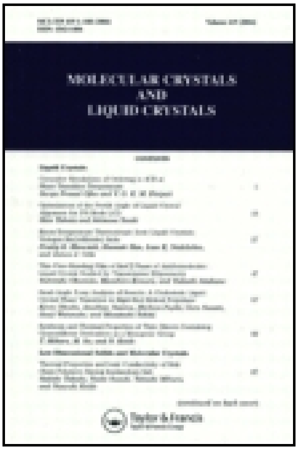

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Binary Mixtures of Hard Rods: A Short Account

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Binary Mixtures of Hard Rods: A Short Account

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Results of recent calculations aimed at predicting the liquid-crystalline phase behavior of binary mixtures of hard spherocylinders are shortly reviewed. These calculations have been made by adopting a simple, re-summed second-virial Onsager-type theory, and include, among the usual isotropic and nematic phases, smectic phases too. The paradigmatic hard spherocylinders with diameter D and length of the cylindrical part equal to 5D have been taken as reference component, to which hard spherocylinders of different geometry are added. The liquid-crystalline phase diagram of the bidisperse mixtures so generated have been traced in all range of composition as a function of pressure. Various phenomena, such as strong demixing, presence of triple, critical and azeotropic points, and smectic phases with different symmetries, have been observed.

Keywords: entropic phase transitions; liquid crystal mixtures

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1. INTRODUCTION

The hard spherocylinder (HSC) is a basic liquid-crystalline model, especially relevant to the domain of lyotropic liquid crystals. It is formed by capping both ends of a cylinder of length L and diameter D with two hemispheres of the same diameter; it can also be seen as that object generated by a sphere of diameter D rolling on a line of length L.

The HSC model was devised by Onsager in his work on the effect of shape on the phase behavior exhibited by dispersions of elongated colloidal particles [1]. He showed that the expression of the excluded volume between a pair of HSCs is both very simple. This fact, together with the insightful realization that, at least in an isotropic fluid of HSCs, the reduced virial coefficients of order higher than two should quickly tend to zero as the ratio L/D tends to diverge, made it possible to write down a simple and exact expression for the free energy of a fluid of very long and thin HSCs. The latter involves the ideal term, which contains the orientational entropy contribution, and the excess term, solely represented by the leading virial coefficient. Thanks to a proper parameterization of the orientational distribution function, this free energy expression was successfully solved for the isotropic-nematic coexistence, thus demonstrating that the latter may be the result of just a competition between orientational (favoring the isotropic phase) and packing (favoring the nematic phase) entropic terms.

Notwithstanding Onsager theory is applicable only to slender rods [2], the underlying mechanism put forward to explain liquid crystallinity is general, as demonstrated by later computer simulations on hard body particle systems [3]. In these studies, it was observed that a nematic phase is stable also in fluids of hard rods with moderate aspect ratio. In addition, it was unambiguously demonstrated that the very HSC model is particularly attractive in that a system of HSCs can exhibit even a smectic-A phase.

The above-mentioned deficiency of the Onsager theory together with these simulational findings clearly prompted the search for theories able to reproduce with a good accuracy the outlined scenario. Among the various attempts, the theory of Parsons [4], later reformulated by Lee [5], has been singled out for its accuracy and simplicity. It is a second-virial, re-summed theory, where the virial coefficients of order higher than two are mapped onto those of a hard sphere fluid [6]. It was originally devised and applied to one-component systems undergoing an isotropic-to-nematic phase transition [5,7–9]. Of considerable importance is also the capability of the Parsons-Lee (PL) theory to provide a faithful account of the thermodynamics of the isotropic-to-smectic A and nematic-to-smectic A phase transition in pure systems of HSCs [10]. Together with that of Onsager, the PL theory has been employed to study isotropic and nematic phases in binary mixtures of hard particles [11]. The very few computer simulations available [12,13] suggest that, also in these cases, the theory provides valid results.

