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# Recombination of dimers as a mechanism for the formation of several nematic phases

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A mixture of nonelongated monomers $A$ and $B$ capable of formation of three kinds of mesogenic dimers $AA$, $BB$, and $AB$ is investigated. We show the possibility of a temperature-induced transition from one nematic phase consisting mostly of dimers $AB$ composed of dissimilar monomers to a different nematic phase consisting mostly of dimers $AA$ and $BB$ composed of similar monomers. The binding energy of dimers $AB$ is supposed to be lower (the binding of monomers $A$ and $B$ is more preferable) than that of dimers $AA$ and $BB$ (the binding of monomers $A$ with each other and monomers $B$ with each other is less preferable). On the contrary, the interactions of dimers $AA$ themselves with each other, dimers $BB$ with each other, and dimers $AA$ with dimers $BB$ are supposed to be stronger (the interaction energy is lower) than those of dimers $AB$ with each other and with dimers $AA$ and $BB$. If inequality of binding energies is stronger than inequality of interactions between various dimers, but the corresponding energy difference is small, the entropy can play a crucial role in the formation of particular dimer kinds and can drive the transitions between two nematic phases. The theoretical prediction is well reproduced experimentally.

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## I. INTRODUCTION

Dimerization of molecules drastically changes the properties of liquid crystals and causes many interesting phenomena. The population of dimers usually depends on the surrounding conditions such as temperature and external field and therefore can be useful for the creation of sensing devices. The existence of dimers in nematic liquid crystals is confirmed experimentally, for example, by x-ray [1–3] and dielectric [4,5] measurements. Specific conformations were predicted for many dimers [6,7] and it was shown that materials composed of dimers can exhibit various nematic phases [8] because of their structural reorganization. Liquid crystal dimers have been found to exhibit a rich variety of frustrated smectic phases [9]. In many cases dimers should not be considered as stable particles, but rather as molecular pairs having enhanced probability of coupling. This coupling can take place due to specific interactions of particular atoms or atomic groups of one molecule with some atoms or atomic groups of the neighboring molecule. For example, in Refs. [10–12] the formation of dimers due to strong dipole-dipole interactions was studied and it was shown that the coexistence of dimers (molecular pairs) and monomers (separate molecules) can essentially influence the nematic-isotropic transition temperature.

It is known that nonelongated molecules can form liquid crystal phases due to the formation of mesogenic dimers. For example, separate molecules of organic acids can form elongated dimers due to specific hydrogen bonds [13]. An x-ray study shows the existence of several crystal structures in alkoxybenzoic acids [14,15]. It was also noticed that organic acids consisting of dimers and higher oligomers can exhibit the so-called texture transition within the nematic phase [16–21]. This transition is explained with the formation of smecticlike molecular complexes in the nematic phase. The transition from an achiral liquid crystal state into a chiral one due to the transformation of the closed dimers in open dimers was also reported in Refs. [22,23] and undulated smectic structures for some alkoxybenzoic acids were observed in Ref. [24]. Also in the crystal phase a strong memorization of the chiral nematic texture was observed in Ref. [22]. The influence of heterodimers on the nematic mesophase stability in the mixtures of hydrogen-bonded organic acids was investigated in Ref. [25] and the role of heterodimers in the formation of the ringed spherulitic and undulated textures in the nematic phase was reported in Ref. [26].

Here we present our results of dielectric permittivity measurements in mixtures of alkoxybenzoic acids 6OBAC and 7OBAC. We noticed some temperature-induced transition within the nematic state for the mixtures with greatly unequal fractions of the components. Anisotropy of the dielectric permittivity exhibits a stepwise sign reversal at the transition temperature. This transition is observed neither for pure 6OBAC and 7OBAC nor for their mixture with equal fractions and thus should be different from the texture transition reported in the literature. In the present paper we derive a theoretical approach explaining this transition by recombination of dimers. We consider two types of monomers $A$ and $B$ capable of formation of three kinds of dimers $AA$, $BB$, or $AB$ with the possibility of recombination under temperature variation. The balance between all kinds of dimers is supposed to depend on the relative strength of the interaction between dimers and binding energies of each dimer.

The paper is organized as follows. In Sec. II experimental observation of the temperature-induced transitions between two nematic phases will be presented. In Sec. III the theoretical approach outlining the mechanisms responsible for the recombination of dimers and for the corresponding transition between two nematic phases will be presented. The temperature dependences of the nematic order parameters and

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of the dimer fractions will be discussed. In Sec. IV theoretical results will be compared with experimental observations. Finally, in Sec. V a summary is given and conclusions will be made.

## II. EXPERIMENTAL RESULTS

Let us first demonstrate our experimental results obtained by dielectric measurements [27]. The mixtures of alkoxybenzoic acids 6OBAC and 7OBAC in several particular proportions were placed into a cell representing a 0.25-mm-thick plane condenser with a surface area of 0.44 cm$^2$. The uniform orientation was maintained by constant magnetic field. The dielectric constant was determined by the bridge method (immittance measurements) at 1.2 V and 1 kHz frequency. The cell was placed into a thermostat and the temperature was increased stepwise. The corresponding temperature dependence of the dielectric anisotropy is presented in Fig. 1(a). In pure 6OBAC (curve 1) the transition from a crystal to a nematic phase happens between 110 °C and 115 °C, where the dielectric anisotropy drops down to the lower values, and the transition from the nematic to the isotropic phase happens at about 155 °C, where dielectric anisotropy becomes equal to zero. In pure 7OBAC (curve 6) the transition from the smectic-*C* phase to the nematic phase happens between 95 °C and 100 °C and the transition from the nematic phase to the isotropic phase happens at about 145 °C. These transition temperatures are in good agreement with the literature data. For both pure materials 6OBAC and 7OBAC the dielectric anisotropy demonstrates small positive values ($\Delta\varepsilon \leqslant 0.3$) in the whole range of the nematic phase. On the contrary, a 50/50 mixture of 6OBAC and 7OBAC (curve 4) demonstrates large negative values of the dielectric anisotropy (about −1.4) in the whole range of the nematic phase. In the mixtures with nonequal proportions of the components (curves 2, 3, and 5) the dielectric anisotropy in the nematic phase is negative at low temperatures and it changes stepwise to positive values at high temperatures. In particular, when the inequality of fractions is great (80/20, curve 2), the dielectric anisotropy appears to be negative in the very narrow temperature interval and positive in the large temperature interval, while for a lesser inequality of fractions (60/40, curve 3; 35/65, curve 5) the temperature range of the negative dielectric anisotropy increases.

Detailed analysis of longitudinal and transverse dielectric susceptibilities [see Figs. 1(b) and 1(c)] shows that only the longitudinal contribution is essentially different below and above this additional transition, while the transverse contribution in the nematic phase is almost the same for each proportion of the components and does not exhibit any additional transition. It is natural to suppose that a number of monomers in the mixtures of 6OBAC and 7OBAC tend to combine in cross dimers [consisting of dissimilar monomers (see Fig. 2)]. In this case the small value of the longitudinal dielectric susceptibility (and consequently the negative dielectric anisotropy) can originate from the lower longitudinal polarizability of the cross dimers.

