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Phase behaviour of hard board-like particles[†]

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We examine the phase behaviour of colloidal suspensions of hard board-like particles (HBPs) as a function of their shape anisotropy, and observe a fascinating spectrum of nematic, smectic and columnar liquid-crystalline phases, whose formation is entirely driven by excluded volum effects. We map out the phase diagram of short and long HBPs by gradually modifying their shape from prolate to oblate and investigate the long-range order of the resulting morphologies along the phase directors and perpendicularly to them. The intrinsic biaxial nature of these particles promotes the formation of translationally ordered biaxial phases, but does not show solid evidence that it would, per se, promote the formation of the biaxial nematic phase. Our simulations show light on the controversial existence of the discotic smectic phase, whose layers are as thick as the minor particle dimension, which is stable in a relatively large portion of our phase diagrams. Additionally, we modify the Onsager theory to describe the isotropic-nematic phase transition of freely rotating biaxial particles as a function of the particle width, and find a relatively strong first order signature, in excellent agreement with our simulations. In an attempt to shed light on the elusive formation of the biaxial nematic phase, we apply this theory to predict the uniaxial-biaxia nematic phase transition and confirm, again in agreement with simulations, the prevailing stability of the translationally ordered smectic phase over the orientationally ordered biaxial nematic phase.

1 Introduction

Colloids are two-phase systems consisting of a dispersed phase, usually droplets or particles, suspended in a continuous medium. They are ubiquitous in our everyday life and play a paramount role in a rich variety of technological applications, especially related to food, paint and cosmetic formulations. According to the IUPAC, at least one of the dimensions of the molecules or particles in the dispersed phase should be roughly between 1 nm and 1 μ m¹. Particles of this size experience stochastic collisions with the molecules of the dispersing medium. The resulting random drifting stems from a thermal energy contribution of the order of few k_BT per particle and is referred to as Brownian motion, af-

pollen grains suspended in water and performing persistent and random jump-like moves². Colloids can be classified according to the physical state of both the continuous and dispersed phases For example, emulsions and foams are dispersions of, respectively small liquid and gas droplets in an other liquid. When the dispersed phase consists of very small solid particles suspended in liquid, the colloid is generally referred to as suspension. A crucial requirement to effectively use colloids in many relevant applications is their thermodynamic and kinetic stability, which is large extent determined by the delicate balance between entropic and enthalpic contributions to their mutual interactions. Controlling these interactions by, for example, adding an electrolyte or a polymer that modifies the particle surface or shape, determines a rich phase behaviour and is key to exploiting, e.g., optical, mechanical, and thermal properties of a colloid. As a consequence, colloids can show a very intriguing phase and aggregation behaviour, surprisingly similar to that of molecular and atomic systems. This similarity has a striking relevance in materials science: it is crucial to unveiling a number of dynamical processes, such as

ter the British botanist Robert Brown. In 1827, Brown observed.

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crystallisation, involving atoms or molecules that are too fast to be detected via conventional microscopy, and provides the opportunity to design functional materials for advanced electro-optical devices³.

Colloidal suspensions of anisotropic particles are particularly attractive for a wide spectrum of applications, including, for instance, photonic band gap materials to manipulate the propagation of light and control the emission of photons at visible wavelengths⁴. Although methods to synthesise anisotropic colloidal particles have been known since the 1990s, most of them lacked the features (high yield and shape selectivity) to efficiently exploit technological applications⁵⁻⁷. The recognition of the impact of the particle shape anisotropy on engineering materials with novel or improved properties sparked off the development of chemical⁸, physical⁹, and biosynthetic¹⁰ techniques to fabricate ad hoc building blocks, such as superballs¹¹, lock-and-key particles¹², fused spheres¹³, and cuboids^{14–17}. Such novel shapes enabled the further enrichment of the already complex phase behaviour of colloids, which includes liquid crystals (LCs)¹⁸, equilibrium gels¹⁹, and porous liquids²⁰. Side by side with experiments, theory and simulation have greatly contributed to understanding the effects of shape on the phase behaviour of colloidal suspensions, often offering preliminary screenings through the huge number of experimental variables ^{21–24}. Very recently, Avendaño and coworkers reported the fascinating phase behaviour of a less conventional family of anisotropic particles: interlocking planar nanorings²⁵. These nonconvex colloidal particles are able to form smectic LCs of remarkably high porosity, which have a very promising potential in gas adsorption and storage.

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Biaxial colloidal particles, such as bent-core and board-like particles, displaying three orthogonal internal axes, have the potential to form a particularly interesting LC phase, the biaxial nematic phase, N_B, which exhibits an orientational order along three directors and thus two distinct optical axes. Nevertheless, stable N_B phases are rarely observed because competing structures, such as the smectic (Sm) phase, limit or preclude its existence. Theory indicates that some particle geometries might be more successful than others in observing this phase. In particular, the self-dual shape, a geometry almost exactly in between prolate and oblate, was shown to promote the formation of the N_B phase, although into a relatively limited region of stability²⁶. Variational cluster expansion theory and Monte Carlo (MC) simulations applied to binary mixtures of hard lath-shaped particles, perfectly aligned along their major axis, suggested that the stability of the N_B phase could be enhanced by size dispersity²⁷. These preliminary intuitions were later experimentally confirmed by Vroege and coworkers, who observed a remarkably stable N_B phase in colloidal suspensions of board-like goethite particles with selfdual shape²⁸. Surprisingly, the range of stability found experimentally significantly exceeded that predicted by previous theories and simulation studies^{26,27} and was later ascribed by Belli et al to the remarkable size dispersity of the goethite particles²⁹. The mean-field theory applied by Belli and based on the Zwanzig restricted orientation model³⁰, pointed out the crucial role of polydispersity in stabilising the N_B phase, which was found to be metastable with respect to the Sm phase for monodisperse HBPs. Adding a non-adsorbing depletant to a pure system of HBPs was shown to have a similar effect and enhance the stability of the N_B phase significantly³¹.

If we restrict our attention to monodisperse systems, many hard biaxial particles investigated over the last twenty years were shown to form stable N_B phases. For instance, Camp and Allen detected a stable N_B phase in suspensions of hard biaxial ellipsoids³², while Peroukidis and Vanakaras in fluids of hard spheroplatelets³³. This particular geometry, consisting of board-like particles with rounded corners, was also examined, in the context of the scaled-particle theory (SPT) within the Zwanzig model, by Taylor and Herzfeld²⁶. By incorporating translational ordering into the framework of SPT, these authors noticed a remarkable reduction in the stability region of the N_B phase, which was almost completely replaced by the uniaxial and biaxial Sm phase. As far as HBPs are concerned, Vanakaras et al observed the existence of the N_B phase in monodisperse systems of perfectly aligned HBPs, which were not allowed to rotate about their two shorter axes²⁷. Escobedo and coworkers calculated the phase diagram of freely rotating oblate and prolate parallelepipeds with square cross section and unveiled a rich variety of LC phases, such as the cubaticlike parquet phase, but did not observe the N_B phase^{34,35}. The more recent work by Belli et al, using the Zwanzig model, revealed the existence of the N_B phase of HBPs with self-dual shape and length-to-diameter ratio $L/W = 3^{31}$. All these computational and theoretical studies suggest that a biaxial geometry is most likely a necessary, but not always sufficient, condition to stabilise biaxial phases. Additional degrees of freedom, such as particle alignment, size and shape dispersity, can dramatically alter the phase behaviour of HBPs. Despite the widespread interest within the LC community, the phase behaviour of monodisperse freelyrotating HBPs is far from being fully understood and the question whether these particles can actually form stable N_B phases remains open.