Thus, the PL theory has been considered a suitable tool with which to undertake exploratory studies aimed at predicting the liquid-crystalline phase diagrams that HSC binary mixtures may exhibit when also the certainly existing smectic phases are included in the calculations [14–16]. In the past, the effect of the presence of the latter in mixtures was examined theoretically from a qualitative point of view, or, more extensively but still limitedly, restricting the calculations to a stability analysis of binary mixtures of perfectly aligned HSCs [17–20]. Only a few studies using computer simulation, still in the perfect orientational order approximation, exist [20–22].

After a concise recapitulation in Section II of the PL theory in binary mixtures of layered phases, the results gathered up to now are reviewed in Section III. The article ends with Section IV, where remarks on the present and perspectives on possible future works are discussed.

2. Recall of Basic Theory

The PL theory amounts to writing the Helmholtz free energy, F, of binary mixtures of HSCs that, in the most general cases, form smectic-A phases, as follows:

$$\frac{\beta F}{V} = \sum_i \frac{1}{\delta}\int_0^{\delta} dz\left\{\rho_i(z)[\ln\rho_i(z) - 1] + \int d\mathbf{u} f_i(z,\mathbf{u})\ln f_i(z,\mathbf{u})\right\}$$

$$+\,\Psi(\phi)\sum_i\sum_j \frac{1}{\delta}\int_0^{\delta} dz\rho_i(z)\int_{-\infty}^{+\infty} d\zeta\rho_j(z+\zeta)\alpha_{ij}(z,\zeta,[f_i,f_j]). \quad (1)$$

In Eq. (1) i, j are integers ($i,j = 1,2$) which label the two components; the parameter $\beta = 1/kT$ is the inverse thermal energy, with k the Boltzmann's constant and T the temperature; V is the volume, and δ the layer spacing, the mesophase director, $\mathbf{n}$, being aligned along the z axis of the laboratory frame of reference. The single sum in Eq. (1) is the ideal contribution, while the last double sum is the excess contribution. Both terms depend on the distribution functions, $\rho_i(z)$ and $f_i(z,\mathbf{u})$, in which the total single-particle distribution function has been factorized. $\rho_i(z)$ gives the probability density to find a particle of the species i at position z along the director, while $f_i(z, \mathbf{u})$ is the orientational distribution function of those specific, so located particles, with $\mathbf{u}$ the unit vector defining the orientation of a HSC. The two types of distribution function are normalized as follows:

$$\frac{1}{\delta}\int_0^{\delta} dz \rho_i(z) = \rho_0 \mathrm{x}_i; \qquad \int d\mathbf{u} f_i(z, \mathbf{u}) = 1, \tag{2}$$

with ρ_0 the total density of the system, and x_i the mole fraction of the HSCs of type i. The particle interactions are taken into account explicitly only at the second-virial level, while the effect of higher order correlations is compensated for through the pre-factor $\Psi(\phi)$. ϕ is the total packing fraction of the fluid, i.e., $\phi = \rho_0 \sum_i \mathrm{x}_i v_i$, with v_i the volume of a HSC of type i. The functional expression of Ψ is related to the Carnahan-Starling expression of the excess free energy of a hard sphere fluid [23]; both the latter and Onsager's expression are recovered in the respective appropriate limits. The key quantity in Eq. (1) is the function $\alpha_{ij}(z, \zeta, [f_i, f_j])$. It is interpreted as the area obtained by cutting the excluded volume of two particles, one of them having its center of mass located at position z along the director, with a plane perpendicular to the director and positioned at a distance ζ, resolved along the director, from the center of mass of the aforementioned particle (Fig. 1), and averaged over the orientational distribution functions of both particles.

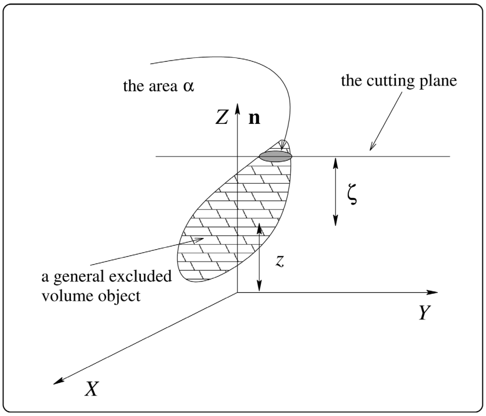

FIGURE 1 Scheme explaining the meaning of the function α.

