

PHYSICAL REVIEW E

STATISTICAL PHYSICS, PLASMAS, FLUIDS, AND RELATED INTERDISCIPLINARY TOPICS

THIRD SERIES, VOLUME 58, NUMBER 3 PART B

SEPTEMBER 1998

ARTICLES

Bicritical points in a nematic rod-disk mixture

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(Received 22 July 1997; revised manuscript received 25 November 1997)

The influence of the rod-disk excluded volume on the existence of a bicritical point in a mixture of rodlike and disklike particles has been examined using the second virial theory. Within the approximation in which the interaction kernel is expanded to second order in a basis of symmetry-adapted functions, it is shown from a combination of bifurcation analysis and numerical solution of the Euler-Lagrange equations for the free energy that there exists a value of the rod-disk excluded volume parameter for which the bicritical point disappears. [S1063-651X(98)04008-2]

PACS number(s): 64.70.Md, 64.60.Cn, 61.30.Cz

I. INTRODUCTION

In recent years much effort has been put into the investigation of biaxial nematic phases both experimentally and theoretically. A necessary but not sufficient condition in pure systems is that particles should exhibit biaxial symmetry. In addition, the interparticle interaction parameters must fulfill very special relations (see, e.g., [1]). Obtaining stable, pure biaxial thermotropic nematic liquid crystals in practice has remained a formidable challenge.

Much better chances of success are foreseen when dealing with mixtures of rodlike and disklike particles. Experimental evidence for the existence of the biaxial phase was clearly established by Yu and Saupe [2] for the lyotropic mixture of potassium laurate, decanol, and water (D_2O). Because amphiphilic compounds in aqueous solution tend to aggregate, this system contains cylindrical micelles whose shape changes from cylindrical rodlike to bilayer disklike as a function of temperature or concentration. It is not obvious what kind of micelles are formed in the region of the biaxial phase and whether their cylindricality is maintained. However, since the shape anisotropy necessary for biaxial phase formation is really very special and the micelles existing close to the uniaxial nematic–biaxial nematic transition are cylindrical, thus very far from fulfilling these conditions, one can be fairly confident that the biaxiality observed in amphiphilic systems is caused either by mixing of rodlike and disklike micelles or by some other phenomenon connected with a change of identity of the micelles. In the case of thermotropics, the very existence of biaxial phases is still in doubt: Let us note that the molecules of the classic para-azoxyanisole,

4-methoxybenzlidene-4'-n-butylaniline, or cyanobiphenyl homologs, with their rigid and planar pairs of benzene rings, are in fact biaxial but do not form biaxial phases.

Theoretically, the biaxial phase has been found in several models of rod-disk mixtures. The pioneering work of Alben [3] assumed purely steric interactions between particles located at the sites of a lattice whose principal axes are constrained to lie along one of the space-fixed x , y , or z directions. The corresponding phase diagram exhibits four phases: isotropic, calamitic (rodlike) uniaxial nematic, discotic (disklike) uniaxial nematic, and biaxial. Upon compressing the system from the isotropic phase, there is a first-order transition into an ordered phase that has the symmetry of the majority component. There is, however, one special point, called the Landau point or bicritical point, where the transition is second order into the biaxial phase. The uniaxial-biaxial phase boundaries come together in a sharp cusp at this point.

All subsequent theoretical work on mixtures has confirmed the above topology of the phase diagram. Quantitative differences arise owing to details of the models or of the approximations employed. In 1982 [4] Rabin, McMullen, and Gelbart applied the y expansion to a mixture of hard rods and disks with continuous positional and orientational degrees of freedom. A complete analysis of the same model, albeit at the level of the second-virial coefficient, has been performed by Stroobants and Lekkerkerker [5], who gave a detailed description of the behavior of the order parameters, free energies, and phase boundaries as functions of composition, density, and some chosen shape anisotropy. Note, however, that the y expansion does not change the bifurca-

tion diagrams or order parameters but simply rescales the density. In the above continuous models, excluded volumes are approximated by their Legendre polynomial expansion truncated at second order.

In studies of mixtures it is essential to investigate the stability of the biaxial phase with respect to demixing. This is most important from the experimentalist's point of view and also for potential applications. Using the Zwanzig model [6], van Roij and Mulder [7] estimated the critical value of the length-to-width ratio of particles for which a stable biaxial phase might appear. When present, the biaxial phase is stable in a triangular region of the composition-density phase diagram. Attempts at a more realistic description of nematogenic molecules need to include not only steric interactions but also attractive forces and comprise results such as the van der Waals theory [8] and the mean-field theory of the Ruygrok modification of Lennard-Jones interactions [9] or of Gay-Berne mixtures [10]. Within the Maier-Saupe theory, Palfy-Muhoray and de Bruyn [11] have given a negative answer to the question of whether there is a stable biaxial phase. Results of computer simulations of various mixtures have also highlighted stability problems [12]. In all these approaches, biaxiality is driven by interactions between unlike particles.

One of the characteristic features of the phase diagrams of rod-disk liquid crystal mixtures, already mentioned above, is the existence of the bicritical, or Landau, point, where biaxial, uniaxial, and isotropic phases meet. When the particles have the same proper volume, in the second virial approximation, the bicritical point is found at composition 1/2. In this case the transition from the isotropic phase to the anisotropic one is second order due to the fact that the cubic term in the expansion of the free energy in the leading-order parameter vanishes. So far it has been thought that the second-order character justifies that the anisotropic phase involved has to be of biaxial symmetry. In this paper I show that, if in a hard-rod-hard-disk mixture the spherical harmonic expansion of the excluded volume is truncated at second order, then for a sufficiently large rod-disk excluded volume the anisotropic phase is uniaxial.

