Biaxial, Twist-bend, and Splay-bend Nematic Phases of Banana-shaped Particles Revealed by Lifting the "Smectic Blanket"

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We perform an extensive computational study on the phase behavior of hard banana-shaped particles, and show that biaxial, twist-bend, and splay-bend nematic phases are metastable with respect to a smectic phase for a system of hard bent spherocylinders. However, if the smectic phase is destabilized—either by polydispersity in the particle length or by curvature in the particle shape—stable biaxial, twist-bend, and splay-bend nematic phases are obtained. This provides a unified and consistent picture on the subtle role of particle shape on the phase behavior of bent rods.

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In 1949 Onsager [1] predicted that fluids of uniaxial hard rods undergo an entropy-driven first-order phase transition from the isotropic (I) to the nematic phase (N) at sufficiently high density, as later verified in experiments [2–10] and simulations [11–15]. The nematic phase is a homogeneous fluid phase with orientational order. One can distinguish between a (rodlike) prolate nematic phase (N_+) when the longest particle axes are aligned along a common direction, and a (plateletlike) oblate nematic phase (N_-) when the shortest particle axes are aligned. Much work has since then been devoted to unveiling the rich variety of other nematic phases that can be stabilized by particles with different shapes and symmetries [16–28]. One of the first questions concerned the case of biaxial particles, for which the cylindrical symmetry is broken. In 1970 Freiser [16] showed by a generalized Maier-Saupe [29] theory that biaxial particles can exhibit a second-order phase transition from an isotropic to a biaxial nematic phase (N_b), in which both particle axes are aligned along two mutually orthogonal nematic directors. In the following years, the stability of the N_b phase was theoretically predicted for hard biaxial particles of various shapes [27,30–32].

Despite numerous theoretical predictions, the N_b phase turned out to be elusive in experiments, supposedly because of a subtle competition with the positionally ordered smectic phase (Sm) [33–35]. Only in 2004, Madsen *et al.* [36] and Acharya *et al.* [37] claimed the first observation of a thermotropic N_b phase in a system of bent-core mesogens, i.e., a class of polar biaxial "banana"-shaped molecules with a C_{2v} symmetry. Various claims of observations of a thermotropic N_b phase were later reported in systems of bent-core mesogens [38–45], promoting the idea that the C_{2v} symmetry plays a crucial role in the stabilization of N_b phases.

Although the validity of these claims is still a matter of debate [46–56], they encouraged new experimental, theoretical, and computational studies on bent-core mesogens, evolving into a "banana mania" in which more than 50 new liquid crystalline phases were discovered [57]. The observation of the twist-bend nematic phase ($N_{\rm TB}$) [58–68] is particularly exciting. The $N_{\rm TB}$ phase is a chiral nematic phase characterized by a wave number $q = 2\pi/p$, a pitch length p, a cone angle θ_0, and an oblique heliconical arrangement of the nematic director field $\hat{\mathbf{n}}(z) = \sin(\theta_0)\cos(qz)\mathbf{e}_x + \sin(\theta_0)\sin(qz)\mathbf{e}_y + \cos(\theta_0)\mathbf{e}_z$ [see Fig. 1(a)]. The possibility of this phase was postulated by Meyer [17] in 1976 and independently by Dozov [18] in 2001 for banana-shaped particles that favor a spontaneous bend deformation of the nematic director field. As a pure bend deformation cannot uniformly fill 3D space, the geometrical frustration caused by the local bend deformations is resolved via the emergence of a complementary left- or right-handed twist deformation.

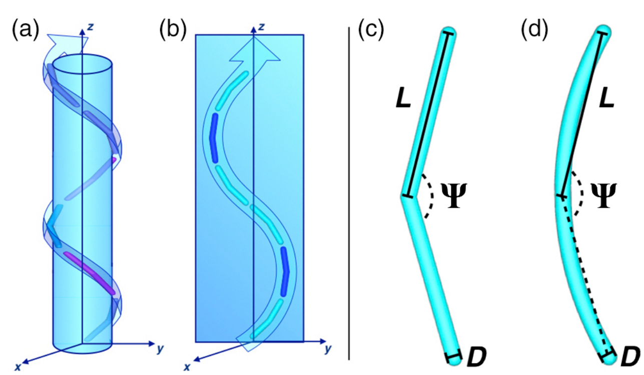

FIG. 1. Structure of the (a) chiral twist-bend $N_{\rm TB}$, and of the (b) biaxial splay-bend $N_{\rm SB}$ phase, as shown by the spatial modulations of the nematic director field. Schematic of a hard bent spherocylinder (c) and a hard curved spherocylinder (d).

