Coupling between splay deformations and density modulations in splay-bend phases of bent colloidal rods

Carmine Anzivino,[1, *] René van Roij,[2] and Marjolein Dijkstra[1, †]
[1]*Soft Condensed Matter, Debye Institute for Nanomaterials Science,*
Utrecht University, Princetonplein 1, 3584 CC Utrecht, The Netherlands
[2]*Institute for Theoretical Physics, Utrecht University,*
Princetonplein 5, 3584 CC Utrecht, The Netherlands
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Using a grand-canonical Landau-de Gennes theory for colloidal suspensions of bent (banana-shaped) rods, we investigate how spatial deformations in the nematic director field affect the local density of twist-bend and splay-bend nematic phases. The grand-canonical character of the theory naturally relates the local density to the local nematic order parameter S. In the splay-bend phase, we find S and hence the local density to modulate periodically along one spatial direction. As a consequence the splay-bend phase has the key symmetries of a smectic rather than a nematic phase. By contrast we find that S and hence the local density do not vary in space in the twist-bend phase, which is therefore a proper nematic phase. The theoretically predicted one-dimensional density modulations in splay-bend phases are in agreement with recent simulations.

Dispersions of rodlike colloidal particles can spontaneously order into nematic liquid-crystal phases upon compressing a dilute isotropic fluid phase [1, 2]. The nematic bulk phase is a homogeneous fluid that exhibits long-range orientational order of the long axes of the rods, which on average align along a so-called nematic director $\hat{\mathbf{n}}$ that is uniform in space. An important characteristic of the nematic phase is its up-down symmetry, which identifies $\hat{\mathbf{n}}$ with $-\hat{\mathbf{n}}$, to be contrasted with polar order of for instance a magnet. The simplest nematic phase does not only feature up-down symmetry but also azimuthal symmetry about $\hat{\mathbf{n}}$. This uniaxial symmetry is broken in the case of a biaxial nematic phase, which features not only ordering of the long axes of the rods along $\hat{\mathbf{n}}$ but also of their short axes along a direction $\hat{\mathbf{m}} \perp \hat{\mathbf{n}}$, with $\pm\hat{\mathbf{m}}$ equivalent [1]. This Letter, however, concerns the interesting and intricate case in which the azimuthal symmetry about $\hat{\mathbf{n}}$ is broken by a *polar* ordering of the short axes of the rods in a preferred direction $\mathbf{P} \perp \hat{\mathbf{n}}$, with non-equivalent $\mathbf{P}$ and $-\mathbf{P}$. This type of ordering is well known to be strongly coupled, via the so-called bend flexoelectric effect [3], to spontaneous bend deformations of the nematic director field, such that $\hat{\mathbf{n}}(\mathbf{r})$ is no longer a spatial constant if $\mathbf{P} \neq 0$ [4]. As a pure bend deformation cannot uniformly fill 3D space, Meyer [5] and later independently Dozov [6] argued that these local bend deformations should be accompanied by either a twist or a splay deformation. In the former case they theoretically postulated the stabilization of a spatially modulated twist-bend nematic (N_{TB}) phase, that displays a heliconical structure of $\hat{\mathbf{n}}(\mathbf{r})$ with bend and twist deformations in the molecular orientation. In the latter case, they predicted a spatially modulated splay-bend nematic (N_{SB}) phase that is characterized by alternating layers of splay and bend.

After its theoretical prediction, the N_{TB} phase has actually been observed experimentally in several molecular systems [7–14], and has meanwhile become well-established as a new type of orientationally ordered fluid phase. By contrast, the N_{SB} phase has never been observed in the absence of a strong external constraint, such as an electric field [15–17], a planar surface anchoring [18] or a topological constraint [19]. Rather, a huge variety of smectic phases was found either in systems of thermotropic bent-core mesogens [4, 20, 21] and in systems of bent silica rods [22, 23]. Therefore, many doubts subsist on the existence and true nature of the N_{SB} phase. Recently, however, simulations of systems of hard bent spherocylinders revealed that N_{TB} and N_{SB} phases can be thermodynamically stable in bulk, provided the smectic (Sm) phase is destabilized either by polydispersity in particle length or by curvature in the particle shape [24]. Inspired by these simulation results, a stable N_{SB} phase has experimentally been sought for and actually observed, for the first time in a lyotropic system of smoothly curved colloidal rods [25] and later in polydisperse bent silica rods [26]. Recently, simulations and a Maier-Saupe theory showed that the (alleged) N_{SB} phases of monodisperse curved rods display (weak) density modulations [27], which cannot be described by current Oseen-Frank and Landau-de Gennes type theories. The existing theoretical descriptions [5, 6, 28] are direct extensions of Oseen-Frank theory for the elastic deformations of $\hat{\mathbf{n}}(\mathbf{r})$; they only account for the *direction* of the ordering and ignore the *degree* of ordering that is characterised by the scalar nematic order parameter S. Landau-de Gennes (LdG) theories for thermotropic liquid crystals do account for S but lack any coupling with density ρ [29–33].