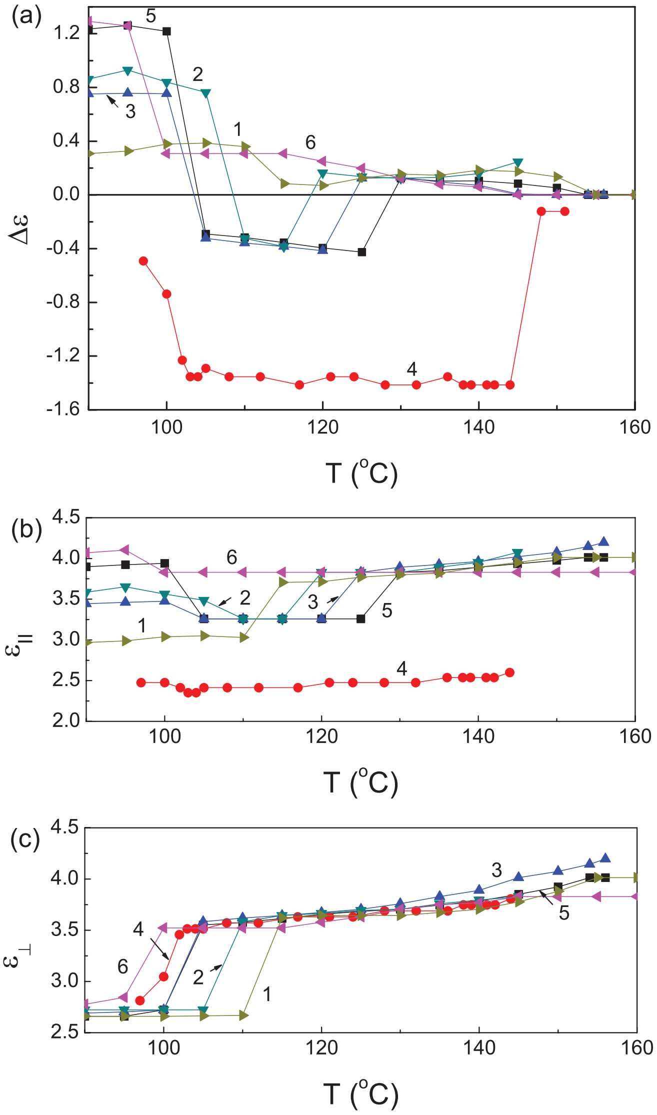

FIG. 1. (Color online) Temperature dependences of the (a) dielectric anisotropy $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ and (b) longitudinal $\varepsilon_\parallel$ and (c) transverse $\varepsilon_\perp$ dielectric susceptibilities at various weight proportions between materials 6OBAC and 7OBAC: 100/0 (curve 1), 80/20 (curve 2), 60/40 (curve 3), 50/50 (curve 4), 35/65 (curve 5), and 0/100 (curve 6).

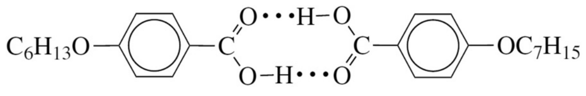

FIG. 2. Cross dimer *AB* composed of dissimilar monomers 6OBAC and 7OBAC.

We expect that nonsymmetrical dimers can have *permanent* longitudinal dipole moments, which prevent further separation of charges in the electric field due to accumulation of charges. Any separation of charges (due to either the molecular or external field) causes repulsion between arising charges of the same sign localized in particular areas (see the inset in Fig. 3) and attraction between charges of opposite sign in different areas (the latter is obviously weaker due to the larger distance between separate areas than the distances between charges within their areas). Both repulsive and attractive potentials are proportional to the square of the arising charge value. The work of the external electric field should be equal to the change of the total potential between charges. The absolute values of both repulsive and attractive potentials change in the same way in

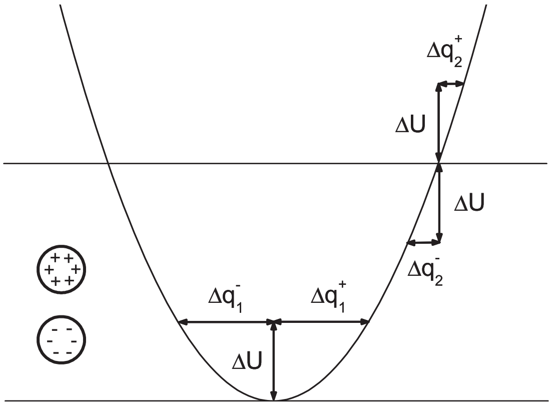

FIG. 3. Illustration showing how permanent longitudinal dipoles prevent further separation of charges in the electric field. Voltage $\Delta U$ applied to a charged system causes induction of charges $\Delta q_2^+$ or $\Delta q_2^-$, which are smaller than charges $\Delta q_1^+$ and $\Delta q_1^-$ induced by the same voltage in an uncharged system, because the interaction of charges is proportional to the square of the charge.

the presence of an external electric field (either increase both or decrease both). An illustration of the quadratic dependence of the total interaction potential between charges (which is expected to be repulsive in general) on the value of the charge is presented in Fig. 3. The external voltage $\Delta U$ applied to the uncharged system (when the potential is minimal) causes the creation of charges $\Delta q_1^+$ or $\Delta q_1^-$ (depending on the direction of the electric field). One can see that the same voltage $\Delta U$ applied to the charged system (when the potential is essentially larger) causes the creation of charge $\Delta q_2^+$ or $\Delta q_2^-$; both are essentially smaller than $\Delta q_1^+$ and $\Delta q_1^-$. The smaller the charges arising in the electric field, the smaller the dielectric permittivity is. Therefore, the longitudinal dielectric permittivity of dimers $AB$ having permanent dipoles should be smaller than that of dimers $AA$ and $BB$ having no permanent dipoles. Permanent longitudinal dipole moments themselves cannot contribute to the dielectric susceptibility in the nonpolar nematic phase since a half of them are oriented along the electric field and half are oriented against the electric field.

Suppose that dimers consisting of dissimilar monomers are more favorable at low temperatures, while dimers consisting of similar monomers are more favorable at high temperatures. In this case the dimers can recombine from dissimilar to similar ones at some temperature (at least for particular proportions of the components). The corresponding transition should obviously shift to the lower temperatures when proportions are greatly unequal (because a smaller number of cross dimers can exist in this case) and it should shift to the higher temperatures if the two fractions are comparable with each other. Figure 1 suggests that at equal proportions recombination happens already in the isotropic phase (curve 4), where the dielectric anisotropy cannot be observed.

In the next section we derive a theoretical approach explaining a recombination between dimers consisting of similar and dissimilar monomers, using a combination of molecular-statistical theory and molecular modeling. In particular, we are going to answer the question of which dimers are more favorable at given fractions of two monomers: similar dimers consisting of dissimilar monomers or dissimilar dimers each consisting of similar monomers. We will show that the answer can be different depending on the temperature because of the entropy.

