Orientational and thermodynamic properties of rod - plate mixtures

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Abstract. The molecular-statistical model of a fluid composed of rectangular parallelepipeds, that is continuous in translations and discrete in orientation distribution, is employed in calculations relating to regions corresponding to the stability of uniaxial and biaxial nematic phases in model mixtures of uniaxial rod-like and plate-like particles, interacting via steric repulsion. The calculations are performed taking into account three-particle correlations. It is shown that for fixed overall mole fraction, the value of the configurational Gibbs free energy of a biaxial phase is equal to that of a system with a miscibility gap containing two uniaxial nematic phases, one rich in rod-like molecules and the other in plate-like ones. The results of the present study are compared with those of studies of related model systems.

1. Introduction

The phase diagrams of model nematic mixtures containing oblate and prolate molecules continue to attract considerable research activity. The studies are motivated by the interest in the discussion of the formation of a biaxial nematic phase (B), which may result from the mixing of axially symmetric particles, even though the pure components exhibit only uniaxial nematic phases [1–7]. In the case of one-component fluids the formation of a biaxial phase is predetermined by biaxiality of molecules (defined through either biaxiality of their molecular shape or anisotropy of their polarizability [8]), whereas in binary systems this phenomenon is due to the interaction of unlike particles which causes mutually orthogonal orientation of their principal axes. The idea was initiated by Alben in the framework of the lattice model [1], and confirmed in studies based on the Onsager theory [2, 3] and a model of the van der Waals type [4].

Experimental evidence for the occurrence of a biaxial phase has been obtained only for some lyotropics for a region separating uniaxial nematic phases, one formed of rod-like micelles and the other of lamellae [9]. However, the interpretation of these results on the molecular level is complicated because of the size and shape dependency of micelles on the overall composition of the system. As for thermotropic nematic liquid crystals, the study of a mixture of calamitic and discotic nematogens by the use of the polarized microscopy technique has revealed the split into two uniaxial nematic phases [10].

Parallel and subsequent theoretical studies have been carried out on the basis of various approaches. The mean-field model [5] as well as Monte Carlo simulations [7] have shown a

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close relationship between the peculiarities of nearest-neighbouring interactions of rods and disks and the thermodynamic stability of a biaxial nematic. The analysis of hard-rod–plate mixtures recently performed on the basis of the Onsager–Zwanzig theory has indicated that below a certain critical value of the asphericity factor of constituent particles, the probability of formation of a biaxial nematic is limited by an entropy-driven split into two coexisting rod-like (N_+) and plate-like (N_-) uniaxial nematic phases [6].

The present study is focused on the re-investigation of phase regions of biaxial and uniaxial symmetry in a binary mixture composed of sterically interacting uniaxial rods and plates which are represented by rectangular parallelepipeds. The faces of the particles are parallel to the X-, Y-, and Z-axes of a space-fixed coordinate frame. The calculations are based on models of multicomponent systems of blocks, suggested earlier by Tumanyan and Sokolova [11, 12]. The hole lattice version of this model has been developed using the Flory–Alben combinatorial method [1] for calculating the number of configurations. The method has been adapted so as to take into account all of the possible orientations of the triplets of particles on a cubic lattice. For a particular case of a system composed of uniaxial blocks, the lattice model results are shown to be identical to those of Mitra and Allnatt [13] who utilized the so-called complete star approximation based on the summation of Mayer full stars in the virial expansion of the configurational entropy. The quasichemical treatment of attractive interactions carried out in reference [14] indicated that the lattice approach offers considerable latitude as a formal structure suitable for correlating orientational and thermodynamic functions of some real nematic mixtures.

In the present paper we used the continuous version of the corresponding lattice theory, i.e. a mixture of parallelepipeds with continuous translation coordinates. The assumption that the principal axes of the particles are parallel to the X-, Y-, and Z-axes made it possible to obtain expressions for thermodynamic functions of nematic mixtures in a rather simple form. One advantage of this approach is that calculations can be carried out without complicated estimations of the third virial coefficient for mixtures in approaches using virial expansion methods. The model proved to be successful in studying trends of nematic ordering and the lines of coexistence of the isotropic and uniaxial nematic phases in mixed nematic systems [15].

The statement of the present problem is influenced mostly by modern microscopic theories of the mesogenic state, which attribute the correlation structure of nematics to the anisotropy of intermolecular repulsion forces [16, 17]. This concept stimulates the study of athermal mixtures, i.e. systems which have solely hard-core interactions. Such fluids of anisometric hard particles play an important role as reference systems in the elaboration of and applying methods to the model description of mesomorphic mixtures.

2. The molecular-thermodynamic framework

In the present study, we employ a model of a nematic mixture of hard rectangular parallelepipeds, their principal axes being directed along the X-, Y-, and Z-axes of a space-fixed coordinate frame [12]. The binary fluid is composed of $N = N_1 + N_2$ particles having a volume v_k ($k = 1, 2$) and sizes $A_1^{(k)} \times A_2^{(k)} \times A_3^{(k)}$; the limits $A_1^{(1)} > A_2^{(1)} = A_3^{(1)}$ and $A_1^{(2)} < A_2^{(2)} = A_3^{(2)}$ correspond to uniaxial rods and plates, respectively. In the general case, where $A_1^{(1)} \neq A_2^{(1)} \neq A_3^{(1)}$, each particle can adopt six discrete orientations.

