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A simple mean field theory is introduced to describe a biaxial nematic phase in mixtures of a low-molecular-weight liquid crystalline molecule (LC) and a rigid-rodlike polymer (ROD), such as carbon nanotubes (CNTs) and liquid crystalline polymers. When the two components favor perpendicular orientations, we predict a biaxial nematic phase on the temperature-concentration plane, depending on the anisotropic interaction between ROD and LC.

Keywords Biaxiality; carbon nanotubes; liquid crystal; phase separation; rodlike polymer

1. Introduction

A biaxial nematic phase has been predicted theoretically by Freiser [1], based on a generalized Maier-Saupe theory for thermotropic nematic liquid crystals. Since then, the existence of a stable biaxial nematic phase has been a challenge from experimental [2–11], computational [12–14], and theoretical point of view [15–18] (*for recent review see* [19]). Biaxiality occurs if anisotropic particles orient along a second axis perpendicular to a main director. In a recent experiment the biaxial nematic phase has been observed in colloidal dispersions of board-like particles [20]. For its fast response [21] the biaxial nematic phase can have a significant advantage in display applications.

Recently, we have presented a mean field theory to describe phase separation in a mixture of a low-molecular-weight liquid crystal (LC) and a long rigid-rodlike polymer (ROD), such as carbon nanotube (CNT) [22–25] or liquid crystalline polymers. For ROD/LC mixtures we have predicted three nematic phases, N_0, N_1, N_2. We used the orientational order parameter S_1 for LC and S_2 for ROD [26]. (Note that the notation is changed from that used in Ref. [26]). The nematic phase, N_0, shows ROD and LC parallel to each other: $S_1 > 0$ and $S_2 > 0$. On the other hand, when the order parameter of one component is positive, determining the nematic director, and the order parameter of the second component is negative, we have

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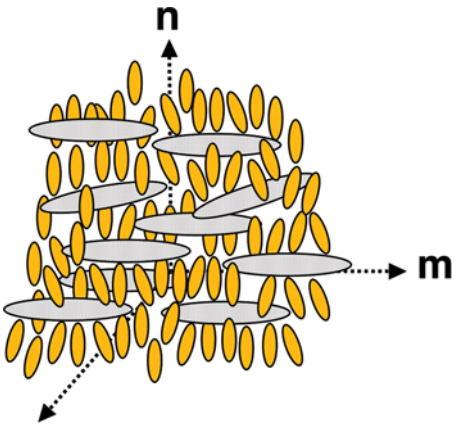

Figure 1. Biaxial nematic phase in mixtures of long rods and short LCs, which favor perpendicular orientations. Rods on an easy plane induce the additional ordering in the direction **m** perpendicular to the major director **n** of LCs. (Figure appears in color online.)

planar nematic phases, where the second component is randomly oriented within the plane perpendicular to the director. We then have a nematic phase, N_1, with $S_1 > 0$ and $S_2 < 0$, where the nematic director can be defined by an average orientation of LC, and a nematic phase, N_2, with $S_1 < 0$ and $S_2 > 0$, where the nematic director can be given by an average orientation of ROD. On increasing the concentration of rods, the nematic phase, N_1, changes to N_2 [26]. In N_1 and N_2 we can expect either a uniaxial or a biaxial nematic phase.

Figure 1 shows schematically the biaxial nematic in a ROD/LC mixture, where the two components favor mutually perpendicular orientations. In the N_1 phase we can expect the excluded volumes between rods to increase on increasing concentration of rods. Hence, long-range ordering of rods along the minor director **m**, perpendicular to the major director **n** of LC can form, yielding a biaxial nematic (N_{1b}) phase. In the N_2 phase, we can have a biaxial nematic (N_{2b}) phase, where the additional ordering of LC appears in the direction **n** (which is the minor director in this case), perpendicular to the major director **m** of ROD.

Although, biaxiality has been studied in quantum spin system [27], thermotropic LCs [7–11,14], lyotropic LCs [2,3], anisotropic colloidal dispersions [20], liquid crystalline polymers [6,28], and mixtures of rodlike and disk-like molecules [29–31], it has not been studied for ROD/LC mixtures.