## III. THEORETICAL APPROACH

### A. Molecular-statistical theory

Let us consider a mixture of anisotropic dimers $AA$, $BB$, and $AB$ and assume that each pair of dimers can recombine into a different pair of dimers. For simplicity we assume that all monomers $A$ and $B$ always combine in some dimers. We expect that fractions of all dimers can strongly vary with variation of temperature because of different interactions between various dimers and different binding energies of each kind of dimer. Let us enumerate each kind of dimer with index $i$ equal to 1 for dimers $AA$, 2 for dimers $BB$, and 3 for dimers $AB$. The free-energy density of the mixture can be written in the following form:

$$F = \rho k_B T \sum_{i=1}^{3} p_i \int d^2\mathbf{a}_1 f_i(\mathbf{a}_1 \cdot \mathbf{n}) \ln[p_i f_i(\mathbf{a}_1 \cdot \mathbf{n})] + \frac{1}{2}\rho^2 \sum_{i,j=1}^{3} p_i p_j \int d^2\mathbf{a}_1 \int d^2\mathbf{a}_2 \int d^3\mathbf{r}_{12} f_i(\mathbf{a}_1 \cdot \mathbf{n}) \times f_j(\mathbf{a}_2 \cdot \mathbf{n}) U_{ij}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12}) - \rho \sum_{i=1}^{3} p_i E_i, \tag{1}$$

where $\rho$ is the average concentration of dimers, $k_B$ is the Boltzmann constant, $p_i$ is the fraction of dimers $i$, $f_i(\mathbf{a}_1 \cdot \mathbf{n})$ is the orientational distribution function for the long axes $\mathbf{a}$ of dimers $i$ with respect to director $\mathbf{n}$, $\mathbf{r}_{12}$ is the vector connecting dimer 1 with dimer 2, $U_{ij}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12})$ is the effective interaction potential of dimer 1 of kind $i$ with dimer 2 of kind $j$, and $E_i$ is the absolute value of the binding energy of dimers $i$. The first term in Eq. (1) is the orientational entropy, the second term is the internal energy, and the third term is the sum of the binding energies of all dimers per unit volume. Minimizing the free energy (1) with respect to each distribution function $f_i(\mathbf{a} \cdot \mathbf{n})$ under the normalizing constraint $\int d^2\mathbf{a} f_i(\mathbf{a} \cdot \mathbf{n}) = 1$, approximating the interaction potentials averaged with respect to vector $\mathbf{r}_{12}$ by the Legendre polynomials

$$-\int d^3\mathbf{r}_{12} U_{ij}(\mathbf{a}_1,\mathbf{a}_2,\mathbf{r}_{12}) \approx J_{ij}^{(0)} + J_{ij}^{(2)} P_2(\mathbf{a}_1 \cdot \mathbf{a}_2), \tag{2}$$

and introducing the order parameter for each kind of dimer $S_i \equiv \int d^2\mathbf{a} P_2(\mathbf{a} \cdot \mathbf{n}) f_i(\mathbf{a} \cdot \mathbf{n})$, one obtains the following recurrent equations for the order parameters:

$$S_i = \frac{1}{I_i^{(2)}} \int_{-1}^{1} dt\, P_2(t) \exp\left[\frac{\rho P_2(t)}{k_B T} \sum_{j=1}^{3} p_j J_{ij}^{(2)} S_j\right], \tag{3}$$

where $t \equiv \mathbf{a} \cdot \mathbf{n}$ and normalizing integrals $I_i^{(2)}$ are determined as follows:

$$I_i^{(2)} \equiv \int_{-1}^{1} dt \exp\left[\frac{\rho P_2(t)}{k_B T} \sum_{j=1}^{3} p_j J_{ij}^{(2)} S_j\right]. \tag{4}$$

Using the solution (3), one can eliminate all the distribution functions from Eq. (1) and rewrite the free-energy density of the mixture of dimers in the following form:

$$F = \rho k_B T \sum_{i=1}^{3} p_i \ln \frac{p_i}{I_i} + \frac{1}{2}\rho^2 \sum_{i,j=1}^{3} p_i p_j \big[ J_{ij}^{(0)} + J_{ij}^{(2)} S_i S_j \big], \tag{5}$$

where

$$I_i \equiv I_i^{(2)} \exp\left\{ \frac{\rho}{k_B T} \left[ E_i + \sum_{j=1}^{3} p_j J_{ij}^{(0)} \right] \right\}. \tag{6}$$

Since the numbers of monomers $A$ and $B$ participating in various dimers are fixed, the dimer fractions are not independent of each other:

$$p_{AA} + p_{AB}/2 = \phi_A, \quad p_{BB} + p_{AB}/2 = \phi_B, \tag{7}$$

where $\phi_A$ and $\phi_B = 1 - \phi_A$ are the fractions of monomers $A$ and $B$, respectively, participating in various dimers. Minimizing the free energy (5) with respect to fractions $p_{AA}$, $p_{BB}$, and $p_{AB}$ under two constraints (7) and using Eq. (3), one obtains the following recurrent equation:

$$\frac{p_{AB}^2}{p_{AA} p_{BB}} = \frac{I_3^2}{I_1 I_2}. \tag{8}$$

Equation (8), together with two constraints (7) and three equations (3), determines the temperature dependence of three order parameters $S_{AA}$, $S_{BB}$, and $S_{AB}$ and three dimer fractions $p_{AA}$, $p_{BB}$, and $p_{AB}$.

The system of equations (3), (7), and (8) can be solved numerically for each particular temperature $T$. The resulting temperature dependences of the order parameters and dimer fractions essentially depend on the percentage of each kind of monomer ($A$ and $B$) in the mixture. One can check that in the simplest limit cases of pure material $A$ ($\phi_A = 1$ and $\phi_B = 0$) or pure material $B$ ($\phi_A = 0$ and $\phi_B = 1$) there is only one kind of dimer (either $AA$ or $BB$), whose nematic order parameter is determined by the conventional Maier-Saupe equation, and the ratios between various isotropic interactions $J_{ij}^{(0)}$ ($i,j = 1,2,3$), anisotropic interactions $J_{ij}^{(2)}$, and dimer binding energies $E_i$ play no role in these two cases. A similar result for each order parameter follows from Eqs. (3), (7), and (8) in the limit case of indistinguishable dimers, i.e., in the case when all coefficients $J_{ij}^{(0)}$ are equal to each other, all coefficients $J_{ij}^{(2)}$ are equal to each other, and all binding energies $E_i$ are equal to each other. In this case, however, from Eq. (8) it follows that $p_{AB}$ is the square root of a multiple of $p_{AA}$ and $p_{BB}$, which means that from an entropy point of view it is favorable to have as many dimers of each kind as possible. In particular, if $\phi_A = \phi_B = 0.5$, then each dimer fraction is equal to 1/3. This limit fraction value itself has no physical meaning since all dimers are not distinguishable. At the same time, the physical meaning arises if dimers are slightly distinguishable and each dimer fraction tends to 1/3.

### B. Interplay between interactions of various dimers and their binding energies

It is interesting to analyze how the difference between dimers influences this tendency. Let us first analyze the isotropic mixture of dimers ($S_{AA} = S_{BB} = S_{AB} = 0$). In this case one can rewrite the free energy (5) in the following simple form:

$$\frac{F}{\rho k_B T} = \sum_{i=1}^{3} p_i \ln p_i - \frac{\alpha}{4T} p_s^2 - \frac{\gamma}{2T} p_s, \tag{9}$$

where $p_s \equiv p_1 + p_2 = p_{AA} + p_{BB}$ is the fraction of symmetrical dimers $AA$ and $BB$ and

$$\begin{aligned} \alpha &\equiv \frac{2\rho}{k_B}\big[\Delta J_{ss,sa}^{(0)} + \Delta J_{aa,sa}^{(0)}\big], \\ \gamma &\equiv \frac{2\rho}{k_B}\big[-\Delta E_{a,s} + \Delta J_{ss,sa}^{(0)} + \Delta\phi_{AB}\Delta\tilde{J}^{(0)}\big] \end{aligned} \tag{10}$$

are the two parameters depending on the excess $\Delta\phi_{AB} \equiv \phi_B - \phi_A$ of monomers $B$ over monomers $A$ and, in the case of an isotropic mixture, on the four inequalities completely characterizing the relative isotropic properties of all dimers, in correspondence with the following definitions:

$$\begin{aligned} \Delta J_{ss,sa}^{(k)} &\equiv \overline{J_{ij}^{(k)}} - \overline{J_{i3}^{(k)}}, \\ \Delta J_{aa,sa}^{(k)} &\equiv J_{33}^{(k)} - \overline{J_{i3}^{(k)}}, \\ \Delta\tilde{J}^{(k)} &\equiv \tfrac{1}{2}\big(J_{22}^{(k)} - J_{11}^{(k)}\big) - \big(J_{23}^{(k)} - J_{13}^{(k)}\big), \\ \Delta E_{a,s} &\equiv E_3 - \overline{E_i}, \quad i,j = 1,2, \end{aligned} \tag{11}$$

where isotropic $J_{ij}^{(0)}$ and anisotropic $J_{ij}^{(2)}$ coefficients of the approximation for the interaction between a dimer of kind $i$ and a dimer of kind $j$ are in correspondence with Eq. (2) and the averages over symmetrical ($s$) dimers $AA$ and $BB$ are defined as follows:

$$\begin{aligned} \overline{J_{ij}^{(k)}} &\equiv \tfrac{1}{4}\big(J_{11}^{(k)} + J_{22}^{(k)}\big) + \tfrac{1}{2} J_{12}^{(k)}, \\ \overline{J_{i3}^{(k)}} &\equiv \tfrac{1}{2}\big(J_{13}^{(k)} + J_{23}^{(k)}\big), \\ \overline{E_i} &\equiv \tfrac{1}{2}(E_1 + E_2). \end{aligned} \tag{12}$$

Only in the isotropic case, however, can the description be simplified by introducing only two parameters $\alpha$ and $\gamma$ according to Eq. (10). Both parameters $\alpha$ and $\gamma$ are different from zero in the case of distinguishable dimers.

### C. Determination of the signs of inequalities $\Delta J_{ss,sa}^{(k)}$, $\Delta J_{aa,sa}^{(k)}$, and $\Delta E_{a,s}$ from a molecular model

It is reasonable to suppose that the binding energy of asymmetrical dimers $AB$ is stronger than that of symmetrical dimers $AA$ and $BB$ (due to the polar structure of dimer $AB$ allowing a polar distribution of the electric charge along its principal axis). As a result, one monomer (let us say, $A$) can obtain a negative charge, while another monomer ($B$) can obtain a positive charge. The Coulomb attraction between monomers $A$ and $B$ enlarges their binding energy and thus $\Delta E_{a,s} > 0$, in correspondence with definition (11).

Now let us find out how the presence of the longitudinal dipole moment in each dimer $AB$ influences the balance between the interactions of various dimers. The interaction between particular dimers averaged with respect to their mutual position is approximated by Eq. (2), where the isotropic and anisotropic parts are present. The elongated rigid cores of all dimers ($AA$, $BB$, and $AB$) are expected to attract each other mainly due to the dispersion interactions, so the deepest

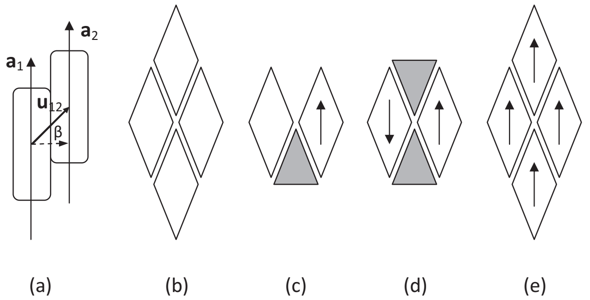

FIG. 4. (a) Nearest location of two dimers with principal axes parallel to each other, optimal packing of symmetrical dimers ($AA$ and/or $BB$) with (b) each other and (c) asymmetrical dimers $AB$, and optimal packing of dimers $AB$ with (d) antiparallel and (e) parallel dipoles. Areas where the presence of particular dimers is restricted by the dipole-quadrupole interaction are colored in gray.

minimum interaction potential between any pair of dimers should correspond to their nearest location with principal axes parallel to each other [see Fig. 4(a)]. Let us analyze how the electrostatic interaction between various dimers influences their total interaction. Since all dimers are electrically neutral, the electrostatic interaction between dimers is mainly represented by dipole-dipole and dipole-quadrupole interactions. Since the distribution of the short axes of all dimers is expected to be isotropic, it is sufficient to consider the uniaxial quadrupole moment $q_{\alpha\beta} = Q(a_\alpha a_\beta - \delta_{\alpha\beta}/3)$, the same for each kind of dimer, where $a_\alpha$ and $a_\beta$ are the projections of the principal axis $\mathbf{a}$ on coordinate axes $\alpha$ and $\beta$ and $\delta_{\alpha\beta}$ is the Kronecker symbol. For the same reason it is sufficient to consider the longitudinal dipole moment $\boldsymbol{\mu} = \mu\,\mathbf{a}$ for each dimer $AB$, while dimers $AA$ and $BB$ should not possess any dipole moments on average.

In the framework of the model described above, the electrostatic interaction of dimer $AB$ having principal axis $\mathbf{a}_1$ with a symmetrical dimer ($AA$ or $BB$) having principal axis $\mathbf{a}_2$ contains an additional term with respect to the electrostatic interaction of symmetrical dimers with each other ($AA$ with $AA$, $BB$ with $BB$, or $AA$ with $BB$): a dipole-quadrupole interaction [28]

$$U_{\mu Q}^{as} = \frac{3\mu Q}{r^4}\{2(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_2\cdot\mathbf{u}_{12}) + (\mathbf{a}_1\cdot\mathbf{u}_{12})[1-5(\mathbf{a}_2\cdot\mathbf{u}_{12})^2]\}, \tag{13}$$

where $\mathbf{u}_{12}$ is the unit vector connecting the dipole of one dimer with the quadrupole of another dimer, which are both located in the centers of cores of the corresponding dimers for simplicity. The potential (13) can be repulsive or attractive depending on the sign of angle $\beta$ [see Fig. 4(a)] and the signs of dipole $\mu$ and quadrupole $Q$, while the absolute value of $U_{\mu Q}^{as}$ is maximal at parallel principal axes $\mathbf{a}_1$ and $\mathbf{a}_2$. This fact should effectively enlarge the minimal approach for two dimers at one sign of angle $\beta$ and reduce it at the opposite sign of angle $\beta$. In other words, dimers $AB$ in contact with dimers $AA$ or $BB$ should behave as if the shape of both interacting dimers were less symmetrical than that of dimers $AA$ and $BB$ in contact with each other. An illustration of optimal packing of symmetrical dimers with each other and with asymmetrical dimers $AB$ is presented in Figs. 4(b) and 4(c), respectively, from where one concludes that packing (both isotropic and anisotropic) of dimers $AB$ with dimers $AA$ or $BB$ should not be as good as that of symmetrical dimers with each other. Therefore, it is reasonable to suppose $\Delta J_{ss,sa}^{(k)} > 0$ (for both $k = 0$ and 2).

