Polydispersity Stabilizes Biaxial Nematic Liquid Crystals

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Inspired by the observations of a remarkably stable biaxial nematic phase [van den Pol *et al.*, Phys. Rev. Lett. **103**, 258301 (2009)], we investigate the effect of size polydispersity on the phase behavior of a suspension of boardlike particles. By means of Onsager theory within the restricted orientation (Zwanzig) model we show that polydispersity induces a novel topology in the phase diagram, with two Landau tetracritical points in between which oblate uniaxial nematic order is favored over the expected prolate order. Additionally, this phenomenon causes the opening of a huge stable biaxiality regime in between uniaxial nematic and smectic states.

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Since its first prediction back in the early 1970s [1–3], the biaxial nematic (N_B) phase has strongly attracted the interest of the liquid crystal (LC) community [4]. In contrast to the more common uniaxial nematic (N_U) phase, where cylindrical symmetry with respect to the nematic director determines optical uniaxiality, the N_B phase is characterized by an orientational order along three directors and consequently by the existence of two distinct optical axes. The prospect of inducing orientational ordering along three directions, while maintaining a nematic fluidlike mechanical behavior [5], renders biaxial nematics preeminent candidates for next generation LC-based displays [6]. Although experimental evidence of stable N_B phases was reported already 30 years ago in lyotropic LCs [7], in thermotropics this result was achieved in systems of bent-core molecules only a few years ago [8]. Actually, when trying to experimentally reproduce an N_B phase, one often encounters practical problems related to its unambiguous identification [4] and to the presence of competing thermodynamic structures [9–11]. Stabilizing N_B states is therefore an open, challenging scientific problem with huge potential applications. Motivated by the exciting results of a recent experiment on a colloidal suspension [12], we use here a mean-field theory to investigate the role played by size polydispersity on the stability of biaxial nematics in systems of boardlike particles. We show that a difference in the particle volume of a binary mixture can favor oblate uniaxial orientational ordering over prolate, in sharp contrast with the behavior of the pure systems. This phenomenon gives rise to a new phase-diagram topology due to the appearance of two Landau tetracritical points, leading to a wider region of N_B stability. This feature is shown to hold also for a larger number of components, thus offering an explanation to the results of Ref. [12]. Finally, we argue that our findings could furnish a new way to look for biaxiality in thermotropic LCs.

At low density in lyotropics, and at high temperature in thermotropics, the N_B phase appears as a crossover regime in between ''rodlike'' and ''platelike'' behavior [2]. In fact, one can distinguish between the N_U phase developed by rods, in which particles align the longest axis along a common direction (uniaxial nematic prolate, N_+), and that developed by plates, in which particles align the shortest axis (uniaxial nematic oblate, N_-). A natural candidate system for developing an N_B phase is a binary mixture of rods and plates [13]; however, in most cases a demixing transition into two uniaxial nematic phases, i.e., N_+ and N_-, prevents its stabilization [10,11]. Alternatively, a stable N_B state is expected in a system of particles with cuboid (i.e., rectangular parallelepiped) shape defined by the lengths of the principal axes $L \geq W \geq T$, as depicted in Fig. 1(a) [3]. In this case, it is convenient to introduce a shape parameter ν, defined by $\nu = \frac{L}{W} - \frac{W}{T}$. By increasing the packing fraction and disregarding the possible stability of inhomogeneous phases, a system of cuboids undergoes an $I \rightarrow N_+ \rightarrow N_B$ sequence of phases if $\nu > 0$, whereas an

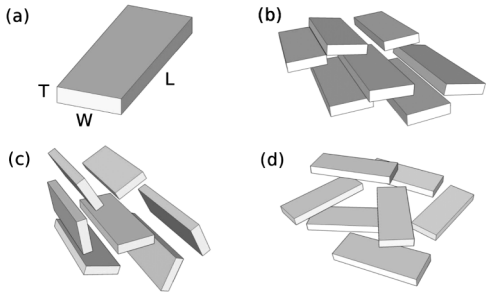

FIG. 1. (a) Cuboidal particle with dimensions $L \times W \times T$. (b) Schematic representation of a system of freely rotating cuboids in the biaxial nematic phase N_B, (c) the uniaxial nematic prolate N_+, and (d) the uniaxial nematic oblate N_-. In this Letter the rotational degrees of freedom are discretized according to the Zwanzig model [18].

