Effect of shape biaxiality on the phase behavior of colloidal liquid-crystal monolayers

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We extend our previous work on monolayers of uniaxial particles [J. Chem. Phys., 2014, 140, 204906] to study the effect of particle biaxiality on the phase behavior of liquid-crystal monolayers. Particles are modelled as board-like hard bodies with three different edge lengths $s_1 \geq s_2 \geq s_3$, and the restricted-orientation approximation (Zwanzig model) is used. A density-functional formalism based on the fundamental-measure theory is used to calculate phase diagrams for a wide range of values with the largest aspect ratio $k_1 = s_1/s_3 \in [1,100]$. We find that particle biaxiality in general destabilizes the biaxial nematic phase already present in monolayers of uniaxial particles. While plate-like particles exhibit strong biaxial ordering, rod-like ones with $k_1 > 21.34$ exhibit reentrant uniaxial and biaxial phases. As particle geometry is changed from uniaxial- to increasingly biaxial-rod-like, the region of biaxiality is reduced, eventually ending in a critical-end point. For $k_1 > 60$, a density gap opens up in which the biaxial nematic phase is stable for any particle biaxiality. Regions of the phase diagram, where packing-fraction inversion occurs (i.e. packing fraction is a decreasing function of density), are found. Our results are compared with the recent experimental studies on nematic phases of magnetic nanorods.

I. Introduction

Biaxial hard-particle systems have received considerable theoretical and experimental attention since their first theoretical prediction by Freiser. The characteristic feature of the biaxial phase is that two directions of orientational ordering occur associated with two molecular symmetry axes. The importance of studying biaxial nematic phases is that they might be used in practical applications, such as fast electro-optical devices.

The theoretical exploration of stable biaxial nematic order has been based on biaxial hard-body and Gay–Berne-type soft potential models, using specific particle shapes such as spheroplatelets, biaxial ellipsoids and bent-core particles. The biaxial nematic phase has also been found in binary mixtures of uniaxial plate-like and rod-like particles. However, the experimental realization of this exotic phase has proved to be rather complicated. The first observation dates back to the study of Yu and Saupe, who observed that a mixture of potassium laurate, 1-decanol, and water exhibited a region of biaxial order between two uniaxial phases. Recent studies on the same system found the formation of non-equilibrium biaxial textures under the action of mechanical perturbations which after relaxation end in uniaxial configurations. Later, a biaxial nematic order was observed in low molecular weight thermotropic liquid crystals where the constituting particles had biaxial symmetry. Regarding the shape of the constituting particles, banana-shaped mesogenic molecules are found to form a thermotropic biaxial nematic phase, while board-shaped colloidal particles have been used successfully in the stabilization of lyotropic biaxial nematic phases. However, some recent experiments suggest that the biaxial phases found in ref. 21–24 are in fact uniaxial and that the surface-induced birefringence is associated with smectic layering near both confining surfaces which in turn creates a nonuniform molecular tilt along the surface normal.

The recent experimental observation of biaxial nematic order in suspensions of board-like goethite nanorods has prompted several theoretical studies in order to determine the global phase behavior of hard board-shaped particles and also to identify those processes which promote the formation of the biaxial nematic phase. Interestingly, an increasing polydispersity in shape and size favors the biaxial nematic phase over other ordered phases. In addition to this, binary mixtures
consisting of board-shaped particles with added polymers can stabilize biaxial order very efficiently.33 Even the biaxiality of the nematic phase can be tuned by applying an external magnetic field.34

By inserting goethite nanorods into a soft lamellar matrix of non-ionic surfactant, it is also possible to examine the effect of dimensional reduction on the stability of mesophases.35–37 The confined nanorods between the bilayers of a lamellar phase have been shown to undergo a first-order in-plane (two-dimensional) isotropic–nematic phase transition, where the isotropic and nematic phases correspond to planar and biaxial nematic phases, respectively. In the light of an increasing amount of knowledge about the ordering properties of board-shaped goethite nanorods in confined geometries, it is worth studying the phase behaviour of hard board-shaped particles in quasi-two-dimensions using theoretical methods, and this is the motivation of our work.

In the present study we use density-functional theory in the fundamental-measure version to examine the orientational and positional ordering properties of confined hard-board colloidal particles with discrete orientations. The confinement is such that the centers of the board particles are always on a flat surface. We mainly focus on the effect of shape biaxiality on the stability of the biaxial nematic phase, but we also determine the stability regions of other mesophases such as the uniaxial nematic and positionally-ordered smectic, columnar and solid phases using bifurcation analysis. An important result is that an increasing biaxiality does not promote the formation of biaxial nematic phases due to the free-volume maximizing effect of the packing entropy.

This paper is organized as follows. The particle model and expressions for the relevant order parameters measuring biaxial ordering are presented in Section II. Section III presents the results, which include the evolution of the phase diagrams with particle biaxiality and the density dependence of the order parameters for different particle shapes. Some conclusions are drawn in Section IV. Details on the density-functional theory and bifurcation analysis are presented in the Appendices.

II. Model and theory

Colloidal particles are modelled as biaxial hard boards with edge-lengths \( \sigma_1 \geq \sigma_2 \geq \sigma_3 \) and centres of mass located on a flat surface perpendicular to the \( z \) axis. Particles are allowed to rotate (within the restricted-orientation approximation) in the full 3D solid angle, but constrained to move on a plane. By restricting the possible orientations to be the three Cartesian axes, and considering the symmetries of the particles, six possible orientations, depicted in Fig. 1, are possible. The system can then be mapped onto a six-component mixture, with species labelled by \( \mu \nu \) (with \( \mu, \nu = x, y, z \) and \( \mu \neq \nu \)), where the indexes refer to the orientation of the longest and intermediate particle lengths, respectively. The density of 'species' \( \mu \nu \) is written as \( \rho_{\mu \nu} = \rho \gamma_{\mu \nu} \), with \( \rho \) the 2D total density. \( \{ \gamma_{\mu \nu} \} \) is a set of molar fractions that fulfills the constraint \( \sum_{\mu, \nu} \gamma_{\mu \nu} = 1 \).

The particular cases of prolate \( (\sigma_1 = L \text{ and } \sigma_2 = \sigma_3 = \sigma) \) and oblate \( (\sigma_1 = \sigma_2 = \sigma \text{ and } \sigma_3 = L) \) particles are sketched in Fig. 2(a) and (b), respectively.

To characterise the particle shape, two aspect ratios are defined, \( k_1 = \sigma_1/\sigma_3 \) and \( k_2 = \sigma_2/\sigma_3 \), which fulfill the inequalities \( 1 \leq k_2 \leq k_1 \). Further, the degree of particle biaxiality will be characterised by the parameter

\[
\theta \equiv (k_1 - 1)^{-1} \left( \frac{k_1}{k_2} - k_2 \right).
\]

For fixed \( k_1 \), the \( \theta \) parameter varies from \(-1\) (when \( k_2 = k_1 \), corresponding to uniaxial plate-like geometry) to \( \theta = 1 \) (when \( k_2 = 1 \), pertaining to uniaxial rod-like geometry). The value \( \theta = 0 \) corresponds to perfect biaxiality, i.e. \( k_2 = \sqrt{k_1} \); when \( k_2 > \sqrt{k_1} \) particles are considered to be oblate or prolate, respectively.