The orientation distribution is described by $\{s_{\alpha k}\}$ ($s_{\alpha k} = N_{\alpha k}/N_k$, $\sum_\alpha s_\alpha = 1$), a set of fractions of particles of sort k with orientation α.

The unit vectors $\boldsymbol{e}_{1k}, \boldsymbol{e}_{2k}, \boldsymbol{e}_{3k}$ lie along the edges $A_1^{(k)}, A_2^{(k)}, A_3^{(k)}$ of a particle, and the

director of the predominant orientation n is parallel to the Z-axis. Then a procedure of labelling orientations can be performed so that $\alpha = 2i - 1, 2i$ $(i = 1, 2, 3)$, if $|(n, e_{ik})| = 1$. Then for an axial-symmetry nematic phase of biaxial particles,

$$s_1 = s_2 \qquad s_3 = s_4 \qquad s_5 = s_6 \tag{1}$$

and for an axial-symmetry phase of uniaxial particles,

$$s_1 = s_2 \qquad s_3 = s_4 = s_5 = s_6. \tag{2}$$

The ordering of principal axes of uniaxial particles with respect to n is defined in terms of statistical averages [1, 4, 12, 14]:

$$S_k = (3s'_{1k} - 1)/2 \qquad (k = 1, 2) \tag{3}$$

where the notation $s'_1 = 2s_1$ is employed.

In a biaxial phase having two mutually orthogonal axes of the preferred orientation, additional characteristics of the ordering of uniaxial particles are introduced, namely

$$T_k = s'_{2k} - s'_{3k} \tag{4}$$

where $s'_{2k} = 2s_{3k}$, $s'_{3k} = 2s_{5k}$. The parameters T_k express the orientation order of the principal axes of the rods and plates in the plane XY. In the case of a uniaxial nematic phase, the condition $T_1 = T_2 = 0$ holds, while for an isotropic phase one has $S_1 = S_2 = T_1 = T_2 = 0$.

For the configurational Helmholtz free energy, F_{conf}, the continuum limit of the function, corresponding to the lattice version of the same basic model [12, 14], is used. As shown in the appendix, the model with continuous translation coordinates can be obtained by taking the zero limit of the lattice cell volume, holding the density constant. In the general case of a mixture of rectangular blocks with D_{2h} symmetry, the configurational Helmholtz free energy, $F_{conf}(\{s_{\alpha k}\})$, and the pressure equation of state are given by

$$\frac{F_{conf}}{NkT} = \sum_k y_k \left\{ \sum_{\alpha=1}^{6} s_{\alpha k} \ln s_{\alpha k} - 1 + \ln \frac{\varphi_k}{v_k(\bar{V} - 1)} \right\}$$
$$+ f_k \left[\frac{1}{\bar{V} - 1} \sum_{i=1}^{3} (a_i b_i) + \frac{1}{(\bar{V} - 1)^2} \prod_{i=1}^{3} a_i \right] \tag{5}$$

$$\frac{Pa^3}{kT} = \sum_k \frac{\varphi_k}{f_k(\bar{V} - 1)} + \sum_{i=1}^{3} \frac{a_i b_i}{(\bar{V} - 1)^2} + \frac{2}{(\bar{V} - 1)^3} \prod_{i=1}^{3} a_i \tag{6}$$

where V is the volume of a system:

$$\bar{V} = V \bigg/ \sum_k N_k v_k = 1/\eta$$

where η is the density (the packing fraction),

$$a_i \equiv \sum_{k=1}^{2} \varphi_k \sum_{\alpha=1}^{6} s_\alpha / f_\alpha^{(i)} \qquad b_i = \sum_{k=1}^{2} \varphi_k \sum_{\alpha=1}^{6} s_\alpha f_\alpha^{(i)} / f_k \tag{7}$$

and y_k and $\varphi_k = y_k v_k / \sum_i y_i v_i$ are the mole and volume fractions of the component of kind k, α is the unit length, $f_k = v_k/a^3$, and $f_{\alpha k}^{(i)}$ is the dimensionless length of an edge of a molecule of the component k with orientation α constrained to be parallel to the direction i $(i = X, Y, Z)$. The input model parameters are the aspect ratios, $\gamma_k = A_1^{(k)}/A_2^{(k)}$, and the ratios of molecular volumes, v_1/v_2.

Since the internal energy in an athermal model is identically zero, thermodynamic properties may be expressed in terms of the reduced temperature:

$$T^* = kT/Pv \tag{8}$$

independently of the separate values of P and T.

To check the stability of the possible phase states, the configurational terms of the normalized Gibbs free energy

$$G_{conf}/NkT = (F_{conf} + PV)/NkT \tag{9}$$

are evaluated and compared at fixed values of T^* and the overall mole fraction of the system.