$I \to N_- \to N_B$ sequence is found if $\nu < 0$ (I stands for the isotropic phase) [14]. A schematic representation of these nematic phases is given in Figs. 1(b)–1(d). The case $\nu = 0$ describes the optimal "brick" shape exactly in between "rodlike" and "platelike." In this case the N_U phase is suppressed and substituted by a second-order IN_B transition [14].

The first experimental realization of the hard-cuboid model was found only recently in a colloidal suspension of boardlike mineral goethite particles [12]. By producing particles with shape parameter $\nu \simeq 0.1$ close to zero ($\langle L\rangle \times \langle W\rangle \times \langle T\rangle = 254 \times 83 \times 28$ nm^3 and size polydispersity of 20%–25%), the authors were able to produce an N_B phase stable over a pressure range surprisingly much wider than to be expected from theory [9,15] and simulations [16] for particles whose shape parameter deviates even slightly from zero. Even more interestingly, the authors affirm that no N_U phase was observed, contrasting Ref. [14]. They suggest that a possible reason for this disagreement should be found in ingredients whose effects have never been studied so far because of their complexity, i.e., fractionation, sedimentation, and polydispersity. These unexpected results motivate our interest in analyzing the effect of the above mentioned ingredients, in particular, polydispersity, on the stability of the N_B phase in a fluid of hard cuboids.

We consider an M-component suspension of N_α colloidal cuboidal particles of species $\alpha = 1, \ldots, M$ with dimensions $L_\alpha \times W_\alpha \times T_\alpha$ ($L_\alpha > W_\alpha > T_\alpha$) in a volume V at temperature T. The total number density of colloids is $n = \sum_\alpha N_\alpha/V$, the mole fraction of species α is $x_\alpha = N_\alpha/(nV)$, and the packing fraction is $\eta = n\sum_\alpha x_\alpha L_\alpha W_\alpha T_\alpha$. The theoretical framework used in this Letter consists of Onsager theory of LCs [17], which is a density functional theory truncated at second-virial order. In order to facilitate the calculations we follow Zwanzig by restricting the orientations of the particles to the six in which their principal axes are aligned along a fixed Cartesian frame [18]. Although quantitative agreement with real systems is not expected because of the simplifications introduced in the model, the same model was shown to successfully predict nontrivial phenomena such as demixing in rod-plate mixtures [10], orientational wetting due to confinement, and capillary nematization [19]. Moreover, we expect that transitions between different nematic phases and smectic phases are better described by this model than transitions from isotropic to nematics. In density functional theory the free energy of the system is expressed as a functional of the local density $\rho_i^\alpha(\mathbf{r})$ of particles of species $\alpha = 1, \ldots, M$ with orientation $i = 1, \ldots, 6$ as [20]

$$\frac{\mathcal{F}[\rho]}{k_B T} = \int d\mathbf{r} \sum_{\alpha,i} \rho_i^\alpha(\mathbf{r})\{\ln[\rho_i^\alpha(\mathbf{r})\Lambda_\alpha^3] - 1\} + \frac{\mathcal{F}^{\mathrm{ex}}[\rho]}{k_B T}, \quad (1)$$

where k_B is the Boltzmann constant and Λ_α^3 the thermal volume of species α. At second-virial order the excess free energy $\mathcal{F}^{\mathrm{ex}}$ reads

$$\frac{\mathcal{F}^{ex}[\rho]}{k_B T} = -\frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \sum_{\alpha,\alpha',i,i'} f_{ii'}^{\alpha\alpha'}(\mathbf{r}-\mathbf{r}')\rho_i^\alpha(\mathbf{r})\rho_{i'}^{\alpha'}(\mathbf{r}'), \quad (2)$$