The purpose of this paper is to study the influence of the rod-disk excluded volume on the existence of the bicritical point in a mixture of rods and disks. The paper is organized as follows. Section II summarizes the theoretical background for the case considered and introduces a complete bifurcation analysis. Section III presents numerical results. Finally, Sec. IV contains a summary of the conclusions.

II. SECOND VIRIAL THEORY OF A HARD ROD-DISK MIXTURE

A. L2 rod-disk model

In this paper I consider a binary mixture of hard rods (A particles) and hard disks (B particles). The length of a rod is L_A and its width is D_A and those of a disk are L_B and D_B , respectively. The total number of particles in the system is $N = N_A + N_B$, the total density $\tilde{\rho} = N/V$, and the mole fractions of rods and disks $x_A = N_A/N$ and $x_B = N_B/N$, respectively. Such a system is the simplest model of a rod-disk mixture and has been quite widely studied [4,5]. The goal of this paper is to extend the knowledge of hard rod-disk mix-

tures by showing the possibility of a different type of phase diagram and analyzing the influence of the rod-disk interaction parameter on the bicritical point.

The free energy functional for a binary system comes from density-functional theory [4,5,7,11] (it is also derivable from the basic principles of the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy [9]) and for the hard rod-disk mixture takes the form

$$\begin{aligned} \frac{\beta\mathcal{F}}{N} = & x_A \ln x_A + x_B \ln x_B + x_A \int \psi_A \ln \psi_A d\vec{\omega} \\ & + x_B \int \psi_B \ln \psi_B d\vec{\omega} + \frac{1}{2} \tilde{\rho} x_A^2 \langle E^{AA} \rangle + \frac{1}{2} \tilde{\rho} x_B^2 \langle E^{BB} \rangle \\ & + \tilde{\rho} x_A x_B \langle E^{AB} \rangle - \lambda_A \left(\int \psi_A d\vec{\omega} - 1 \right) \\ & - \lambda_B \left(\int \psi_B d\vec{\omega} - 1 \right) + \ln \frac{N}{4\pi V} - 1, \end{aligned} \quad (1)$$

where ψ_A and ψ_B are the single-particle orientational distribution functions of rods and disks, $\vec{\omega}$ is the unit vector along the main axis of a given particle, and λ_A, λ_B are the Lagrange multipliers that ensure normalization of the orientational distribution functions. The interaction terms have the form

$$\langle E^{ij} \rangle = \ell_{ij} \int d\vec{\omega}_i \int d\vec{\omega}_j \psi_i E^{ij}(\vec{\omega}_i, \vec{\omega}_j) \psi_j, \quad (2)$$

where $\ell_{ij} E^{ij}(\vec{\omega}_i, \vec{\omega}_j)$ is the excluded volume of two particles i and j with fixed orientations and ℓ_{ij} alone stands for the angular average of the excluded volume of those two particles. For rod-rod, disk-disk, and rod-disk excluded volumes the following formulas hold:

$$\langle E^{AA} \rangle = \frac{4}{\pi} \ell_{AA} \int d\vec{\omega}_{1A} \int d\vec{\omega}_{2A} \psi_{1A} \sin \gamma(\vec{\omega}_{1A}, \vec{\omega}_{2A}) \psi_{2A}, \quad (3)$$

$$\langle E^{BB} \rangle = \frac{4}{\pi} \ell_{BB} \int d\vec{\omega}_{1B} \int d\vec{\omega}_{2B} \psi_{1B} \sin \gamma(\vec{\omega}_{1B}, \vec{\omega}_{2B}) \psi_{2B}, \quad (4)$$

$$\langle E^{AB} \rangle = 2 \ell_{AB} \int d\vec{\omega}_{1A} \int d\vec{\omega}_{2B} \psi_{1A} |\cos \gamma(\vec{\omega}_{1A}, \vec{\omega}_{2B})| \psi_{2B}, \quad (5)$$

with

$$\ell_{AA} = \frac{\pi}{4} D_A L_A^2, \quad \ell_{BB} = \frac{\pi^2}{16} D_B^3, \quad \ell_{AB} = \frac{\pi}{16} D_B^2 L_A, \quad (6)$$

where $\gamma(\vec{\omega}_i, \vec{\omega}_j)$ is the angle between $\vec{\omega}_i$ and $\vec{\omega}_j$. Minimization of the functional (1) yields the set of equations

$$\begin{aligned} \ln \psi_{1A} = & -\frac{8}{\pi} \tilde{\rho} x_A b \int \sin \gamma(\vec{\omega}_{1A}, \vec{\omega}_{2A}) \psi_{2A} d\vec{\omega}_{2A} \\ & -4\tilde{\rho} x_B \not\propto b \int |\cos \gamma(\vec{\omega}_{1A}, \vec{\omega}_{2B})| \psi_{2B} d\vec{\omega}_{2B} + \frac{\lambda_A}{x_A}, \end{aligned} \quad (7)$$

$$\begin{aligned} \ln \psi_{1B} = & -\frac{8}{\pi} \tilde{\rho} x_B r b \int \sin \gamma(\vec{\omega}_{1B}, \vec{\omega}_{2B}) \psi_{2B} d\vec{\omega}_{2B} \\ & -4\tilde{\rho} x_A \not\propto b \int |\cos \gamma(\vec{\omega}_{1A}, \vec{\omega}_{1B})| \psi_{1A} d\vec{\omega}_{1A} + \frac{\lambda_B}{x_B}, \end{aligned} \quad (8)$$

which are the self-consistent integral equations for the distribution functions ψ_{1A} and ψ_{1B} and I also used the notation of [5]: $\ell_{AA}=b$, $\ell_{BB}=rb$, and $\ell_{AB}=\not\propto b$. When the excluded volumes of the particles of the same kind in the isotropic phase are equal, $r=1$. Introducing the dimensionless density $\rho=b\tilde{\rho}$, one is left with the only one parameter $\not\propto$, which is a function of molecular shapes and determines the value of the rod-disk excluded volume.