In this paper we present a simple mean field theory to describe phase diagrams with the biaxial nematic phase of ROD/LC mixtures. We predict an unstable, a metastable, and a stable biaxial nematic phase on the temperature-concentration plane, depending on the interaction between a ROD and a LC.

2. Free Energy

We consider a binary mixture of N_1 LC molecules of length L_1 and diameter d_1 and N_2 rods of length L_2 and diameter d_2: $L_2 >> L_1$. The volume of the LC molecule and that of the rod are given by $v_1 = (\pi/4)\, d_1{}^2 L_1$ and $v_2 = (\pi/4)\, d_2{}^2 L_2$, respectively. Here, we assume that $d \equiv d_1 = d_2$. Let $\rho_1(\mathbf{u})$ and $\rho_2(\mathbf{u})$ be the number density of LC and

ROD, respectively, with the orientational unit vector $\mathbf{u} = \{\theta, \varphi\}$, defined by the polar angle θ ($0 < \theta < \pi$) and the azimuthal angle φ ($0 < \varphi < 2\pi$).The free energy, F, of the dispersion at the level of second virial approximation is given by

$$\beta F(N_1, N_2)/V = \sum_{i=1,2} c_i[\beta\mu_i^\circ + \ln c_i - 1] + \sum_{i=1,2} c_i \ln[4\pi f_i(u)]d\Omega + \frac{1}{2}\sum_{i,j=1,2} c_i c_j \int\int f_i(u) f_j(u')\beta_{ij}(u,u')d\Omega d\Omega', \quad (1)$$

where $c_i = N_i/V$ is the number density, $d\Omega = \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\varphi$, μ_i° is the standard chemical potential of a particle type i ($i = 1, 2$), $\beta \equiv 1/k_B T$; T is the absolute temperature, k_B is the Boltzmann constant, $\beta_{ij} = 1 - \exp[-\beta u_{ij}]$ is the Mayer-Mayer function, u_{ij} is the interaction energy between particles i and j, and $f_i(\mathbf{u})$ is the orientational distribution function of the component i.

For the interaction between LC molecules in Eq. (1) we take the attractive Maier-Saupe interaction [32]

$$\beta_{11} = -\nu_1 v_1 P_2(\cos\ \gamma), \quad (2)$$

where γ is the angle between the molecular orientation vectors $\mathbf{u}$ and $\mathbf{u}'$, $V_1 = U_1/k_B T > 0$ and $P_2(\cos\ \gamma) = 3(\cos^2\ \gamma - 1/3)/2$. For the interaction between long rods we take both the attractive interaction and excluded volume into account. It yields

$$\beta_{22} = 2L^2 d|\mathbf{u} \times \mathbf{u}'| - \nu_2 v_2 P_2(\cos\gamma), \quad (3)$$

where the first term represents the excluded volume interaction between rods [33] and $v_2 \equiv U_2/k_B T > 0$. The interaction between LC molecules and rods is given by

$$\beta_{12} = -\nu_{12} v_{12} P_2(\cos\gamma), \quad (4)$$

where the coupling constant $v_{12} = U_{12}/k_B T$ can be positive or negative [26]. Here we assume that the excluded volume between LC molecules can be neglected.

Now we expand $|\mathbf{u} \times \mathbf{u}'| = \sin\gamma$ in Legendre polynomials up to the second-order: $\sin\gamma \cong \pi/4 - 5\pi/32 P_2(\cos\gamma)$, and make use of the addition theorem for spherical harmonics

$$P_2(\cos\gamma) = P_2(\cos\theta)P_2(\cos\theta') + 2\sum_{k=1}^{2} \frac{(2-k)!}{(2+k)!} P_2^k(\cos\theta) P_2^k(\cos\theta')\cos[k(\varphi - \varphi')]. \quad (5)$$