The electrostatic interaction of two dimers $AB$ with each other contains two additional terms with respect to the electrostatic interaction of symmetrical dimers with each other: the dipole-dipole interaction

$$U_{\mu\mu}^{aa} = \frac{\mu^2}{r^3}\{(\mathbf{a}_1\cdot\mathbf{a}_2) - 3(\mathbf{a}_1\cdot\mathbf{u}_{12})(\mathbf{a}_2\cdot\mathbf{u}_{12})\} \tag{14}$$

and the dipole-quadrupole interaction

$$U_{\mu Q}^{aa} = \frac{3\mu Q}{r^4}\{2(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_2\cdot\mathbf{u}_{12}) + (\mathbf{a}_1\cdot\mathbf{u}_{12}) \times [1-5(\mathbf{a}_2\cdot\mathbf{u}_{12})^2] + 2(\mathbf{a}_2\cdot\mathbf{a}_1)(\mathbf{a}_1\cdot\mathbf{u}_{21}) + (\mathbf{a}_2\cdot\mathbf{u}_{21})[1-5(\mathbf{a}_1\cdot\mathbf{u}_{21})^2]\}, \tag{15}$$

where $\mathbf{u}_{21} = -\mathbf{u}_{12}$. If at $\mathbf{a}_1\|\mathbf{a}_2$ the dipoles of two dimers $AB$ are also parallel to each other, then the potential (15) is equal to zero. On the contrary, if at $\mathbf{a}_1\|\mathbf{a}_2$ the dipoles are antiparallel, the dipole-quadrupole interaction of dimers $AB$ with each other is twice that of dimers $AB$ with dimers $AA$ or with dimers $BB$ [compare to Eq. (13)]. Thus, on average, there should be no qualitative difference between the dipole-quadrupole interaction of dimers $AB$ with each other and with dimers $AA$ or $BB$. Therefore, $\Delta J_{aa,sa}^{(k)}$ at least should not be negative, which is in fact sufficient for our consideration. However, the dipole-dipole interaction can further optimize the packing of dimers $AB$ with each other since it is attractive on average over all configurations, where the presence of dimers is not restricted by the dipole-quadrupole interaction [see the illustration of optimal packing of dimers $AB$ with antiparallel and parallel dipoles in Figs. 4(d) and 4(e), respectively]. In particular, couplings of the nearest unfavorable antiparallel longitudinal projections of dipoles (along the vector connecting dipoles) are restricted [Fig. 4(d)], while couplings of the nearest favorable parallel longitudinal projections of dipoles are not restricted [Fig. 4(e)]. Couplings of the nearest transverse projections of dipoles (perpendicular to the vector connecting dipoles) equalize each other in Figs. 4(d) and 4(e). Therefore, it is reasonable to suppose $\Delta J_{aa,sa}^{(k)} > 0$ (for both $k = 0$ and 2).

### D. Recombination of dimers with temperature variation

Minimizing the free energy (9) with respect to $p_s$ under constraint (7), one obtains the simple equation

$$\frac{p_s^2 - \Delta\phi_{AB}^2}{4(1-p_s)^2} = \exp\left(\frac{\alpha}{T}p_s + \frac{\gamma}{T}\right) \tag{16}$$

determining the temperature dependence of $p_s$ in the isotropic phase. If temperature tends to infinity, the right-hand side of Eq. (16) tends to one and, as a result,

$$\lim_{T\to\infty} p_s = \tfrac{2}{3}\left[2 - \sqrt{4 - 3\left(1 + \Delta\phi_{AB}^2/4\right)}\right], \tag{17}$$

which is equal to one at $|\Delta\phi_{AB}| = 1$ (all monomers combine in either dimers $AA$ or dimers $BB$), equal to 2/3 at $\Delta\phi_{AB} = 0$ (fractions of dimers $AA$, $BB$, and $AB$ are equal to each other and equal to 1/3), and varies between one and 2/3 at other proportions of components $A$ and $B$.

From the presentation (9) for the free energy we can expect the phase transition from small $p_s$ to large $p_s$ with temperature variation if coefficients $\alpha$ and $\gamma$ have opposite signs. As discussed in the previous subsection, it is reasonable to suppose $\Delta E_{a,s} > 0$, $\Delta J^{(0)}_{ss,sa} > 0$, and $\Delta J^{(0)}_{aa,sa} > 0$. In this case we obtain positive $\alpha$, while $\gamma$ can be negative at an appropriate ratio of parameters $\Delta E_{a,s}$ and $\Delta J^{(0)}_{ss,sa}$. We also expect that inequality $\Delta \tilde{J}^{(0)}$ [see Eq. (11)] should be small and play almost no role because it reflects only the differences between similar pairs of dimers (two pairs of symmetrical dimers and two pairs both containing one symmetrical dimer and one asymmetrical dimer). At positive $\alpha$ and negative $\gamma$ we can introduce the dimensionless temperature $T/\alpha$ and the solution of Eq. (16) in terms of $T/\alpha$ depends only on the ratio $\gamma/\alpha$.

Let us first abstract from the influence of a small inequality $\Delta \tilde{J}^{(0)}$ and consider equal fractions of materials $A$ and $B$ [see Eq. (10)]. At $\gamma/\alpha \approx 0$ (when disproportion $\Delta J^{(0)}_{ss,sa}$ is comparable to disproportion $\Delta E_{a,s}$) the fraction of dimers $AB$, $p_{AB} = 1 - p_s$, starts from very small values at low temperatures and increases, tending to 1/3 at high temperatures [see Fig. 5(a)]. If disproportion $\Delta J^{(0)}_{ss,sa}$ is smaller than disproportion $\Delta E_{a,s}$, there can be several kinds of solutions. In the range $-2/3 < \gamma/\alpha < 0$ [see Figs. 5(b) and 5(c)] there exist three solutions for $p_{AB}$ within some temperature range (two free-energy minima and one maximum between them). The binding energy disproportion $\Delta E_{a,s}$ favors large $p_{AB}$ [the upper line in Figs. 5(b) and 5(c)], while the interaction