The statistical mechanics of the monolayer is dealt with using a version of density-functional theory. This version is based on the fundamental-measure theory for hard cubes.38 The resulting free-energy functional is expressed as a function of the set of molar fractions \( \{ \gamma_{\mu \nu} \} \), and the equilibrium state of the monolayer is obtained by minimising the free energy with respect to this set with the constraint \( \sum_{\mu, \nu} \gamma_{\mu \nu} = 1 \) and for fixed

![Fig. 1 Six Zwanzig species \( \mu \nu \) (with \( \mu, \nu = x, y, z \) and \( \mu \neq \nu \)) of hard board-like particles of dimensions \( \sigma_1 \geq \sigma_2 \geq \sigma_3 \).

![Fig. 2 Projection of orientation-restricted uniaxial hard boards on the monolayer. (a) Uniaxial prolate particles \( (\sigma_1 = L \text{ and } \sigma_2 = \sigma_3 = \sigma) \). (b) Uniaxial oblate particles \( (\sigma_1 = \sigma_2 = \sigma, \sigma_3 = L) \). The projected areas are conveniently shaded.](image-url)
scaled density $\rho^* = \rho_0^* s^2$, where $\rho = N/A$ is the two-dimensional density ($N$ is the number of particles and $A$ the area of the monolayer). The chemical potentials $\mu_{\alpha}$ of all species and the lateral pressure $p$ of the monolayer can then be calculated, and phase equilibria can be obtained. Details on the density functional used are given in Appendix A. The stability analysis and bifurcation theory derived to obtain the biaxial nematic spinodal and the nematic stability against non-uniform fluctuations can be found in Appendices B and C.

A useful measure of the ordering properties of the equilibrium phases are the order parameters, which help us to identify the two possible nematic phases in our system: the uniaxial nematic phase, $N_u$, and the biaxial nematic phase, $N_b$. In the case of biaxial particles two order parameter tensors can be defined,

$$\hat{Q}_{xy} = \frac{1}{2} \left( \langle u_x u_y \rangle - \delta_{xy} \right), \quad \hat{B}_{xy} = \frac{1}{2} \left( \langle n_x n_y \rangle - \langle m_x m_y \rangle \right),$$

where $u_x, n_x$, and $m_x$ are the $x$-components of the unit vectors $u$, $n$, and $m$ along the longest, intermediate and smallest particle lengths. Averages are taken over the orientational distribution function, given by the set $\{\gamma_{\mu\nu}\}$. For our restricted-orientation approximation, it can be easily shown that the tensors are diagonal:

$$\hat{Q} = \begin{pmatrix} \frac{Q - A_Q}{2} & 0 & 0 \\ 0 & \frac{-Q + A_Q}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\hat{B} = \begin{pmatrix} \frac{B - A_B}{2} & 0 & 0 \\ 0 & \frac{-B + A_B}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

where $Q$ and $B$ are uniaxial nematic order parameters,

$$Q = \frac{Q_{xx}}{2} \left( 3 \sum_{\mu \neq \nu} \gamma_{\mu\nu} - 1 \right),$$

$$B = \frac{B_{xx}}{2} \left( \sum_{\mu \neq \nu} \gamma_{\mu\nu} - \sum_{\mu \neq \nu} \gamma_{\mu\nu} \right),$$

with $Q$ the usual uniaxial order parameter (note that $B \neq 0$ for both $N_u$ and $N_b$ phases), while

$$A_Q \equiv Q_{xx} - Q_{yy} = \frac{3}{2} \left( \sum_{\nu \neq x} \gamma_{\nu x} - \sum_{\nu \neq y} \gamma_{\nu y} \right),$$

$$A_B \equiv B_{xx} - B_{yy} = \frac{1}{2} \left( \sum_{\nu \neq x} \gamma_{\nu x} - \sum_{\nu \neq y} \gamma_{\nu y} + \sum_{\mu \neq x} \gamma_{\mu x} - \sum_{\mu \neq y} \gamma_{\mu y} \right),$$

are biaxial nematic order parameters, both different from zero only for the $N_b$ phase.

A comment on the definition of the above order parameters in relation to the particle geometry is in order. For uniaxial rods ($\theta = 1$), the vector $u$ points along the main symmetry axis (longest particle length), the other two being equivalent. Thus, the above definitions for $\{Q, B, A_Q, A_B\}$ are correct in the limit $\theta \to 1$, and they will be used for any $\theta > 0$. However, for uniaxial oblate particles ($\theta = -1$), the main particle axis should be taken to lie along the shortest particle length $m$, the other two being equivalent: $u$ and $m$ should be interchanged for $\theta < 0$, and all four order parameters can be obtained from the same formulas as before but replacing $\gamma_{\mu\nu}$ by $\gamma_{\nu\mu}$ (with $\nu \neq \mu$). In this way we obtain, for example, that $Q \to -\frac{1}{2}$ for perfect planar nematic ordering, as it should be.

In the following, the parameter $A_0^* \equiv 2A_Q/3$ will be used to measure the degree of biaxiality for uniaxial plate-like and rod-like particles ($\theta = \pm 1$), while in the case of biaxial particles ($-1 < \theta < 1$) the parameter $A_B$ will be used. It can be shown that, for perfect biaxial order, $|A_B| \to 1$ and 0.5 for rods and plates, respectively, while $|A_0^*| \to 1$ for both particles. In any case, we always plot absolute values of biaxial order parameters in the figures.

Finally, a useful measure of packing in the monolayer is $\eta$, the area fraction covered by particles on the monolayer (packing fraction). It can be shown that $\eta$ is related to $\rho^*$, $Q$ and $B$ by

$$\eta = \frac{\rho^*}{3} \left( \kappa_1 (\kappa_2 + 1) - \kappa_2 - [\kappa_1 (\kappa_2 + 1) - 2\kappa_2] Q - 3\kappa_1 (\kappa_2 - 1) B \right).$$

(7)

This equation is used later to explain packing-fraction inversion effects that take place for some particle symmetries.

III. Results

A. Effect of particle biaxiality on the biaxial phase

First we chose a pair of values for the largest aspect ratio, $\kappa_1 = 5$ and 10, and varied particle biaxiality $\theta$ from $-1$ (plate-like uniaxial symmetry) to 1 (rod-like uniaxial symmetry). For each value of $\kappa_1$ and $\theta$, bifurcation analysis provides the values of scaled density $\rho^*$ and mol fractions $\{\gamma_{xx} = \gamma_{yy} \neq \gamma_{xy} = \gamma_{yx}\}$ corresponding to the $N_u \to N_b$ bifurcation point. The nature (continuous vs. first order) of the transition was always checked via direct minimization of the free-energy density with respect to all the molar fractions $\{\gamma_{\mu\nu}\}$, which confirmed the continuous character of the transition from $|\gamma_{xx} - \gamma_{yy}| \sim (\rho^* - \rho_0^*)^{1/2}$ (with $\rho_0^*$ the scaled density at bifurcation) near and above the bifurcation point.