After substitution of the relation

$$V\Big/\sum N_k = \left(V\Big/\sum N_k v_k\right)\sum v_k\left(N_k\Big/\sum N_k\right) = \frac{1}{\eta}\sum y_k v_k \tag{10}$$

and by using the definition

$$\Phi_1 = Pv_1/kT \tag{11}$$

for the compressibility factor of the component of kind 1, the Gibbs energy can be written in the form

$$\frac{G_{conf}}{NkT} = \frac{F_{conf}}{NkT} + \frac{\Phi_1}{\eta v_1}\sum y_k v_k = \frac{F_{conf}}{NkT} + \frac{(\Phi_1)_{NI}}{t^*}\left(y_1 + \frac{v_1}{v_2}y_2\right) \tag{12}$$

where

$$t^* = T^*/(T_{NI}^*)_1 = (\Phi_{NI})_1/\Phi_1 \tag{13}$$

is the reduced temperature normalized with respect to the reduced transition temperature of the component of kind 1 ('NI' stands for nematic–isotropic).

To elucidate the correspondence between the present model and other modern descriptions of anisometric-particle fluids, we compare it with approach based on the third-order truncation of the Y-series given by Gelbart and Barboy [18].

Let us consider the particular case of an isotropic one-component hard-particle fluid. According to reference [18], the usual virial equation of state

$$Pv/kT = \sum_{n\geqslant 1} B_n \eta^n \tag{14}$$

can be resummarized in the form

$$Pv/kT = \sum_{n\geqslant 1} C_n Y^n \tag{15}$$

where $Y = \eta/(1-\eta)$.

The relationships between the second and third coefficients of the two series are

$$C_2 = B_2 - 1 \qquad C_3 = B_3 - 2B_2 + 1. \tag{16}$$

For an isotropic phase of the system under study, equation (6) can be rearranged to give

$$\frac{Pv}{kT} = y + \frac{(\gamma+2)(\gamma^{-1}+2)}{3}y^2 + \frac{2}{27}\gamma(\gamma^{-1}+2)^3 y^3. \tag{17}$$

By comparing expression (17) with the truncated Y-expansion (15) and taking into account the relationships (16), the following expressions for the reduced values of B_2 and B_3 can easily be derived:

$$B_2 = \frac{(\gamma+2)(\gamma^{-1}+2)}{3} + 1 \qquad B_3 = \frac{2}{27}\gamma(\gamma^{-1}+2)^3 + \frac{2}{3}(\gamma+2)(\gamma^{-1}+2) + 1. \tag{18}$$

These expressions are identical with those of the discrete representations for B_2 and B_3 obtained in [19] in the framework of Mayer cluster theory of gas mixtures. In this study, a one-component fluid of blocks having D_{4h} symmetry was treated as a mixture of three types of block, each restricted to pointing in a fixed direction.

As follows from (18), for a fluid of hard parallel cubes one has $B_2 = 4$ and $B_3 = 9$. These values are identical to the well-known results of reference [20].
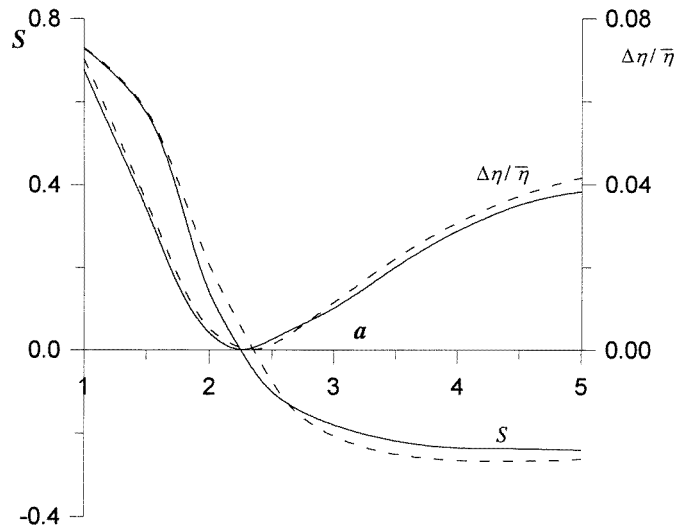
Figure 1. Numerical results of the present model (solid lines) and the Y-approximation [15] (dashed lines) for $\Delta\eta/\bar{\eta}$ (the r.h.s. ordinate scale) and S (l.h.s.) for a one-component fluid of hard blocks with dimensions $5 \times x \times 1$.

Let us consider the another case for comparison, namely a fluid of blocks with D_{2h} symmetry having dimensions $5 \times x \times 1$, where $1 \leqslant x \leqslant 5$. Thus, the shape of the particles changes from rod-like to plate-like. Earlier, a fluid of such particles was studied by Gelbart and Barboy [18] in order to view the effect of particle biaxiality on the characteristics of the NI transition order. Figure 1 shows the variations of the order parameter and relative density discontinuity with the parameter x, calculated in the present approach, along with the results replotted from reference [18]. Without discussing the limitations of the discrete-orientation models which are studied in reference [8], one can see that lowering the symmetry of the particles results in the reduction of the degree of first-order character of the NI transition. As is shown in figure 1, the present model provides satisfactory agreement with the data from the Y-expansion method.