The single-particle functions have been parameterized as follows:

$$\ln \rho_i(z) = \lambda_i \cos\left(2\pi \frac{z}{\delta}\right) + c_i, \tag{3}$$

$$\ln f_i(z, \mathbf{u}) = \gamma_i \ln f_i(\mathbf{u}) + d_i \tag{4}$$

where the constants c_i, d_i are just the logarithms of the corresponding normalization constants. The parameters λ_i and γ_i bear a one-to-one correspondence with the usual smectic, τ_1, and nematic, S, order parameters:

$$\begin{aligned} \tau_{1i} &= \frac{1}{\delta}\int_0^{\delta} dz \cos\left(2\pi\frac{z}{\delta}\right)\rho_i(z); \\ S_i &= \int d\mathbf{u}\left[\frac{3}{2}(\mathbf{u}\cdot\mathbf{n})^2 - \frac{1}{2}\right] f_i(\mathbf{u}). \end{aligned} \tag{5}$$

Note that no coupling has been assumed between positional and orientational variables. Because of these parameterizations, the free energy becomes a function of the positional and orientational order parameters of the two HSCs which form the mixture, as well as of the layer spacing and the total packing fraction, i.e., $F = F(\mathbf{K})$, with $\mathbf{K} = \{\rho_0, \delta, \tau_{11}, \tau_{12}, S_1, S_2\}$. It has been also assumed that the function $\alpha_{ij}(\zeta, S_i, S_j)$ is not a function of the orientational order parameters of the two components separately but a function of the average orientational order parameter, i.e., $\alpha_{ij}(\zeta, (S_i + S_j)/2)$.

In the case of a mixture it is more convenient to pass to the Gibbs free energy density, g. This is a function of the above-mentioned set of parameters $\mathbf{K}$, as well as of the pressure. For all of the binary mixtures considered, g has been minimized with respect to the set of parameters, for many values of pressure, in the range $P^* = \beta P D^3 \in [0, 4]$ and composition, $x = x_1 \in [0, 1]$, D being the unit of length (vide infra). During this operation, isotropic, nematic and smectic-A phases of different structure have been considered. Then, at any pressure considered, phase coexistences have been searched for by appropriately equating chemical potentials.

3. PRESENTATION AND DISCUSSION OF THE RESULTS

In all binary mixtures discussed in the following, the component 1 is a HSC with $D_1 = D = 1$ (in the following all lengths are expressed in units of D) and $L_1 = 5$. These numbers are, to a certain degree, paradigmatic, the HSC particle that they define being the one most studied both by theory and computer simulations. Several examples of HSC acting as the second component have been considered. They range from HSCs having $D_2 = 1$ but $L_2 \neq 5$, to HSCs with a total length, $D_2 + L_2$, equal to 6, but with a diameter different from unity (and consequently a value of L_2 differing from 5), and finally a HSC having the same volume as component 1 but different values of D_2 and L_2.

In Figure 2, the phase diagram of the binary systems obtained by mixing component 1 with HSCs of $D_2 = 1$ and $L_2 = 3.5$, 7 and 10 (top, central and bottom panels, respectively) is shown.

Upon addition to a system of HSCs with $L_1 = 5$ of HSCs with $L_2 = 3.5$, two coexistence regions arise, one separating isotropic and nematic phases, and the other nematic and smectic-A phases. Their width increases with pressure at first. Upon a further increase of pressure, while the width of isotropic-nematic coexistence region remains fairly constant, that of the nematic-smectic-A coexistence region reaches a maximum around $P^* = 2.5$, and subsequently shrinks. The two coexistence regions meet at $P^* \approx 2.9$, where a triple point emerges, with a nematic phase simultaneously in equilibrium with an isotropic phase, richer in the shorter component, and a smectic-A phase, richer in the longer component. Upon further increasing the pressure a direct isotropic-smectic-A phase transition occurs, as in the case of a pure system of HSCs with $L_2 = 3.5$ and $D_2 = 1$ [7,24].