A basic tool that is used to operate on the orientational-dependent objects are the Wigner standard rotation matrix elements $\mathcal{D}_{m,n}^j(\Omega)$ [13], which are certain complex functions of the Euler angles $\Omega=(\theta, \phi, \psi)$. In practice, usage of them causes troubles and is very inconvenient. Taking also into account their complex character, it is apparent that the need for real symmetry-adapted functions has arisen. In the case of the biaxial symmetry the following definitions have been given by [1] and [14]. In the first,

$$\Delta_{m,n}^j(\Omega) = (\frac{1}{2}\sqrt{2})^{2+\delta_{m0}+\delta_{n0}} \sum_{\sigma, \sigma'=\{-1,1\}} \mathcal{D}_{\sigma m, \sigma' n}^j(\Omega), \quad (9)$$

only even indices j, m, n are allowed ($0 \leq m, n \leq j$); in the second, it is shown that odd values of j are also possible ($2 \leq m, n \leq j$):

$$\begin{aligned} \Delta_{m,n}^j(\Omega) = & (\frac{1}{2}\sqrt{2})^{2+\delta_{m0}+\delta_{n0}} \\ & \times \sum_{\sigma, \sigma'=\{-1,1\}} (-1)^{j(\sigma'-\sigma)/2} \mathcal{D}_{\sigma m, \sigma' n}^j(\Omega). \end{aligned} \quad (10)$$

For the analysis of the D_{2h} symmetry of the biaxial phase, application of the following generators is recommended [14]: rotation of π around the z axis $\Omega_z(\pi)$, rotation of π around the y axis $\Omega_y(\pi)$, and inversion I . These three symmetry operations change Euler angles as $(\pi+\phi, \theta, \psi)$, $(\pi-\phi, \pi-\theta, \pi+\psi)$, and $(\pi+\phi, \pi-\theta, \pi-\psi)$, respectively, and the following equalities for the Wigner matrix elements hold:

$$\begin{aligned} \mathcal{D}_{m,n}^j(\Omega_y(\pi)\Omega) &= (-1)^{j+m} \mathcal{D}_{-m,n}^j(\Omega), \\ \mathcal{D}_{m,n}^j(\Omega_z(\pi)\Omega) &= (-1)^m \mathcal{D}_{m,n}^j(\Omega), \end{aligned} \quad (11)$$

$$\mathcal{D}_{m,n}^j(I\Omega) = (-1)^{j+n} \mathcal{D}_{m,-n}^j(\Omega).$$

States before and after the symmetry transformations should be equivalent and thus appropriate conditions for the indices allowed in Wigner matrices emerge in Eqs. (9) and (10).

A standard way of solving Eqs. (7) and (8) is to expand interaction kernels and functions into a series of symmetry-adapted functions for the biaxial phase [1,14] and then to solve iteratively the set of self-consistent equations, whose number depends on the maximum order of terms included in the series. The general expansion of the excluded volumes in the present case (functions $\sin \gamma$ and $|\cos \gamma|$),

$$E(\vec{\omega}_i \cdot \vec{\omega}_j) = \sum_{l \geq 0} E_l^{ij} P_l(\vec{\omega}_i \cdot \vec{\omega}_j), \quad (12)$$

would also contain odd-order Legendre polynomials. However, because of the symmetry properties imposed on the distribution functions, all integrals containing these terms effectively vanish.

Following [5], I retain terms up to second order only ($l=2$). Thus the model interaction no longer describes real hard rods or disks and becomes of the Maier-Saupe type; henceforth I will call it the $L2$ rod-disk model.

Because molecules are uniaxial, their orientational order (uniaxial or biaxial) is described in terms of angular averages of only two symmetry-adapted functions

$$P_2(\theta) = \frac{1}{2}(3 \cos^2 \theta - 1), \quad D(\theta, \phi) = \frac{1}{2}\sqrt{3} \sin^2 \theta \cos 2\phi, \quad (13)$$

coinciding with $\Delta_{0,0}^2(\Omega)$ and $\Delta_{2,0}^2(\Omega)$ in [1]. (For biaxial molecules, the full set of four symmetry-adapted functions would be required.)

Within the $L2$ model the functions appearing in the kernels of integrals (7) and (8) and relevant for the biaxial symmetry are

$$\sin \gamma = \frac{\pi}{4} - \frac{5\pi}{32} P_2(\cos \gamma), \quad (14)$$

$$|\cos \gamma| = \frac{1}{2} + \frac{5}{8} P_2(\cos \gamma). \quad (15)$$

The relation between Legendre polynomials depending on the cosine of the relative angle γ of two particles i and j [as in Eqs. (14) and (15)] and symmetry functions dependent on the orientations of the individual particles $\theta_i, \phi_i, \theta_j, \phi_j$ is

$$P_l(\vec{\omega}_i \cdot \vec{\omega}_j) = \sum_{l,m} \frac{4\pi}{2l+1} (-1)^m Y_m^l(\theta_i, \phi_i) Y_{-m}^l(\theta_j, \phi_j), \quad (16)$$

where Y_m^l are the standard spherical harmonic functions ($-l \leq m \leq l$) [13]. In particular, one can rewrite Eq. (16) as

$$\begin{aligned} P_l(\vec{\omega}_i \cdot \vec{\omega}_j) &= P_l(\cos \theta_i) P_l(\cos \theta_j) \\ &+ \sum_{m=1}^l \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta_i) P_l^m(\cos \theta_j) \\ &\times 2 \cos[m(\phi_i - \phi_j)], \end{aligned} \quad (17)$$

where P_l^m are the associated Legendre polynomials.