Additionally, our results confirm the existence of the longdebated discotic Sm phase, consisting of layers as thick as the particle minor axis. While the most common Sm phases are characterised by layers as thick as the particle length, we observe the formation of Sm phases whose layers' thickness is given by the minor particle dimension, *T*. This intriguing phase, referred to as discotic or oblate smectic (Sm⁻) LC, was first predicted by Taylor and Herzfeld, who applied scaled particle theory in conjunction with a cell description of translational order to study the phase behaviour of mutually orthogonal hard spheroplatelets²⁶. As far as hard cuboids are concerned, the Sm⁻ phase was detected in systems of hard parallelepipeds (L = W = 5T) by lattice MC simulations within the restricted-orientation Zwanzig model³⁶ and later predicted by the Fundamental Measure Theory (FMT) also in the context of the Zwanzig approximation^{37,38}. John and Escobedo performed off-lattice MC simulations of hard tetragonal parallelepipeds with unrestricted orientations and provided a beautiful picture of their rich phase behaviour^{34,35}. However, these authors could not confirm the theoretical predictions on the existence of the Sm⁻ phase, suggesting that the stability of this phase could be due to the reduced orientational freedom embedded in the FMT. Our simulation and theoretical findings shed light on the controversial existence of the Sm⁻, which, at least for the geometries examined here, exhibits a relevant stability and further enriches the already complex phase behaviour of HBPs.

In the present study, we perform extensive MC simulations of freely rotating HBPs to unveil their intriguing phase behaviour, which is characterised by a plethora of liquid crystal phases and peculiar oblate-to-prolate-to-oblate phase transitions. We also propose an expansion of the Onsager theory¹⁸ to investigate the isotropic-to-nematic and uniaxial-to-biaxial transitions in suspensions of HBPs. While the latter transition is analysed in the context of HBPs perfectly aligned along their major axis, as previously assumed also by other researchers²⁷, the isotropic-to-nematic transition does not involve any possible restriction on the orientation of the particles, which are left free to rotate. This is a paramount difference with respect to other theoretical treatments that predicted the isotropic-to-nematic transition by employing the restricted-orientation Zwanzig model, which allows for only six orthogonal orientations^{29,36–38}. Unfreezing the particle's degree of freedom is crucial to fully understand the nature of the isotropic-nematic coexistence region, which is found to be significantly larger than that predicted by previous studies on identical^{29,31} or similar^{26,39} geometries, and reveals a significant first-order signature. Moreover, one novel feature of the present theory, as compared to previous virial expansions on axially symmetric particles⁴⁰, is that in the nematic phases, we do not assume free rotation about the aligned molecular axis - i.e. we take into account the molecular biaxiality order parameter.

2 Simulation

2.1 Model

We perform simulations of systems containing between N = 1100and N = 3500 freely rotating HBPs with width W, thickness T, and length L. In particular, T is kept constant and is the unit length of the systems studied. Two different particle lengths are considered here: $L_1^* \equiv L_1/T = 9$ and $L_2^* \equiv L_2/T = 12$. Finally, the particle width, $W^* \equiv W/T$, varies in the range $1 \le W_1^* \le 9$ and $1 \le$ $W_2^* \le 12$, for particles with reduced length L_1^* and L_2^* , respectively. By tuning W^* in this range, the particle shape gradually changes

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from a prolate (rod-like) to an oblate (plate-like) geometry, as shown in Fig. 1.



Fig. 1 Model HBPs with thickness *T*, length *L*, and width W = T, 3*T*, and *L*, from left to right. *T*, the unit length, is kept constant in all the systems studied in this paper. The particle length in this figure is L = 9T but systems containing longer particles (L = 12T) have also been investigated. The particle width is a simulation parameter assuming a spectrum of values between W = T (rod-like, prolate particles) and W = L (plate-like, oblate particles). $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are the unit vectors along *W*, *T*, and *L*, respectively.

2.2 Methodology

We performed MC simulations in the isobaric-isothermal ensem ble constraining a costant number of particles into a rectangula. box with periodic boundaries. Phase transitions were usually determined by gradually expanding a solid crystalline (K) phase up to an isotropic (I) phase, but some systems were also compressed to enhance the accuracy of the phase boundaries. The range of pressures explored is very broad and depends on the particle geometry (see ESI[†]). Each MC cycle consisted of N attempts of dia placing and/or rotating the randomly selected particles, plus an attempt to modify the three box lengths independently. Trans lational and rotational moves as well as volume changes wer accepted if no overlap was detected. To test for particle overlaps, we applied the separating axes method described by Gottschalk et al.⁴¹ and adapted by John and Escobedo to study the phase be haviour of tetragonal parallelepiped particles with square cross section³⁴. We refer the interested reader to the Appendix Ref.³⁴ for further details. During the equilibration run, we calculated the uniaxial (S_2) and biaxial (B_2) order parameters as well as the packing fraction $\eta = Nv_0/V$, with $v_0 = T \times W \times L$ and V the volume of the simulation box. The systems were considered to be equilibrated when η , S_2 and B_2 reached a steady value within reasonable statistical fluctuations.

We have calculated the nematic order parameter and nematic director associated to each molecular axis by applying the standard procedure of diagonalizing a traceless symmetric secondrank tensor defined as

$$\mathbf{Q}^{\lambda\lambda} = \frac{1}{2N} \left\langle \sum_{i=1}^{N} (3\hat{\boldsymbol{\lambda}}_{i} \cdot \hat{\boldsymbol{\lambda}}_{i} - \mathbf{I}) \right\rangle$$
(1)

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where $\hat{\lambda} = \hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ is the unit orientation vector of particle *i*, **I** the second-rank unit tensor, and the angular brackets indicate ensemble average. Diagonalization of $\mathbf{Q}^{\lambda\lambda}$ provides three eigenvalues and three associated eigenvectors. The nematic order parameter S_2 is the largest positive eigenvalue of $\mathbf{Q}^{\lambda\lambda}$ and the corresponding eigenvector determines the uniaxial nematic director⁴². In particular, the nematic order parameter $S_{2,L}$ is the largest eigenvalue of the tensor \mathbf{Q}^{zz} , while the corresponding eigenvector $\hat{\mathbf{n}}$ is the nematic director associated to the preferential orientation of the particle axis $\hat{\mathbf{z}}$. Similarly, diagonalizing \mathbf{Q}^{tx} and \mathbf{Q}^{yy} , the nematic order parameters $S_{2,W}$ and $S_{2,T}$ and the nematic directors $\hat{\mathbf{m}}$ and $\hat{\mathbf{l}}$ can be determined. By employing these same symmetric tensors, three biaxial order parameters can also be calculated ³². For instance, the biaxial order parameter associated to the nematic director along L, $\hat{\mathbf{n}}$, reads

$$B_{2,L} = \frac{1}{3} \left(\hat{\mathbf{m}} \cdot \mathbf{Q}^{xx} \cdot \hat{\mathbf{m}} + \hat{\mathbf{l}} \cdot \mathbf{Q}^{yy} \cdot \hat{\mathbf{l}} - \hat{\mathbf{m}} \cdot \mathbf{Q}^{yy} \cdot \hat{\mathbf{m}} - \hat{\mathbf{l}} \cdot \mathbf{Q}^{xx} \cdot \hat{\mathbf{l}} \right)$$
(2)