The spinodal instabilities of uniform nematic phases $N_u$ and $N_b$ with respect to density modulations of crystal (K), columnar (C) or smectic (S) symmetries were also obtained from the appropriate bifurcation theory (Appendix C). The results are plotted in Fig. 3(a) for $\kappa_1 = 5$ and (b) for $\kappa_1 = 10$. In the first case there exists a small region (shaded in the figure), close to $\theta = -1$, in which $N_b$ is stable. The $N_u-N_b$ bifurcation line crosses the curve associated with the spinodal instability to the non-uniform phases at $\theta \approx -0.5$. The figure also shows the lack of biaxial
ordering in rod-like ($\theta > 0$) particles, since the $N_b$ bifurcation point occurs at densities higher than that of the $C$–$S$–$K$ spinodal. For $k_1 = 10$ the region of stability of $N_b$ is considerably enlarged (spanning the interval $\theta < 0$); this is because the aspect ratio of the projected rectangles with the smallest area is larger. Again rod-like particles ($\theta > 0$) do not exhibit biaxial ordering.

The orientational ordering of plate-like biaxial particles can be better visualized by drawing some particle configurations to show how the system evolves as density increases. To this purpose we sketch three projected area configurations of biaxial boards with $k_1 = 10$ and $k_2 = 6$ (which corresponds to the shape parameter $\theta = -0.481$) for three different values of the scaled density, $\rho^* = 0.025$, 0.04, and 0.055, corresponding to the panels (a), (b) and (c) of Fig. 4 respectively. Note that the molar fractions of different species, $\gamma_{jk}$, approximately coincide with those obtained from free-energy minimization. For $\rho^* = 0.025$ [panel (a)] the equilibrium configuration corresponds to a $N_u$ phase. The molar fractions of cross-sections with smallest area, $\sigma_2 \times \sigma_3$ (shown in light gray), are oriented along $x$ and $y$ axes with equal probability. Thus $\gamma_{xx} = \gamma_{yy}$. The same occurs with the other projected areas: the intermediate one, $\sigma_1 \times \sigma_3$ (shown in dark gray), corresponding to molar fractions $\gamma_{xz} = \gamma_{yz}$, and the biggest one, $\sigma_1 \times \sigma_2$ (shown in medium gray), corresponding to molar fractions $\gamma_{xy} = \gamma_{yx}$. Note that the $N_u$ is more populated by

\[ \begin{array}{ccc}
\text{(a)} & \text{(b)} & \text{(c)} \\
\end{array} \]

Fig. 3 (a) Phase diagrams in the plane scaled density $\rho^*$ vs. particle biaxiality parameter $\theta$ for $k_1 = 5$. Density axis is in the logarithmic scale. Solid curve: continuous $N_u$–$N_b$ transition. Dashed curve: spinodal instability from the uniform to the non-uniform phases (either $K$, $C$ or $S$). The region of $N_b$ stability is shaded. (b) The same as (a), but for $k_1 = 10$. (c) Uniaxial $Q$ (solid curve) and biaxial $\Delta Q^*$ (dashed curve) order parameters as a function of scaled density $\rho^*$ for uniaxial plate-like ($\theta = -1$) and rod-like ($\theta = 1$) particles with $k_1 = 10$. The density axis is in the logarithmic scale. Filled circles on the curves indicate the instabilities to non-uniform phases. (d) The same as [c], but for plate-like ($\theta = -0.5$, dashed curve) and rod-like ($\theta = 0.5$, dotted curve) biaxial particles.

Fig. 4 Sketch of projected area configurations of biaxial boards with $k_1 = 10$ and $\theta = -0.481$ corresponding to $\rho^* = 0.025$ [N$_u$ (a)], 0.04 [N$_u$ (b)] and 0.055 [N$_u$ (c)]. The three different projections are shown in light, dark and medium gray colors corresponding to the smallest, intermediate and biggest projected areas respectively.
species with the smallest cross-sectional area and thus the major axes of boards point perpendicular to the monolayer. On the other hand the species with the biggest cross-sectional areas are practically absent while the population of the rest of the species, those with intermediate cross-sectional area, is between the other two. Thus we have that \( \gamma_y \approx \gamma_x > \gamma_{yx} > \gamma_{xy} > \gamma_{yx} \). For density \( \rho^* = 0.04 \) [panel (b)] the orientational symmetry is broken along the \( y \)-axes and consequently the number of projected rectangles with their major axes pointing to \( y \) increases at the expense of those pointing to \( x \)-axis. This is the \( N_b \) phase for which the set of molar fractions fulfills \( \gamma_y > \gamma_x > \gamma_{yx} > \gamma_{xy} > \gamma_{yx} \). Finally for the highest density \( \rho^* = 0.055 \) the majority of rectangles point to the \( y \)-axis and thus the biaxial ordering is almost perfect.

To show the ordering properties of the system in more detail, Fig. 3(c) and (d) contain the behavior of the uniaxial and biaxial order parameters \( Q, A_{\phi^*} \) and \( A_\phi \), as a function of \( \rho^* \) for uniaxial (\( \theta = \pm 1 \)) and biaxial (\( \theta = \pm 0.5 \)) symmetries, respectively, and for \( k_1 = 10 \). As already reported in a previous publication,39 uniaxial plates continuously become ordered with density, their main axes lying preferentially on the surface of the monolayer [see case \( \theta = -1 \) in Fig. 3(c)]. As the density increases from zero, the uniaxial order parameter \( Q \) decreases continuously from zero and saturates at \(-0.5\) for high densities, which means that the shortest particle axes lie on the monolayer. In this configuration the total particle area projected on the surface is minimized (with a vanishingly small fraction of plates with main axes perpendicular to the monolayer). When \( Q \) is almost saturated (\( \rho^* \approx 0.02 \)), the in-plane rotational symmetry of particle axes is broken and the system exhibits a \( N_0 \rightarrow N_b \) transition.

For rod-like particles, case \( \theta = 1 \) in Fig. 3(c), the following behavior is observed: the uniaxial order parameter \( Q \) continuously increases from zero at vanishingly small densities, saturating to 1 as density increases. There are two clear differences with respect to the plate-like geometry: (i) axes of uniaxial particles are now preferentially oriented perpendicular to the monolayer (thus decreasing the total occupied area), and (ii) there is no orientational symmetry breaking: we can discard the presence of a \( N_b \) phase for rods with \( k_1 = 10 \).