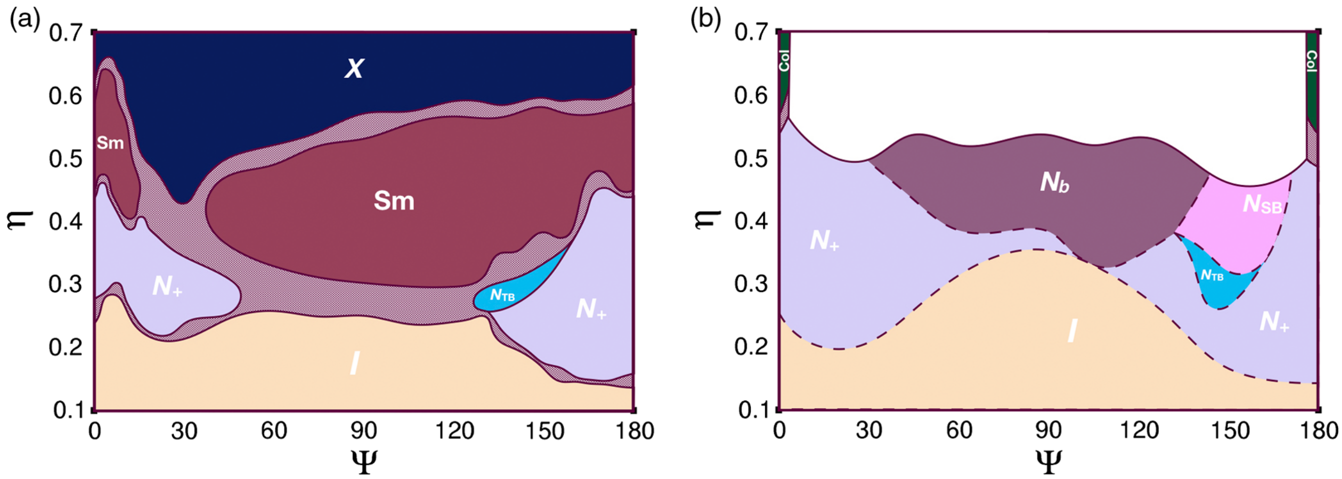

FIG. 2. Phase diagram of hard bent spherocylinders in the packing fraction η—opening angle Ψ representation from MC simulations for a (a) monodisperse with $L/D = 10$ and (b) polydisperse system with $\langle L \rangle/D = 10$ and $\sigma_L = 0.36\langle L \rangle$, displaying I (yellow), N_+ (lilac), Sm (red brown), columnar Col (dark green), and crystal X (dark blue) phases, but also twist-bend N_{TB} (light blue), biaxial N_b (purple), and splay-bend N_{SB} (pink) nematic phases. The coexistence regions are colored light brown. The white region corresponds to parts of the phase diagram that are unaccessible because of kinetic arrest upon compression. Dashed lines correspond to continuous transitions. The opening angle values used in the simulations are reported in the Supplemental Material [72].

Understanding the formation mechanism of the N_{TB} phase of bent-core mesogens could therefore provide fundamental insights on the spontaneous chiral symmetry breaking in systems of achiral particles.

Meyer and Dozov [17,18] postulated that the geometric frustration arising from bend deformations could also be resolved via a complementary splay deformation, yielding a so-called splay-bend nematic phase (N_{SB}), characterized by alternating domains of splay and bend and nematic director field $\hat{\mathbf{n}}(z) = \sin(\theta_0 \sin(qz))\mathbf{e}_y + \cos(\theta_0 \sin(qz))\mathbf{e}_z$ [see Fig. 1(b)]. The N_{SB} phase—which unlike the N_{TB} phase preserves the chiral symmetry—is also an N_b phase. Dozov predicted stability regimes of both the N_{TB} and N_{SB} phase for banana-shaped particles, but unlike the N_{TB} phase neither experimental nor computational evidence of a stable bulk N_{SB} phase has yet been reported, thereby raising doubts on its very existence.