In this Letter we investigate the nematic nature of the N_{SB} phase displayed in colloidal systems, by employing

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[*] Present Address: Department of Physics "A. Pontremoli", University of Milan, via Celoria 16, 20133 Milan, Italy; Electronic mail: `carmine.anzivino@gmail.com`

[†] Electronic mail: `m.dijkstra@uu.nl`

a recently introduced grand-canonical LdG theory [34] applied to lyotropic curved rods [35], that does involve a coupling between S and ρ. We show that S and therefore also ρ varies periodically along one spatial direction in the N_{SB} phase, such that the N_{SB} phase has actually the symmetries of a smectic rather than a nematic phase. This is not the case, however, for the N_{TB} phase, for which we find that S does not vary in space, and is therefore a proper nematic phase.

We follow Ref. [35] and extend the Oseen-Frank theory of Selinger and co-workers [28] to a mesoscopic LdG theory where the director $\hat{\mathbf{n}}$ is replaced by the standard second-rank, symmetric, and traceless tensor $\mathbf{Q}(\mathbf{r})$ with Cartesian components $Q_{\alpha\beta}(\mathbf{r})$ for $\alpha,\beta = x,y,z$. The eigenvector of $\mathbf{Q}$, corresponding to the maximum modulus of a non-degenerate eigenvalue, defines the nematic director $\hat{\mathbf{n}}$ of the system [1]. A vector field $\mathbf{P}(\mathbf{r})$ with Cartesian coordinates $P_\gamma(\mathbf{r})$ for $\gamma = x,y,z$ describes the polar order in a direction perpendicular to $\hat{\mathbf{n}}$. In order to describe lyotropic systems that become ordered with increasing density, we follow Ref. [34] and set up a Landau expansion for which we use the chemical-potential dependent grand potential $\Omega(\mu)$ rather than the temperature dependent Helmholtz (or Gibbs) free energy $F(T)$. More specifically, for a system of hard bent rods modeled as curved or kinked rods of contour length L and diameter D, at chemical potential μ in a macroscopic volume V, and at fixed temperature T, we write the excess-over-isotropic LdG grand potential as $\Delta\Omega(\mathbf{Q},\mathbf{P}) = \int_V d\mathbf{r}(\Delta\omega_b + \omega_{eP})$, where $\Delta\omega_b$ denotes a bulk term

$$\begin{aligned}\beta B_2\Delta\omega_b =& \frac{2}{3}a\beta(\mu^*-\mu)Q_{\alpha\beta}Q_{\beta\alpha} - \frac{4}{3}b\; Q_{\alpha\beta}Q_{\beta\lambda}Q_{\lambda\alpha}\\ &+ \frac{4}{9}d\; Q_{\alpha\beta}Q_{\beta\alpha}Q_{\lambda\rho}Q_{\rho\lambda},\end{aligned} \tag{1}$$

and ω_{eP} an elastic-polar term

$$\begin{aligned}\beta B_2\omega_{eP} =& \frac{2}{9}l_1(\partial_\alpha Q_{\beta\lambda})(\partial_\alpha Q_{\beta\lambda}) + \frac{2}{9}l_2(\partial_\alpha Q_{\alpha\lambda})(\partial_\beta Q_{\beta\lambda})\\ &+ e_2 P_\alpha\left(\delta_{\alpha\beta} + \frac{2}{S_0}Q_{\alpha\beta}\right)P_\beta + e_4 P_\alpha P_\alpha P_\beta P_\beta\\ &- \lambda P_\alpha(\partial_\beta Q_{\alpha\beta}) + \kappa(\partial_\alpha P_\beta)(\partial_\alpha P_\beta).\end{aligned} \tag{2}$$