The uniaxial and biaxial order parameters are also shown as a function of \( \rho^* \) for \( k = 10 \) in the case of biaxial particles with \( \theta = \pm 0.5 \) [see Fig. 3(d)]. Here the situation is similar to the uniaxial case: (i) plate-like particles (\( \theta = -0.5 \)) exhibit \( N_0 \) planar ordering and a \( N_0 \rightarrow N_b \) transition when \( Q \) is almost saturated. However, the \( N_b \) phase looses its stability against non-uniform phases at higher densities. (ii) Rod-like particles (\( \theta = 0.5 \)) possess uniaxial out-of-plane ordering and a direct transition from the \( N_0 \) phase to the non-uniform phases (\( K, C \) or 8). Note that \( N_b \) is metastable with respect to these phases.

From these results we can conclude that, in contrast to intuition, the main effect of particle biaxiality in plate or rod monolayers is the destabilization of the \( N_b \) phase: note in Fig. 3(a) and (b) how the shaded region of \( N_b \) stability, bounded by the two spinodal curves, shrinks as \( \theta \) increases from the uniaxial case \( \theta = -1 \). There is a clear physical interpretation of this behavior. For uniaxial plates, with dimensions \( \sigma \times \sigma \times L (L < \sigma) \), there are two identical rectangular and mutually perpendicular projections of dimensions \( L \times \sigma \), which have different molar fractions for a given density, and consequently a \( N_b \) phase appears. The other (large) projection, of dimensions \( \sigma \times \sigma \), has a vanishingly small molar fraction. When particle biaxiality increases keeping fixed the largest aspect ratio (\( k_1 = \sigma_1/\sigma_3 = 10 \); without loss of generality we suppose \( \sigma_3 \) to be constant), decreasing \( \sigma_2 \) from \( \sigma_1 \), the original projected rectangular species of equal areas now becomes different, with dimensions \( \sigma_1 \times \sigma_3 \) (intermediate species) and \( \sigma_2 \times \sigma_3 \) (smallest species). Note that biggest species, with dimensions \( \sigma_1 \times \sigma_2 \), will continue to have a vanishingly small molar fraction. To minimize the excluded volume interactions between particles, the fraction of \( \sigma_2 \times \sigma_3 \) species should increase with respect to the other, and the total density has to increase to stabilize the \( N_0 \) phase (we remind that a larger aspect ratio favours the \( N_a-N_b \) symmetry breaking).

It is fruitful to compare (at least qualitatively) our results with those of the recent experiment of goethite nanorods confined between the bilayers of a lamellar phase made from the nonionic surfactant.35–37 These particles orient perpendicularly to an applied magnetic field along the lamellae axis so that negative uniaxial order parameters can be obtained, resulting in stacked sheets of liquid-like quasi-two-dimensional rods. Particle sizes were estimated by optical and X-ray diffraction methods to be \( 315 \times 38 \times 18 \) nm\(^3\) resulting, in our notation, in aspect ratios \( k_2 = 17.5 \) and \( k_3 = 2.1 \), and \( \theta = 0.37 \) (i.e. relatively biaxial particle sizes). Rod interactions are approximately hard, but interact with the lamellae in complex ways, probably resulting in effective attractions between the rods in a sheet; intersheet interactions also exist, although they are probably weak. The authors find an ‘isotropic’ phase (corresponding to the uniaxial nematic phase \( N_0 \) in our monolayer) and a ‘nematic’ phase (our biaxial \( N_b \) phase) and suggest a possible continuous phase transition between the two at a packing fraction which was not possible to estimate in the experiment. This particle geometry would correspond closely to the phase diagram of Fig. 5(a) and (d). In our diagram, the experimental value of \( \theta \) is slightly larger than the predicted limiting point for the biaxial phase. A number of factors could explain the difference: modified attractive interactions and size polydispersity in the experimental nanorod system, both of which could enhance the stability of the biaxial phase, and/or defects in the theoretical approach.

B. Topology of the phase diagram

In this section the topology of the phase diagram as a function of \( k_1 \) is analysed. Fig. 5 shows phase diagrams in the \( \rho^*-\theta \) \([a-c]\) and \( \eta-\theta \) \([d-f]\) planes for \( k_1 = 20, 55 \) and 70. For \( k_1 = 20 \) \([a] \) and \( [d] \) the phase diagrams retain the same topology as for the case \( k_1 = 10 \), see Fig. 3(b).

As shown in our recent work,39 a monolayer of uniaxial rods in the restricted-orientation approximation exhibits a peculiar phase behaviour for \( k_1 = 21.34 \), with a reentrant \( N_0 \) phase and an intermediate \( N_b \) phase. This behaviour persists in the case of
bicontinuous rods. For example, Fig. 5(b) and (e) pertain to the case $\kappa_1 = 55$, and the aforementioned system would be similar to the case $\theta = 1$ (uniaxial rods). The $N_b$ stability region shrinks for increasing particle biaxiality (decreasing $\theta$), totally disappearing at a critical-end point (shown by an open circle). The presence of a biaxial phase in monolayers of uniaxial rods is easy to explain: For high aspect ratios and densities such that the total packing fraction of the projected rectangular species $L \times \sigma$ is close to $\eta_{2D}$ (that of the I–N transition of hard rectangles in 2D), an orientational symmetry breaking at the surface of the monolayer takes place. Of course the presence of the square, $\sigma \times \sigma$, species should be taken into account. However, at low densities and high aspect ratios, the packing fraction of squares is small compared to that of rectangles. When the total density is increased, the packing fraction of squares increases (as uniaxial nematic ordering is promoted), while the packing fraction of rectangles decreases. Then the packing fraction of rectangles jumps below $\eta_{2D}$ and consequently the $N_b$ phase looses its stability with respect to the $N_u$ phase.

Now we discuss the stability region of the biaxial nematic phase on the prolate side. When particle biaxiality is increased ($\theta$ decreases from 1), rectangular species becomes inequivalent and the largest one, of dimensions $\sigma_1 \times \sigma_2$, rapidly decreases in the molar fraction with respect to the intermediate one, of dimensions $\sigma_1 \times \sigma_3$. Therefore the total density should increase so that the total area fraction of the projected rectangular species follows the order of $\eta_{2D}$, and the $N_u$–$N_b$ transition density increases. On the other hand, the alignment of particles along $z$ is enhanced with the increased biaxiality such that the packing fraction of the smallest species grows at the expense of the other two, and consequently the $N_b$–$N_u$ transition curve moves to lower densities. For a particular value of particle biaxiality the two transition curves, for the $N_u$–$N_b$ and $N_b$–$N_u$ transitions, coalesce into a single critical end-point [see Fig. 5(b)].