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 $B_{2,W}$ and $B_{2,T}$ can be calculated by similar expressions. Following previous works ^{43–45}, it is sufficient to monitor a single biaxial order parameter to assess phase biaxiality. In other words, we only need to examine the fluctuations of the two particle unit vectors perpendicular to the main nematic director. If, for instance, the particles are on average aligned along their $\hat{\mathbf{z}}$ axis and thus the main nematic director is $\hat{\mathbf{n}}$, then the fluctuations of the other two particle axes, $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$, in the plane defined by $\hat{\mathbf{m}}$ and $\hat{\mathbf{l}}$, should be considered. In this case, $S_{2,L} = 1$ and $B_{2,L} = 0$ would give a perfect uniaxial phase, while $S_{2,L} = 1$ and $B_{2,L} = 1$ a perfectly aligned biaxial phase. Similar considerations hold if the main nematic director is $\hat{\mathbf{m}}$ or $\hat{\mathbf{l}}$. In what follows, we refer to the biaxial order parameter associated to the main nematic director as B_2 .

Order parameters, alone, are not sufficient to distinguish between two uniaxial or biaxial phases, such as a nematic (N) from a smectic (Sm) phase. To this end, after equilibration, we addressed the existence and nature of long-range structural correlations by calculating the pair distribution functions along the nematic directors, $g_{\parallel,L}(r_{\parallel,L}^*)$, $g_{\parallel,W}(r_{\parallel,W}^*)$ and $g_{\parallel,T}(r_{\parallel,T}^*)$, and perpendicularly to them, $g_{\perp,L}(r_{\perp,L}^*)$, $g_{\perp,W}(r_{\perp,W}^*)$ and $g_{\perp,T}(r_{\perp,T}^*)$, with $r_{\parallel}^* = r_{\parallel}/T$ and $r_{\perp}^* = r_{\perp}/T$ the longitudinal and transverse distances, respectively, between pairs of particles. Finally, to investigate the local structure of columnar (Col) and K phases, we have also calculated an order parameter that can distinguish between the relative positions between the particles in planes perpendicular to the nematic director:

$$\psi_n = \frac{1}{N_j} \sum_{k}^{N_j} \exp(in\theta_{jk})$$
(3)

where N_j is the number of nearest neighbours around particle k, θ_{ik} is the angle formed by the vectors connecting j and k and

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a reference axis, and n = 4 or 6 to determine the occurrence of, respectively, quadratic or hexatic symmetry.

3 Theory

3.1 Isotropic-nematic phase transition

3.1.1 Uniaxial particles

The Onsager theory of nematic LCs¹⁸ is based on an expression for the Helmholtz energy *A* which contains two competing terms. One arises from the mixing of particles of different orientations, similar to an entropy of mixing, while the other arises from excluded volume interactions and is expressed via a virial expansion. Onsager showed that the Helmholtz energy of a system containing *N* particles at volume *V* (and hence with a number density $\rho = N/V$), can be given as

$$a = \frac{\beta A}{N} = \ln \Lambda^3 \rho - 1 + \sigma [f(\mathbf{\Omega})] + \sum_{n=2}^{\infty} \frac{1}{n-1} B_n \rho^{n-1}.$$
 (4)

Here, β is the inverse temperature, $\ln \Lambda^3 \rho - 1$ is the ideal gas contribution with Λ the de Broglie wavelength, and $\sigma[f(\Omega)]$ is the entropy of mixing-like term with $f(\Omega)$ giving the one-particle orientational distribution function and Ω the particle orientation. The final term is the virial expansion which corrects for manybody interactions, with B_n denoting the n^{th} virial coefficient. The key component in this expression is the one-particle orientational distribution $f(\Omega)$. For uniaxial particles, Onsager used a trial function of the form

$$f(\mathbf{\Omega}) = \frac{\alpha \cosh(\alpha \cos \theta)}{4\pi \sinh \alpha},$$
 (5)

where θ is the angle between the nematic director and the director through the particle symmetry axis and α is a free parameter which describes the degree of nematic ordering, with $\alpha = 0$ for isotropic orientational ordering and $\alpha = \infty$ for perfect nematic alignment. α can be related to the nematic order parameter as

$$S = \int f(\mathbf{\Omega}) P_2(\cos \theta) d\mathbf{\Omega},$$

= $1 + \frac{3}{\alpha^2} - \frac{3}{\alpha \tanh \alpha},$ (6)

where $P_2(\cos \theta) = (3\cos^2 \theta - 1)/2$ is the second Legendre polynomial. This trial function can be used to calculate the entropy of mixing-like term as

$$\sigma[f(\mathbf{\Omega})] = \int f(\mathbf{\Omega}) \ln[4\pi f(\mathbf{\Omega})] d\mathbf{\Omega},$$

= $\ln\left(\frac{\alpha}{\tanh(\alpha)}\right) + \frac{\tan^{-1}(\sinh\alpha)}{\sinh\alpha} - 1,$ (7)

where $d\mathbf{\Omega} = \sin\theta d\theta d\phi$, with ϕ the azimuthal angle. The virial coefficients can be calculated from

$$B_n = \frac{1-n}{n!V} \int \cdots \int f(\mathbf{\Omega}_1) \dots f(\mathbf{\Omega}_n) V_n d\mathbf{\Omega}_1 \dots d\mathbf{\Omega}_n d\mathbf{r}_1 \dots d\mathbf{r}_n, \quad (8)$$

with *V* the volume, and \mathbf{r}_i and $\mathbf{\Omega}_i$ the position and orientation of particle *i*. V_n is given as

$$V_n = \sum_{S_n} \prod_{i< j}^n f_{ij}.$$
(9)

The sum over S_n denotes the sum over all star integrals with n points (see e.g. Refs.^{46–48}), and f_{ij} is the Mayer f-bond between particles i and j, which for hard particles is -1 when the particles overlap, and 0 when they do not. The virial coefficients can be calculated using MC integration for a range of α values, which gives the Helmholtz free energy entirely as a function of density ρ and α . By minimizing Eq. (4) with respect to α for a given density, we obtain the free energy and degree of nematic ordering as a function of ρ , from which we can also calculate the pressure as

$$P = \rho + \sum_{n=2}^{\infty} B_n \rho^n, \tag{10}$$

and the chemical potential as

$$\mu = \ln \Lambda^3 \rho + \sigma \left[f(\mathbf{\Omega}) \right] + \sum_{n=2}^{\infty} \frac{n}{n-1} B_n \rho^{n-1}.$$
 (11)

Coexistence between the I and N phases can be located by equating these two properties in the I and N phases; that is

$$P(\rho_I) = P(\rho_N),$$

$$\mu(\rho_I) = \mu(\rho_N), \qquad (12)$$

where $\rho_{I,N}$ are the isotropic and nematic coexistence densities.