Moreover, the attribution of the rich phase behavior of bent-core mesogens to their shape and symmetry is questioned by an earlier study by Lansac *et al.* [69], who mapped out the phase behavior of hard bent spherocylinders [see Fig. 1(c)] using Monte Carlo (MC) simulations, finding large stable regions of polar and antipolar smectic phases ($\mathrm{Sm}_{\mathrm{P/AP}}$) rather than N_b, N_{TB} and N_{SB} phases. Smectic phases were also observed experimentally in systems of bent silica rods [70,71].

To summarize, a fragmented and inconclusive picture arises from previous investigations on bent-core particles, in which a zoo of novel and exotic nematic phases appears to be cloaked under a vast "smectic blanket" in computer simulations. In this Letter, we first confirm the huge stability of the Sm phase of hard bent spherocylinders in simulations. Next, inspired by an earlier Onsager theory [32] which predicts the existence of N_b phases when the Sm phase is not taken into account, we proceed by "lifting" the smectic blanket. We destabilize the Sm phase, either by a polydisperse distribution of particle lengths or by curvature in the particle shape, thereby opening pathways towards all the theoretically predicted exotic nematic phases, including—for the first time—the N_{SB} phase.

We consider a system of hard bent spherocylinders consisting of two spherocylinders with a length-to-diameter ratio L/D, a rigid opening angle Ψ, and a shared capping sphere [see Fig. 1(c)]. We study the phase behavior of hard bent spherocylinders with $L/D = 5$ via NPT-MC simulations, resulting in a phase diagram as a function of the opening angle $\Psi \in [0, \pi]$ and packing fraction η—shown in the Supplemental Material [72]—completely dominated by I and Sm phases, with only small pockets of prolate nematic N_+ phases at $\Psi \in [3\pi/4, \pi]$ and close to $\Psi \sim \pi/6$ and $\Psi \sim 0$. This is consistent with Ref. [69]—where the regime $\Psi > \pi/2$ was investigated—except for the stable columnar phase reported in Ref. [69], which turned out to be an artifact of finite-size effects [73]. However, these findings differ from the work by Teixeira *et al.* [32], who presented a phase diagram based on Onsager theory featuring N_+, N_-, and N_b phases for $L/D \to \infty$ and $\Psi \in [\pi/2, \pi]$.

Inspired by Ref. [32], which is only exact in the Onsager limit of infinite L/D, and by Dussi *et al.* [27], who showed that N_b phases can only be stabilized for sufficiently anisotropic particles, we perform NPT-MC simulations of a system of hard bent spherocylinders with $L/D = 10$. The resulting phase diagram is presented in Fig. 2(a). Our simulations reveal neither N_- nor N_b phases, largely because of the enormous stability of the Sm phase. In fact, Fig. 2(a) reveals a direct I-Sm phase transition at η as low as

$\simeq 0.30$. The direct low-η I-Sm transition deviates from the behavior of straight rods [15], for which smectic order sets in at $\eta \simeq 0.45$ for $L/D \in [6, \infty]$. Also, the onset of the Sm phase moves to lower η when the rods are bent ($\Psi = 0 \to \pi/2$ and $\Psi = \pi \to \pi/2$), showing that crooked rods favor Sm phases. Interestingly, we do find a small region of stable N_{TB} phase for $\Psi \in [130°, 150°]$, demonstrating that the symmetry and polarity of boomerangs can be sufficient to break the chiral symmetry and stabilize the N_{TB} phase, provided that the aspect ratio is sufficiently pronounced. Note that we find an I-N-N_{TB}-Sm phase sequence at $\Psi = 150°$, whereas the nematic phase region shrinks and disappears for $\Psi \lessapprox 135°$, where we observe an I-N_{TB}-Sm phase sequence with a direct I-N_{TB} transition. This is in agreement with the predictions of a molecular theory for V-shaped particles [23], which predicts that the phase sequence I-N-N_{TB} (for decreasing temperature) is replaced by a direct I-N_{TB} transition when Ψ changes from 140° to 130°. Moreover, the packing fraction dependence of the pitch length p of the N_{TB} phase [72] is in remarkable agreement with the theory of Ref. [23], which predicts a decreasing pitch length from $p \sim 10L$ to $\sim 5L$ when moving deeper into the N_{TB} phase for $\Psi = 140°$ and 135°, and a nearly constant pitch length of $p \sim 5L$ for $\Psi = 130°$. On the other hand, we find smaller cone angles θ_0 than the ones predicted by theory [23].