The above theory allows for the numerical analysis of the properties of a hard rod-disk mixture. I would like to apply it to investigate the influence of the rod-disk excluded volume on the bicritical point.

To learn about the structure of the possible phase diagrams for the mixture considered I will have to look at the solutions of Eqs. (7) and (8). Note first that the trivial solutions $e^{\psi_0^{A,B}} = 1/4\pi$ corresponding to the isotropic phase always exist for any density and compositions. Then, at some higher densities, the forms of the distribution functions will gain orientational-dependent contributions indicating anisotropic phases solutions. These solutions will continuously bifurcate from the isotropic branch. However, only in the case of the second-order transitions do the bifurcation points coincide with the transition points. One may assume that close to the bifurcation points the anisotropic solutions would contain only linear orientational order terms or symmetry-adapted functions of the lowest order. Thus Eqs. (7) and (8) in the vicinity of the bifurcation will take the form of a simple set of two linear equations. In the following subsections I will present the way of finding bifurcation points due to isotropic (*I*) –uniaxial nematic (UN) bifurcation and then, likewise, for the UN–biaxial nematic (BN) bifurcation.

B. Analysis of bifurcation to the uniaxial phase

Let us assume that close to the isotropic bifurcation point the orientational distribution functions of the uniaxial nematic phase have the form

$$\psi = e^{(\psi_0 + \epsilon P_2)}, \quad (18)$$

where ϵ is an (infinitesimally small) scalar order parameter and e^{ψ_0} is the orientation distribution function of the isotropic phase. Under this assumption and using Eqs. (14), (15), and (17), the self-consistency equations (7) and (8) read

$$\begin{aligned} \psi_0^A + \epsilon^A P_2(1) + \rho x_A \int \left[2 - \frac{5}{4} P_2(1) P_2(2) \right] \\ \times e^{[\psi_0 + \epsilon^A P_2(2)]} d(\cos \theta_2) d\phi_2 \\ + \rho x_B \int \left[2 + \frac{5}{2} P_2(1) P_2(2) \right] \\ \times e^{[\psi_0 + \epsilon^B P_2(2)]} d(\cos \theta_2) d\phi_2 = \frac{\lambda_A}{x_A}, \end{aligned} \quad (19)$$

$$\begin{aligned} \psi_0^B + \epsilon^B P_2(1) + \rho x_B \int \left[2 - \frac{5}{4} P_2(1) P_2(2) \right] \\ \times e^{[\psi_0 + \epsilon^B P_2(2)]} d(\cos \theta_2) d\phi_2 \\ + \rho x_A \int \left[2 + \frac{5}{2} P_2(1) P_2(2) \right] \\ \times e^{[\psi_0 + \epsilon^A P_2(2)]} d(\cos \theta_2) d\phi_2 = \frac{\lambda_B}{x_B}. \end{aligned} \quad (20)$$

For small values of x one can approximate $e^x = 1 + x + \dots$ and the above set of equations splits into the isotropic part and the more interesting nematic part, which contains the

order parameters ϵ^A, ϵ^B and the angular function $P_2(1)$. Multiplying Eqs. (19) and (20) by $P_2(1)$ and integrating over the whole range of the variables θ_1 and ϕ_1 , effectively one can get the set of equations

$$\epsilon^A (1 - \pi \rho x_A I_A) + \epsilon^B \rho x_B 2 \pi I_B \not\approx 0, \quad (21)$$

$$\epsilon^B (1 - \pi \rho x_B I_B) + \epsilon^A \rho x_A 2 \pi I_A \not\approx 0, \quad (22)$$

where $I_{A,B} = e^{\psi_0^{A,B}} = 1/4\pi$. Equations (21) and (22) yield ρ^* , the bifurcation density, as the root of the characteristic equation $\det M = 0$, where M is the matrix of coefficients multiplying $\epsilon^{A,B}$:

$$M = \begin{pmatrix} 1 - \pi \rho x_A I_A & \rho x_B 2 \pi I_B \not\approx \\ \rho x_A 2 \pi I_A \not\approx & 1 - \pi \rho x_B I_B \end{pmatrix}. \quad (23)$$

The characteristic equation reads:

$$(1 - \pi \rho x_A I_A)(1 - \pi \rho x_B I_B) - \not\approx^2 \rho^2 4 \pi^2 x_A x_B I_A I_B = 0. \quad (24)$$

The lowest positive solution of Eq. (24) gives the density at which one can expect a bifurcation from the isotropic to the uniaxial nematic phase.

