

Supplemental Material

Entropic Stabilization of Biaxial Nematics: a Competition with Uniaxial and Positional Order for Extremely Long Particles

Simone Dussi^{1,3,†}, Nikos Tasios^{1,†}, Tara Drwenski^{2,†}, René van Roij², Marjolein Dijkstra¹

¹*Soft Condensed Matter, Debye Institute for Nanomaterials Science,
Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands*

²*Institute for Theoretical Physics, Utrecht University,
Princetonplein 5, 3584 CC Utrecht, The Netherlands**

SIMULATION METHODS

To study the phase behavior of polyhedral hard rods (either cuboids or triangular prisms) we employed standard Monte Carlo (MC) simulations either in the *NPT* or *NVT* ensemble. System sizes range from $N \simeq 2000$ to $N \simeq 5000$ and several million MC steps are performed before obtaining equilibrated configurations. For *NVT*-MC simulations, each MC step consists on average of $N/2$ attempts of translating a random particle and $N/2$ attempts of rotating a random particle. In the case of *NPT*-MC simulations, an additional attempt is performed at each step in order to either scale isotropically the box volume or change only one edge of the cuboidal simulation box. Equilibrium average density, order parameters and diffraction patterns are calculated based on around one hundred equilibrated configurations. For systems of rhombic particles, cluster moves are used in *NPT*-MC to perform volume changes move [1, 2]. Particles interact only via a hard-core potential and overlaps are detected using algorithms based either on triangular-triangular intersection-detection, using the RAPID library [3], or based on the GJK algorithm [4, 5], depending on the particle model. In addition to MC simulations, rhombic platelets (and some selected cases of cuboids) are simulated with state-of-the-art Event-Driven Molecular Dynamics (EDMD) [2]. The GJK overlap-detection algorithm is combined with conservative advancement and near-neighbor list to efficiently simulate around $N \sim 2 \cdot 10^3$ rhombic particles in the *NVT* ensemble. The moment of inertia and the mass of all particles is set to 1 and the system is simulated for over $10^4 \tau$, where $\tau = v_p^{1/3}/v_0$ is the reduced time unit, with v_p particle volume and v_0 the initial velocity of each particle (velocities are initialized by using random unit vectors whereas angular velocities are initially set to zero). The equilibrium pressure is calculated from the particle collisions in the equilibrated configurations.

ORDER PARAMETERS AND PHASE IDENTIFICATION

To quantify the orientational and positional order in the system we use several order parameters. The nematic

order parameters for the biaxial particle models considered here are obtained by first constructing the following tensors

$$\mathcal{Q}_{\alpha\beta}^{\hat{\mathbf{a}}} = \frac{1}{N} \sum_{i=1}^N \left[\frac{3}{2} \hat{\mathbf{a}}_{i\alpha} \hat{\mathbf{a}}_{i\beta} - \frac{\delta_{\alpha\beta}}{2} \right], \quad (1)$$

where $\alpha, \beta = x, y, z$ component and $\hat{\mathbf{a}} = \hat{\mathbf{u}}, \hat{\mathbf{v}}, \hat{\mathbf{w}}$ denotes the three symmetry axes of the particle (see also Fig. 1 of the main text) and where N is the number of particles and $\delta_{\alpha\beta}$ is the Kronecker delta. By diagonalizing each of these tensors we obtain three eigenvalues $\lambda_a^+ \geq \lambda_a^0 \geq \lambda_a^-$. We identify the (scalar) order parameter associated with the nematic order of the axis $\hat{\mathbf{a}}$ as the maximum of these eigenvalues: $S^{\hat{\mathbf{a}}} \equiv \lambda_a^+$. The corresponding eigenvector is the nematic director $\hat{\mathbf{n}}_{\hat{\mathbf{a}}}$. These order parameters are used to distinguish between oblate and prolate nematic phases, and only partially for biaxial nematic phases. In fact, to precisely quantify the degree of (macroscopic) biaxial alignment of a nematic phase an additional (scalar) order parameter $\mathcal{B}$ is employed. Notice that different notations and slightly different approaches are employed to calculate the biaxial order parameter in computer simulations [6–10]. We follow the procedure in Refs. [6, 7] that consists in first identifying an appropriate orthonormal basis for the laboratory reference frame that is aligned with the two main directions of the biaxial phase. For each configuration, we identify the largest $S^{\hat{\mathbf{a}}}$ and we define the z -axis of the laboratory reference frame as $\hat{\mathbf{Z}} \equiv \hat{\mathbf{n}}_{\hat{\mathbf{a}}}$, with $\hat{\mathbf{a}}$ the principle main axis of the particle. Then, we identify the second largest nematic order parameter $S^{\hat{\mathbf{b}}}$ and we define the second axis of the laboratory reference frame as $\hat{\mathbf{Y}} \equiv \hat{\mathbf{n}}_{\hat{\mathbf{b}}} - (\hat{\mathbf{n}}_{\hat{\mathbf{b}}} \cdot \hat{\mathbf{Z}}) \hat{\mathbf{Z}} \simeq \hat{\mathbf{n}}_{\hat{\mathbf{b}}}$. Analogously, we define the third axis of the laboratory frame by orthogonalizing the third nematic director: $\hat{\mathbf{X}} \equiv \hat{\mathbf{n}}_{\hat{\mathbf{c}}} - (\hat{\mathbf{n}}_{\hat{\mathbf{c}}} \cdot \hat{\mathbf{Z}}) \hat{\mathbf{Z}} - (\hat{\mathbf{n}}_{\hat{\mathbf{c}}} \cdot \hat{\mathbf{Y}}) \hat{\mathbf{Y}}$, with $\hat{\mathbf{c}}$ the third symmetry axis of the particle. Finally, we compute

