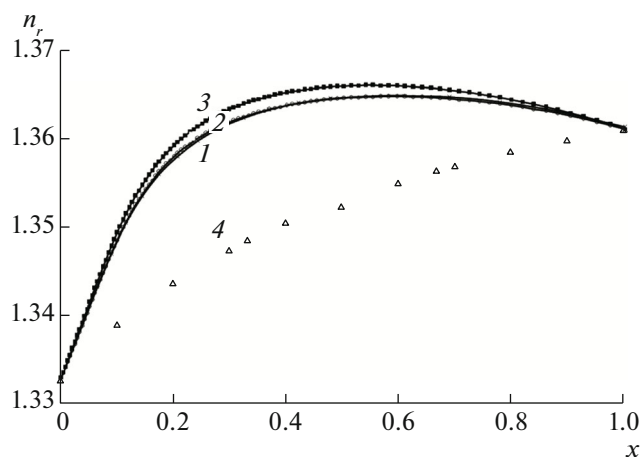
(iv) the presence of a fine structure of the curve  $Z(x)$  in the molar-fraction range  $x_p < x < 2x_p$  can be interpreted as a result of the formation of two phases with similar properties, which continuously undergo phase transitions: drops of one phase arise and regress in the other.

Note that our  $Z(x)$  values are in satisfactory agreement with those found in [15] according to qualitative considerations.

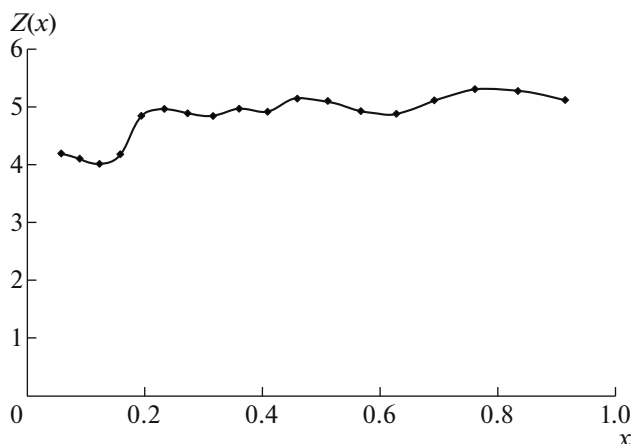
Let us supplement the obtained results with the concentration dependence of the refractive index of aqueous solution of ethanol found from (14). Using the polarizability and  $\Delta^{(2)}$  values listed in Table 2, we find that the experimental dependence of the refractive index is almost exactly reproduced (Fig. 4). One can make sure that the formulas proposed by us describe the refractive indices of methanol and sugars with almost the same accuracy.

To conclude, we should note that consideration of the irreducible two-particle components of molecular polarizability is fundamentally necessary for the sufficiently accurate reproduction of the refractive index of (a) single-component liquids and (b) binary solutions. The simple electrostatic approach to estimating the two-particle polarizability is fairly satisfactory. From the physical point of view, this is a result of a rather weak overlap of the electron shells of neighboring molecules. Within our approach, it is also possible to estimate the average number of nearest neighbors in single-component liquids and solutions. In the case of water and diluted aqueous solutions of alcohols ( $x \ll 0.1$ ), formula (28) yields  $Z(x) \approx 4$ , which corresponds to the experimental data [18, 19]. This satisfactory agreement between the calculated and experimental data is likely to remain for arbitrary binary solutions with close-to-spherical molecules.

Let us briefly consider the applicability of the proposed approach to describing the constant of molecular refraction or the refractive index by the example of another representative of one-atomic alcohols: methanol. In this case, the  $\Delta^{(2)}$  value calculated in the same way as for ethanol is smaller than that for ethanol by an order of magnitude. This is due to the fact that the



**Fig. 4.** Dependence of the refractive index of the aqueous solution of ethanol on the molar fraction of alcohol: (1) experimental data [10, 12], (2, 3) calculation from formula (14) with (2) the  $\Delta^{(2)}$  values listed in Table 2 and (3)  $\Delta^{(2)} = 0$ , and (4) calculation of the refractive index from the simplified additive formula  $n_r(x) = n_r(a)x + n_r(w)(1 - x)$  used in [16, 17].



**Fig. 5.** Dependence of coordination number  $Z(x)$  on the molar fraction in the aqueous solution of methanol determined according to (28).

sizes of water and methanol molecules are close. Therefore, it is urgent to increase the accuracy of determining  $\zeta$ . Here, we restrict ourselves to the determination of only the average number of nearest neighbors  $Z(x)$ . We will choose  $\Delta^{(2)}$  so as to make  $Z(x \rightarrow 0) \rightarrow 4$ . One can easily make sure that the appropriate value is  $\Delta^{(2)} = 0.02$ . The corresponding behavior of  $Z(x)$  for the aqueous solution of methanol is shown in Fig. 5.

Note that consideration of the irreducible components of two-particle polarizability is important for

not only analysis of permittivity and the refractive index, but also the description of high-frequency asymptotics of the spectra of molecular light scattering in gases and liquids [20–22].

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