To better visualize the ordering properties of the biaxial prolate boards we show in Fig. 6 some projected area configurations of biaxial rods with $\kappa_1 = 40$ and $\kappa_2 = 3$ (thus $\theta = 0.265$) for three densities: $\rho^* = 0.007$ [N$_b$ (a)], 0.01 [N$_b$ (b)] and 0.025 [N$_u$ (c)]. The relationship between cross-sectional areas and the molar fractions of different species are the same as those corresponding to the already discussed oblate case: the fluid is rich in smallest projected-area species (and thus the majority of boards have their long axis pointing perpendicular to the monolayer). However now the orientational symmetry-breaking is promoted by the presence of intermediate species (the dark gray ones) corresponding to boards with longest axis laying on the surface monolayer while its second, intermediate axis, is perpendicular to it. Note that although the number of intermediate species are much less than those with the smallest projected areas their packing fractions exhibit the opposite relationship. Also note that when the density is increased from 0.007 to 0.01 the degree of biaxial ordering has negligible increment [compare the panels (a) and (b)] and it could even decrease up to the point of disappearing [compare the panels (b) and (c)]. This is a direct consequence of a phase diagram topology in which a $N_b$ phase is sandwiched between two $N_u$ phases.

It is interesting to note from Fig. 5(a–c) that the $N_u$–$N_b$ spinodal in the region $\theta < 0$ deforms as $\kappa_1$ increases and eventually develops a loop at $\theta = 0$ [see Fig. 5(b) for $\kappa_1 = 55$]. This means that there is a small $\theta$-interval (between the two critical end-points shown with open circles) where both nematic phases are reentrant. Also, there is a particular value
of the aspect ratio, $k_1^* \approx 60$, for which the two critical end-points in the plate-like ($\theta < 0$) and rod-like ($\theta > 0$), on the corresponding $N_b$ spinodals, coalesce into a single point. For $k_1 > k_1^*$ a density gap appears in the phase diagram where $N_b$ is stable for any $\theta$, as shown in Fig. 5(c) for $k_1 = 70$. Now both nematic phases are reentrant in wide intervals of $\theta$.

We should mention that the nature of the $N_u$–$N_b$ transition is always continuous, except for $k_1 \leq 40$ in a very small range of particle biaxiality corresponding to the density loop mentioned above. This is shown in Fig. 7(a) where a detail of the phase diagram for $k_1 = 55$ is shown. The hatched area represents the $N_u$–$N_b$ coexistence region.

For high enough $k_1$ and particles with $\theta \approx 0$ the phase diagrams present an interesting feature, namely a packing-fraction inversion. This is shown in Fig. 5(e) and (f) for $k_1 = 55$ and 70. In this region the lower $N_u \rightarrow N_b$ and upper $N_b \rightarrow N_u$ transition curves in the $\rho^*\sim\theta$ plane change their relative locations when plotted in the $\eta\sim\theta$ plane. This peculiar phenomenon can be clearly visualized in Fig. 7(b), where the packing fraction $\eta$ is plotted against $\rho^*$. As we can see, once the $N_u$–$N_b$ transition takes place, the transition packing fraction exhibits a maximum and then decreases down to the value at the $N_b$–$N_u$ transition. For larger $\rho^*$ the packing fraction exhibits the usual monotonic behaviour. This effect can be explained by resorting to eqn (7), which shows that $\eta$ is a function of $\rho^*$ and the two order parameters $Q$ and $B$. It is then possible for the packing fraction to decrease with $\rho^*$ when the order parameters are positive and increase sufficiently strongly with $\rho^*$ (i.e. uniaxial ordering is strongly promoted so that the number of particles of the species with the smallest projected area increases rapidly enough), in such a way that the total increase in the number of particles is compensated.

One interesting feature of the phase diagrams shown in Fig. 5 is that, for particular values of the parameters ($k_1, \theta$), the total number of transitions between uniform phases ($N_u$ and $N_b$) can be one or three (the latter case associated with reentrant phases). The curve in the $k_1\sim\theta$ plane separating both regions is just the continuous boundary of critical end-points (see Appendix B for details on their calculation), and is plotted in Fig. 8(a), where the regions corresponding to one or three phase transitions are correspondingly labelled.

To finish this section, we compare in Fig. 8(b) the biaxial orientational order, as measured by the biaxial order parameter $A_{Bv}$, of plate-like ($\theta = -0.5$, solid curve), perfectly biaxial ($\theta = 0$, dotted curves) and rod-like ($\theta = 0.5$, dashed curve) particles, all of them having $k_1 = 70$. There are important differences between the three cases: while the biaxial order of plate-like particles increases from the bifurcation point and finally saturates at its maximum value, rod-like particles exhibit a rather small biaxial order in the range of densities where the $N_b$ phase
is stable. Finally, for $\theta = 0$ a small region of biaxial order (with a relatively small order parameter) is followed by a second transition to a second $N_b$ phase possessing a high degree of biaxiality up to the transition to a non-uniform phase. This trend is general for any $\kappa_1 > 21.34$: The $N_b$ phase of rod-like particles exhibits only a small degree of global biaxial ordering, quantified through the order parameter $\Delta_B$. Therefore, its stability is questionable for the freely-rotating case.

IV. Conclusions

In this work we studied the effect of particle biaxiality on the phase behaviour of liquid-crystal colloidal monolayers, using fundamental-measure density-functional theory for hard board-like biaxial particles with restricted orientations. Various phase diagrams were obtained for different values of the two parameters that describe the particle shape: the largest particle aspect ratio $\kappa_1$ and the particle biaxiality $\theta$. This study is an extension of our previous work in which monolayers of uniaxial rod-like and plate-like particles were analysed.\(^{39}\) In contrast to that expected, particle biaxiality destabilizes the biaxial phase in the cases where the latter is present, a phenomenon directly related with the competition between (i) the biaxiality promoted by the two-dimensional spatial constraint on particle centres of mass, and (ii) the biaxial ordering promoted by particle biaxiality for high enough densities. For biaxial particles the rectangular projected areas are inequivalent, and the mixing entropy stabilizes, mainly for plate-like geometry, the 2D isotropic phase.

For rod-like geometry the $N_b$ phase has a small degree of biaxial order and occurs in a narrow interval of densities. Again an increase in particle biaxiality reduces the stability interval which eventually disappears at a critical end point. For high enough values of the largest aspect ratio, $\kappa_1 \approx 60$, the phase diagram exhibits a density gap in which the $N_b$ is stable for any value of particle biaxiality $\theta$. The transitions between nematic phases are continuous, except for a small range of values of $\theta$ about zero and for large values of $\kappa_1$, where a first-order $N_u$-$N_b$ transition appears. A packing fraction inversion phenomenon also exists. The rapid increase of particle alignment along $z$, resulting in a large fraction of the projected species with the smallest area, compensates the total increment in number of particles, resulting in a decrease of $\eta$ with $\rho^*$.

The presence of a $N_b$ phase in the rod-like region of the phase diagram ($\theta > 0$) should be taken with care, as it could be a direct consequence of the restriction on particle orientations. As shown by Monte Carlo simulations and Parsons–Lee density-functional theory, uniaxial freely-rotating plate-like ellipsoidal particles adsorbed on a monolayer without orientational restrictions do exhibit a $N_b$ phase, while their rod-like counterparts do not.\(^{40}\) However it would be necessary to explore a larger variety of particle geometries, without imposing orientational constraints, to finally discard the presence of a biaxial nematic phase.