We express $\Delta\omega_b$ and ω_{eP} in units of $\beta^{-1} = k_B T$ with k_B the Boltzmann constant, and in units of the second virial coefficient $B_2 = \pi L^2 D/4$ of long needles in the isotropic (I) fluid phase, which is a convenient unit of volume for systems of rodlike particles. We use the Einstein summation convention for repeated indices, and indicate the Landau phenomenological parameters by $a, b, d, l_1, l_2, e_2, S_0, e_4, \lambda$ and κ. We note that only the quadratic term $Q_{\alpha\beta}Q_{\beta\alpha}$ has a μ-dependent prefactor that changes sign at the nematic spinodal μ^* and drives the phase transitions. Stability of the grand potential expansion in the dilute limit requires $a > 0$ and $e_2 > 0$, while stability with respect to an unlimited growth of $\mathbf{Q}$, $\mathbf{P}$ and $\partial_\alpha P_\beta$ requires that $d > 0$, $e_4 > 0$, and $\kappa > 0$, respectively. The sign of the b term determines the nature of the I-N transition, rodlike for $b > 0$ and platelike for $b < 0$. The coefficients $2/S_0$ and λ represent the $\mathbf{Q}$-$\mathbf{P}$ coupling and the bend flexoelectric $\mathbf{P}$-$\nabla\mathbf{Q}$ coupling, respectively. In order to describe a favored polarization perpendicular to the nematic director, leading to a bend flexoelectric effect, we set $S_0 > 0$. Finally the coefficients l_1 and l_2 are related to the Oseen-Frank elastic constants [36, 37] through the relations $\beta B_2 K_{11} = \beta B_2 K_{33} = (2l_1 + l_2)S^2$ and $\beta B_2 K_{22} = 2l_1 S^2$. As shown in Ref. [35], a complete mapping exists between our LdG theory and the Oseen-Frank theory of Selinger and co-workers [28].

Minimization of the grand potential $\Delta\Omega(\mathbf{Q},\mathbf{P})$ with respect to $\mathbf{Q}$ at $\mathbf{P} \equiv 0$, $\nabla\mathbf{Q} \equiv \mathbf{0}$, and $\nabla\mathbf{P} \equiv \mathbf{0}$, gives a first order I-N transition at $\beta\mu_{IN} \equiv \beta\mu^* - b^2/(4ad)$ [34, 35]. The nematic order parameter equals $S_I(\mu) = 0$ for $\mu \le \mu_{IN}$, and

$$S_N(\mu) = \frac{3b}{8d}\left(1 + \sqrt{1 - \frac{32ad\beta(\mu^*-\mu)}{9b^2}}\right) \tag{3}$$

for $\mu > \mu_{IN}$. In order to describe the “Onsager”-type I-N phase transition of uniaxial hard needles [2, 38] we follow Ref. [34] and set $a = 1.436, b = 5.851, d = 3.693$, and $\beta\mu^* = 6.855$. As shown in Ref. [35], the uniaxial N phase becomes unstable with respect to an N_{TB} or N_{SB} phase at a critical μ where the renormalized bend elastic constant $K_{33}^{\mathrm{eff}} = 0$. The N_{TB} phase is described by a chiral nematic director and polarization vector

$$\begin{aligned}\hat{\mathbf{n}}_{\mathrm{TB}}(z) &= \big(\sin\theta\cos(qz),\ \sin\theta\sin(qz),\ \cos\theta\big),\\ \mathbf{P}_{\mathrm{TB}}(z) &= P(z)\big(\sin(qz), -\cos(qz), 0\big),\end{aligned} \tag{4}$$

with q and θ the variational wave number and tilt angle, respectively, and $P(z)$ the variational magnitude of the polarization. The N_{SB} phase is described by an achiral nematic director and polarization vector

$$\begin{aligned}\hat{\mathbf{n}}_{\mathrm{SB}}(z) &= \big(\sin\phi(z),\ 0,\ \cos\phi(z)\big),\\ \mathbf{P}_{\mathrm{SB}}(z) &= P(z)\cos(qz)\big(-\cos\phi(z), 0, \sin\phi(z)\big),\end{aligned} \tag{5}$$

where $\phi(z) = \theta\sin(qz)$. The system either stabilizes an N_{TB} phase, if l_1 and l_2 are such that $K_{11} > 2K_{22}$, or an N_{SB} phase, if l_1 and l_2 are such that $K_{11} < 2K_{22}$ [35]. The N-N_{TB} as well as N-N_{SB} phase transitions are continuous and proceed in both cases without any jump in $S(\mu)$.