3.1.2 Biaxial particles

The above calculations are relatively straighforward for uniaxial particles, and the Onsager trial function given in Eq. (5) allows for Eq. (7) to be solved analytically. Furthermore, when calculating the virial coefficients, it is very computationally efficient to weight the particle orientations generated for the MC integration procedure by $f(\mathbf{\Omega})$, and we can obtain an analytical expression from Eq. (5) to pick random numbers from the distribution for a given α value.

For biaxial particles, the particle orientation is no longer described simply by the polar and azimuthal angles, but by the three Euler angles θ , ϕ and γ , the third of which denotes rotation around the long axis of the particle. A uniaxial N phase

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of biaxial particles must take into account ordering of θ and γ (with additional ordering of ϕ denoting biaxial nematic ordering). Since the Onsager trial function only accounts for ordering of θ , we therefore require an additional term in the distribution which also takes γ into account. We choose the following trial function

$$f(\mathbf{\Omega}) = \frac{\cosh(\alpha\cos\theta)\cosh(\beta\sin\theta\cos\gamma)}{C},$$
 (13)

where α and β are free parameters describing the degree of ordering and *C* is a normalization parameter defined by $\int f(\Omega) d\Omega = 1$. This can then be inserted into Eqs. (7) and (8) to obtain σ and the virial coefficients as a function of α and β , from which the Helmholtz free energy can be obtained from Eq. (4). By then minimizing *a* with respect to α and β at a fixed density ρ , and calculating the pressure and chemical potential from Eqs. (10) and (11), we can obtain the I-N coexistence densities from Eq. (12) The integrals involving Eq. (13) cannot, to our knowledge, by solved analytically, so instead we must use numerical integration: and interpolation to calculate σ and B_n as continuous functions of α and β .

3.2 Uniaxial-biaxial nematic phase transition

In order to describe the transition from a uniaxial to a biaxial nematic phase (N_U-N_B transition), we must describe the alignment of the minor axis of the biaxial particle, which is defined by the azimuthal angle ϕ . A full description of the phase transition would require a form of the one particle distribution function which de pends on all three of the Euler angles. In practice we find that, for the type of particles considered here, the N phase is highly or dered, and hence we examine N_U-N_B transitions from a perfective aligned nematic phase to a NB phase. That is, from a translationally disordered phase where the particle long axes are perfect aligned but where the short axes are disordered, to a translationally disordered phase where the particle long axes are perfect. aligned and the short axes show a degree of alignment. Thus we can describe the phase via a one particle distribution function which depends only on ϕ and a single free parameter α , which we choose to be the following

$$f(\mathbf{\Omega}) = \frac{\alpha \exp\left(\frac{\alpha|2\phi - \pi|}{\pi}\right)}{4\pi(e^{\alpha} - 1)}.$$
 (14)

This can be inserted into Eqs. (7) and (8) to obtain σ and the virial coefficients as a function of α , and we follow the above procedure to obtain the uniaxial and biaxial nematic coexistence densities.

3.3 Nematic-smectic and nematic-columnar phase transition

 N_B phases are often unstable with respect to smectic or columnar phases, and hence we also examine the N-Sm and N-Col phase transitions. We use a bifurcation analysis to calculate the density at which a perfectly aligned nematic phase first becomes unstable with respect to smectic or columnar ordering. We may calculate σ for positionally ordered phases by

$$\sigma = \int \rho(\mathbf{r}) \ln[\rho(\mathbf{r})] d\mathbf{r}, \qquad (15)$$

where ${\bf r}$ is the particle position. The virial coefficients can be calculated from

$$B_n = \frac{1-n}{n!V} \int \cdots \int \rho(\mathbf{r}_1) \dots \rho(\mathbf{r}_n) V_n d\mathbf{r}_1 \dots d\mathbf{r}_n, \qquad (16)$$

where V_n is given by Eq. (9). Following Ref.⁴⁹, we define the following expression for the density ρ of a smectic phase

$$\boldsymbol{\rho} = \boldsymbol{\rho}_0 \left(1 + \boldsymbol{\varepsilon} \boldsymbol{\xi}(\mathbf{r}) \right), \tag{17}$$

where ρ_0 is the average density of the system, ε is a small constant and $\xi(\mathbf{r})$ for the smectic phase is given by

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$$\xi(\mathbf{r}) = \cos(kz + \delta), \tag{18}$$

where $k = 2\pi/d$, with *d* the spacing between smectic layers, and δ is a phase shift. For the columnar phase $\xi(\mathbf{r})$ is

$$\xi(\mathbf{r}) = \frac{\cos(kx+\delta) + \cos(ky+\delta)}{2},$$
(19)

where the symbols have the same meaning as before and d is now the spacing between the columns. We make the assumption that the columns form a square 2d-lattice which has an even spacing of columns in both directions of the columnar plane, which is valid based on our simulation results.

These are then inserted into Eqs. (15) and (16), which are in turn inserted into Eq. (4) to obtain the Helmholtz free energy. This gives us an expansion in powers of ε , with

$$a = a_0 + \varepsilon a_1 + \varepsilon^2 a_2. \tag{20}$$

Here, the zeroth order term in ε , a_0 , corresponds to the free energy of the nematic phase and the first order term a_1 can be shown to be equal to 0. The second order term a_2 is given by

$$a_2 = \frac{\rho}{2} \int \xi(\mathbf{r})^2 d\mathbf{r} + \sum_{n=2}^{\infty} \frac{1}{n} B'_n \rho^n, \qquad (21)$$

where B'_n is related to the virial coefficients and is given by

$$B'_{n} = \frac{1-n}{n!V} \int \cdots \int \zeta V_{n} d\mathbf{r}_{1} \dots d\mathbf{r}_{n}, \qquad (22)$$

where V_n is given by Eq. (9) and ζ is

$$\zeta = \frac{1}{n(n-1)} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \xi(\mathbf{r}_i) \xi(\mathbf{r}_j).$$
(23)

The term a_2 will be positive at low densities and negative at high densities. The density at which $a_2 = 0$ corresponds to the point at which the positionally ordered phases will first become stable with respect to the positionally disordered nematic phase. We therefore calulate a_2 and locate the density at which it is equal to zero, giving us the nematic-smectic instability density ρ_{Sm} and the nematic-columnar instability density ρ_{Col} .

4 Results

In this section, we analyse and discuss the rich phase behaviour observed in colloidal suspensions of HBPs of length $L_1^* = 9$ and $L_2^* = 12$. In particular, we first present the order parameters and radial distribution functions to accurately distinguish the phases found at equilibrium, and then the phase diagrams and equations of state as obtained by simulation and theory.