The most significant difference between the theoretical predictions in literature and the phase diagram of Fig. 2(a) concerns the enormous stability of the Sm phase, which covers most of the nematic regimes. We anticipated that this "smectic blanket" can be lifted by destabilizing the Sm phase. Since polydispersity is well known to destabilize the Sm phase [74,75] and favor the formation of N_b phases [76,77], a polydisperse length distribution of bent spherocylinders may open a pathway to the hitherto elusive nematic phases. Performing accurate investigations of the equilibrium phase behavior of polydisperse systems requires sophisticated theoretical and computational methods [75,78,79]. As we only intend to take a peek below the smectic blanket, we start by fixing the polydisperse length distribution and ignoring fractionation. We perform NPT-MC simulations on systems of hard bent spherocylinders with particle lengths drawn from a Gaussian distribution of average $\langle L \rangle = 10D$ and standard deviation $\sigma_L = 3.6D$, keeping the lengths of the particles—hence the length distribution—fixed along the simulations. We report the phase diagram in Fig. 2(b), which interestingly shows no Sm phases at the packing fractions studied but exhibits N_b phases at large η. Two stability regions of N_+ phases are found for either $\Psi \lesssim 105°$ and $\Psi \gtrsim 105°$, with in between a region of N_b phase and consequently a Landau critical point at $\Psi_L \approx 105°$, which compares well with the theoretically predicted value [32]. At $\Psi = 150°$ we find again the N_{TB} phase, but with a significantly smaller cone angle θ_0, signaling a weakening of the bend deformations—and

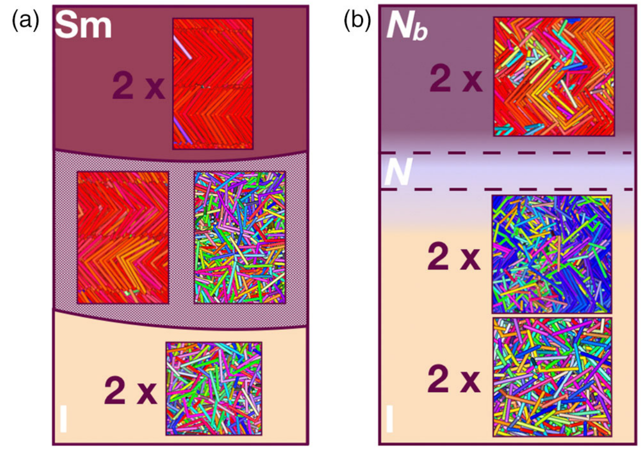

FIG. 3. Configurations of polydisperse bent spherocylinders with $\langle L \rangle/D = 10$ and opening angle $\Psi = 90°$ obtained from two simultaneous simulations in the semigrand canonical ensemble with imposed Gaussian parent distributions of variance (a) $\sigma_L = 0.01\langle L \rangle$ and (b) $\sigma_L = 0.36\langle L \rangle$. At low polydispersity (a) two I states, I-Sm coexistence, and two Sm states are found upon increasing the pressure. At large polydispersity (b) a continuous I-N-N_b transition is found with increasing pressure in both the simultaneous simulations. No fractionation is found in the cases shown here, but the I-Sm coexistence shows fractionation at intermediate polydispersities (see the Supplemental Material [72]).

therefore of the twist-bend ordering—caused by polydispersity. Intriguingly, we also find a N_{SB} phase in an I-N-N_{TB}-N_{SB} phase sequence, confirming that the polarity and C_{2v} symmetry of banana-shaped particles is sufficient to stabilize a N_{SB} phase, as predicted in Ref. [18]. This finding is, to the best of our knowledge, the first observation of a stable bulk N_{SB} phase since its prediction in 1976 [17]. For polydisperse straight rods ($\Psi = 0°$ and $\Psi = 180°$) we recover the phase behavior reported in Ref. [75], with a N-Col phase transition at $\eta \approx 0.6$.