We employ the thermodynamic identity $\partial(\Omega/V)/\partial\mu|_{V,T} = -\rho$ to perform the conversion between chemical potential μ and number density ρ. To this end, we introduce the grand potential density ω_I of the isotropic I state and define $\omega \equiv \omega_I + \Delta\omega_b$, where $\Delta\omega_b$ is the excess bulk grand potential density (1). From $\partial(B_2\omega)/\partial\mu = -c$, with $c \equiv B_2\rho$ the dimensionless particle concentration, we find

$$c(\mu) = c_I(\mu) + aS^2(\mu). \tag{6}$$

The particle concentration of the I phase, $c_I(\mu) = -\partial(B_2\omega_I)/\partial\mu$, can be calculated within Onsager theory, by using an isotropic distribution function, such that $\beta\mu(c_I) = \log(c_I/4\pi) + 2c_I$ [38]. By inverting this relation we obtain $c_I(\mu)$ straightforwardly. Together with Eq. (6), we can determine c, for every value of μ for which $S(\mu)$ is known. We observe that Eq. (6) not only allows us to convert a dependence on the chemical potential into a dependence on the particle density, but also expresses a coupling between the scalar order parameter S and the particle concentration c. In this Letter we employ this coupling to obtain insight into the structure of the $N_{\rm SB}$ phase.

In contrast to earlier works [6, 28–33, 35] we consider here a z-dependent nematic order parameter $S(z)$ in the definition of the tensorial order parameter $Q_{\alpha\beta}(z) = S(z)\big(3n_\alpha(z)n_\beta(z)/2 - \delta_{\alpha\beta}/2\big)$, as well as a z-dependent magnitude $P(z)$ of the polarization vectors $\mathbf{P}_{\rm TB}$ and $\mathbf{P}_{\rm SB}$ in Eqs. (4) and (5). In order to study the relative stability of the $N_{\rm TB}$ and $N_{\rm SB}$ phases, we insert $\hat{\mathbf{n}}_{\rm TB}$ and $\hat{\mathbf{n}}_{\rm SB}$, respectively, into $\mathbf{Q}$. After insertion of $\mathbf{Q}$ and $\mathbf{P}$ into $\Delta\Omega(\mathbf{Q},\mathbf{P})$, we perform, at fixed chemical potential μ, a full grand-potential minimization. To this end we numerically solve the system of Euler-Lagrange equations

$$\frac{\delta\Delta\Omega}{\delta S(z)} = \partial_z \frac{\delta\Delta\Omega}{\delta(\partial_z S(z))}; \qquad \frac{\delta\Delta\Omega}{\delta P(z)} = \partial_z \frac{\delta\Delta\Omega}{\delta(\partial_z P(z))}, \qquad (7)$$

for many combinations of fixed wave number q and tilt angle θ, from which we identify the grand-potential minimum of the $N_{\rm TB}$ phase characterized by $q_{\rm TB}(\mu), \theta_{\rm TB}(\mu), S_{\rm TB}(\mu;z)$ and $P_{\rm TB}(\mu;z)$, and that of the $N_{\rm SB}$ phase at $q_{\rm SB}(\mu), \theta_{\rm SB}(\mu), S_{\rm SB}(\mu;z)$ and $P_{\rm SB}(\mu;z)$.