3. Results and discussion

The data from the present study refer to the following three binary rod–plate mixtures, whose constituent species have the same anisometry factor: I: $\gamma_1 = 3, \gamma_2 = 1/3$; II: $\gamma_1 = 5, \gamma_2 = 1/5$; and III: $\gamma_1 = 10, \gamma_2 = 1/10$.

In table 1 the results of calculations for several thermodynamic parameters at the NI transition are collected together for the pure components of the mixtures studied. As the information concerning the comparison of fluids of rectangular rods and plates is not

Table 1. Comparison of the calculated NI transition parameters in the present model of a rectangular-block system (A) with the results of the Y-expansion method (B [21], C* [22]) and Monte Carlo simulations (D [23]) for a fluid of hard ellipsoids of revolution.

γ	Method	Φ	$\bar{\eta}$	$10^2(\Delta\eta/\bar{\eta})$	S
3	A	4.304	0.440	2.4	0.673
	B	8.107	0.473	3.4	0.641
	D	9.786	0.512	1.9	—
1/3	A	3.476	0.409	2.4	0.449
	B	6.081	0.433	2.1	0.456
	D	9.294	0.505	1.6	—
5	A	1.224	0.275	7.0	0.730
	C	2.093	0.297	9.4	0.647
1/5	A	1.025	0.249	4.2	0.525
	C	2.007	0.281	9.2	0.642
10	A	0.371	0.143	15.6	0.802
	C	0.891	0.179	16.8	0.718
1/10	A	0.324	0.126	10.3	0.635
	C	0.794	0.157	16.6	0.714

*Method B, as compared to method C, corresponds to the revised third virial coefficient of an ellipsoid-of-revolution fluid.

reported, the results from reference [21] for systems of ellipsoids of revolution are also included in the table to allow one to compare qualitatively the trends in the change of thermodynamic properties following the passage from rod- to plate-like molecules with the same anisometry factor. It can be seen that although the present model is somewhat artificial because of the restricted orientations of particles, it nonetheless provides a qualitative description of the tendencies in the phase transition parameters, which agree with those obtained from other methods and computer simulation. The evidence for this comes from the results of table 1, showing that the compressibility factor, the density, and the discontinuity in the density reduce during the transformation from rods to plates as well as during that from prolate to oblate particles. The discrepancy in the phase transition parameters for fluids of rods and plates with the same value of the anisometry factor manifests the effect of three-particle correlations on the behaviour of nematic fluids. The difference is known to be missing in the second virial approximation [21].

The thermodynamic properties of the mixtures under consideration are discussed in terms of the reduced temperature t^* which is defined in relations (8) and (13). The reduced transition temperatures of the constituent components in each mixture were set equal, which was achieved by ascribing relevant values to the ratios of the molecular volumes. Indeed, for fixed pressure, the relation $v_1/v_2 = (\Phi_1)_{NI}/(\Phi_2)_{NI}$ holds as long as the scaled pressure $(\Phi_k)_{NI}$ of a pure component k depends on γ_k only [12]. The ratios v_1/v_2 in the systems I, II, and III equal 1.2384, 1.1943, and 1.1451, respectively.

The calculated fragments of the reduced temperature–concentration phase diagrams are shown in figure 2. The regions a, b, and c corresponding to the non-zero values of the 'biaxiality parameters' T_1 and T_2 are those of biaxial phases. They fill the gap between the stability areas of the uniaxial phases N_+ and N_-. The boundaries of the biaxial phases
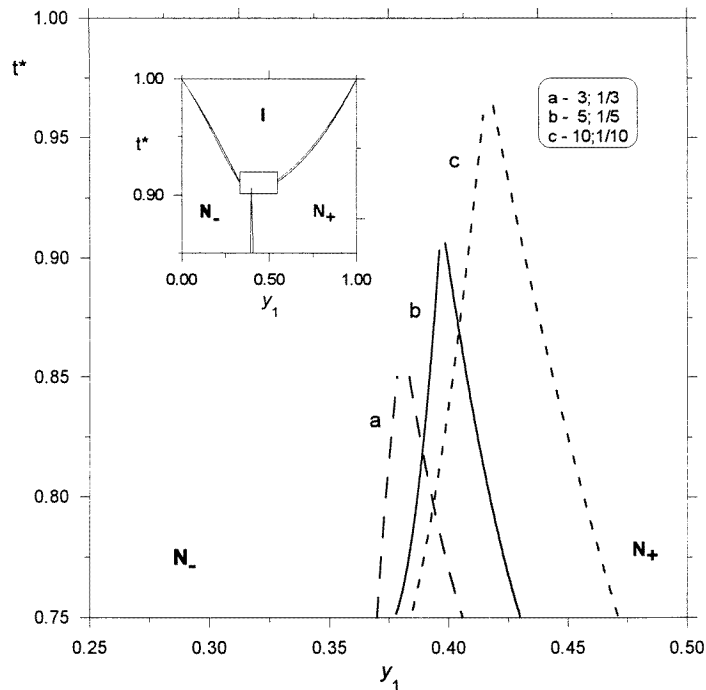
Figure 2. Fragments of the t^*–y phase diagram for mixtures of rods with $\gamma_1 = 3$, 5, and 10, and plates with $\gamma_2 = 1/3$, 1/5, and 1/10, respectively. The inset shows the t^*–y diagram for $\gamma_1 = 5, \gamma_2 = 1/5$. The rectangular region contains either the critical point corresponding to the intersection of N_+–B and N_-–B boundaries, or the short tie-line with a eutectic-type point displaying the coexistence of N_+, N_-, and isotropic phases.