C. Analysis of bifurcation to the biaxial phase

Let us now write the biaxial solution close to the bifurcation point in the form $\psi_B = \exp(\psi_n + \epsilon D)$ [where ψ_n is the uniaxial-nematic orientational distribution function, assumed known, and D is as in Eq. (13)]. Then, by the above isotropic-uniaxial phase analysis, one can obtain the biaxial-nematic bifurcation equations as

$$\begin{aligned} \epsilon^A D(1) - \pi \rho x_A \int [Y_2^2(1) Y_{-2}^2(2) + Y_2^2(2) Y_{-2}^2(1)] \\ \times [1 + \epsilon^A D(2)] e^{\psi_n^A} d(\cos \theta_2) d\phi_2 \\ + 2 \pi \rho x_B \not\approx \int [Y_2^2(1) Y_{-2}^2(2) + Y_2^2(2) Y_{-2}^2(1)] \\ \times [1 + \epsilon^B D(2)] e^{\psi_n^B} d(\cos \theta_2) d\phi_2 = 0, \end{aligned} \quad (25)$$

$$\begin{aligned} \epsilon^B D(1) - \pi \rho x_B \int [Y_2^2(1) Y_{-2}^2(2) + Y_2^2(2) Y_{-2}^2(1)] \\ \times [1 + \epsilon^B D(2)] e^{\psi_n^B} d(\cos \theta_2) d\phi_2 \\ + 2 \pi \rho x_A \not\approx \int [Y_2^2(1) Y_{-2}^2(2) + Y_2^2(2) Y_{-2}^2(1)] \\ \times [1 + \epsilon^A D(2)] e^{\psi_n^A} d(\cos \theta_2) d\phi_2 = 0, \end{aligned} \quad (26)$$

where I used Eq. (16) for the excluded volumes. The expression with spherical harmonics $Y_2^2(1) Y_{-2}^2(2) + Y_2^2(2) Y_{-2}^2(1)$ is equal to $2C \sin^2 \theta_1 \sin^2 \theta_2 \cos 2(\phi_1 - \phi_2)$, where $C = 15/32\pi$. Again, multiplying both sides of Eqs. (25) and (26) by the function $D(1)$ and integrating over the full set of orientational variables, bearing in mind that $\cos(\alpha + \beta)$

$=\cos \alpha \cos \beta + \sin \alpha \sin \beta$ and $\int_0^{2\pi} \sin 2\phi \cos 2\phi = 0$, the following set of equations for the uniaxial-biaxial bifurcation is obtained:

$$\epsilon^A(1 - \pi\rho x_A W_A) + \epsilon^B \rho x_B 2\pi W_B = 0, \quad (27)$$

$$\epsilon^B(1 - \pi\rho x_B W_B) + \epsilon^A \rho x_A 2\pi W_A = 0, \quad (28)$$

where $W_{A,B} = 4\pi C \int_0^1 \sin^4 \theta e^{(\psi_n^{A,B})} d \cos \theta$ and $e^{\psi_n^{A,B}}$ are the equilibrium orientational distribution functions of species A and B in the uniaxial nematic phase. Then the characteristic equation for Eqs. (27) and (28) reads

$$(1 - \pi\rho x_A W_A)(1 - \pi\rho x_B W_B) - \rho^2 4\pi^2 x_A x_B W_A W_B = 0. \quad (29)$$

To find the bifurcation points of the uniaxial-biaxial transition one needs to know explicitly the orientational distribution functions of species A and B in the uniaxial nematic phase $e^{(\psi_n^{A,B})}$. They are found from the consistency equations (7) and (8) restricted to uniaxial symmetry. Then one can search for bifurcation points for different compositions by examining the roots of Eq. (29). Since $W_{A,B}$ are dependent on ρ through the orientational distribution functions, one has to look for solutions of Eq. (29) self-consistently. The technique is to find numerically a value for W for a given ρ and x_A and then put it into the bifurcation equation and find the desired root. If it is not the same as the density used, change ρ and repeat the procedure until you get the desired density.

Equation (29) becomes Eq. (24) if one replaces W_A and W_B by their isotropic counterparts I_A and I_B . This means that a certain phase represented by the function D bifurcates from the isotropic phase exactly at the points where the uniaxial phase bifurcates. A similar result has been obtained in [5] for the equimolar composition, where the authors regarded it as sufficient proof that the transition is *always* to the phase of biaxial symmetry. The above analysis shows that the theoretically obtained densities for the isotropic–uniaxial nematic bifurcation are the same as isotropic–biaxial nematic bifurcation densities for *any* composition. From [1] one knows that it is possible to express the uniaxial solution close to the bifurcation points in terms of the ‘‘biaxial’’ D function by performing appropriate rotations of the reference system. This is responsible for the fact that the solution of the I -UN bifurcation analysis coincides with the result for the I -BN bifurcation. Moreover, one can conclude that I -BN bifurcation analysis is not an appropriate tool for finding bifurcation points from the isotropic to a real biaxial phase and one has to look for another sufficient tool. It turns out that this can only be provided by consideration of the UN-BN bifurcation. If the set of solutions of the UN-BN bifurcation intersects the set of solutions of the I -UB bifurcation, then one can be sure that these points refer to the bifurcation from the isotropic to the phase of biaxial symmetry.