We start by considering the coefficients $l_1 = 0.165L^2, l_2 = 0.427L^2, e_2 = 1, S_0 = 0.99, e_4 = 0.5, \kappa = 0.3L^2$, and $\lambda = 0.18L$. It follows that $K_{11}/K_{22} = 2.294$ and that, as shown in Fig. S2(a) in the Supplemental Material (SM) [39], a second-order N-$N_{\rm TB}$ phase transition takes place at $\beta\mu = 5.663 \equiv \beta\mu_{NN_{\rm TB}}$. We plot $S_{\rm TB}$ and $P_{\rm TB}$ as a function of $z \in [0, 2\pi/q_{\rm TB}]$ for several values of the chemical potential $\mu \equiv \mu_{NN_{\rm TB}} + \Delta\mu$ in Figs. S4(a) and S4(b), respectively. We clearly find that $S_{\rm TB}$ and $P_{\rm TB}$ are constant along z for every μ. As a consequence, the corresponding density profile $c_{\rm TB}$ is also a spatial constant. Interestingly, we show in the SM and in Fig. S5 [39] that the extremal solutions $q_{\rm TB}(\mu)$, $\theta_{\rm TB}(\mu)$, $S_{\rm TB}(\mu)$, $P_{\rm TB}(\mu)$, and $c_{\rm TB}(\mu)$ exactly coincide with those obtained when S and P are assumed z-independent in $\mathbf{Q}$ and $\mathbf{P}_{\rm TB}$, respectively. In particular we observe from Fig. S5(a) that $S_{\rm TB}(\mu)$ coincides with $S_N(\mu)$ of Eq. (3). We conclude that spatial twist and bend modulations do not affect the scalar nematic order.

Subsequently, we reset the elasticity parameters to $l_1 = 0.1L^2$ and $l_2 = 0.0427L^2$ such that $K_{11}/K_{22} = 1.214$ and, as shown in Fig. S2(b), a second-order N-$N_{\rm SB}$ phase transition takes place at $\beta\mu = 5.354 \equiv \beta\mu_{NN_{\rm SB}}$. In Fig. 1(a) we plot for several chemical potentials $\mu \equiv \mu_{NN_{\rm SB}} + \Delta\mu$ the (shifted) scalar nematic order parameter $S_{\rm SB} - S_N$ as a function of $z \in [0, 2\pi/q_{\rm SB}]$. The periodic modulation of $S_{\rm SB}$ is manifest, with an amplitude that vanishes at $\Delta\mu = 0$ and increases to 0.0075