The present model can qualitatively describe the phase behavior of Langmuir monolayers of biaxial molecules with one of their extremes attached to the surface. The molecules can freely rotate but only exhibits two-dimensional diffusion on the surface of the monolayer. Also the present model can describe the entropic-driven phase transitions of colloidal biaxial particles highly confined by external potentials which act on the center of masses but allow particles to freely rotate. There are several mixtures with one of their species adsorbed at their fluid–fluid interfaces. In these cases the external confining potentials acting on these species are usually proportional to the projected particle areas. To describe these systems within the present DF formalism we need to include the adsorption energy contribution (the attractive external potential) as $\beta F_{\text{ext}} = -\varepsilon \sum_{\mu\nu} a_{\mu\nu} \int_A d\rho_{\mu\nu}(r) = -\varepsilon \sum_{\mu\nu} N_{\mu\nu} a_{\mu\nu}$, with $\varepsilon > 0$ the amplitude in reduced thermal units of the adsorption energy and $N_{\mu\nu}$ the number of species $\mu\nu$ present in the total area $A$, while $a_{\mu\nu} = a_{\mu\nu}^s a_{\mu\nu}^e$ is the projected area of species $\mu\nu$. This term will certainly change the phase behavior of the system and we postpone its elucidation as future work.

We hope that our study will serve as a guide for future experimental studies of confined board-shaped colloidal systems, such as goethite nanorods\(^{35-37}\) and the recently synthesized lead carbonate nanoplatelets.\(^{41}\)
Appendix A : density-functional theory 

We use a density functional (DF) based on fundamental-measure theory for the Zwanzig model ( particle orientations along the three Cartesian axes) which fulfills the $3D \rightarrow 2D$ dimensional crossover. In this formalism the excess part of free-energy density depends on a set of weighted densities calculated by convoluting the density profiles of the two-dimensional projections of the six species with certain weighting functions, the latter depending on the geometry of a single particle: 

$$n_s(r) = \sum_{\mu \nu} \int dr' \rho_{\mu \nu}(r') \omega^{(2)}_{\mu \nu}(r - r'),$$

$$\omega^{(0)}_{\mu \nu}(r) = \frac{1}{4} \delta \left( |r_{\mu \nu} - |x| \right) \delta \left( |r_{\mu \nu} - |y| \right).$$

$$\omega^{(1)}_{\mu \nu}(r) = \frac{1}{2} \Theta \left( |r_{\mu \nu} - |x| \right) \delta \left( |r_{\mu \nu} - |y| \right).$$

$$\omega^{(2)}_{\mu \nu}(r) = \Theta \left( |r_{\mu \nu} - |x| \right) \Theta \left( |r_{\mu \nu} - |y| \right).$$

where $\delta(x)$ and $\Theta(x)$ are the Dirac delta and Heaviside functions, respectively, while we have introduced the tensor $r_{\mu \nu} = \sigma_3 + (\sigma_2 - \sigma_1) \delta_{\mu \nu} + (\sigma_1 - \sigma_3) \delta_{\mu \nu}$, with $\tau = x, y$ and $\delta_{\mu \nu}$ the Kronecker delta. In the uniform limit the density $n_s = \sum_{\mu \nu} \rho_{\mu \nu} M^{(2)}_{\mu \nu}$, with 

$$M^{(0)}_{\mu \nu} = 1, \quad M^{(1)}_{\mu \nu} = \sigma_3 \rho_{\mu \nu}, \quad M^{(2)}_{\mu \nu} = \sigma^x \rho_{\mu \nu}. \quad (A2)$$

The excess part of the scaled free-energy density for a 2D mixture of six particle projections, 

$$\Phi_{\text{exc}} = \beta F_{\text{exc}} \sigma_3^2 / A = \sigma_3^2 \left( -n_0 \ln(1 - n_2) + n_{1u} n_{1s} / 1 - n_2 \right), \quad (A3)$$

where $F_{\text{exc}}$ is the uniform limit of the excess part of the DF and $A$ (the total area) can be written as 

$$\Phi_{\text{exc}} = \rho^* \left[ -\ln(1 - \eta) + y \Psi_{1s} \Psi_{1y} \right]. \quad (A4)$$

where the scaled density is defined as $\rho^* = \rho \sigma_3^2$ and the packing fraction, $\eta = \rho^* \Psi_{1x}$ is the uniform limit of the weighted density $n_s(r)$. Also we have defined $y = \rho^*(1 - \eta)$, and the following functions 

$$\Psi_{1x} = (\gamma_{xy} + \gamma_{xz}) k_1 + (\gamma_{yx} + \gamma_{yz}) k_2 + \gamma_{xy} + \gamma_{yz}, \quad (A5)$$

$$\Psi_{1y} = (\gamma_{yx} + \gamma_{yz}) k_1 + (\gamma_{xy} + \gamma_{xz}) k_2 + \gamma_{yx} + \gamma_{xz}, \quad (A6)$$

$$\Psi_{2} = (\gamma_{xy} + \gamma_{xz}) k_2 + (\gamma_{yx} + \gamma_{yz}) k_1 + (\gamma_{yx} + \gamma_{xz}) k_2. \quad (A7)$$

The ideal part of the free-energy density in reduced units is 

$$\Phi_{\text{id}} = \beta F_{\text{id}} \sigma_3^2 / A = \rho^* \left[ \ln \rho^* - 1 + \sum_{\mu, \nu} \gamma_{\mu \nu} \ln \gamma_{\mu \nu} \right]. \quad (A8)$$

The minimization of the total free-energy density, $\Phi^* = \Phi_{\text{id}}^* + \Phi_{\text{exc}}^*$ with respect to the molar fractions $\gamma_{\mu \nu}$, together with the constraint $\sum_{\mu \nu} \gamma_{\mu \nu} = 1$, provide the following set of equations that have to be solved to obtain their equilibrium values: 

$$\gamma_{\mu \nu} = e^{-\beta \mu} / \sum_{\eta} e^{-\beta \eta}, \quad (A9)$$

$$\gamma_{\mu \nu} = y[\Psi_{1x} \gamma_{\mu \nu}^y + \Psi_{1y} \gamma_{\mu \nu}^x + (1 + y \Psi_{1x} \Psi_{1y}) k_{\mu \nu}^x k_{\mu \nu}^y], \quad (A10)$$

where we have denoted $k_{\mu \nu}^x = 1 + (\kappa_1 - 1) \delta_{\mu \nu} + (\kappa_2 - 1) \delta_{\mu \nu}$. 

The chemical potentials of the species $\tau \nu$ evaluated at the equilibrium $\{\gamma_{\mu \nu}^{(eq)}\}$ are 

$$\beta \mu_{\tau \nu} = \beta \mu_0 = \ln \left( \frac{y}{\sum_{\eta} e^{-\beta \eta}} \right), \quad \forall \tau, \nu \quad (A11)$$

Finally, the pressure in reduced units can be computed as 

$$p^* = \beta p \sigma_3^2 = y + y^2 \Psi_{1x} \Psi_{1y}, \quad (A12)$$

Both quantities are required to calculate the coexistence densities in the case of first-order phase transitions.