4.1 Phase Characterisation

The initial configurations for the simulations consisted of particles arranged in a cubic-like lattice with a highly degree of orientational and translational order. These systems were first relaxed at high pressure to determine the stability region of the K phase and then gradually expanded to liquid-crystalline and isotropic phases. In some cases, such a sequence of isobaric paths was inverted to improve our calculations and thus better locate the phase boundaries. We characterised the phases at equilibrium by calculating the order parameters and radial distribution functions. The evolution of the uniaxial order parameters $S_{2,L}$, $S_{2,T}$ and $S_{2,W}$, and the biaxial order parameter B_2 , in systems containing HBPs with length L_1^* and L_2^* is presented, respectively, in Figs. 2 and 3 as a function of the packing fraction η . Each frame in both figures refers to a different particle width, decreasing from frame (a) to (d) and producing a transition from oblate (platelike) to prolate (rod-like) anisotropies. In particular, uniaxial and biaxial order parameters are extremely low and basically indistinguishable in the I phase. At larger packing fractions, whose precise value depends on the particle architecture, but generally in the range $\eta = (0.2, 0.35)$, one of the uniaxial order parameters S_2 increases significantly, indicating the occurrence of a N phase. Oblate (N⁻) and prolate (N⁺) nematic phases show a surprisingly large uniaxial order parameter along their main nematic director ($\hat{\mathbf{n}}$ or $\hat{\mathbf{l}}$) in the range $S_2 = (0.6, 0.9)$, but usually $S_2 > 0.8$. This sound difference clearly distinguishes the N phase from the I phase.

At substantially larger packing fractions, the behaviour of both uniaxial and biaxial order parameters becomes strongly dependent on the particle shape anisotropy and therefore on the phases at equilibrium. For instance, in Fig. 2a (oblate HBPs), B_2 in-

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Fig. 2 Uniaxial order parameters as a function of the packing fraction for colloidal suspensions of HBPs with length L_1^* and width $W_1^* = 9$ (a), 7 (b), 4.5 (c), and 1 (d). Black, red, and blue symbols refer to $S_{2,L}$, $S_{2,T}$, and $S_{2,W}$, respectively, while the green symbols refer to the dominant biaxial order parameter. The vertical dashed lines indicate phase transitions.



Fig. 3 Uniaxial order parameters as a function of the packing fraction for colloidal suspensions of HBPs with length L_2^* and width $W_2^* = 12$ (a), 8 (b), 5 (c), and 1 (d). Black, red, and blue symbols refer to $S_{2,L}$, $S_{2,T}$, and $S_{2,W}$, respectively, while the green symbols refer to the dominant biaxial order parameter. The vertical dashed lines indicate phase transitions.

creases abruptly from 0.01 to approximately 0.54 at $\eta = 0.515$, marking the transition from an oblate nematic (N⁻) to an oblate columnar (Col⁻) phase. By contrast, in Fig. 2d (prolate HBPs), the same biaxial order parameter does not show any noticeable change across the I-N⁺ and N⁺-Sm⁺ phase transitions and only increases at $\eta > 0.7$, where a prolate columnar (Col⁺) phase is formed. Interestingly enough, the largest and smallest uniaxial order parameters can also undergo a mutual inversion as a result of an oblate-prolate transition and consequent rearrangement of the nematic directors (see Fig. 2c). At very large packing frac-

tions, all the order parameters assume values above 0.9 and a K phase is formed.

To unambiguously determine the degree of positional order within a given LC and thus distinguish between N, Sm, Col and K phases, we calculated the pair distribution functions in the directions parallel and perpendicular to the nematic directors. In particular, the $g_{\parallel,L}(r)$ in the top frame of Fig. 4 reveals the typical layered structure of a prolate smectic (Sm⁺) phase and clearly distinguishes it from a N⁺ phase, whose $g_{\parallel,L}(r)$, by contrast, is essentially flat (dashed line in the same frame). In Sm⁺ phases, it is possible to find transverse (interlayer) particles that are trapped in between neighbouring layers (see top-right snapshot in Fig 4), a scenario also detected in colloidal suspensions of uniaxia, prolate particles ^{50–52}. Nevertheless, the probability of observing such transverse particles is so low that the corresponding radial distribution function cannot actually reveal their presence.



Fig. 4 Parallel pair distribution functions along the main nematic director of prolate (top) and oblate (bottom) smectic liquid crystals of HBPs with L_1^* and $W_1^* = 1$ (top), and L_1^* and $W_1^* = 5.5$ (bottom). Dashed and solid lines refer to the $g_{\parallel}(r)$ calculated in the nematic and smectic phase, respectively. Packing fractions: 0.37 (N⁺), 0.525 (Sm⁺), 0.400 (N⁻), are 0.493 (Sm⁻). The insets show typical equilibrium configurations of each phase, with the colour gradient indicating the orientation of the particle major axis.

The radial distribution function displayed in the bottom frame of Fig. 4 (solid line) reveals a different pattern, where periodic peaks are indentified at multiples of the particle thickness. Although the layer thickness of the most recurrent Sm phases is determined by the particle length, here we find a Sm phase whose layers are as thick as the minor particle dimension, *T*, referred to as discotic or oblate smectic phase (Sm⁻). The existence of this phase has been rather controversial over the last decade as evidenced by the lack of full agreement between FMT predictions^{37,38} and MC simulations^{34,35}. The results shown here indicate that the Sm⁻ phase is remarkably stable across a wide range of particle's geometries.

Oblate and prolate Sm phases can also be distinguished from each other by analysing the relevant uniaxial order parameters, which are $S_{2,T}$ for the former and $S_{2,L}$ for the latter. In particular, for Sm⁻ phases $S_{2,T} > S_{2,L}$, whereas for Sm⁺ phases $S_{2,L} > S_{2,T}$, as observed, respectively, in frames (b) and (d) of Fig. 2 or Fig. 3. The existence of Sm⁻ and Sm⁺ phases suggests that, for intermediate geometries between the rod-like and plate-like shape, a biaxial smectic (Sm_B) phase, similar to what previously detected in systems of hard perfect tetragonal parallelepipeds³⁵, might also exist. This is indeed the case for the two particle lengths, L_1^* and L_2^* , investigated here. As a matter of fact, the uniaxial order parameters in Fig. 2c and Fig. 3c, which refer, respectively, to the particle geometries $(L_1^*, W_1^*) = (9, 4.5)$ and $(L_2^*, W_2^*) = (12, 5)$, unveil a strong orientational correlation between each of the three particle axes and confirm the formation of a Sm_B phase at $0.55 < \eta < 0.57$ for the shortest and $0.42 < \eta < 0.45$ for the longest HBPs. The existence of the Sm_B phase is further confirmed by the analysis of the biaxial order parameters, B_2 , provided in the same figures along with those of Sm⁻ and Sm⁺ phases for comparison. The Sm_B is a very peculiar phase with long-ranged translational order in the direction of the particle major axis, as the Sm⁺ phase, and long-ranged orientational order along three directions. Within each layer, there is not significant positional order and the in-layer pair distribution function decays to 1 at relatively short distances (not shown here). This lack of in-layer positional order distinguishes the Sm_B phase from a crystal phase. Typical configurations of Sm⁻ and Sm_B phases of HBPs are shown in Fig. 5. A visual inspection of the top view of the Sm_B phase seems to indicate the occurrence of a quasi-long-range orientational order along two perpendicular axes, resembling the tetratic arrangement of hard-rectangle⁵³ and hard-square⁵⁴ systems. Our preliminary calculations would confirm this scenario, but further investigation is needed to provide a more complete insight into this interesting behaviour.