are determined by extrapolation of the parameters T_1 and T_2 to zero. This procedure corresponds to the location of branching points in the set of five non-linear equations, providing the minimum of G_{conf}/Nk_BT with respect to the sets $\{S_k\}$ and $\{T_k\}$ for fixed reduced temperature t^*.

Figure 3 displays the dependencies of the parameters T_1, T_2 and S_1, S_2 on composition in the vicinity of the N_+–B transition for system II. The positive values of S_1 indicate that the long axes of the rods are constrained to lie along the Z-axis, whereas the negative values of S_2 show that the principal axes of the plates are mainly orthogonal to the Z-axis. As follows from the calculations, on crossing the N_+–B boundary, the quantities S_k change continuously, this behaviour of the order parameters being appropriate to the transformation of uniaxial nematics into biaxial phases [1–5]. Figure 2 shows that the area of a biaxial nematic depends on the aspect ratio of the constituent species.

Comparing the areas of the biaxial nematics depicted in figure 2, one can notice that increase in asymmetry of both components favours the extension of the biaxial regions accompanied with a shift to the higher-temperature range. In connection with these features of the phase diagram, it is noteworthy that in the previous studies [1–4] the properties of the uniaxial-component mixtures were discussed in the second virial approximation, which is valid only for mixtures composed of very long rods and flat disks (plates) at low densities. Another feature of the phase diagrams under consideration is that, unlike
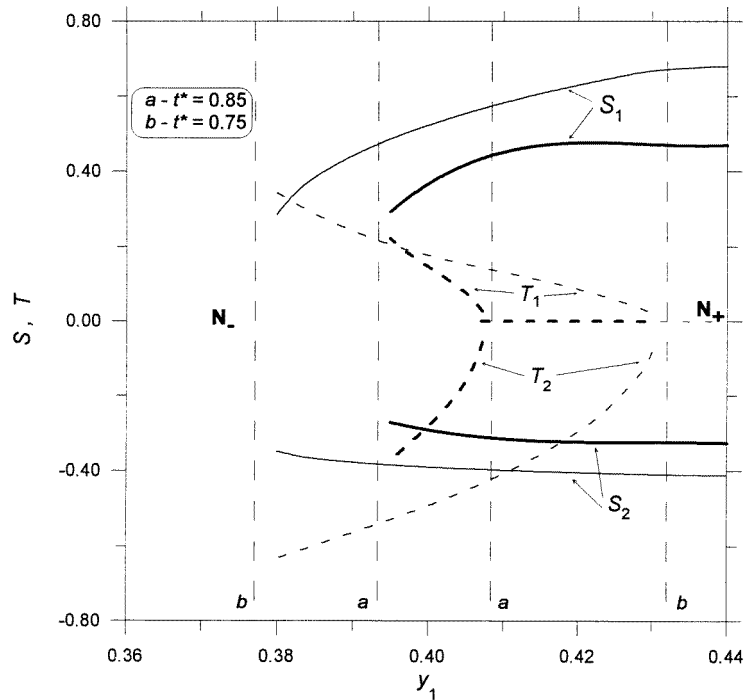
Figure 3. The order parameters S_1, T_1, S_2, T_2 against concentration for a mixture with the component aspect ratios $\gamma_1 = 5, \gamma_2 = 1/5$ at $t^* = 0.75$ and $t^* = 0.85$. The points a and b correspond to the N_+–B and N_-–B boundaries at $t^* = 0.85$ and $t^* = 0.75$, respectively.

what was reported in [2, 3], the regions of biaxial phases are asymmetric with respect to the equimolar composition. This situation may be the consequence of the effect of three-particle correlations, which is manifested, in part, in the difference between the thermodynamic properties (e.g., between the parameters at the NI transition) of one-component rod and plate fluids with the same asphericity factor (see table 1).

The above results are all based upon numerical procedures. The analytical conditions for the stability boundaries of a biaxial phase, necessary for reaching an unambiguous judgment concerning a second-order transition between the uniaxial nematic phase and the biaxial nematic phase (N_+–B and N_-–B), may be derived in terms of the Landau theory generalized for systems with multicomponent order parameters [4]. As for the present problem, the analysis of the set of equations locating the minimum of the Gibbs energy for all of the possible states of the system is hampered by the complicated expression for G_{conf}. However, a number of conclusions outlining the thermodynamic stability of the phases may be worked out by comparing the dependencies of the normalized Gibbs energy as a function of composition.