Interesting features, *prima facie* unexpected, characterize the phase diagram of bidisperse systems of HSCs having the same diameter and moderately different length, as in the case of the mixture shown in the central panel of Figure 2. The first is the appearance of an azeotropic point along the nematic-smectic A coexistence curve; the other is the smectic A-smectic A critical point, at $P^* \approx 3$. At higher pressures an equilibrium establishes between a smectic-A phase, very rich in the shorter component, and a smectic-A phase where the composition of HSCs with $L_1 = 5$ and $L_2 = 7$ is comparable.

The smectic A-smectic A coexistence region just discussed moves toward lower pressure as the length of the second component increases. It inevitably tends to interfere with the nematic-smectic A coexistence region. These two coexisting regions eventually melt together, generating a single, wider coexistence region in the phase diagram plot, as well as a smectic-nematic-smectic triple point. One example of these phenomena is provided by the binary mixture of HSCs with $L_2 = 5$ and $L_2 = 10$, shown in the bottom panel of Figure 2. The other interesting feature of such mixtures concerns the structure of the smectic phase with the shorter particles in large abundance (i.e., large value of x). It is of the A_2 type, i.e., the longer solute rods, still arranged parallel to the director, have their centers of mass located preferentially in between the layers. There is an additional feature

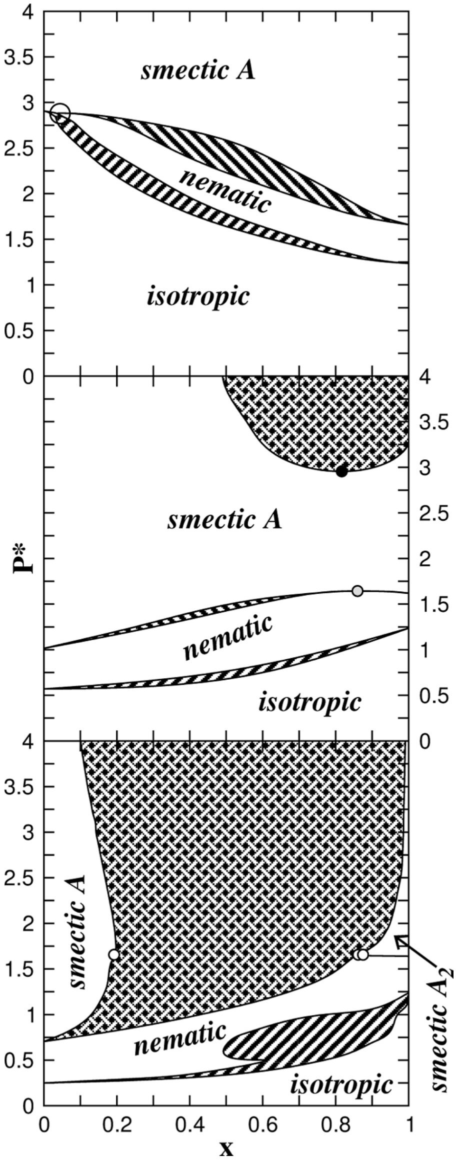

FIGURE 2 Phase diagrams of binary mixtures of HSC particles with the same diameter $D_1 = D_2 = 1$ in the reduced pressure P^* *versus* composition $x = x_1$ plane. The length of component 1 is set to $L_1 = 5$. The length of component 2 is, from top to bottom, $L_2 = 3.5$, 7 and 10. Shaded areas indicate coexistence regions. Empty or white circles indicate triple points; the black circle indicates a critical point; the grey circle indicates an azeotropic point.

worth to be noticed in the mixtures of HSCs having the same diameter and a sufficiently different length. It is the re-entrant behavior that characterizes the isotropic-nematic coexistence region. It is not new and has previously been commented upon profusively [11].