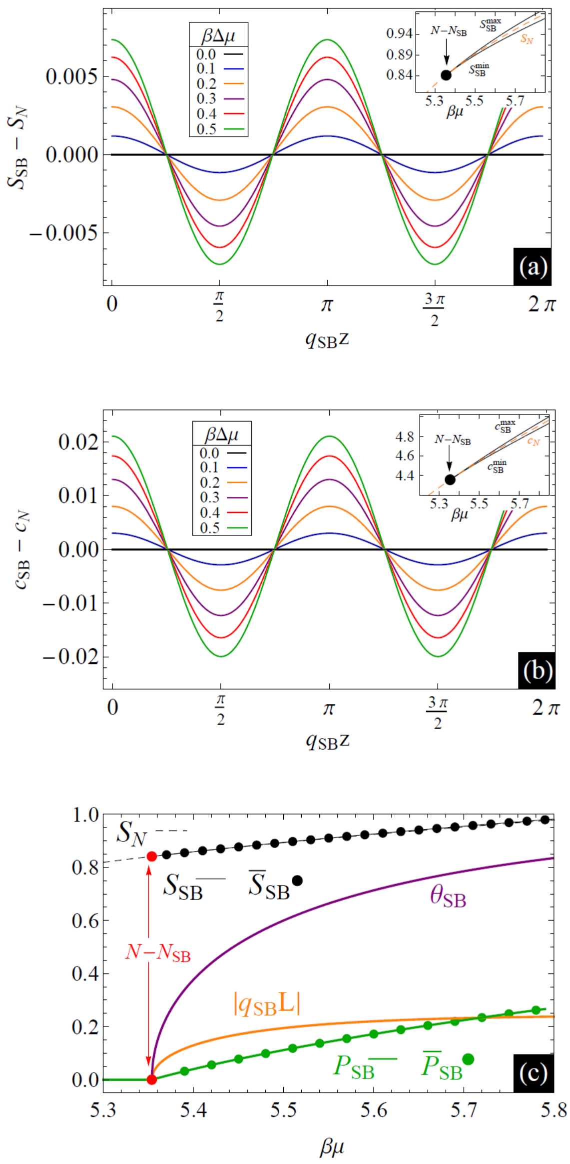

FIG. 1: The excess scalar nematic order parameter $S_{\rm SB} - S_N$ (a) and the excess particle concentration $c_{\rm SB} - c_N$ (b) in the splay-bend phase $N_{\rm SB}$ as a function of position $z \in [0, 2\pi/q_{\rm SB}]$, for several values of the chemical-potential excess $\Delta\mu \equiv \mu - \mu_{NN_{\rm SB}}$ above the N-$N_{\rm SB}$ transition, at wave numbers $q = q_{\rm SB}$ of the director modulations (see Eq.(5)) given by the orange curve in (c). The period-average $\bar{S}_{\rm SB}$ and $\bar{P}_{\rm SB}$ of the nematic order parameter $S_{\rm SB}(z)$ and the polarisation $P_{\rm SB}(z)$ are presented by the dots in (c), which are indistinguishable from the corresponding full curves that follow from the assumption of a spatial constant $S_{\rm SB}$ and $P_{\rm SB}$. The violet curve in (c) represents the opening angle $\theta_{\rm SB}$. The expansion coefficients are $l_1 = 0.1L^2, l_2 = 0.0427L^2, e_2 = 1, S_0 = 0.99, e_4 = 0.5, \kappa = 0.3L^2$ and $\lambda = 0.18L$. The insets of (a) and (b) show the μ-dependence of the minima and maxima of the modulating profiles $S_{\rm SB}(z)$ and $c_{\rm SB}(z)$.

at $\Delta\mu = 0.5k_BT$, see also SM [39]. The inset shows the minimum and maximum of $S_{\rm SB}(z)$ as a function of μ, the difference being small but clearly discernible. Note that the wavelength of the modulation of the scalar order parameter equals half of the pitch $2\pi/q_{\rm SB}$ of the nematic director. This can be explained by the fact that one period of a nematic director modulation corresponds to two alternating bend and splay domains with opposite polar order. Fig. 1(b) shows the corresponding (shifted) density profiles $c_{\rm SB}(z) - c_N$, obtained from Eq. (6) with c_N the density of the metastable N phase. Fig. 1(b) clearly reveals spatial density modulations with the same wavelength as $S_{\rm SB}(z)$ and an amplitude that grows from zero at $\Delta\mu = 0$ to a few percent of c_N at $\Delta\mu = 0.5k_BT$; the inset shows the minimum and the maximum of the density profile as a function of μ, which confirms the density variations on the order of a few percent. From the periodic modulation of $c_{\rm SB}$ along z, it follows that the $N_{\rm SB}$ phase has all the symmetries of a smectic (or lamellar) phase. However, in contrast to ordinary smectic phases with periods on the order of the particle length L, the wavelength $\pi/q_{\rm SB}$ of the density modulation in the splay-bend phase is much larger than L. This becomes manifest from the orange curve in Fig. 1(c), which presents the μ-dependence of the wave number $q_{\rm SB}$, which is infinitesimally small at the N-$N_{\rm SB}$ transition and grows to typically $|q_{\rm SB}L| \simeq 0.2$ in the splay-bend phase; this corresponds to density modulations with wavelengths of the order $\pi/q_{\rm SB} \simeq 15L$ well in the splay-bend phase and a diverging wavelength upon approach of the transition to the N phase. Fig. 1(c) also shows the tilt angle $\theta_{\rm SB}$ and the period-average of the profiles of the nematic order parameter $S_{\rm SB}(z)$ and the polarisation $P_{\rm SB}(z)$; Fig. S7 of the SM [39] shows $P_{\rm SB}(z)$ in the $N_{\rm SB}$ phase, which also exhibits spatial modulations. The infinitesimally small $q_{\rm SB}$, $\theta_{\rm SB}$, and $P_{\rm SB}(z)$ at the N-$N_{\rm SB}$ transition are in line with the continuous character of the N-$N_{\rm SB}$ transition. Additionally, Fig. 1(c) shows that the period-average of the profiles $S_{\rm SB}(\mu; z)$, $P_{\rm SB}(\mu; z)$ and $c_{\rm SB}(\mu; z)$ as well as $q_{\rm SB}$ and $\theta_{\rm SB}$, see SM [39], actually coincide with the solutions $S_{\rm SB}(\mu)$, $P_{\rm SB}(\mu)$, $c_{\rm SB}(\mu)$, and $q_{\rm SB}(\mu)$ and $\theta_{\rm SB}(\mu)$, that are obtained when S and P are assumed z-independent in $\mathbf{Q}$ and $\mathbf{P}_{\rm SB}$. In particular the period-average of $S_{\rm SB}(\mu; z)$ is very close to $S_N(\mu)$ of Eq. (3), as can be seen in Fig. 1(c), where their tiny difference is only discernible at the largest μ's and stems from the small-θ approximation of the grand-potential density [35].