From the above considerations an important question arises, namely, how to distinguish between the real biaxial phase and a uniaxial phase in the rotated frame. Both of them contain nonzero averages of the $D(\theta, \phi)$ function. The simplest possibility is to compare values of the free energy of the different phases or to use formulas that relate order pa-

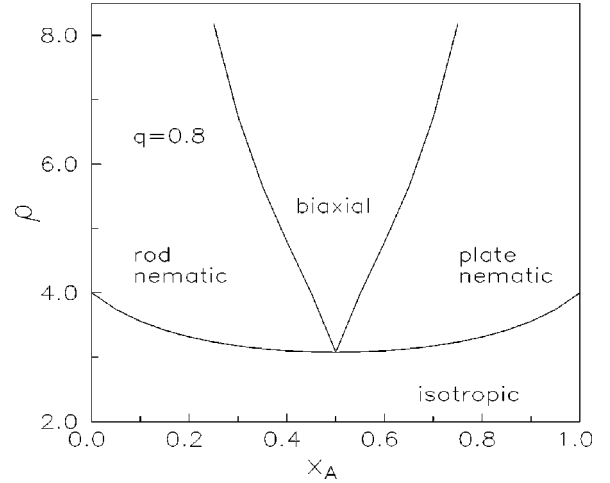


FIG. 1. Bifurcation diagram for the rod-disk excluded volume parameter $q=0.8$.

rameters in the frame where the preferred orientation of the molecules is along the z axis to the ones obtained in the rotated frame.

III. BIFURCATION DIAGRAMS AND ORDER PARAMETERS

A typical bifurcation diagram (here the rod-disk parameter $q=0.8$) obtained on the basis of solutions of Eqs. (24) and (29) is shown in Fig. 1. So far, all papers that introduce different models of rod-disk mixtures present phase diagrams of a similar structure [5,7,11,15]. (Remember that the bifurcation points differ slightly from the transition points for first-order transitions.)

Since the proper volumes of particles are the same, the diagram is symmetric around the composition $x=1/2$. The isotropic–uniaxial transition line has the form of a well with a minimum at $x=1/2$. At this point there is also a transition from the isotropic phase straight into the biaxial phase. At higher densities the biaxial phase is sandwiched between rod-rich and disk-rich uniaxial phases.

The isotropic-to-uniaxial transition is first order, which means that, as far as ordering is concerned, there are jumps in the order parameters. The only exception is the point x

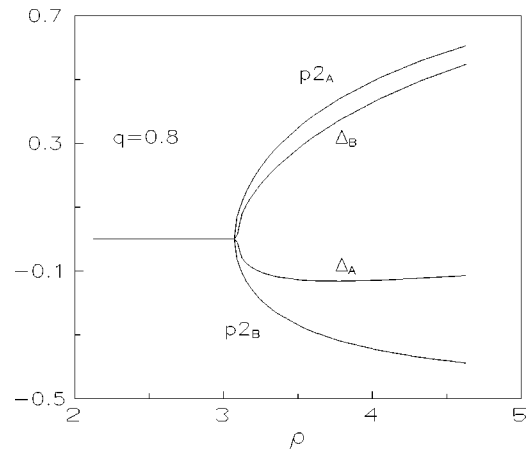


FIG. 2. Order parameters vs density for the equimolar point $x=1/2$ and the rod-disk excluded volume parameter $q=0.8$.

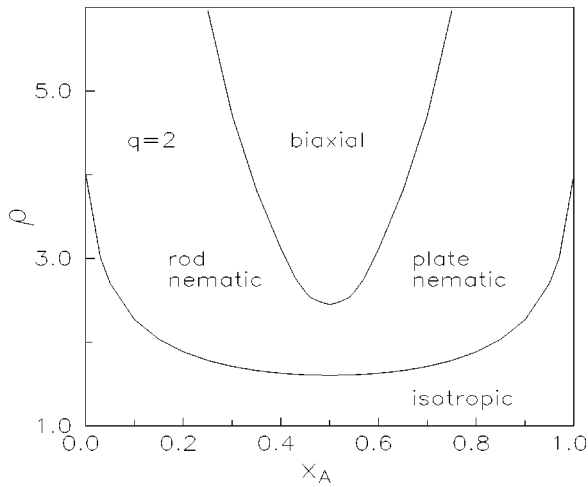


FIG. 3. Bifurcation diagram obtained for the parameter $q=2$ without the four-phase bicritical point.

$=1/2$ (equimolar point). In this case the transition point and the bifurcation point coincide and the transition is second order. Order parameters rise from zero on increasing the density of the system. This is a consequence of the vanishing of the cubic term in the free energy, which has been the source of the belief that the anisotropic phase occurring at this point has to be of biaxial symmetry. Transitions from the uniaxial to the biaxial phase are always second order.

Figure 2 shows the behavior of the order parameters vs density at the point $x=1/2$. The nonzero values of D_A and D_B indicate a biaxial phase that bifurcates straight from the isotropic phase. The order parameters presented are the averages of the leading symmetry-adapted functions [Eq. (13)] performed with the obtained solutions for the distribution functions:

$$P_{2i} = \int P_2(\theta) \psi_i(\theta, \phi) d\vec{\omega},$$

$$D_i = \int D(\theta, \phi) \psi_i(\theta, \phi) d\vec{\omega} \quad (i=A, B). \quad (30)$$

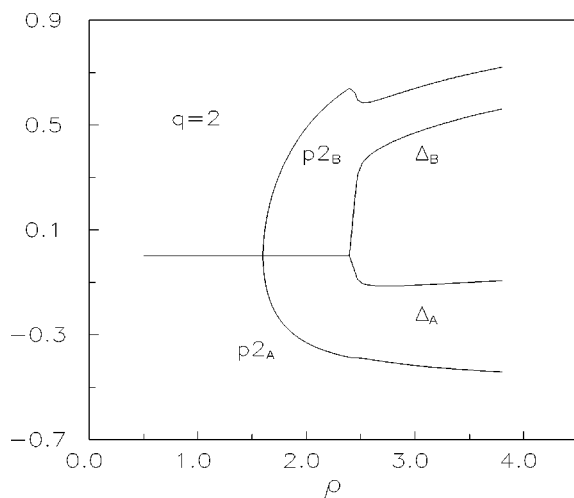


FIG. 4. Order parameters vs density for the equimolar point $x=1/2$ and the rod-disk excluded volume parameter $q=2$.