The liquid-crystalline phase behavior of bidisperse mixtures of HSCs having the same total length is driven by the difference in the diameter. The addition to a sample of HSCs with $L_1 = 5$ and $D_1 = 1$ of thicker HSCs, such as those having $D_2 = \frac{4}{3}$ (and $L_2 = \frac{14}{3}$, so that their total length is also equal to 6), has the effect of destabilizing the nematic phase with respect to both the smectic-A and isotropic phases. In this particular mixture, whose phase diagram is shown in the top panel of Figure 3, the prolongation of this effect upon further addition of thicker rods results in a triple point where the nematic phase is in simultaneous equilibrium with an isotropic and smectic-A phase, and the consequent direct transition from the isotropic to the smectic-A phase for values of x sufficiently close to zero (note that for the thicker-rod component the length-to-breadth ratio is equal to 3.5, for which no stable nematic phase is obtained [7,24]).

The reduction of the diameter of a HSC leads to an increase of the values of the reduced pressure at which a pure sample undergoes a transition from the isotropic to the nematic phase, and from the latter to the smectic-A phase. Thus, in a mixture consisting of the reference HSCs and HSCs having $D_2 = 0.5$ and $L_2 = 5.5$ (Figure 3, central panel), apart from a very narrow isotropic-nematic coexistence region, a nematic-smectic A coexistence region occurs, in the range of pressures considered in the plot, at increasingly higher pressures as the composition x decreases (i.e., the thinner rods become more abundant).

An ulterior decrease of the value of D leads to a significant rise of the pressure at which the pure system of slender HSCs undergoes an isotropic-nematic phase transition. Consequently, in the pressure range represented in the graph, the phases exhibited by the fluid with a more abundant thicker component (isotropic, nematic and smectic A in the present case) appear sequentially in equilibrium with, essentially, an isotropic phase formed almost exclusively by thin rods. This is the case for the mixture composed of HSCs with $D_1 = 1$ and $L_1 = 5$, and HSCs with $D_2 = 0.15$ and $L_2 = 5.85$ (Figure 3, bottom panel). The isotropic-isotropic coexistence region is bounded by a lower critical point, while isotropic-isotropic-nematic and isotropic-nematic-smectic-A triple points are additional interesting features.

The characteristics seen to be salient for mixtures of equally wide or equally long HSCs compound together in more general binary mixtures, such as the one formed by two HSCs of equal volume. One example is provided in Figure 4, where the phase diagram of the

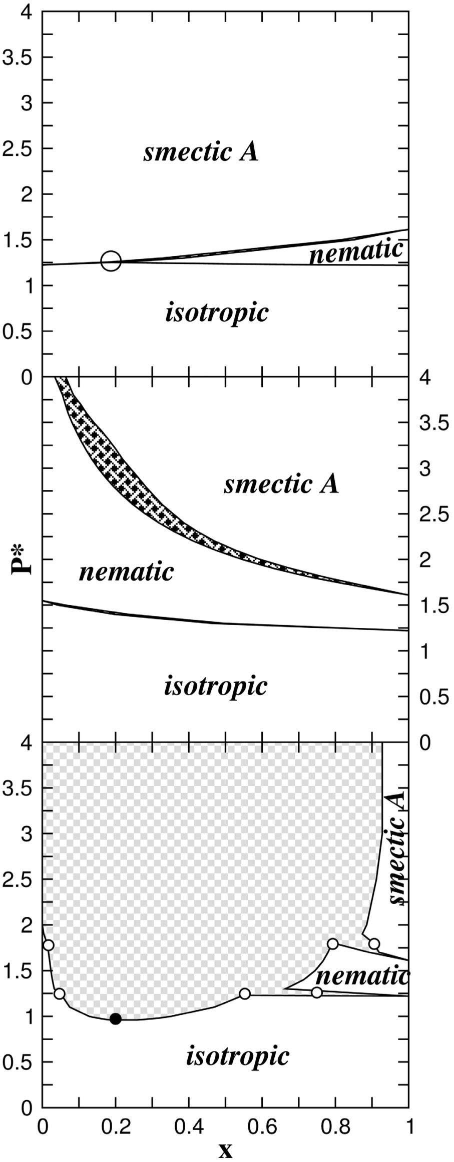

FIGURE 3 Phase diagrams of binary mixtures of HSC particles with the same total length in the reduced pressure P^* *versus* composition $x = x_1$ plane. The length and breadth of component 1 are set to $L_1 = 5$ and $D_1 = 1$, respectively. The length and breadth of component 2 are, from top to bottom: $L_2 = 14/3 \simeq 4.67$ and $D_2 = 4/3 \simeq 1.33, L_2 = 5.5$ and $D_2 = 0.5$, and $L_2 = 5.85$ and $D_2 = 0.15$. Shaded areas indicate coexistence regions. Empty or white circles indicate triple points; the black circle indicates a critical point.