The terms proportional to the associated Legendre polynomials (P_2^k) will vanish in the uniaxial nematic phase, where the orientational distribution function does not depend on the azimuthal angle. In the biaxial nematic phase, however, the terms P_2^2 give a finite contribution. The orientational order parameter S_i ($i = 1, 2$) of the uniaxial nematic phase is given by [34]

$$S_i = \int P_2(\cos\ \theta) f_i(\theta, \varphi) d\Omega. \quad (6)$$

The biaxial order parameter is given by

$$\Delta_i = \int D(\theta, \varphi) f_i(\theta, \varphi) d\Omega, \tag{7}$$

where $D(\theta, \varphi) \equiv (\sqrt{3}/2) \sin^2 \theta \cos(2\varphi)$. Using the tensor order parameter $S_{i,\alpha\beta} = (3/2)S_i(n_\alpha n_\beta - \delta_{\alpha\beta}/3)$, ($\alpha, \beta = x, y, z$), we have $\Delta_i = S_{i,yy} - S_{i,xx}$ and $S_i = S_{i,zz}$ [34]. Here $S_{i,zz}$ describes alignment of molecules along the z axis (major director), whereas the non-zero value of Δ_i gives ordering along the x or y axis. Then Eq. (5) can be given by $P_2(\cos \gamma) = P_2(\cos \theta)P_2(\cos \theta') + D(\theta, \varphi)D(\theta', \varphi')$. Using the order parameters S_i, Δ_i we can identify: (a) the isotropic (I) phase with $S_i = \Delta_i = 0$; (b) the uniaxial (N_1) phase: $S_1 > 0$, $S_2 < 0$, $\Delta_i = 0$; (c) the uniaxial (N_2) phase: $S_1 < 0$, $S_2 > 0$, $\Delta_i = 0$; (d) the biaxial (N_{1b}) phase: $S_1 > 0$, $S_2 < 0$, $\Delta_i \neq 0$; and (e) the biaxial (N_{2b}) phase: $S_1 < 0$, $S_2 > 0$, $\Delta_i \neq 0$.

To describe phase behavior of the ROD/LC blends, we calculate the free energy of mixing for the binary mixtures [35]:

$$\Delta F = F(N_1, N_2) - Fi(0, N_2) - Fi(N_1, 0), \tag{8}$$

where the $F_i(N_1, 0)$ and $F_i(0, N_2)$ are the reference free energies of the pure LC and the pure ROD in the isotropic phase, respectively. Substituting Eqs. (1–7) into (8), we obtain

$$\begin{aligned} a^3 \beta \Delta F / V = {} & \frac{\phi_1}{n_1} \ln \phi_1 + \frac{\phi_2}{n_2} \ln \phi_2 + \chi \phi_1 \phi_2 \\ & + \sum_{i=1}^{2} \frac{\phi_i}{n_i} \int f_i(u) \ln[4\pi f_i(u)] d\Omega - \frac{1}{2} \nu_1 \phi_1^2 (S_1^2 + \Delta_1^2) \\ & - \nu_{12} \phi_1 \phi_2 (S_1 S_2 + \Delta_1 \Delta_2) - \frac{1}{2} (\nu_2 + 5/4) \phi_2^2 (S_2^2 + \Delta_2^2), \end{aligned} \tag{9}$$

where $\chi = U_0 / k_B T$ is the isotropic Flory-Huggins interaction between ROD and LC [36], $\phi_1 = \upsilon_1 N_1 / V$ and $\phi_2 = \upsilon_2 N_2 / V$ are the volume fractions of LC and ROD, respectively. Using the axial ratio $n_1 = L_1/d$ of LC molecules and $n_2 = L_2/d$ of rods, the volume of the molecules is given by $\upsilon_1 = a^3 n_1$ and $\upsilon_2 = a^3 n_2$, where $a^3 = (\pi/4)d^3$. Here we assumed that the system is incompressible i.e., $\phi_1 + \phi_2 = 1$. Then the total volume of the system is given by $V = a^3(n_1 N_1 + n_2 N_2)$. The terms υ_2 and 5/4 in Eq. (9) correspond to the attractive and excluded volume interactions between rods, respectively. When $\nu_{12} < 0$, LCs prefer to align, on average, perpendicular to rods, which lowers the free energy. Then the values of S_1 and S_2 have opposite sign. This corresponds to N_1 or N_2 phase.