where $f_{ii'}^{\alpha\alpha'}(\mathbf{r}) = \exp[-u_{ii'}^{\alpha\alpha'}(\mathbf{r})/(k_B T)] - 1$ is the Mayer function, defined in terms of the pairwise potential $u_{ii'}^{\alpha\alpha'}(\mathbf{r})$. By neglecting spatial modulations, i.e., by imposing $\rho_i^\alpha(\mathbf{r}) = \rho_i^\alpha$, the free energy Eq. (1) reduces to an Onsager-type functional whose minimization (under the constraints that $\sum_i \rho_i^\alpha = n x_\alpha$ for all $\alpha = 1, \ldots, M$) allows us to identify the spatially homogeneous equilibrium phase [21]. Since at sufficiently high density one expects spatially inhomogeneous phases to be thermodynamically favored, we apply bifurcation theory [14] to determine the limit of stability of the homogeneous equilibrium phases with respect to smectic fluctuations. By considering spatial density modulations only along the z axis, i.e., $\rho_i^\alpha(\mathbf{r}) = \rho_i^\alpha(z)$ in Eq. (1), the smectic bifurcation density is the minimum density at which the Hessian second-derivative matrix of the free energy has an eigenvalue equal to zero [21].

Our analysis starts by considering the simplest case of polydispersity, i.e., a mixture of $M = 2$ components with mole fractions x_1 and $x_2 = 1 - x_1$, respectively. Among the different ways one can parametrize polydispersity, our preliminary analysis suggests to consider volume polydispersity (i.e., same particle shape but different volume). Therefore, we study the phase behavior of a binary mixture of hard cuboids whose dimensions are

$$\begin{aligned} L_1 &= L(1+s), & W_1 &= W(1+s), & T_1 &= T(1+s), \\ L_2 &= L(1-s), & W_2 &= W(1-s), & T_2 &= T(1-s), \end{aligned} \quad (3)$$

where the parameter $s \in [0, 1)$ describes the degree of bidispersity. Notice that Eq. (3) implies the same aspect ratios for both species $L_1/T_1 = L_2/T_2 = L/T$ and $W_1/T_1 = W_2/T_2 = W/T$ (hence $\nu_1 = \nu_2 = \nu$). Here we set $L/T = 9.07$ and $W/T = 2.96$ ($\nu = 0.1$) in order to reproduce the experimental system of Ref. [12], thereby neglecting the small effect of the ionic double layer used by the authors to interpret the experimental data.

Figure 2 shows density-composition phase diagrams of binary mixtures ($M = 2$) of boardlike particles with the experimental shape parameter $\nu = 0.1$ for various bidispersity parameters (a) $s = 0.15$, (b) 0.18, (c) 0.20, and (d) 0.30, featuring isotropic (I), uniaxial nematic (N_+ and N_-), biaxial nematic (N_B) and smectic (Sm) phases. Because of the near-perfect "biaxial" shape of the particles, fractionation is extremely weak and invisible on the scale of Fig. 2 [21]. At the extreme mole fractions $x_1 = 0$ and $x_1 = 1$ (pure systems) all phase diagrams feature the phase sequence $I \to N_+ \to$ Sm that is well known and expected for board-shaped particles with $\nu > 0$, with the N_B phase metastable with respect to the Sm phase

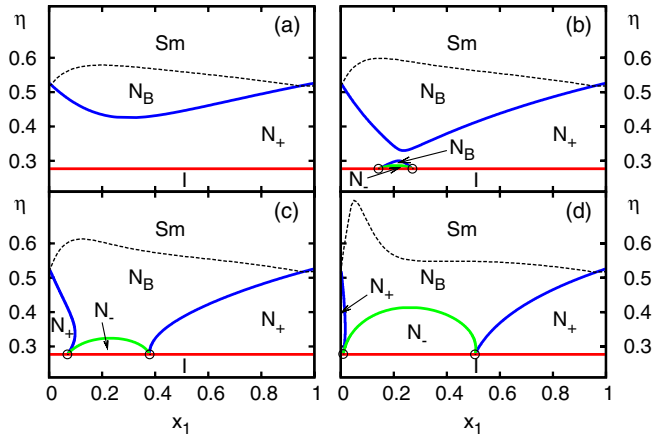

FIG. 2 (color online). Phase diagram of a binary mixture of hard cuboids in terms of packing fraction η vs mole fraction of the larger component x_1 showing isotropic (I), uniaxial (N_+ and N_-) and biaxial (N_B) nematic and smectic (Sm) phases. The size of the particles is defined by Eq. (3) with $L/T = 9.07$, $W/T = 2.96$ ($\nu = 0.1$) and bidispersities (a) $s = 0.15$, (b) $s = 0.18$, (c) $s = 0.20$, (d) $s = 0.30$. The solid lines separate different homogeneous phases, the dashed lines indicate the limit of stability of the homogeneous phases with respect to smectic fluctuations, whereas the open circles represent the Landau tetracritical points.