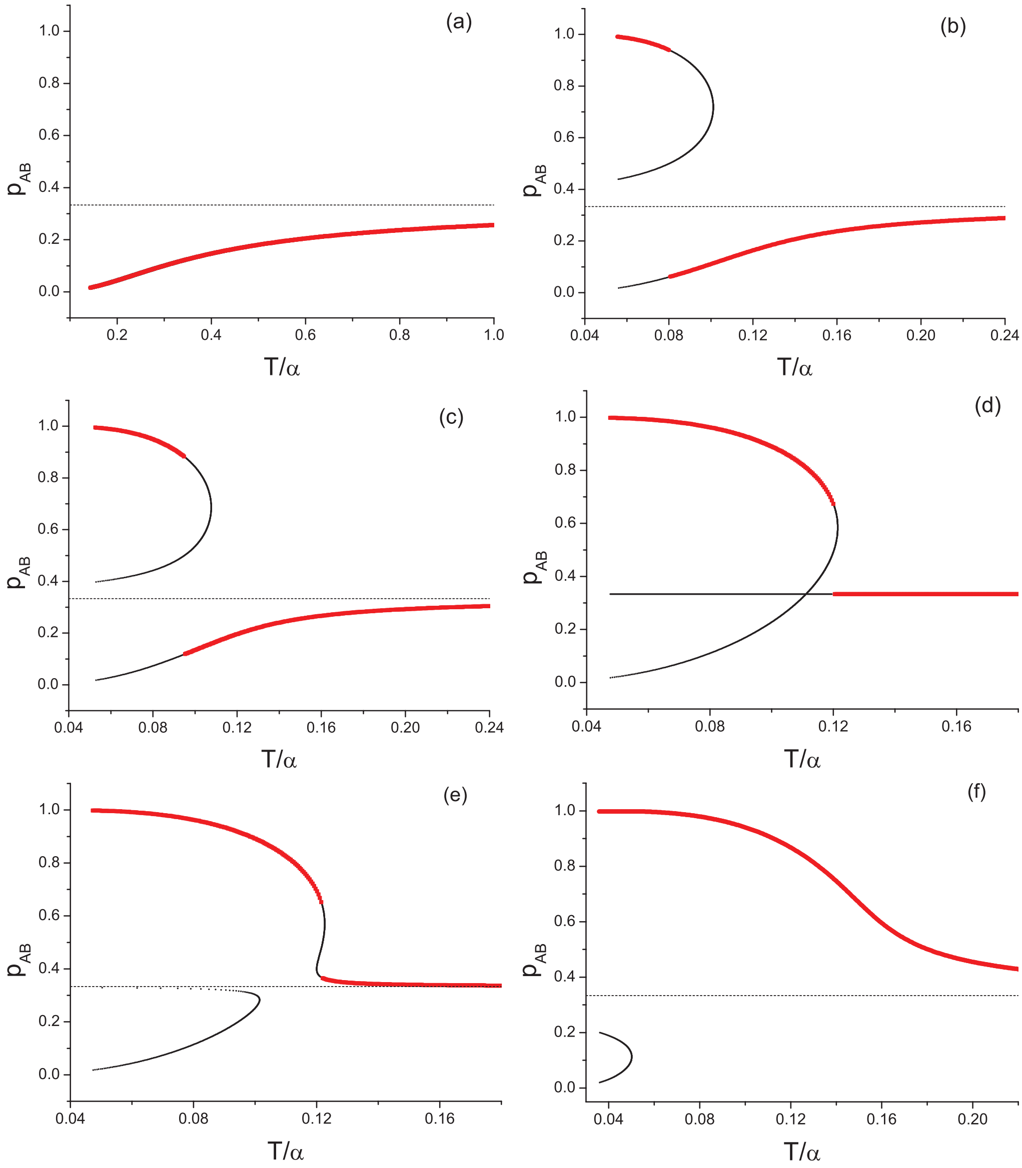

FIG. 5. (Color online) Temperature dependence of the fraction of dimers $AB$ in the isotropic mixture of materials $A$ and $B$ at $\Delta\phi_{AB} = 0$ and (a) $\gamma/\alpha = 0$, (b) $\gamma/\alpha = -0.61$, (c) $\gamma/\alpha = -0.63$, (d) $\gamma/\alpha = -2/3$, (e) $\gamma/\alpha = -0.67$, and (f) $\gamma/\alpha = -0.75$. Red thick lines correspond to the global minimum free energy, black thin lines correspond to the maximum or the secondary minimum free energy, and dashed horizontal lines depict level $p_{AB} = 1/3$ to which $p_{AB}$ tends at high temperature.

energy disproportion $\Delta J^{(0)}_{ss,sa}$ favors small $p_{AB}$ [the lower line in Figs. 5(b) and 5(c)]. The solution corresponding to the global free-energy minimum is presented by the red thick line and one notes that the first-order transition from the phase with large $p_{AB}$ to the phase with small $p_{AB}$ happens at some temperature. This transition is driven by the entropy [the first term in Eq. (9)], which favors the existence of two different kinds of dimers ($AA$ and $BB$) instead of single one ($AB$) and thus shifts the balance between the two free-energy minima when the temperature increases. The transition temperature itself increases with the decreasing ratio $\gamma/\alpha$ [compare Figs. 5(b) and 5(c)]. At high temperatures $p_{AB}$ tends to 1/3, similarly to the case presented in Fig. 5(a), because equal fractions of dimers $AA$, $BB$, and $AB$ correspond to the most preferable state from the entropy point of view [when both competing second and third energy terms in Eq. (9) are small with respect to the first one].

At a critical ratio $\gamma/\alpha = -2/3$ there is a unique balance between all energies, so equal fractions of all dimers ($p_{AB} = 1/3$) arise already at finite temperatures (just above the transition temperature [see Fig. 5(d)]). At $\gamma/\alpha < -2/3$ (disproportion $\Delta J^{(0)}_{ss,sa}$ is essentially smaller than disproportion $\Delta E_{a,s}$) the solution types change [see Figs. 5(e) and 5(f)] and $p_{AB}$ corresponding to the global minimum free energy becomes always above 1/3. In a very narrow ratio range $-0.672 < \gamma/\alpha < -2/3$ the first-order phase transition from large $p_{AB}$ to smaller $p_{AB}$, which is still larger than 1/3, happens [see Fig. 5(e)]. Finally, at $\gamma/\alpha < -0.672$ there is no phase transition anymore [see Fig. 5(f)] and the fraction of dimers $AB$ decreases continuously with increasing temperature and tends to 1/3 at high temperatures, as in the previous cases.

It is important to note, however, that the inequality of fractions $\Delta\phi_{AB}$ strongly influences the transition temperature. In the general case $p_{AB}$ can vary between zero and the value that is twice as large as the smaller monomer fraction ($\phi_A$ at $\Delta\phi_{AB} > 0$ or $\phi_B$ at $\Delta\phi_{AB} < 0$). Several solutions for various $\Delta\phi_{AB}$ at a particular choice of the interaction constants are presented in Fig. 6, where one may note that the transition temperature is largest at $\Delta\phi_{AB} = 0$ and smaller at $\Delta\phi_{AB} \neq 0$ (when the excess of the particular fraction $A$ or $B$ increases the fraction of dimers $AA$ or $BB$ and reduces the fraction of dimers $AB$) and finally the transition temperature tends to zero at $\Delta\phi_{AB} = \pm 1$ (when only dimers $AA$ or $BB$ can exist).

### E. Role of anisotropy

Now let us take into account the anisotropic parts of interactions $J^{(2)}_{ij}$ for each pair of dimers ($i = 1,2,3$). Arguments about the particular choice of inequalities of both isotropic $J^{(0)}_{ij}$ and anisotropic $J^{(2)}_{ij}$ interactions were discussed in Sec. III C, where both $\Delta J^{(2)}_{ss,sa}$ and $\Delta J^{(2)}_{aa,sa}$ were obtained to be positive (symmetrical dimers $AA$ and $BB$ should have better coupling with each other than with asymmetrical dimers $AB$ and asymmetrical dimers $AB$ also should have better coupling with each other than with symmetrical dimers $AA$ and $BB$). One notes from the general presentation considered in Sec. III A that isotropic and anisotropic interactions are auxiliary to each other and the only problem with anisotropic interactions is that temperature dependences of dimer fractions $p_i$ cannot be analyzed in a simple mathematical way. In contrast, anisotropy of the mixture of dimers $AA$, $BB$, and $AB$ allows one to detect the transition from one nematic phase $N_{AB}$ consisting mostly of dimers $AB$ to another nematic phase $N_{AA,BB}$ consisting mostly of dimers $AA$ and $BB$ with variation of temperature simply by observation of dielectric anisotropy. The corresponding temperature dependences of the fraction $p_{AB}$ for various mutual concentrations of components $A$ and $B$ and of the order parameters of each fraction obtained by solving Eqs. (3), (7), and (8) numerically are presented in Figs. 7(a) and 7(b), respectively.