At increasing packing fractions, our HBPs start to self-assemble into Col⁻ or Col⁺ phases. While in the Col⁻ phase the particles are arranged in stacks oriented along their minor axis, the Col⁺ phase is made of columns incorporating prolate particles oriented along their major axis. The pair distribution functions of representative Col⁻ and Col⁺ phases are shown in Fig. 6. Frame (a) refers to particles of length L_1^* and width $W_1^* = 8$, and frame (b) to particles of length L_1^* and width $W_1^* = 2$. Both frames display the $g_{\parallel}(r)$ calculated in the direction of the three nematic directors $\hat{\mathbf{n}}$ (solid lines), $\hat{\mathbf{m}}$ (dot-dashed lines), and $\hat{\mathbf{l}}$ (dashed lines). The intra-column structural correlations are very weak, typical of a liquid-like system, while the inter-column correlations are relatively strong and indicate a long-range ordered arrangement with the particles roughly located at multiple distances of $W_1^* = 8$ and

(a)

Fig. 5 Front and top views of biaxial (a) and oblate (b) Sm liquid crystals containing 2000 HBPs of length L_1^* and width $W_1^* = 4$, and L_1^* and width $W_1^* = 5$, respectively. Packing fractions: 0.570 (a) and 0.467 (b). The colour gradient follows the orientation of the particle major axis.

 $L_1^* = 9$ (top frame) or $W_1^* = 2$ and $T_1^* = 1$ (bottom frame) from each other. In the top frame, the slight shift of the peak between $g_{\parallel,\hat{\mathbf{n}}}(r)$ and $g_{\parallel,\hat{\mathbf{m}}}(r)$ might indicate a preferential particle orientation in the planes perpendicular to the columns, a sort of alignment between identical faces of the particles. To better address this point, we quantified the angular correlation between the particle unit vectors perpendicular to $\hat{\mathbf{l}}$ by calculating the orientation distribution function $\chi(\hat{\mathbf{x}}, \hat{\mathbf{z}}) = \langle (3\hat{\mathbf{x}}_i \cdot \hat{\mathbf{z}}_j - 1)/2 \rangle$, where $\langle ... \rangle$ indicates ensemble average over all measured orientations of particle pairs (i, j). In particular, $\chi(\hat{\mathbf{x}}, \hat{\mathbf{z}}) \simeq 0.1$, indicating a negligible particle alignment across the columns and two equally probable preferential orientations. This picture is not general though. A significant inter-column particle alignment, with a unique preferential orientation, is detected in Col⁺ phases and in Col⁻ phases consisting of HBPs with larger L/W aspect ratios, for instance $(L_1^*, W_1^*) = (9, 7.5)$, and, upon crowding, in the K phase. In these cases, the larger aspect ratio imposes a more efficient packing at similar packing fractions ($\eta \approx 0.6$) and provides a crystal-like distribution across the columns while maintaining a liquid-like translational order along them. In Fig. 7, we compare the front and top views of two Col⁻ and one Col⁺ phases where the orientation distribution function assumes the values $\chi(\hat{\mathbf{x}}, \hat{\mathbf{z}}) \simeq -0.5$ (Fig. 7a and 7c) and $\chi(\hat{\mathbf{x}}, \hat{\mathbf{z}}) \simeq 0.1$ (Fig. 7b).

Interestingly, the top views of the three snapshots in Fig. 7 unveil an inter-columnar quadratic arrangement that has been con-



Fig. 6 Frame (a): parallel pair distribution functions of an oblate columnar liquid crystal phase containing 2000 HBPs of length L_1^* and width $W_1^* = 8$ at $\eta = 0.597$. Frame (b): parallel pair distribution functions of a prolate columnar liquid crystal phase containing 2000 HBPs of length L_1^* and width $W_1^* = 2$ at $\eta = 0.809$. Solid, dot-dashed and dashed lines refer to the directions parallel to the nematic directors $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$ and $\hat{\mathbf{l}}$, respectively.



Fig. 7 Front and top views of oblate (a,b) and prolate (c) columnar liquid crystals of HBPs with length L_1^* and width $W_1^* = 7.5$ (a), $W_1^* = 8$ (b), and $W_1^* = 2$ (c). Packing fractions: $\eta = 0.590$ (a), $\eta = 0.597$ (b), and $\eta = 0.809$ (c). The colour gradient follows the orientation of the particle major axis.

sistently observed in all the Col phases found in this study. To characterise this four-fold symmetry and unambiguously distinguish it from an hexagonally-packed arrangement, we calculated the quadratic, ψ_4 , and hexatic, ψ_6 , order parameters. In Fig. 8, these two order parameters are presented as a function of the

packing fraction η for a number of systems at L_1^* and $W_1^* = 7.5$ and 8, including the Col⁻ phases shown in Fig. 7a and 7b. While both parameters are almost negligible and indistinguishable in the I phase, at increasing packing fractions it becomes evident that the quadratic order has a dominant character and fully prevails in both Col and K phases. The fluctuations observed in the quadratic and hexatic order parameters of the system with $W_1 = 8$ (solid symbols in Fig. 8) are most probably due to a number of unresolved structural defects that persist in the Col⁻ phase beyond our simulation time.



Fig. 8 Quadratic and hexatic order parameters of colloidal suspensions containing 2000 HBPs of length L_1^* and width $W_1^* = 7.5$ (empty circles) and $W_1^* = 8$ (solid circles) at different packing fractions.

Finally, in Fig. 9, we show the parallel (left frame) and perpendicular (right frame) radial distribution functions of a K phase containing short HBPs with width $W_1^* = 5.5$ and packing fraction $\eta = 0.725$. The $g_{\parallel}(r)$ functions display well-defined periodic peaks with relatively large amplitude approximately at multipredistances of 9*T*, 5.5*T* and *T* along the directors $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$ and $\hat{\mathbf{l}}$, respectively. The $g_{\perp}(r)$ functions, less intuitive than the $g_{\parallel}(r)$, are the result of the combined periodicity of two peaks existing in the planes perpendicular to each director.

4.2 Phase diagrams

As predicted by Onsager theory¹⁸, compressing a suspension of hard-body particles promotes the transition to phases with a higher degree of orientational ordering, from isotropic to LC to crystal phases. These phase transformations are driven by an increase in excluded-volume entropy, which is sufficiently large to compensate the reduction in orientational entropy. In line with these arguments, colloidal suspensions of HBPs undergo entropydriven phase transformations that substantially depend on their geometry and, as such, can produce oblate, prolate, and biaxial



Fig. 9 Parallel (left frame) and perpendicular (right frame) pair distribution functions of a crystal phase containing 1800 HBPs of length L_1^* and width $W_1^* = 5.5$ at $\eta = 0.725$. Solid, dot-dashed and dashed lines refer to the directions parallel (left frame) or perpendicular (right frame) to the nematic directors $\hat{\mathbf{n}}$, $\hat{\mathbf{m}}$ and $\hat{\mathbf{l}}$, respectively. The insets show the front and top views of an equilibrium configuration, with different colours indicating the orientation of the particle major axis.

morphologies. The phase diagrams calculated by MC simulations are presented in Figs. 10 and 11 for HBPs of length L_1^* and L_2^* , respectively. In addition, in the top frames of Figs. 12 and 13, we also show the phase diagrams for the same particle geometries as calculated from theory. The bottom frames of these figures compare the predicted boundaries of the I-N phase transition when the HBPs are assumed to be uniaxial (empty symbols) or biaxial (solid symbols).