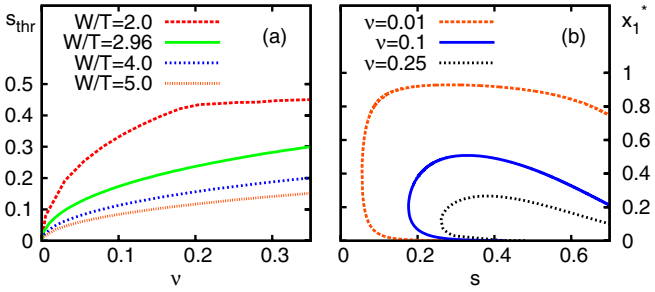

FIG. 3 (color online). (a) Threshold bidispersity s_{thr} for the appearance of a tetracritical point as a function of the shape parameter ν for different fixed values of W/T. (b) Critical mole fraction x_1^* as a function of the bidispersity parameter s for a binary mixture of hard cuboids for different shape of the particles [cf. Eq. (3)].

[9,14,21]. However, for all $s > 0$ there is an intermediate composition regime in which the N_B phase is found to be stable, the more so for increasing s. Whereas the opening up of a stable N_B regime is only quantitative for $s = 0.15$, there is a qualitative change of the phase-diagram topology beyond $s = 0.18$, where two Landau tetracritical points appear [open circles in Figs. 2(b)–2(d)]. In between these critical points a region of stable N_- phase, which is not expected for the rod-shaped particles ($\nu > 0$) of interest, opens up. Clearly, Figs. 2(c) and 2(d) show that this unexpected N_- regime enlarges with bidispersity, accompanying a further increased N_B stability. In other words, excluded-volume interactions in mixtures of board-shaped rods with the same shape and different volume tend to favor N_B stability as a consequence of an unexpected N_+-N_- competition. At higher packing fractions the increased N_B stability with respect to the Sm phase is not a surprise, given that regular packing into layers is hindered by size differences between particles [15].

It is interesting to understand how the remarkable features of the binary mixture described in Fig. 2 change with the shape of the particles. Here we are mainly interested in the following two properties of the phase diagram: (i) the minimum threshold bidispersity s_{thr} at which the Landau tetracritical points appear and (ii) the tetracritical mole fractions x_1^* in terms of the bidispersity s. We change the particle shape ($\nu = L/W - W/T$) by fixing in Eq. (3) one aspect ratio (W/T) and varying the remaining one (L/T). Figure 3(a) shows for $W/T = 2.0$, 2.96, 4.0, and 5.0 a similar trend: the minimum threshold bidispersity s_{thr} increases the more the shape deviates from the optimal brick one. At the same time, the fact that at fixed ν the threshold bidispersity decreases with W/T, indicates that the appearance of the Landau tetracritical points is favored by an increasing aspect ratio of the particles, in qualitative agreement with Ref. [22]. Moreover, by fixing the aspect ratio $W/T = 2.96$, we can observe the tetracritical mole fraction as a function of the bidispersity for different values of $\nu = 0.01$, 0.1, and 0.25 in Fig. 3(b). The closer the shape is to the optimal brick, the wider is the difference in value of the two tetracritical mole fractions x_1^* and, consequently, the stability regime of the N_- phase. Finally, we note that no critical composition is observed if the particles are closer to the "platelike" shape, i.e., if $\nu_1 = \nu_2 = \nu < 0$ one finds the N_- in between the I and N_B phases for every value of s and x_1 (not shown); the N_+ phase does not occur in this case.