However, the introduced polydispersity of $\sigma_L/\langle L \rangle = 0.36$ is twice as large as the terminal polydispersity for the Sm phase of straight rods [75]. Such a relatively large polydispersity could in principle give rise to fractionation in the actual equilibrium phase diagram. To test the stability of the nematic phases observed in Fig. 2(b) with respect to fractionation, we introduce an MC integration scheme which does allow for fractionation and demixing. This scheme is based on the semigrand canonical ensemble (SGCE) introduced in Ref. [80] and the nonequilibrium potential refinement (NEPR) method of Wilding [81], and involves two simultaneous SGCE simulations with a fixed number of particles, the same pressure and temperature, and the same tunable distribution of chemical potentials $\mu(L)$ of particle species. Along with standard variations of volume, particle positions, and particle orientations, we propose independent variations of the length of individual particles $L \to L'$, accepted or rejected with a probability

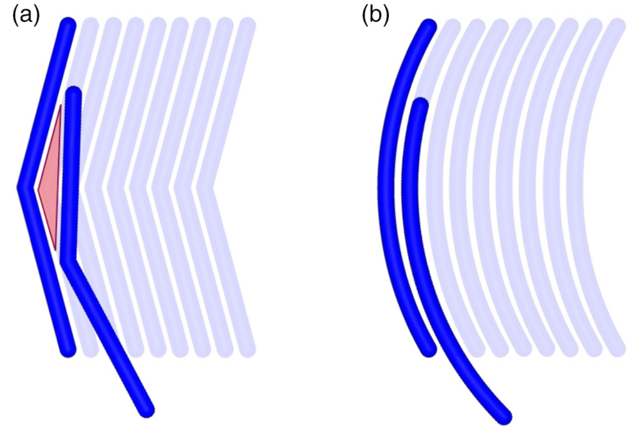

FIG. 4. A bent spherocylinder (a) can only escape out of a Sm layer by creating a void and by displacing other rods, whereas a curved rod (b) can simply slide out of a Sm layer without generating empty spaces and disturbing other rods.

depending on the chemical potential change $\mu(L') - \mu(L)$. The distribution $\mu(L)$ is tuned iteratively via the NEPR algorithm such that the overall distribution of particle lengths in both simulation boxes is a Gaussian *parent* distribution with an imposed average $\langle L \rangle$ and standard deviation σ_L. In this way, after equilibration and convergence of the NEPR algorithm the system can fractionate, if it prefers to do so, into two coexisting phases of different density and composition but with a given parent distribution of particle lengths. For the exemplary case of $\Psi = 90°$ and $\langle L \rangle = 10D$, we apply this scheme and simulate the system at three representative states for a small ($\sigma_L = 0.01\langle L \rangle$) and a large ($\sigma_L = 0.36\langle L \rangle$) polydispersity of the parent length distribution (Fig. 3). At high pressures, the two simulation boxes correspond to smectic phases at low polydispersity and to N_b phases at high polydispersity, both without fractionation, confirming the stability of the N_b phase in Fig. 2(b) with respect to fractionation. At a pressure corresponding to the I-Sm phase coexistence of the monodisperse system the system melts into two intermediate states along the continuous I-N-N_b transition (see the Supplemental Material [72]) at large polydispersity.

Our simulations show that monodisperse systems of hard bent spherocylinders favor Sm phases at η as low as $\simeq 0.30$ [see Fig. 2(a)]. The sharp and abrupt kink in the particle shape, i.e., a single point of infinite curvature between two curvature-free legs, favors the formation of pretransitional smectic clusters, interlocking the particles in the fluid phase and driving the I-Sm phase transition. We therefore speculate that replacing the sharp kink by a smoothly curved shape may be an alternative way to destabilize the Sm phase, postulating the mechanism in Fig. 4.