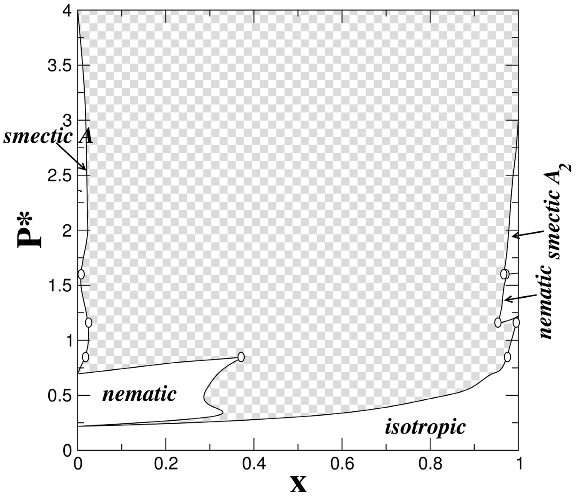

FIGURE 4 Phase diagram of a binary mixture of HSC particles with the same volume in the reduced pressure P^* *versus* composition $x = x_1$ plane. The length and breadth of component 1 are set to $L_1 = 5$ and $D_1 = 1$, respectively. The length and breadth of component 2 are $L_2 = 443/180$ and $D_2 = 2/3$, respectively. The shaded area indicates coexistence regions. White circles indicate triple points.

mixture formed by HSCs with $L_1 = 5$ and $D_1 = 1$, and $L_2 = \frac{443}{180}$ and $D_2 = \frac{2}{3}$ is plotted. Length and diameter bidispersity concur to widen significantly the coexistence region, which is unique and formed by the merging of smectic-smectic, smectic-nematic, and nematic-isotropic coexistence regions. The re-entrant behavior characterizing the latter, as well as the lamellar character of the smectic-A_2 phase, where the shorter and thicker rods are significantly more abundant, both driven by the length bidispersity, have been retained. Of interest is the ondulating character of the curve bounding the coexistence region on the side where the longer and thinner rods are the majority component and form a smectic-A phase. It is presumably originated from the fact that this lamellar phase is progressively in equilibrium with phases of different symmetry: upon increasing pressure, a nematic phase preferentially formed by component 2; isotropic and nematic phases preferentially formed by component 1; and, finally, the above-discussed smectic A_2.

4. CONCLUSIVE REMARKS AND PERSPECTIVES

Recent work on the prediction of the liquid-crystalline phase diagram of hard rod binary mixtures has been reviewed. In the calculations, based on a simple hard spherocylinder model and carried out within a simple second-virial theory, smectic-A phases have been also taken into consideration, thus going beyond previous studies where these phases were deliberately avoided. The phase behavior observed is quite rich. Nematic and smectic orderings have been seen to compete with isotropization and demixing. Various azeotropic, critical and triple points have been observed. Microphase separations have been seen to occur for certain layered phases. Notwithstanding the crudeness of both model particle and theory, these results are of basic relevance to the entire field of lyotropic liquid crystals, either of (bio)organic or mineral origin [11,25,26].

Lots of work remains to be done, though. More ordered phases, like columnar or crystalline, that will show up (certainly the latter) at higher pressures have not been considered, simply because the first type of phase is unlikely to be stable in systems of freely rotating HSCs, or because the present theory is clearly inadequate to handle crystalline phases properly. More sophisticated theories that can be applied to all nonuniform phases and extended to mixtures have simply not been fully developed yet. Different types of interactions should be also considered in future work. Particularly interesting will be the use of PL theory to predict the phase behavior of semiflexible rather than rigid rods, as well as the construction of phase diagrams formed by bidisperse discotic systems.

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