In order to analyze proper polydispersity, and thus more realistically model the experimental system of Ref. [12], we extend our phase-diagram calculations to a system with $M = 21$ components of cuboids. Inspired by our analysis of the binary mixture and by the experiments [12], we fix the aspect ratios of all species to $L_\alpha/T_\alpha = L/T = 9.07$ and $W_\alpha/T_\alpha = W/T = 2.96$, such that (i) all species have the same shape $\nu_\alpha = \nu = 0.1$ and (ii) the size of each species is completely determined by T_α. We consider T_α to be distributed according to a discretized Gaussian function with average $\langle T \rangle = 28$ nm and standard deviation $\sigma\langle T \rangle$, where σ is the size polydispersity. In general the calculation of a (high-dimensional) phase diagram of a multicomponent system is a daunting task [23]. In this case, however, it is justified to ignore fractionation [21], which reduces the problem to minimizing the functional with respect to ρ_i^α at fixed nx_α. The resulting phase diagram in the density-polydispersity representation is shown in Fig. 4(a), featuring again I, N_+, N_-, N_B, and Sm equilibrium states and a tetracritical point at $\sigma \simeq 24\%$, which is surprisingly close to the size polydispersity in the experiments [12]. The strikingly large stability regime

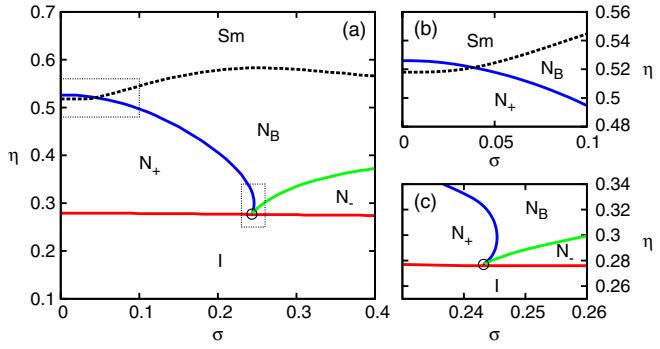

FIG. 4 (color online). (a) Phase diagram of $M = 21$ components of hard cuboids (packing fraction η) with aspect ratios $L_\alpha/T_\alpha = 9.07$ and $W_\alpha/T_\alpha = 2.96$ ($\alpha = 1, \ldots, M$) and Gaussian distributed dimensions with polydispersity σ (see text). The dashed line indicates the limit of stability of the homogeneous phases with respect to smectic fluctuations. The dotted rectangles highlight (b) the absence of the N_B phase at polydispersity $\sigma < 4\%$ due to the direct N_+Sm phase transition and (c) the reentrant character of the N_+N_B transition close to the tetracritical point (open circle).

of the N_B is caused by the reduced stability of Sm and N_+ [cf. Fig. 4(b)], not unlike in the binary case. However, a direct IN_B transition similar to that observed in Ref. [12] is not expected in this model due to the reentrant character of the N_+N_B phase transition [cf. Fig. 4(c)].

In conclusion, by means of a mean-field theoretical approach with discrete orientations we have shown that size polydispersity strongly affects the phase behavior of boardlike particles, driving the emergence of a novel topology of the phase diagram. This topology change is due to the appearance of Landau tetracritical points, which in turn is related to a competition between the prolate "rodlike" ordering typical of the pure components and the oblate "platelike" purely induced by the mixing. In combination with the destabilization of the Sm phase, we can conclude that polydispersity dramatically increases the stability regime of the N_B phase. The usual stability limitations of N_B phases, such as N_+-N_- demixing of rod-plate mixtures and ordering into smectics, are therefore overcome in the present system. Although this work focuses on a particular value of the particles' dimensions, its predictions hold for a more general choice of the relevant parameters, as reported in Fig. 3. Moreover, we do not expect the homogeneous phase behavior to be crucially dependent on the form of the interaction (cuboidal), on the contrary it should be qualitatively similar to other excluded-volume interactions with the same symmetry (e.g., spheroid, spheroplatelet).

Finally, it is tempting to consider this work in the perspective of stabilizing N_B thermotropic liquid crystals. In this case, the soft-core character of the intermolecular interactions does not allow for a univocal definition of "shape," and van der Waals forces can significantly influence the phase diagram. Nonetheless, it is widely accepted that hard-core models contain the essential physical ingredients for a first-approximation description of the structure of a molecular or colloidal fluid [24]. Following this interpretation scheme, it is intriguing to wonder whether it is possible to enhance the N_B stability by considering two- or multicomponent mixtures of molecules with biaxial symmetry and different size. We hope our findings will stimulate further research in this direction.

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