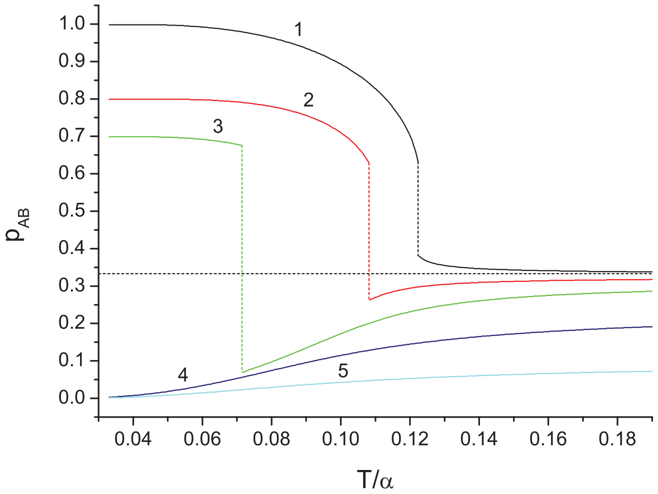

FIG. 6. (Color online) Temperature dependence of the fraction of dimers $AB$ in the isotropic mixture of materials $A$ and $B$ at weight proportions 50/50 (curve 1), 40/60 (curve 2), 65/35 (curve 3), 20/80 (curve 4), and 94/6 (curve 5). Here $\Delta\tilde{J}^{(0)} = 0$ and $\gamma/\alpha = -0.67$. The dashed horizontal line depicts level $p_{AB} = 1/3$ to which $p_{AB}$ tends at high temperature at equal fractions of materials $A$ and $B$.

Several curves in Fig. 7(a) have two discontinuities: one corresponding to the recombination of dimers $AB$ into dimers $AA$ and $BB$ (having the same origin as the phase transitions presented in Figs. 5 and 6) and another one corresponding to the transition from the nematic phase to the isotropic phase (as in classical Maier-Saupe theory). Mathematically, the nematic-isotropic phase transition can be shifted to any temperature by a proportional reduction or enhancement of all anisotropic coefficients $J^{(2)}_{ij}$ with respect to isotropic coefficients $J^{(0)}_{ij}$. Therefore, for an appropriate choice of the coefficients, the recombination can happen in the isotropic phase at small $\Delta\phi_{AB}$ [see curves 1–3 in Fig. 7(a), where the lower-temperature discontinuity is the nematic-isotropic phase transition and the higher-temperature discontinuity is the recombination] or together with the nematic-isotropic phase transition at intermediate $\Delta\phi_{AB}$ (see curve 4, where there is a single discontinuity) or in the nematic phase at large $\Delta\phi_{AB}$ (see curves 5 and 6, where the lower-temperature discontinuity is the recombination and the higher-temperature discontinuity is the nematic-isotropic phase transition). The recombination temperature can also be below the observation range (see curve 7), in particular below the nematic phase range. In addition, the maximum value of $p_{AB}$ decreases, when inequality $|\Delta\phi_{AB}|$

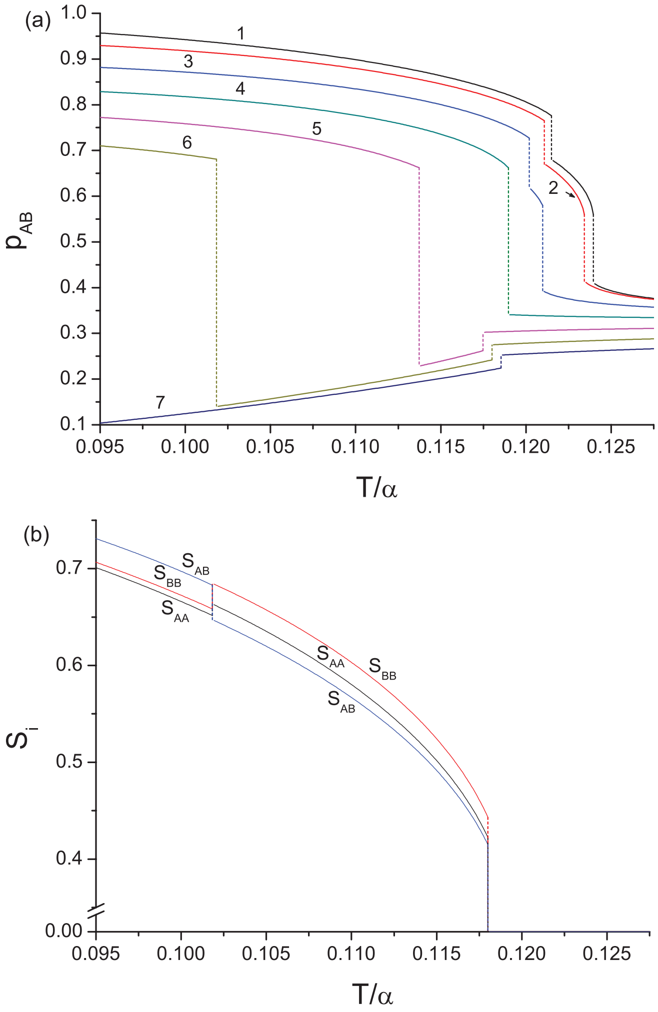

FIG. 7. (Color online) Temperature dependence of (a) the fraction of dimers $AB$ in the anisotropic mixture of materials $A$ and $B$ at $\Delta\phi_{AB} = 0$ (curve 1), 0.05 (curve 2), 0.1 (curve 3), 0.15 (curve 4), 0.2 (curve 5), 0.25 (curve 6), and 0.3 (curve 7) and (b) the nematic order parameters of dimers $AA$, $BB$, and $AB$ at $\Delta\phi_{AB} = 0.25$. Here $\Delta J^{(0)}_{ss,sa}/\alpha' = 0.85$, $\Delta J^{(0)}_{aa,sa}/\alpha' = 0.15$, $\Delta\tilde{J}^{(0)}/\alpha' = -4.2 \times 10^{-2}$, $\Delta E_{a,s}/\alpha' = 1.5$, $\overline{J^{(2)}_{ij}}/\alpha' = 2$, $\overline{J^{(2)}_{i3}}/\alpha' = 1.7$ $(i,j = 1,2)$, $\Delta J^{(2)}_{ss,sa}/\alpha' = 0.3$, $\Delta J^{(2)}_{aa,sa}/\alpha' = 0.05$, and $\Delta\tilde{J}^{(2)}/\alpha' = -10^{-2}$, with $\alpha' \equiv k_B\alpha/2\rho$.

increases, because an excess number of monomers $|\Delta\phi_{AB}|$ of a major fraction cannot participate in the formation of dimers $AB$.

At the recombination temperature the order parameter of dimers $AB$ decreases [see Fig. 7(b)] because below this temperature a large number of dimers $AB$ interact mostly with each other [interaction $J^{(2)}_{33}$ dominates in Eq. (3) for $S_3$], while above this temperature a small number of dimers $AB$ interact mostly with dimers $AA$ and $BB$ [interaction $\overline{J^{(2)}_{i3}}$, in correspondence with definition (12), dominates in Eq. (3) for $S_3$]; the latter is smaller since $\Delta J^{(2)}_{aa,sa} > 0$, in correspondence with definition (11). On the contrary, the order parameters of dimers $AA$ and $BB$ arise at the recombination temperature because below this temperature a small number of dimers $AA$ and $BB$ interact mostly with dimers $AB$ [interaction $\overline{J^{(2)}_{i3}}$ dominates in Eq. (3) for $S_1$ and $S_2$], while above this temperature a large number of dimers $AA$ and $BB$ interact mostly with each other [interaction $\overline{J^{(2)}_{ij}}$ dominates in Eq. (3) for $S_1$ and $S_2$]; the latter is larger since $\Delta J^{(2)}_{ss,sa} > 0$.