$$\mathcal{B} = \frac{1}{3} \left(\hat{\mathbf{Y}} \cdot \mathcal{Q}^{\hat{\mathbf{b}}} \cdot \hat{\mathbf{Y}} + \hat{\mathbf{X}} \cdot \mathcal{Q}^{\hat{\mathbf{c}}} \cdot \hat{\mathbf{X}} - \hat{\mathbf{Y}} \cdot \mathcal{Q}^{\hat{\mathbf{c}}} \cdot \hat{\mathbf{Y}} - \hat{\mathbf{X}} \cdot \mathcal{Q}^{\hat{\mathbf{b}}} \cdot \hat{\mathbf{X}} \right), \quad (2)$$

where $\mathcal{B}$ is normalized such that it ranges from 0 to 1. Low values of $\mathcal{B}$ correspond to an isotropic phase or to a uniaxial phase and high values to a biaxial phase. In Refs. [10, 11] a biaxial nematic phase is further classified

in N_{b-} and N_{b+} , depending on the leading uniaxial order parameter. The authors observed that N_{b-} is always formed at lower densities than N_{b+} , which indicates the preference for oblate order, in agreement with our results. For simplicity, we avoided this additional classification.

To identify the phase transition to a positionally ordered phase we generalize an order parameter that, for example, is often used to identify smectic phases of spherocylinders:

$$\tau^{\hat{\mathbf{a}}} = \max_l \left| \sum_{j=1}^N \exp \left(\frac{2\pi}{l} i \mathbf{r}_j \cdot \hat{\mathbf{n}}_{\hat{\mathbf{a}}} \right) \right|, \quad (3)$$

where l is a real number, $\mathbf{r}_j$ denotes the position of particle j and as before $\hat{\mathbf{n}}_{\hat{\mathbf{a}}}$ indicates the nematic director associated to the axis $\hat{\mathbf{a}}$. A large $\tau^{\hat{\mathbf{a}}}$ indicates one-dimensional positional order (layering) associated to the particle axis $\hat{\mathbf{a}}$. If only one of these order parameters is significantly larger than zero (typically > 0.4), a smectic phase (Sm_+ , Sm_- or Sm_b depending on which particle axis is aligned and if the biaxial order parameter is large) is identified. Two $\tau^{\hat{\mathbf{a}}} > 0$ correspond to a columnar phase and three $\tau^{\hat{\mathbf{a}}} > 0$ to a crystal phase. In addition, the positionally ordered phases are also identified by checking the (projected) diffraction patterns. In particular, the particle positions are projected on the plane defined by the two smallest nematic directors and subsequently we calculate the Fourier transform of a two-dimensional histogram of the projected positions.

Representative configurations, diffraction patterns, and trends for the order parameters of the different models are shown in Figs. 1, 2, 3, 4.

THEORY

In this section, we describe our theoretical techniques and show some additional results for hard cuboids. In density functional theory, we express the free energy as a functional of the single-particle density $\rho(\mathbf{r}, \Omega)$. We assume that the single-particle density has no spatial dependence, i.e. $\rho(\mathbf{r}, \Omega) = \rho\psi(\Omega)$, where $\rho = N/V$ is the average density in a system of N particles and volume V , and $\psi(\Omega)$ is the probability to find a particle with orientation $\psi(\Omega)$ in the interval $d\Omega$. The orientation of rigid, biaxial particles can be given by three Euler angles $\Omega = (\alpha, \beta, \gamma)$, with an integration measure $\int d\Omega = \int_0^{2\pi} d\alpha \int_0^\pi \sin\beta d\beta \int_0^{2\pi} d\gamma = 8\pi^2$. The free energy density can be written as