Figures 4(a) and 4(b) show plots for the possible phases, B, N_-, and N_+, as functions of the mole fraction. As is seen, for both systems the plot of G_{conf}/NkT versus y for the biaxial phase is practically linear, and coincides with the common tangent to the curves G_{conf}/NkT for the uniaxial phases N_- and N_+. In addition to estimations carried out in terms of the Gibbs free energy, the set of equations embracing the usual conditions of heterogeneous equilibrium and those of equilibrium orientation distribution were solved for
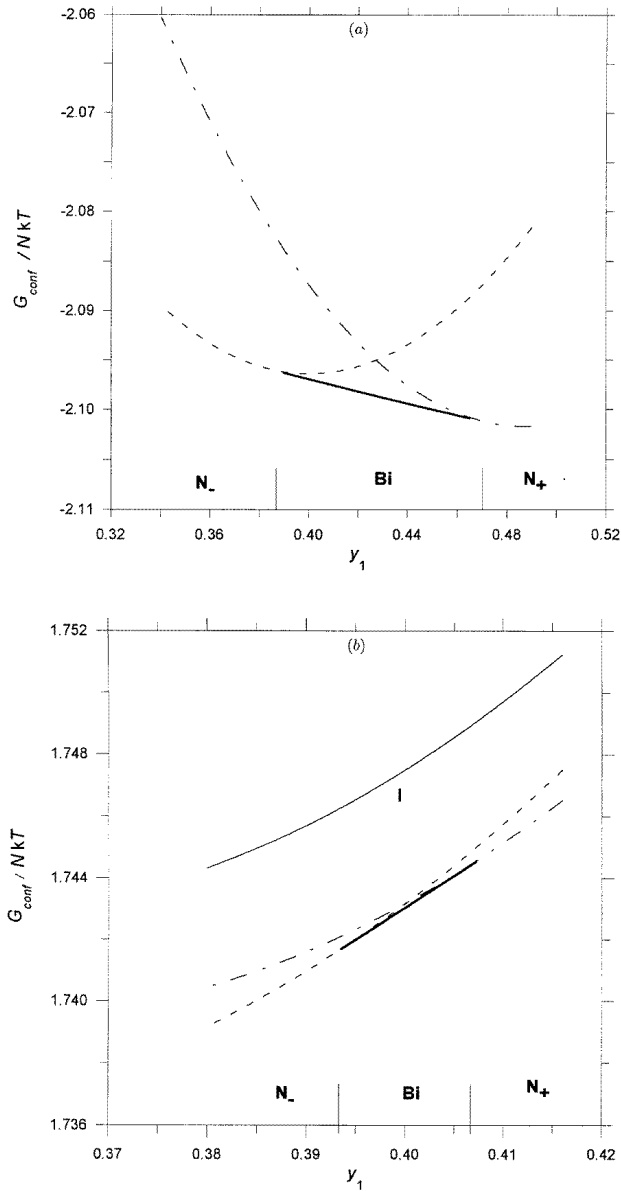
Figure 4. The configurational Gibbs energy versus the concentration of the possible phases in the following mixtures: (a) rods with $\gamma_1 = 10$ and plates with $\gamma_2 = 1/10$ at $t = 0.75$; and (b) rods with $\gamma_1 = 5$ and plates with $\gamma_2 = 1/10$ at $t^* = 0.85$: uniaxial nematic, N_+ (chain line); uniaxial, N_- (dotted line); biaxial (solid line).

all of the systems studied. The results of the calculations confirm that the uniaxial nematic–uniaxial nematic $(N_+ - N_-)$ coexistence curves practically coincide with the boundaries of biaxial phases determined via graph location of branching points in the non-linear equations for the order parameters.

Therefore, the system under study can form either a biaxial nematic phase or a

heterogeneous complex of two uniaxial-symmetry nematics with almost equal probabilities, the situation occurring over a broad interval of related temperatures.

The inset in figure 2 depicts the phase diagram of the system II over the range $0.85 \leqslant t^* \leqslant 1$; the two narrow N_+–I and N_-–I coexistence regions are also indicated here. In connection with the trends discussed above, the area confining a singularity point is singled out. The singularity belongs to one of the following types: (i) critical point resulting from the intercept of the N_+–B and N_-–B second-order phase transition boundaries, and consequently coexistence of the phases I, N_-, N_+, and B; and (ii) eutectic point located on the extremely short tie-line corresponding to the coexistence of the phases I, N_-, and N_+. It is noteworthy that, in accord with the third virial estimations performed by van Roij and Mulder [6] on the basis of the Onsager–Zwanzig model, a biaxial phase may turn out to be stable with respect to demixing into phases N_- and N_+, if the aspect ratio of the rods exceeds 8.8 or that of the plates is less than 1/8.8. However, the results of the present study for the systems composed of highly asymmetric particles (system III in figure 4(b)) do not confirm this statement, evidently.