Since we only find variations in the local density of the $N_{\rm SB}$ phase and not in that of the $N_{\rm TB}$ phase, we investigate the possibility of a direct connection between density modulations and splay deformations. Referring to the SM [39] for more details, we first note that the $S_{\rm SB}(z)$ profiles shown in Fig. 1(a) accurately fit the functional form $S_{\rm SB}(z) = S_{\rm SB}^{\rm max} \cos\big(\theta_S \sin\big(q_{\rm SB}z\big)\big)$ with θ_S a fit parameter. Next, for several values of μ, we plot $S_{\rm SB}(\nabla\cdot\hat{\mathbf{n}}_{\rm SB})$ (full lines) and $H(\nabla S_{\rm SB})\cdot\hat{\mathbf{n}}_{\rm SB}$ (dashed lines) as a function of z in Fig. S10, with H a suitably chosen spatial constant that varies with μ as shown in the inset of Fig. S10. We find that for each μ the condition $S_{\rm SB}(\nabla\cdot\hat{\mathbf{n}}_{\rm SB}) = H(\nabla S_{\rm SB})\cdot\hat{\mathbf{n}}_{\rm SB}$ holds, from which we can derive

$$\nabla\cdot\hat{\mathbf{n}}_{\rm SB}(z) = \frac{H}{2}\frac{\nabla c_{\rm SB}(z)}{(c_{\rm SB}(z) - c_I)}\cdot\hat{\mathbf{n}}_{\rm SB}(z), \qquad (8)$$

through Eq. (6). We observe that an expression similar to the one of Eq. (8) was found by de Gennes [40] and Taratuta and Meyer [41] for polymer nematics. It expresses the coupling between concentration gradients $\nabla c_{\rm SB}$ and splay deformations, given by $\nabla\cdot\hat{\mathbf{n}}_{\rm SB}$, such that splay deformations cannot exist without density gradients.

To conclude, in this Letter we have employed the LdG theory introduced in Ref. [35] for lyotropic colloidal suspensions of bent rods to investigate the repercussions of spatial distortions in the nematic director field on the density of the twist-bend and splay-bend nematic phases. In contrast with the existing theories [6, 28–33], our theory allows to analyze the spatial dependence of the nematic order parameter S and provides a natural coupling between S and the particle density ρ. We show that the $N_{\rm SB}$ phase is characterized by a one-dimensional density modulation such that the originally predicted [5, 6, 28] N-$N_{\rm SB}$ transition is strictly speaking a N-Sm transition. In the case of an $N_{\rm TB}$ phase, instead, we find that S and hence ρ are spatial constant such that this phase is a true nematic phase. Our findings are in agreement with simulations [24] and a Maier-Saupe theory [27]. Furthermore, the existence of a coupling between ∇c and $\nabla\cdot\hat{\mathbf{n}}$, as shown in this Letter, lends strong support that the splay deformations in the nematic director field $\hat{\mathbf{n}}$ are inherently coupled to density modulations.

Finally the theory presented in this Letter could be employed to verify the existence and the nematic nature of a recently experimentally observed splay nematic phase [32, 42–47] and a recently postulated twist-splay-bend phase [27]. In addition, biaxiality and external constraints could be taken into account. While we do not expect biaxial order to change the smectic nature of $N_{\rm SB}$ phase, it could influence the "shape" of the density modulations. Understanding the repercussions of external constraints on the local density of the bulk $N_{\rm SB}$ phase, instead, could be very important to connect the findings presented in this Letter to those of Refs. [15–19].

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