Minimizing (9) with respect to $f_i(\mathbf{u})$ with the normalization condition $\int f_i(\mathbf{u}) d\Omega = 1$, we obtain the orientational distribution functions for LC

$$f_1(u) = \frac{1}{W_0} \exp\left[\Gamma_{1,n} P_2(\cos\theta) + \Gamma_{1,b} D(u)\right], \tag{10}$$

and for ROD

$$f_2(u) = \frac{1}{I_0}\exp[\Gamma_{2,n}P_2(\cos\theta) + \Gamma_{2,b}D(u)], \tag{11}$$

where

$$\Gamma_{1,n} = n_1[\nu_1\phi_1 S_1 + \nu_{12}\phi_2 S_2], \tag{12}$$

$$\Gamma_{1,b} = n_1[\nu_1\phi_1\Delta_1 + \nu_{12}\phi_2\Delta_2], \tag{13}$$

$$\Gamma_{2,n} = n_2[(\nu_2 + 5/4)\phi_2 S_2 + \nu_{12}\phi_1 S_1], \tag{14}$$

$$\Gamma_{2,b} = n_2[(\nu_2 + 5/4)\phi_2\Delta_2 + \nu_{12}\phi_1\Delta_1]. \tag{15}$$

The constants I_0 and W_0 can be obtained from the normalization condition. Substituting Eqs. (10) and (11) into (9) we get

$$\begin{aligned} a^3\beta\Delta F/V = {} & \frac{\phi_1}{n_1}\ln\ \phi_1 + \frac{\phi_2}{n_2}\ln\ \phi_2 + \chi\phi_1\phi_2 + \frac{1}{2}\nu_1\phi_1^2(S_1^2 + \Delta_1^2) \\ & + \nu_{12}\phi_1\phi_2(S_1S_2 + \Delta_1\Delta_2) + \frac{1}{2}(\upsilon_2 + 5/4)\phi_2^2(S_2^2 + \Delta_2^2) \\ & - \frac{\phi_1}{n_1}\ln\frac{W_0}{4\pi} - \frac{\phi_2}{n_2}\ln\frac{I_0}{4\pi}, \end{aligned} \tag{16}$$

We calculate the phase diagrams of this system for different concentrations by using the standard common-tangent construction to find coexisting phases (binodal lines). The spinodal region, which separates unstable and metastable states can be calculated from the inflection point condition, $(\partial^2 f/\partial^2\phi_2)_T = 0$, for the free energy [35]. For numerical calculations we introduce the reduced temperature $\tau = T/T_{NI}$, where T_{NI} stands for the nematic-isotropic phase transition (NIT) temperature of the pure LC. Using τ, the interaction parameter ν_1 is given by $\nu_1 = 4.55/(n_1\tau)$ [26]. In the following we set $n_1 = 2$, $n_2 = 10$, $\upsilon_2 = 0$, and $\chi = \nu_1/10$ for a good solvent condition.

3. Phase Behavior

In this section we show some results of biaxial nematic phases. Figure 2(a) shows the phase diagram numerically calculated for $\nu_{12}/\nu_1 = -0.5$. Black lines show the binodal and the broken lines show the spinodal. The red (blue) dotted-lines show a first (second)-order phase transition, where the order parameters change discontinuously (continuously). The biaxial nematic phase, which includes the unstable biaxial phase $N_{1b}u$, the metastable biaxial phase $N_{1b}m$, and the stable biaxial phase N_{1b}, is indicated by the blue area. Such biaxial nematic phase is induced by the excluded volume interaction between rods dispersed in the N_1 phase to maximize the entropy, as discussed in Figure 1. For example, at $\tau = 1.05$, we have the phase separation ($I + N_2$) between I at $\phi_2 = 0.14$ and N_2 at $\phi_2 = 0.63$. Inside the binodal lines we find the first-order I-N_{1b} phase transition at $\phi_2 = 0.2$ and the first-order N_{1b}-N_2 phase transition at $\phi_2 = 0.5$. Between the spinodal lines (broken-lines), we