The conclusions of the study described in [6] assert that the mechanism of athermal nematic solution demixing is mostly predetermined by pair interactions of anisometric molecules, i.e. the difference in excluded volumes of similar as well as unlike particles. To elucidate the effect of three-particle correlations on the demixing of the biaxial phase and the topology of the phase diagrams for nematic mixtures of components with different shapes, it would be interesting to undertake further computer simulations, and concurrently work out new molecular-statistical models. Here the analogy with results of analysis referring to binary athermal mixtures of hard spheres with different radii [24] seems expedient. The cited work shows that on exceeding certain ratios of radii the mixture may split, with the occurrence of the miscibility gap being dependent on the precision of the description of collective molecular interactions.

4. Conclusions

The analysis of the configurational Gibbs free energy has been carried out in the third virial approximation for a discrete-orientation model mixture of uniaxial rods and plates, with continuous translational coordinates. It is revealed that the value of G_{conf}/NkT for a biaxial phase is practically equal to that for the equilibrium heterogeneous complex of the two uniaxial nematic phases, N_+ and N_-, at the same overall mole fraction. These results, as well as the data concerning the positions of biaxial phases in the t^*–y phase diagrams, indicate that the three-particle correlations incorporated in the model may produce certain dissimilarities in the phase behaviour of such fluids when compared with results gained within the second virial approximation.

The major evident shortcoming of the model is that it does not provide a transition to a continuous distribution over orientations. Nonetheless, the approach employed here is simple enough for the calculations of the order parameters of both components and thermodynamic properties in nematic hard-particle mixtures. Besides, the model can also be used in studying the behaviour of biaxial nematogens in binary mixtures—this work has recently been started by Goetz and Hoatson in the framework of the mean-field theory [25]. In this sense, it may be of some help in modelling and interpreting the behaviour of mixtures composed of materials with differing geometries [26], and the development of their novel applications.

Acknowledgments

Appendix

A model system is an n-component mixture of $\{N_k\} = N_1, N_2, \ldots, N_n$ hard asymmetric particles; each particle is allowed to have only m discrete orientations, $\{\alpha\} = 1, 2, \ldots, m$, and $\sum_{k=1}^{n} \sum_{\alpha=1}^{m} N_{\alpha k} = N$.

Following Cotter [27], the configurational partition function of such a system can be written in the form

$$Q_N = \left(1 \bigg/ m^n \prod_k \prod_\alpha N_{\alpha k}!\right) \int \mathrm{d}\mathbf{r}^N \, \exp\left[-\frac{1}{kT} U_N(\mathbf{r}^N, \{\bar{N}_{\alpha k}\})\right] \tag{A1}$$

where $U_n(\mathbf{r}^N, \{\bar{N}_{\alpha k}\})$ is the N-particle potential energy of the interaction, the $\mathbf{r}^N = \mathbf{r}_1, \mathbf{r}_2, \ldots$ are the positions of the molecular mass centres. The bars over the $N_{\alpha k}$ denote the distribution maximizing $\ln Q_N$.

Let us view this system on a simple cubic lattice, and assume that the accuracy of locating a mass centre of a particle equals Δv, the volume of a lattice cell. Then integration over coordinates in the configurational partition function reduces to the summation over configurations of a lattice gas, and the expression (A1) in the general case of a system of biaxial blocks ($m = 6$) can be rearranged to the form

$$Q_N = \left((\Delta v)^N \bigg/ 6^N \prod_k \prod_{\alpha=1}^{m} N_{\alpha k}!\right) \sum_{U_n} g(\{\bar{N}_{\alpha k}\}; \Delta v) \exp\left[-\frac{1}{kT} U_N(\{\bar{N}_{\alpha k}\})\right] \tag{A2}$$

where $g(\{\bar{N}_{\alpha k}\}; \Delta v)$ is the total number of configurations with equal energy. The summation is performed over all of the configurational energies U_N of the system, with the equilibrium (the most probable) orientational distribution of particles $\{\bar{N}_{\alpha k}\}$.

In the athermal system, the term $g(\{\bar{N}_{\alpha k}\}; \Delta v)$ equals the number of ways to adopt $\{N_{\alpha k}\}$ indistinguishable particles on a lattice. Thus, one has

$$Q_N = \left((\Delta v)^N \bigg/ 6^N \prod_k \prod_{\alpha=1}^{m} N_{\alpha k}!\right) g(\{\bar{N}_{\alpha k}\}; \Delta v). \tag{A3}$$