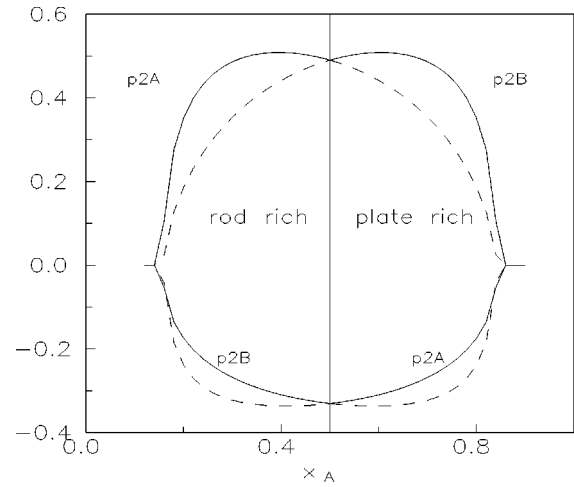


FIG. 5. Composition-dependent order parameters of the uniaxial region (density $\rho=2$).

In Fig. 3 I show the possibility for the bifurcation diagram, obtained in the case of an increased rod-disk parameter $q=2$. In spite of the fact that the general outlook of the picture is similar to that previously discussed, a different qualitative feature occurs. For the composition $x=1/2$ there is no longer a common point for the isotropic, uniaxial, and biaxial phases (no bicritical point) and the whole uniaxial-biaxial transition curve is shifted towards higher densities. Both isotropic-uniaxial and uniaxial-biaxial transitions are now second order. This can also be seen from Fig. 4, where all order parameters rise from zero without a jump. In this figure one can see that on increasing the density, the phase that bifurcates from the isotropic solution at $\rho^*=1.6$ is of uniaxial symmetry and then the biaxial solution appears for $\rho^*=2.45$. Thus solution of the self-consistency equations justifies, as had been expected, the absence of a bicritical isotropic-biaxial point.

An interesting question is what happens to the order parameters of species A and B in the uniaxial phase in the density range between the isotropic-uniaxial and uniaxial-biaxial curves and how the system stops being rodlike and

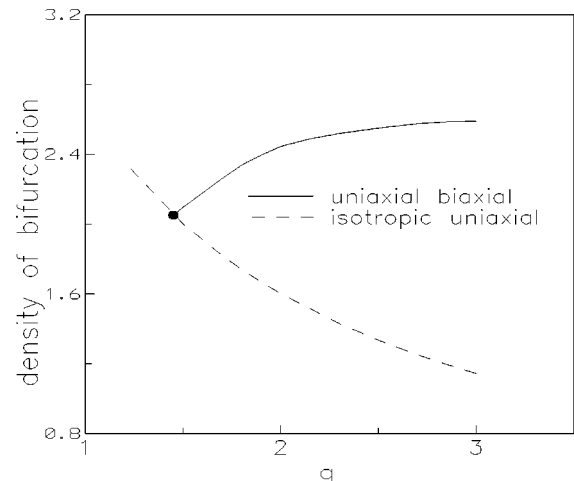


FIG. 6. Dependence of the isotropic uniaxial and uniaxial biaxial bifurcation densities vs excluded volume parameter q for the composition $1/2$.

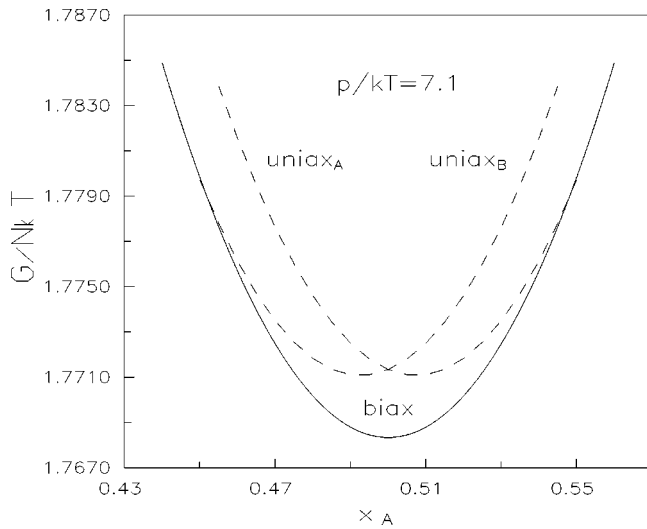


FIG. 7. The Gibbs energy vs composition obtained at fixed pressure 7.1 for the mixture without a bicritical point ($\varphi=2$).

becomes disklike. Changing smoothly the composition x_A and keeping the density at $\rho=2$, I obtained the following behavior of the order parameters (Fig. 5). Nonzero values of the order parameters appear at the isotropic-uniaxial nematic transition points and form a shark-jaw-like picture. In the rod-rich phase the uniaxial order parameter for rods P_{2A} is greater than zero, whereas the one for disks P_{2B} is less than zero. In the left half of the picture they are shown as solid lines. However, there exists another possibility when the order parameters have signs opposite to these. This is obtained by using two reference frames. The first one, which we will call the rod-phase reference frame, has the z axis along the preferred direction of rods in the rod phase. In the second one, the disk-phase reference frame, the z axis points along the preferred direction of disks in a discotic phase, which is perpendicular to the z axis of rods (lies in the xy plane of the rod frame). The dashed lines are the order parameters obtained in the frame of character opposite to that of the phase. The right half of the picture is a mirror image of the left half: rodlike features are changed into disklike features. This symmetry about the equimolar point is caused by the condition of equal proper volumes of the particles. Being restricted to one reference frame, for instance, the rod-phase frame, the rod-rich phase approaches the equimolar point with a positive value of the main (uniaxial) order parameter and jumps to a negative value in the discotic phase. In this sense one may say that there is a first-order transition at the equimolar point. However, this transition does not refer to the symmetry of the phases since both of them are cylindrical.