Appendix B: bifurcation to the biaxial phase

Here we perform a bifurcation analysis from the uniaxial nematic ($N_u$) to the biaxial nematic ($N_b$) phase. The latter phase has two nematic directors, perpendicular and parallel to the monolayer, respectively. By solving eqn (B12) and (B17) below we find the values of the scaled density $\rho^*$ and two independent molar fractions at the bifurcation (spindal). Note that in the case of continuous $N_u - N_b$ phase transitions, this formalism provide the exact location of the transition point.

Let us define the new variables $u_{\pm} = (\gamma_{xx} + \gamma_{yy}) / 2, v_{\pm} = (\gamma_{xx} - \gamma_{yy}) / 2$, and $r_{\pm} = (\gamma_{xy} + \gamma_{yz}) / 2$ which for $N_u$ symmetry ($\gamma_{xx} = \gamma_{yy} = \gamma_{zz}$ and $\gamma_{xy} = \gamma_{yz} = \gamma_{xz}$) are equal to $\gamma_{xx}, \gamma_{zz}$, and $\gamma_{xy}$ for the $+$ sign, and strictly zero for the $-$ sign. Also let us define the quantities 

$$s_{\pm} = u_{\pm}(k_2 \pm 1) + v_{\pm}(k_1 \pm 1) + r_{\pm}(k_1 \pm k_2). \quad (B1)$$

Then we find that 

$$\Psi_{1x} \Psi_{1y} = s_{+}^2 - s_{-}^2, \quad \Psi_{2} = 2(u_{\pm} k_2 + v_{\pm} k_1 + r_{\pm} k_1 k_2), \quad (B2)$$

The ideal part of the free-energy density in these new variables, has the form 

$$\Phi_{\text{id}}^* = \rho^* \left[ \ln \rho^* - 1 + \sum_{\nu = \pm} \left[ (u_{\nu} + v_{\nu} - u_{\nu} + v_{\nu}) \ln(u_{\nu} + v_{\nu} - u_{\nu} + v_{\nu}) + (v_{\nu} + v_{\nu}) \ln(v_{\nu} + v_{\nu} - u_{\nu} + v_{\nu}) \right] \right], \quad (B3)$$

while the excess part has the same expression (A4). Minimizing the total free energy density $\Phi_{\text{id}}^* + \Phi_{\text{exc}}^*$ with respect to $u_{\pm}, v_{\pm}$ and $r_{\pm}$, we obtain 

$$\ln(u_{\pm}^2 - u_{-}^2) + 2y[1 + y(s_{+}^2 - s_{-}^2)] k_1 + 2y s_{1}(k_2 + 1) + 2A = 0, \quad (B4)$$
\[ \ln(v_1 - v_2) + 2y[1 + y(s_1^2 - s_2^2)]k_1 + 2ys_s(k_1 + 1) + 2A = 0, \]

(B5)

\[ \ln(r_1 - r_2) + 2y[1 + y(s_1^2 - s_2^2)]k_1k_2 + 2ys_s(k_1 + k_2) + 2A = 0, \]

(B6)

\[ \ln\left(\frac{u_s + u}{u_s - u}\right) - 2y(s_1 - 1) = 0, \]

(B7)

\[ \ln\left(\frac{v_s + v}{v_s - v}\right) - 2y(s_2 - 1) = 0, \]

(B8)

\[ \ln\left(\frac{r_s + r}{r_s - r}\right) - 2y(s_1 - k_2) = 0, \]

(B9)

where \( A \) is a Lagrange multiplier which guarantees the constraint \( 2(u_s + v_s + r_s) = 1 \). Considering the case of vanishingly small biaxial ordering, i.e. \( u_s \sim 0, v_s \sim 0 \) and \( r_s \sim 0 \) (which is correct near and above the bifurcation point), we can expand eqn (B7)-(B9) up to the first order in these variables to obtain in the matrix form \( \mathbf{A} = 0 \), where we have defined the vector \( \mathbf{h} = (u_s, v_s, r_s) \) and a matrix \( \mathbf{A} \) in the form

\[
\mathbf{A} = \begin{pmatrix}
1 - yu_s(k_2 - 1)^2 & -yu_s(k_1 - 1)(k_2 - 1) & -yu_s(k_1 - k_2)(k_2 - 1) \\
-yv_s(k_1 - k_2)(k_1 - 1)(k_2 - 1) & 1 - yv_s(k_1 - 1)^2 & -yv_s(k_1 - k_2)(k_1 - 1) \\
-yr_s(k_1 - k_2)(k_1 - k_2)(k_1 - 1) & -yr_s(k_1 - k_2)(k_1 - 1) & 1 - yr_s(k_1 - k_2)^2,
\end{pmatrix}
\]

where the explicit expressions for the functions \( h_i(\mathbf{u}, \mathbf{v}, \mathbf{r}) \) (\( i = 1, 2 \)) are:

\[
f_1(u_s, v_s) \equiv u_s - C^{-1}(u_s, v_s)e^{-\xi(u_s, v_s)} = 0,
\]

\[
f_2(u_s, v_s) \equiv v_s - C^{-1}(u_s, v_s)e^{-\xi(u_s, v_s)} = 0,
\]

\[
f_3(u_s, v_s) \equiv v_s - C^{-1}(u_s, v_s)e^{-\xi(u_s, v_s)} = 0,
\]

\[
f_4(u_s, v_s) \equiv C(u_s, v_s) = 2[e^{-\xi_1(u_s, v_s)} + e^{-\xi_2(u_s, v_s)} + e^{-\xi_3(u_s, v_s)}],
\]

(B12)

where we have defined

\[
\xi_1(u_s, v_s) = y[k_2(1 + ys'_2) + (k_2 + 1)s_s],
\]

(B13)

\[
\xi_2(u_s, v_s) = y[k_1(1 + ys'_2) + (k_1 + 1)s_s],
\]

(B14)

\[
\xi_3(u_s, v_s) = y[k_1k_2(1 + ys'_2) + (k_1 + k_2)s_s],
\]

(B15)

and it is convenient to rewrite \( s_s \), considering that \( u_s + v_s + r_s = 1/2 \), as

\[
s_s = -\frac{k_1 + k_2}{2}(k_1 - 1)u_s - (k_2 - 1)v_s.
\]

(B16)

Once the values of \( u_s \) and \( v_s \) are found by solving the set (B12), the packing fraction at which the bifurcation occurs can be calculated from

\[
\eta = \frac{y\Psi_2}{1 + y\Psi_2},
\]

(B17)

\[
\Psi_2 = k_1k_2 - 2k_1(k_1 - 1)u_s - 2k_2(k_2 - 1)v_s.
\]