Now we trace the transformation to the continuous transitional coordinates of mass centres in the expression for the partition function of a lattice gas of a mixture of parallelepipeds. Let a cubic lattice contain M sites overall, its volume being $V = M \Delta v$. Each particle occupies $L_k = \prod_{i=1}^{3} r_{\alpha k}^{(i)}$ adjacent cells of a lattice, and the product $r_{\alpha k}^{(i)}(\Delta v)^{1/3}$ is the dimension of a particle of sort k having orientation α ($\alpha = 1, \ldots, 6$) along a direction i. The volume of a particle is: $v_k = L_k \Delta v$. For $g(\{N_{\alpha k}\})$ we use the following estimation [11, 12, 14]:

$$g(\{N_{\alpha k}\}) = (N_0 + B_{123})! \prod_{i=1}^{3} (N_0 + B_i)! \bigg/ \left(N_0! \prod_k \prod_{\alpha=1}^{6} N_{\alpha k}! \prod_{i<j}^{3} (N_0 + B_{ij})!\right). \tag{A4}$$

Here $N_0 = M - \sum_k N_k L_k$ is the number of vacant sites on a lattice, and

$$B_i = \sum_k \sum_{\alpha=1}^{6} N_{\alpha k} L_k / r_{\alpha k}^{(i)}$$

$$B_{ij} = \sum_k \sum_{\alpha=1}^{6} N_{\alpha k} L_k [1/r_{\alpha k}^{(i)} + 1/r_{\alpha k}^{(j)} - 1/(r_{\alpha k}^{(i)} r_{\alpha k}^{(j)})]$$

$$B_{123} = \sum_k \sum_{\alpha=1}^{6} N_{\alpha k} \left[L_k - \prod_{i=1}^{3} (r_{\alpha k}^{(i)} - 1) \right].$$

In accord with (A3), the configurational Helmholtz energy of a lattice gas, F_{latt}, can be expressed as follows:

$$F_{latt}/kT = -\ln g(\{N_{\alpha k}\}) - N \ln \Delta v + N \ln 6 + \sum_k \sum_{\alpha=1}^{6} \ln N_{\alpha k}!. \qquad (A5)$$

The properties of a lattice gas converge to the properties of a fluid with continuous translation coordinates of particles as the volume of a lattice cell is decreased [28] and the number of lattice sites covered by a particle for constant volume of a particle, v_k, is increased.

The transition to the continuous distribution of the mass centres of molecules can be performed by taking to the limit:

$$F_{conf} = \lim_{\Delta v \to 0} F_{latt} = \lim_{z \to 0} F_{latt} \qquad (A6)$$

where $z = (\Delta v)^{1/3}/a$ is the dimensionless edge of a cubic lattice cell.

For convenience we introduce the following dimensionless quantities:

$$f_{\alpha k}^{(i)} = r_{\alpha k}^{(i)} z \qquad f_k = \prod_{i=1}^{3} f_{\alpha k}^{(i)} = L_k z^3 = v_k/a^3.$$

The terms N_0 and $N_0 + B_n$ ($n = 1, 2, 3, 12, 13, 23, 123$) from equations (A2) and (A3) are represented in the form

$$N_0 = \left(\sum_k N_k f_k \right) Z_0/z^3 \qquad N_0 + B_n = \left(\sum_k N_k f_k \right) Z_n/z^3 \qquad (A7)$$

where

$$Z_0 = V \bigg/ \sum_k N_k v_k - 1 = \bar{V} - 1$$

$$Z_i = Z_0 + za_i$$

$$Z_{ij} = Z_0 + za_i + za_j - z^2 b_l \qquad l \neq i \neq j \qquad (A8)$$

$$Z_{123} = Z_0 + z \sum_{i=1}^{3} a_i - z^2 \sum_{i=1}^{3} b_i + z^3 \sum_k \varphi_k/f_k.$$

The notation a_i, b_i was introduced in relationships (7). Employing the forms (A7) and (A8) along with the Stirling formula, we rewrite equation (A4) in the following form:

$$F_{latt}/kT = \sum_k N_k \sum_{\alpha=1}^{6} s_{\alpha k} (\ln s_{\alpha k} - 1)$$

$$+ \sum_k N_k \ln(\varphi_k/v_k) - \sum_k N_k f_k \left\{ \sum_n h_n (Z_n \ln Z_n - Z_n)/z^3 \right\} \qquad (A9)$$

where $h_1 = h_2 = h_3 = h_{123} = -h_0 = -h_{12} = -h_{13} = -h_{23} = 1$.

Furthermore, we take the limit $z \to 0$ (the zero value of a lattice cell volume) in accord with equation (A6) for constant packing fraction η. After evaluation of an indeterminable

expression of the type 0/0 in the factor $\{\sum_n h_n(Z_n \ln Z_n - Z_n)/z^3\}$ of equation (A9), one gets an expression identical with equation (5):

$$F_{conf}/kT = \sum_k N_k \left\{ \sum_{\alpha=1}^{6} s_{\alpha k}(\ln s_{\alpha k} - 1) + \ln \frac{\varphi_k}{v_k(\bar{V} - 1)} \right\}$$
$$+ f_k \left[\frac{1}{\bar{V} - 1} \sum_{i=1}^{3} (a_i b_i) + \frac{1}{(\bar{V} - 1)^2} \prod_{i=1}^{3} a_i \right]. \tag{A10}$$

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