Fig. 10 Phase diagram of HBPs with length L_1^* , and width $1 \le W_1^* \le 9$.

As far as short HBPs ($L^* = 9$) are concerned, the simulation results in Fig. 10 indicate that the I-N phase transition occurs at packing fractions that gradually increase in the prolate region from approximately 0.28 to 0.38, and then decrease in the oblate region down to 0.27. Above the I-N coexistence region, which is relatively small, but significant enough to suggest a strong firstorder character, we find the N- and N+ phases, respectively at $W_1^* \leq 3$ and $W_1^* > 3$. The prolate N phase has a relatively small stability region and transforms into a Sm⁺ phase at approximately $\eta = 0.40$. The stability of the oblate N phase appears to increase with the particle width and at $\eta > 0.40$ can transform into a Sm⁺, Sm⁻ or Col⁻ phase, depending on the degree of particle anisotropy. All these features are perfectly predicted by the theoretical phase diagram in Fig. 12, whose quantitative agreement with the simulation results is excellent. The only tangible discrepancy between theory and simulation arises from the location of upper phase boundary of the N region, which is slightly overestimated by the theory. However, we stress that in this case, we are only calculating the spinodal instability densities at which a uniaxial N phase consisting of aligned particles becomes unstable with respect to a layered structure. Similar considerations are still valid for the phase diagrams of long HBPs ($L^* = 12$), reported in Figs. 11 (simulation) and 13 (theory).

The phase diagrams of short ($L^* = 9$) and long ($L^* = 12$) HBPs exhibit a number of common features, but also some key differences mostly related to the region of stability of the nematic and columnar phases and the location of the I-N phase transition. More specifically, the I-N phase transition appears to shift to lower packing fractions at increasing particle length and, because the lower boundaries of the positionally ordered phases are not particularly influenced, the region of stability of the nematics increases too. Previous theoretical predictions based on the Zwanzig approximation locate the I-N transition of HBPs with $(L^*, W^*) = (9,3)$ at $\eta \approx 0.28^{31}$, while the results of more recent MC simulations of hard spheroplatelets, similar, but not identical, to our HBPs, are much closer to our estimations of $\eta \approx 0.35 - 0.40$, depending on the L/W aspect ratio³⁹. In both these works, the I-N transition was observed to be of a weak first-order, with an insignificant density difference between I and N phases. Although our theory confirms the first-order character of the I-N transition over the whole range of geometries examined, it reveals an I-N coexistence region that is not negligible and thus suggests a rather strong first-order signature. This is also confirmed by the analysis of the equations of state (see ESI⁺), which unveil the existence of slight discontinuities or sudden changes in the slope of η vs P^* . The strong first-order character of the I-N transition can dramatically determine the kinetics of formation of the N phase, most probably characterised by the occurrence of temporary metastable domains persisting over relatively long time scales. Further investigation is however necessary to address this qualitative intuition. The extension of the I-N coexistence region can be more easily appreciated in the bottom frame of Figs. 12 and 13, where we compare the effect of assuming a uniaxial or

biaxial particle geometry on the location of the I and N phase boundaries. We notice that relatively strong first-order I-N transitions were also reported in the simulation work by John and Escobedo on systems of hard tetragonal parallelepipeds with square cross section and L/W = 6.5 and 8^{34} . We also notice that, according to both theory and simulation, the exact location of the I-N transition depends on the particle width across the complete range of prolate and oblate shapes, again in qualitative agreement with former simulation results on cuboids³⁴.



Fig. 11 Phase diagram of HBPs with thickness *T*, length L = 12T, and width $1 \le W_2^* \le 12$.

It is also interesting to highlight that assuming a uniaxial rather than biaxial geometry, when investigating the I-N transition of freely-rotating HBPs, determine a shifting of the coexistence region towards larger packing fractions. In Fig. 12b, this assumption especially influences the I-N phase boundaries of rod-like particles with square cross section, but does not have any significant effect at or close to the self-dual shape. Restricting the orientations of HBPs to six seems to have a much more relevant impact on the description of their phase behaviour than assuming them to be uniaxial.

Furthermore, our simulation and theoretical results do not provide any sound evidence of the existence of an I-N_B transition. The boundary between the N⁻ and N⁺ phases is basically located at the particle width $W = \sqrt{LT}$, corresponding to the self-dual shape at which, according to theory^{26,31,55} and simulation^{32,39} on a spectrum of hard-core biaxial particles, including HBPs, a second-order I-N_B phase transition should be observed. Although our extensive simulations could not confirm the existence of the N_B phase, at least for the particular board-like geometries investigated here, they revealed the formation of a Sm_B phase, being approximately constrained between the Sm⁻ and Sm⁺ phases and consisting of HBPs with $W \approx 1.4\sqrt{LT}$. The eventual occurrence of



Fig. 12 (a) Phase diagrams for HBPs with L_1^* calculated from theory. Red squares and green triangles denote the I-N phase transition, blue and orange inverted triangles denote, respectively, the N-Sm and N-Col instability densities, and blue open squares and pink open triangles denote the N_U-N_B transition. (b) Comparison of the predicted I-N phase transition found when considering the board particles as biaxial (solid symbols) and as uniaxial (empty symbols). For the uniaxial predictions, we ignore ordering of the angle γ (rotations about the particle long-axis).

the N⁻-N_B and N⁺-N_B phase transitions were examined theoret ically, by keeping one of the particle axes perfectly aligned with the nematic director and allowing the other two particle axes to reorient. In particular, we observed that the N_B is pre-empted by the Sm phase over all its range and cannot form unless the Sm phase is somehow destabilised (see Figs. 12a and 13a). W_{\odot} did not examine the range of stability of the Sm phase, but only the spinodal instability boundaries at which a perfectly aligned N_U phase first becomes unstable with respect to a layered stru ture. Our predictions locate the N-Sm instability of short HB. at $0.42 < \eta < 0.48$, depending on the particle width (blue in verted triangles in Fig. 12a), in very good agreement with the N⁺-Sm⁺ and N⁻-Sm⁻ phase boundaries reported in Fig. 10. As far as long HBPs are concerned, our theory predicts the occur rence of these density instabilities at similar packing fractions, that is $0.42 < \eta < 0.49$, depending on W_2^* (blue inverted triangles in Fig. 13a), again in excellent agreement with the simulation results. It should be noticed that the N-Sm instability densities at $W_1^* = 3.5$ and $4 \le W_2^* \le 5$ are missing in Figs. 12a and 13a, respectively. Our theory cannot account for the N⁻-Sm⁺ (oblateto-prolate) phase transition, which is observed in simulations, but would only provide the instability density of a hypothetical transition to an oblate smectic phase. Aware of the limitations of our theory, we have therefore decided to omit these points.