The set of end-points separating the regions in the \( k_1-k_2 \) plane, where the system (B12) has a different number of solutions, can be calculated by equating the Jacobian to zero:

\[
\begin{vmatrix}
\frac{\partial f_1}{\partial u_s} & \frac{\partial f_1}{\partial v_s} \\
\frac{\partial f_2}{\partial u_s} & \frac{\partial f_2}{\partial v_s}
\end{vmatrix} = 0.
\]

(B18)

Using eqn (B12) we obtain:

\[
J(u_s, v_s) = 1 + 3u_s v_s (1 - 2u_s - 2v_s)^3(k_1 - 1)^2(k_2 - 1)^2 + u_s (1 - 2u_s)\frac{\partial \xi_{13}}{\partial u_s} + v_s (1 - 2v_s)\frac{\partial \xi_{23}}{\partial v_s} - 2u_s v_s \left(\frac{\partial \xi_{23}}{\partial u_s} + \frac{\partial \xi_{13}}{\partial v_s}\right),
\]

(B19)

where the explicit expressions for the functions \( \frac{\partial \xi_{13}}{\partial u_s} \) and \( \frac{\partial \xi_{23}}{\partial v_s} \) (\( i = 1, 2 \)) are:

To compute the values of \( u_s, v_s \), and \( k_1 \) (we fix the value of \( k_2 \)) for the location of the critical end-point of the \( N_6-N_6 \) transition, we
need to solve eqn (B12) and also the equation:

\[ f(\mu, \nu, \tau) = 0. \]  

**(B21)**

**Appendix C: spinodal instability to nonuniform phases**

The spinodal instability of a uniform phase with respect to density modulations of a given symmetry can be calculated by searching the singularities of the structure factor matrix, whose elements can be calculated as

\[ T_{\nu, \tau}(q, \rho) = \delta_{\nu, \tau} - \rho \sqrt{\gamma_{\nu, \tau}} \tilde{T}_{\nu, \tau}(q, \rho). \]  

**(C1)**

with \( \tilde{T}_{\nu, \tau}(q, \rho) \) the Fourier transforms of the direct correlation functions, calculated from the second functional derivatives of \( F_{\text{exc}}[\{\rho_{\mu}\}] \) with respect to density profiles. The latter can be computed as

\[ -\tilde{T}_{\nu, \tau}(q, \rho) = \sum_{x, y} \frac{\partial^2 F_{\text{exc}}}{\partial n_{\mu} \partial n_{\mu}}(q) \tilde{\phi}_{\nu, \tau}^{(0)}(q), \]  

**(C2)**

where the Fourier transforms of the weighting functions are

\[ \tilde{\phi}_{\nu, \tau}^{(0)}(q) = \tilde{w}_{\nu, \tau}^{(0)}(q) = \prod_{x, y} Z_0 \left( q_x^* \kappa_{\nu, \tau}/2 \right). \]  

**(C3)**

\[ \tilde{\phi}_{\nu, \tau}^{(2)}(q) = \sigma_3^2 \tilde{w}_{\nu, \tau}^{(2)}(q) = \sigma_3^2 \prod_{x, y} \kappa_{\nu, \tau}^{(2)} \left( q_x^* \kappa_{\nu, \tau}/2 \right). \]  

**(C4)**

\[ \tilde{\phi}_{\nu, \tau}^{(4)}(q) = \sigma_3^4 \tilde{w}_{\nu, \tau}^{(4)}(q) = \sigma_3^4 \prod_{x, y} \kappa_{\nu, \tau}^{(4)} \left( q_x^* \kappa_{\nu, \tau}/2 \right). \]  

**(C5)**

\[ \tilde{\phi}_{\nu, \tau}^{(1)}(q) = \sigma_3^2 \tilde{w}_{\nu, \tau}^{(1)}(q) = \sigma_3^2 \prod_{x, y} \kappa_{\nu, \tau}^{(1)} \left( q_x^* \kappa_{\nu, \tau}/2 \right). \]  

**(C6)**

The elements (C1) can be written in the following explicit form:

\[ T_{\nu, \tau} = \delta_{\nu, \tau} + y \sqrt{\gamma_{\nu, \tau}} \left\{ \left( \tilde{\phi}_{\nu, \tau}^{(0)}(q) \tilde{w}_{\nu, \tau}^{(2)}(q) \right) + \left( \tilde{\phi}_{\nu, \tau}^{(4)}(q) \tilde{w}_{\nu, \tau}^{(1)}(q) \right) \right\} \]

\[ + y \left[ \psi_{\nu} \left( \tilde{w}_{\nu, \tau}^{(1)}(q) \tilde{w}_{\nu, \tau}^{(2)}(q) \right) + \psi_{\tau} \left( \tilde{w}_{\nu, \tau}^{(1)}(q) \tilde{w}_{\nu, \tau}^{(2)}(q) \right) \right] \]

\[ + \left( 1 + 2y \psi_{\nu} \psi_{\tau} \right) \tilde{w}_{\nu, \tau}^{(2)}(q) \tilde{w}_{\nu, \tau}^{(2)}(q) \}

**(C7)**

where we have defined

\[ \langle \tilde{w}_{\nu, \tau}^{(0)}(q^*) \tilde{w}_{\nu, \tau}^{(2)}(q^*) \rangle = \tilde{w}_{\nu, \tau}^{(0)}(q^*) \tilde{w}_{\nu, \tau}^{(2)}(q^*) + \tilde{\phi}_{\nu, \tau}^{(4)}(q^*) \tilde{w}_{\nu, \tau}^{(1)}(q^*). \]  

**(C8)**

Therefore the spinodal instability of a uniform phase with respect to density modulations can be found from

\[ |T(q^*, \rho^*)| = 0, \]  

**(C9)**

where \( |T(q^*, \rho^*)| \) denotes the determinant of the 6 × 6 symmetric matrix with elements given by (C7). In this way we find the values \( \rho_0^* \) and \( q_0^* \) at the bifurcation point for which the absolute minimum of \( |T(q^*, \rho^*)| \) as a function of \( q^* \) is equal to zero for the first time. In practice we select \( q^* = (q_x^*, 0) \) or \( q^* = (0, q_y^*) \) with \( q_x^* = 2\pi \sigma_3 / d_{x,y} \) and \( d_x \) and \( d_y \) are the periods of nonuniform phases along \( x \) and \( y \) respectively. The values \( \{i \}_{\nu, \tau} \) at each step of the numerical procedure used to solve eqn (C9) are found from the solution of eqn (A9). Bifurcated phases can have different symmetries: smectic (S) or columnar (C), where density modulations exist along only one spatial direction, which could coincide (S) or not (C) with the alignment directions of the particle projections. Also a crystalline phase (K) with full 2D positional ordering could exist with (orientational ordered K) or without (plastic K) orientational ordering.

**Acknowledgements**

We gratefully acknowledge illuminating discussions with G. Odriozola. Financial support from MINECO (Spain) under grants FIS2010-22047-C01 and FIS2010-22047-C04 is acknowledged. SV acknowledges the financial support from the Hungarian State and the European Union under the TAMOP-4.2.2.A-11/1/KONV-2012-0071.

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