To investigate this, we perform MC simulations of hard curved spherocylinders with a fixed and finite curvature along the entire particle [see Fig. 1(d), where also L is defined]. Previous simulations showed the presence of a stable N_{TB} phase for a system of soft repulsive curved rods [24]. Here, we perform simulations of hard curved rods with $L/D = 10$ and $\Psi = 150°$, and compare their phase behavior with the one of hard bent spherocylinders of "equivalent" shape. From the equations of state [72] we determine the phase behavior of the two systems as a function of η and compare them in Fig. 5. We observe that the smooth finite curvature of the particles not only destabilizes the smectic order but also promotes bend deformations in the nematic phase. As a consequence, the stability region of the N_+ phase shrinks in favor of a wider stability region of the N_{TB} phase, and the first-order N_{TB}-Sm phase transition is replaced by a weakly first-order N_{TB}-N_{SB} phase transition followed by a continuous transition to the Sm phase, with a gradual increase of the smectic order with η (see the Supplemental Material [72]). Typical configurations of the N_{TB} and N_{SB} phases are shown in Fig. 6.

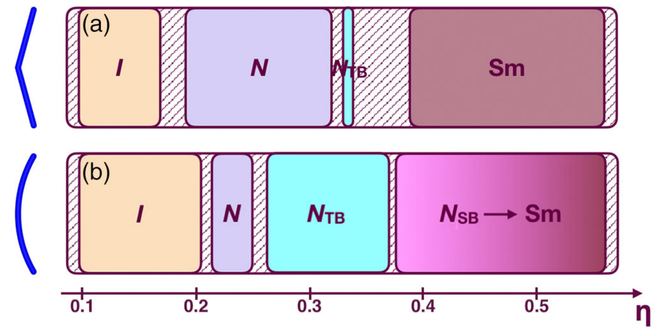

FIG. 5. Phase diagram of (a) hard bent spherocylinders and (b) hard curved spherocylinders for $L/D = 10$ and $\Psi = 150°$ as a function of packing fraction η.

In conclusion, we showed by simulations that the N_b, N_{TB}, and N_{SB} phases are metastable with respect to a stable Sm phase for a system of hard bent spherocylinders. By introducing polydispersity in the particle length or curvature in the particle shape, the smectic order is destabilized and all the exotic N_b, N_{TB} and N_{SB} phases become stable. We confirmed that molecular polarity and anisotropy are fundamental ingredients for the formation of N_b, N_{TB} and N_{SB} phases of bent particles, and that the exotic nematic states of bent-core mesogens can be justified in terms of their shape

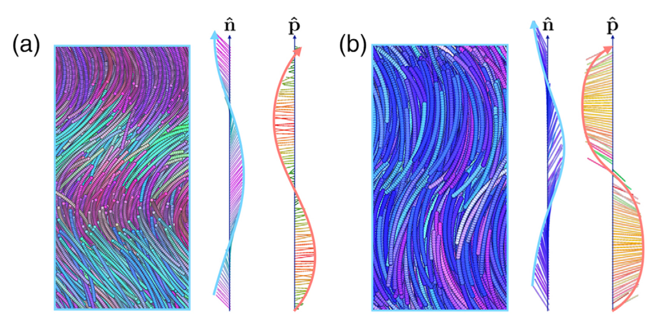

FIG. 6. Configurations of a (a) N_{TB} and (b) N_{SB} phase of hard curved spherocylinders along with the nematic ($\hat{\mathbf{n}}$) and polar ($\hat{\mathbf{p}}$) director fields along the z axis.

and C_{2v} symmetry. We also showed that ingredients that stabilize these exotic nematic phases also enhance the stability of the competing Sm phase. In particular, the sharp kink of crooked rods favors smectic ordering, shedding light on the discrepancy between theory and previous MC simulations. The destabilization of the positionally ordered smectic phase of crooked rods—either via polydispersity or curvature—opens pathways towards a variety of theoretically predicted nematic states in systems of hard particles. Introducing finite curvature in the particle shape destabilizes the smectic phase, and favors the spontaneous formation of bend deformations yielding stable regions of N_{TB} and N_{SB} phases. Our results may provide guidelines and insights to settle the long-standing quest for an experimentally stable N_{SB} phase.

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