Figure 6 shows the dependence of the isotropic-uniaxial and uniaxial-biaxial bifurcation densities on the excluded volume parameter φ for the composition $x=1/2$. For the isotropic-uniaxial curve a descending tendency is observed due to the fact that increasing φ corresponds to lengthening the rods. For $\varphi > 1.4$ there appears a gap between the biaxial and isotropic density regions due to the intervening uniaxial phase.

Figure 7 shows the Gibbs energy plot at fixed dimensionless pressure 7.1 for the case without a bicritical point. The obtained biaxial phase is stable with respect to decomposition into rod- and disk-rich uniaxial phases. This is in accor-

dance with the property highlighted in [15], where increasing the value of the rod-disk excluded volume parameter φ improves the stability of the biaxial phase. Because this model is restricted to nematic phases I do not discuss the problem of stability of the biaxial phase vs the formation of a possible smectic phase or the competition between the formation of the smectic phase and the decomposition of the biaxial phase into two uniaxial ones at high pressure.

IV. CONCLUSIONS

On the basis of the second virial theory of a rod-disk mixture, I show the possibility of a different type of phase diagram without the bicritical isotropic-biaxial point at the equimolar concentration, where the biaxial phase appears to be separated from the isotropic phase by the uniaxial phase. This entails that the transition from the isotropic to uniaxial phase is of second order, i.e., the order parameters change continuously. Such a situation for mixed systems has, to my knowledge, not been explained so far. In the literature there exist some indications of the first-order transition phenomenon between rodlike and disklike phases in one-component systems [16,17]. An early one, which also found the biaxial phase, is due to Li and Freed [16], who consider a lattice model of infinitesimally thin rectangular mesogens interacting via both steric and attractive forces. However, in a lyotropic system of mesogens interacting through purely repulsive forces, the model does not predict the phase with D_{2h} symmetry at all, although such a possibility is well known from theoretical and computer simulations of hard-core biaxial objects. Also in the diagrams exhibiting the biaxial phase they observe an unusual sequence of transitions, namely, the biaxial phase always melts into a discotic one upon lowering the temperature at constant pressure or density. Such results, being far from reality, might be caused by the two-dimensional character of the molecules considered or by deficiencies of the approximations used.

More conventional are the results of Toledano *et al.* [18], who show that a general Landau analysis, albeit of the one-component system, allows for the possibility of a first-order transition line from the calamitic (rodlike) phase to the discotic phase. However, at the same time this line does not end with a bifurcation to the biaxial phase.

The case most closely related to that analyzed here might be, surprisingly, the report of Yu and Saupe [2], where they also mentioned the sodium decylsulfate system in which, besides a phase diagram similar to the lyotropic mixture of potassium laurate, decanol, and water (D_2O), it is possible to observe a direct first-order transition between calamitic and discotic nematic liquid crystals. A similar case has been investigated by Amaral [19].

The discussion presented in this paper might be regarded as a partial theoretical explanation to this experimental finding. Since lyotropic systems with biaxial phases also exhibit the feature of reentrant phenomena, i.e., a sequence of transitions such as isotropic to uniaxial to biaxial to uniaxial to isotropic, a full explanation of the Yu-Saupe phase diagram might be achieved through constructing a mixture theory in which micelles are allowed to change identity.

Here I have analyzed the influence of the rod-disk excluded volume parameter on the type of phase diagram. Per-

forming a uniaxial-biaxial nematic bifurcation analysis on the $L2$ model, I found the critical value of the rod-disk parameter for which the bicritical isotropic-biaxial point disappears. The conclusion I would like to stress here is that the factor that is responsible for the increased stability of the biaxial phase is also responsible for the vanishing of the bicritical point. This conclusion refers to the group of theories restricted to the $L2$ model. Although this may be regarded as a rough approximation, all theoretically found and examined instances of a stable biaxial phase are within the $L2$ model *only*.

Inclusion of higher-order terms in the interaction kernel rather leads to the demixing phenomena of the biaxial phase into two uniaxial ones. What I call second virial theory might be interpreted in two ways. First, it is the Onsager-type model where the interaction parameters used refer to the real interaction potential of the particles. Then disregarding higher virial terms in the free energy functional may introduce significant differences into the analysis, as is known

from (exact) computer simulations. In the second interpretation, the kernel interaction parameters may be regarded as renormalized ones, effectively taking into account the influence of higher virial contributions. Such a renormalized model allows one to obtain very good results, both for the static and for the hydrodynamic properties of a nematic phase [20].

Designing mesogenic molecules whose structure of mutual interaction is dominated by $L2$ terms may be the key to the synthesis of the thermotropic liquid crystal compounds with the so intensely searched for stable biaxial phase. Much work remains to be done to discover the influence of real molecular factors on the interaction kernel parameters, especially those that may promote $L2$ terms.

ACKNOWLEDGMENTS

The author is indebted to Bela Mulder and Paulo Teixeira for reading the manuscript and for their comments.

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