At sufficiently large packing fractions, both oblate and prolate

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Fig. 13 (a) Phase diagrams for HBPs with L_2^* calculated from theory. Red squares and green triangles denote the I-N phase transition, blue and orange inverted triangles denote, respectively, the N-Sm and N-Col instability densities, and blue open squares and pink open triangles denote the N_U-N_B transition. (b) Comparison of the predicted I-N phase transition found when considering the board particles as biaxial (solid symbols) and as uniaxial (empty symbols). For the uniaxial predictions, we ignore ordering of the angle γ (rotations about the particle long-axis).

HBPs can form Col phases. The region of existence of the Col phase and its stability with respect to the Sm phases is very similar for short and long HBPs. The most remarkable difference to mention is the ability of short HBPs to self-assemble into Col⁻ phases in a region of the phase diagram where long HBPs can only form Col⁺ phases, that is for $W < \sqrt{LT}$. More generally, the intriguing result of oblate (prolate) HBPs to self-assemble into prolate (oblate) phases is also detected at lower packing fractions, where oblate HBPs ($W > \sqrt{LT}$) can aggregate into Sm⁺ phases. As a consequence of this peculiar behaviour, some particle geometries undergo oblate-prolate-oblate transitions at increasing pressure. This is for instance the case of systems with particle of size (L_1^*, L_1^*) W_1^* = (9, 4) and (L_2^*, W_2^*) = (12, 4.5), where an N⁻-Sm⁺ followed by a Sm⁺-Col⁻ phase transition is observed. Even more intriguing is the sequence of phase transitions observed for HBPs of size (L_2^*, L_2^*) W_2^* = (12, 3.8), which undergo a remarkable N⁻-Sm⁺-Col⁻-Col⁺ transformation across the range $0.35 < \eta < 0.66$.

The relative Col/Sm phase stability in suspensions of polydisperse colloidal platelets has recently been investigated by density functional theory within the FMT formalism⁵⁶. In monodisperse systems, the particle geometry play a dominant role across the range of anisotropies studied here. Both short and long HBPs are able to self-assemble into Col phases regardless of their prolate or oblate geometry. In addition, for particularly pronounced oblate anisotropies, at which L/W < 1.3, the range of stability of the Col⁻ phase increases significantly and a direct N⁻-Col⁻ transformation, without the occurrence of the Sm⁻ phase, is observed. Our theoretical predictions in Figs. 12a and 13a show that the N⁻-Col⁻ transition is indeed favoured for plate-like particles, whose nematic-columnar instability density is found to be lower than the nematic-smectic instability density at $W_1^* > 7.5$ and $W_2^* > 10$. Depending on the particle width, the columnar phase can be obtained by compressing N⁻, Sm⁻, Sm_B or Sm⁺ phases. The occurrence of all these phase transitions is determined over all the particle width analysed here, from prolate ($W < \sqrt{LT}$) to oblate $(W > \sqrt{LT})$ geometries. HBPs with a quasi self-dual shape, for instance $(L_2^*, W_2^*) = (12, 3.6)$, are very peculiar because at increasing packing, they can orient along either their shortest or longest axis or both and thus can switch from prolate to oblate to biaxial phases. In the range $\sqrt{LT} < W < 4.5T$, these particles undergo a N^- to Sm^+ transition first and then, at larger pressures, a transition from the Sm⁺ to the Col⁻ phase, which has a significant degree of biaxiality. Since we did not study the details of the kinetics of Sm⁺ to Col⁻ phase transformation, we can only speculate that an in-layer reorganisation of the particles takes place at increasing densities and promotes a gradual micro-segregation of the smectic layers in separate stacks. Also prolate HBPs are able to form columnar phases, as was previosly observed in systems of hard tetragonal parallelepipeds 34 . The Col⁺ phase is stable at relatively high density, especially in systems of short HBPs, where the transition to the K phase is only found at $\eta > 0.9$. By contrast, to the best of our knowledge, uniaxial particles are not able to form Col phases^{38,57}, unless a degree of size dispersity^{58,59} or flexibility⁶⁰ is incorporated.

5 Conclusions

In summary, we have investigated the phase behaviour and mapped out the phase diagram of colloidal suspensions of short and long HBPs, which, depending on their length-to-width ratio, are able to self-assemble into oblate, prolate, and biaxial phases with a large degree of positional and/or orientational order. We have characterised these phases by calculating uniaxial and biaxial order parameters as well as the structural correlation between the particles along the phase directors and perpendicularly to them. Short and long HBPs exhibit similar phase diagrams, with an I-N phase transformation at approximately $0.2 < \eta < 0.3$, depending on the particle width, and a transition from prolate to oblate nematic LCs at the so-called self-dual shape, where $W = \sqrt{LT}$. Our theory, a generalisation of Onsager theory to incorporate particle biaxiality, is able to capture both these features very well. In addition, it reveals an I-N coexistence region that is significantly larger than that predicted by previous studies on identical^{29,31} or similar^{26,39} particle geometries, but in agreement with the simulations by John and Escobedo on hard tetragonal parallelepipeds³⁴. This coexistence region, which reveals a

relatively strong first-order character, is virtually independent on the particle width across the complete range of prolate and oblate shapes investigated here.

More surprisingly, we did not observe, neither by simulations nor theory, the formation of a stable biaxial nematic phase. While at the self-dual shape and sufficiently large densities a secondorder I-N_B transition is generally predicted by theory^{26,31,55}, our HBPs undergo transitions from I to N_{II} to Sm phase and no evidence of biaxiality is observed. We notice that, by limiting the particle orientations to six, these theories locate the I-N transition at packing fractions $\eta < 0.3$ at which we still observe I phases. At such moderate densities, the formation of a Sm phase, which we only detect at $\eta > 0.4$, is very unlikely and consequently the N_B phase would be indirectly favoured. We conclude that a biaxial geometry, per se, might not be enough to observe biaxial phases and a degree of size dispersity, as reported experimentally²⁸ and suggested by theory^{27,29}, is crucial to weaken the stability of the Sm phase and thus create the best conditions to form the N_B phase. Contrary to the N_B, the Sm_B phase has been detected for the two particle lengths L_1 and L_2 , although within a very small range of stability.

Finally, we have also shed light on the existence of the discotic (or oblate) smectic phase. The Sm⁻ phase, which consists of particles with their long axes randomly oriented within the smectic layers, has been found in the phase diagram of both short and long HBPs. Although the Sm⁻ phase had been predicted by the FMT and lattice MC simulations, in both cases within the Zwanzig approximation^{36,37}, it was not observed in off-lattice MC simulations of freely rotating hard parallelepipeds with square cross section^{34,35}. The latter geometry promotes instead the formation of a cubatic-like mesophase, the so-called parquet phase, where the particles are arranged in stacks oriented roughly perpendicular to one another and without formation of layers^{34,35}. The board-like geometry of our particles, very different from that of a cuboid, does not promote the formation of this phase, but can definitively confirm the existence of the Sm⁻ phase.

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