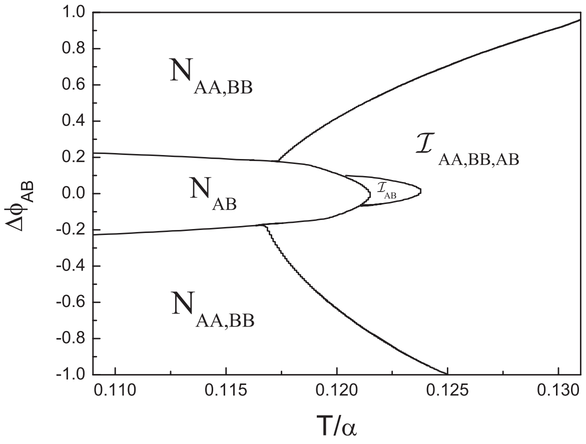

FIG. 8. Phase diagram containing two nematic phases and two isotropic phases at $\Delta J^{(0)}_{ss,sa}/\alpha' = 0.85$, $\Delta J^{(0)}_{aa,sa}/\alpha' = 0.15$, $\Delta\tilde{J}^{(0)}/\alpha' = -4.2 \times 10^{-2}$, $\Delta E_{a,s}/\alpha' = 1.5$, $\overline{J^{(2)}_{ij}}/\alpha' = 2$, $\overline{J^{(2)}_{i3}}/\alpha' = 1.7$ $(i,j = 1,2)$, $\Delta J^{(2)}_{ss,sa}/\alpha' = 0.3$, $\Delta J^{(2)}_{aa,sa}/\alpha' = 0.05$, and $\Delta\tilde{J}^{(2)}/\alpha' = -10^{-2}$, with $\alpha' \equiv k_B\alpha/2\rho$.

The phase diagram is presented in Fig. 8, where one can see that two nematic phases and two isotropic phases can generally be distinguished. In one nematic phase $N_{AB}$ almost all monomers are combined in dimers $AB$, while in the other nematic phase $N_{AA,BB}$ almost all monomers are combined in either dimers $AA$ or dimers $BB$. By analogy, in one isotropic phase $\mathcal{I}_{AB}$ almost all monomers are combined in dimers $AB$, while in the other isotropic phase $\mathcal{I}_{AA,BB,AB}$ all three kinds of dimers are present in almost equal proportions for this particular choice of parameters.

## IV. COMPARISON OF THEORETICAL AND EXPERIMENTAL RESULTS

Suppose that material $A$ is alkoxybenzoic acid 7OBAC, while material $B$ is alkoxybenzoic acid 6OBAC. For an almost pure material $A$ (the lower part of the diagram in Fig. 8) and an almost pure material $B$ (the higher part of the diagram in Fig. 8) only one nematic phase $N_{AA,BB}$ is observed, mostly consisting of symmetrical dimers $AA$ (in the case of domination of material $A$) or dimers $BB$ (in the case of domination of material $B$). As we discussed in Sec. II, in the symmetrical dimers all permanent longitudinal dipoles are compensated for and therefore the electronic clouds should be symmetrical with respect to the middle of each dimer in the absence of the electric field. The external electric field can easily shift the electronic clouds along the principal axes of dimers in this case and therefore the dielectric anisotropy should be positive (as in most of the elongated molecules). From experiment (Fig. 1, curves 1 and 6) one can see that pure materials 6OBAC and 7OBAC have positive dielectric anisotropy in the whole range of the nematic phase.

On the contrary, at almost equal proportions of components $A$ and $B$ (the middle of the diagram in Fig. 8) only a different nematic phase $N_{AB}$ is observed, mostly consisting of asymmetrical dimers $AB$. In the asymmetrical dimers the permanent longitudinal dipoles can exist and therefore the electronic clouds appear to be shifted with respect to the middle of each dimer even in the absence of the electric field. In this case a further shift of the electronic clouds in the external electric field is hindered and therefore the dielectric anisotropy appears to be negative. From experiment (Fig. 1, curve 4) one can see that a 50/50 percentage mixture of 6OBAC and 7OBAC has negative dielectric anisotropy in the whole range of the nematic phase. If the percentage of the components is essentially different from 100/0, 0/100, and 50/50, both nematic phases are observed in the phase diagram in Fig. 8: $N_{AB}$ at lower temperature, since the binding energy of dimers $AB$ is stronger than that of dimers $AA$ and $BB$, and $N_{AA,BB}$ at higher temperature, since entropy favors the existence of two kinds of dimer $AA$ and $BB$ rather than one kind $AB$.

The choice of the coefficients used in Figs. 7 and 8 corresponds to the situation when the inequality of interactions $\Delta J_{ss,sa}^{(k)}$ is not sufficiently large with respect to the inequality of binding energies $\Delta E_{a,s}$ to generate the transition between phases $N_{AB}$ and $N_{AA,BB}$ at equal monomer fractions. In this case only $N_{AB}$ arises, similarly to the case presented in Fig. 1, curve 4. However, if the monomer fractions are not equal, the temperature-induced transition between phases $N_{AB}$ and $N_{AA,BB}$ becomes possible, similarly to the cases presented in Fig. 1, curves 2, 3, and 5, because an excess of the major fraction (let us say, $B$) always has to combine partially into dimers $BB$, whose interaction with dimers $AA$ and $BB$ is stronger than their interaction with dimers $AB$. When the inequality of fractions further increases, only one fraction (let us say, $B$) remains and the transition between phases $N_{AB}$ and $N_{AA,BB}$ again becomes impossible, similarly to the cases presented in Fig. 1, curves 1 and 6.

Qualitatively, the tendency presented in Figs. 7 and 8 is the same, as in experiment (Fig. 1). Therefore, we suggest that alkoxybenzoic acids 6OBAC and 7OBAC should match the parameters used in Figs. 7 and 8 and the two nematic phases observed for unequal fractions of 6OBAC and 7OBAC should be $N_{AB}$ and $N_{AA,BB}$.

## V. CONCLUSION

In the present paper we derived a theoretical approach explaining the recombination in a triple mixture of mesogenic dimers $AA$, $BB$, and $AB$, consisting of nonelongated monomers $A$ and $B$. We assumed that each dimer possesses the finite binding energy and therefore each pair of dimers can recombine to a different pair of dimers with variation of temperature. It is known that entropy can induce the transition from the nematic phase to the isotropic phase in mesogenic materials. Here we outlined another effect that can be driven by entropy in the mixture described above: a transition from one nematic phase $N_{AB}$, where a large fraction of monomers combine in dimers $AB$, to a different nematic phase $N_{AA,BB}$, where almost all monomers combine in either dimers $AA$ or dimers $BB$.

An example of the mixture described above, a mixture of alkoxybenzoic acids 6OBAC and 7OBAC, is investigated experimentally and the temperature-induced phase transition between two nematic phases is registered at unequal proportions of the components. Alkoxybenzoic acids 6OBAC (material $A$) and 7OBAC (material $B$) have very similar chemical structures. However, a small difference between them can play a crucial role. For example, the binding energy of dimers $AB$ can be stronger than that of dimers $AA$ and $BB$ because of the electronic cloud shift between monomers $A$ and $B$. In addition, due to dipole-quadrupole interaction, asymmetric dimers $AB$ should have worse coupling with dimers $AA$ and $BB$ than symmetric dimers with each other ($AA$ with $AA$, $BB$ with $BB$, or $AA$ with $BB$). On the contrary, asymmetric dimers $AB$ should have better coupling with each other than with symmetric dimers due to dipole-dipole interaction. In this case the creation of either the pure fraction $AB$ or the mixture without dimers $AB$ at all is energetically favorable. Therefore, entropy can cause the transition from $N_{AB}$ to $N_{AA,BB}$ with increasing temperature because it favors the existence of two different kinds of dimer $AA$ and $BB$ rather than a single kind of dimer $AB$.

## ACKNOWLEDGMENTS

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