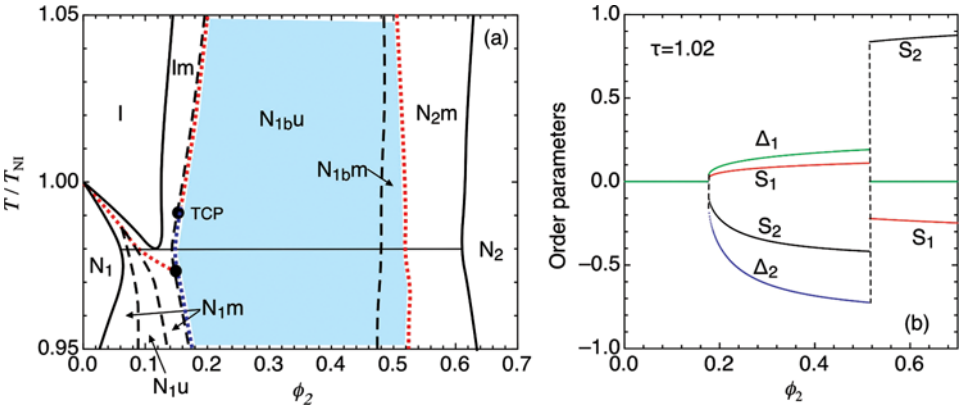

Figure 2. (a) Phase diagram on the temperature ($\tau = T/T_{NI}$) – volume fraction (ϕ_2) plane for $\nu_{12}/\nu_1 = -0.5$ and (b) order parameters at $\tau = 1.02$. See text for the details. (Figure appears in color online.)

have unstable regions $N_{1b}u$ and N_2u, where the system is initially unstable with respect to orientational ordering but metastable to concentration fluctuations when the phase separation progresses.

Between the binodal and spinodal lines, we have metastable regions: isotropic (Im) and nematic (N_2m). Above $\phi_2 = 0.63$, we have a stable N_2 phase. We also find the three-phase coexistence, or triple point (TP), between $N_1 + I + N_2$ at $\tau = 0.98$. Below TP, we have the $N_1 + N_2$ phase separation. At low concentrations the $N_1 + I$ phase separation appears. Inside the binodal curves we also find an unstable nematic region (N_1u) and a metastable one (N_1m). We also find a tricritical point (TCP, solid circles), at which the first-order phase transition (red dotted-line) meets the second-order one (blue dotted-line). Below TCP, we find the second-order N_1-N_{1b} and I-N_{1b} phase transitions. Figure 2(b) shows the order parameters S_1, S_2, Δ_1, and Δ_2 as function of the volume fraction of rods at $\tau = 1.02$. The first-order I-N_{1b} phase transition occurs at $\phi_2 = 0.18$ and the first-order N_{1b}-N_2 phase transition takes place at $\phi_2 = 0.52$.

On increasing the repulsive interaction ν_{12} between ROD and LC, or more favored perpendicular orientations, the TP temperature shifts to higher values and the stable biaxial nematic phase (N_{1b}) appears [37]. A recent Monte Carlo simulation for a mixture of rod-like and disk-like molecules has shown that normal alignment of the two components causes a stable biaxial phase to appear due to the anisotropic interaction between rods and disks [31].

Duran *et al.* [38] have observed in CNT/LC mixtures that the NIT temperature of the LCs is enhanced by the incorporation of CNT and suggested that this enhancement can be attributed to anisotropic coupling between CNT and LC. These studies would demonstrate the validity of our mean field theory.

4. Summary

We have presented a simple mean field theory to describe biaxial nematic phases in rod/LC mixtures. We have predicted a variety of phase separations. When the two components favor a mutually perpendicular orientation, rods dispersed in nematic

LCs can induce biaxiality. The perpendicular alignments of rods and LCs can be achieved by wrapping polymers or surfactants on nanotube's surface [24,25]. Hence it controls the balance between the attractive Van der Waals interaction and the excluded volumes between rods. These modifications can change the strength of the interaction parameter ν_{12} in our model and give a possibility of a novel biaxial phase in this mixture.

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