$$\frac{\beta F[\psi(\Omega)]}{V} = \rho(\ln \mathcal{V}\rho - 1) + \rho \int d\Omega \psi(\Omega) \ln \psi(\Omega) + \rho^2 B_2 + \frac{\rho^3}{2} B_3 + \dots, \quad (4)$$

where $\beta = 1/(k_B T)$ is the inverse thermal energy and $\mathcal{V}$ is an irrelevant thermal volume factor. In the second-

virial approximation, we truncate the excess free energy at B_2 and similarly in the third-virial theory we truncate at B_3 . The second-virial term is

$$B_2 = \frac{1}{2} \int d\Omega_1 \int d\Omega_2 E(\Omega_{12}) \psi(\Omega_1) \psi(\Omega_2), \quad (5)$$

where $\Omega_{12} = \Omega_2^{-1} \Omega_1$ is the relative orientation between two particles with orientations Ω_1 and Ω_2 . The excluded volume $E(\Omega)$ in Eq. (5) is defined as

$$\begin{aligned} E(\Omega_{12}) &= - \int d\mathbf{r}_{12} f(\mathbf{r}_{12}, \Omega_{12}) \\ &= - \int d\mathbf{r}_{12} (\exp[-\beta U(\mathbf{r}_{12}, \Omega_{12})] - 1), \end{aligned} \quad (6)$$

where $f(\mathbf{r}_{12}, \Omega_{12})$ is the Mayer function, $U(\mathbf{r}_{12}, \Omega_{12})$ is the pair potential, and $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ is the vector connecting the centers of the two particles. For hard particles we assume the pair potential to be

$$\beta U(\mathbf{r}_{12}, \Omega_{12}) = \begin{cases} \infty, & \text{1 and 2 overlap;} \\ 0, & \text{otherwise.} \end{cases} \quad (7)$$

For hard cuboids, an analytic expression for $E(\Omega)$ is known [12]. The third-virial term is

$$B_3 = \frac{1}{3} \int d\Omega_1 \int d\Omega_2 \int d\Omega_3 \hat{E}(\Omega_{12}, \Omega_{13}) \psi(\Omega_1) \psi(\Omega_2) \psi(\Omega_3),$$

with

$$\begin{aligned} \hat{E}(\Omega_{12}, \Omega_{13}) &= - \int d\mathbf{r}_{12} \int d\mathbf{r}_{13} [f(\mathbf{r}_{12}, \Omega_{12}) f(\mathbf{r}_{13}, \Omega_{13}) \\ &\quad \times f(\mathbf{r}_{13} - \mathbf{r}_{12}, \Omega_{12}^{-1} \Omega_{13})]. \end{aligned} \quad (8)$$

First, we consider using the Zwanzig model, where we approximate the orientation distribution function of the six discrete, orthogonal orientations as $\psi(\Omega) = \psi_i$ with $i = 1, \dots, 6$. Following Ref. [13], we can define the orientation vectors

$$\begin{aligned} \mathbf{X} &= (L, M, S, L, M, S), \\ \mathbf{Y} &= (M, S, L, S, L, M), \\ \mathbf{Z} &= (S, L, M, M, S, L), \end{aligned} \quad (9)$$

such that the dimensions of a particle with orientation i in the $\hat{x}, \hat{y}, \hat{z}$ directions are X_i, Y_i, Z_i , respectively. Now the excluded volume [Eq. (6)] of two particles with orientations i and j is simply given by [13]

$$E_{ij} = (X_i + X_j)(Y_i + Y_j)(Z_i + Z_j). \quad (10)$$

Similarly, we can write the three-particle excluded volume [Eq. (8)] for our Zwanzig model as

$$\begin{aligned} \hat{E}_{ijk} &= (X_i X_j + X_j X_k + X_i X_k) \\ &\quad \times (Y_i Y_j + Y_j Y_k + Y_i Y_k)(Z_i Z_j + Z_j Z_k + Z_i Z_k). \end{aligned} \quad (11)$$

Using Eqs. (9)-(11), and minimizing the free energy [Eq. (4) with appropriate replacements of $\int d\Omega \rightarrow \sum_{i=1}^6$]

with respect to ψ_i at fixed ρ with the normalization condition $\sum_{i=1}^6 \psi_i = 1$ gives an Euler-Lagrange equation which can be solved iteratively for the equilibrium distribution ψ_i^{eq} . Then ψ_i^{eq} can be used to identify the phase and to obtain the equilibrium free energy.

In our second model, the orientations are continuous rather than discrete and we instead consider expanding all Euler angle dependences in a complete basis of Wigner matrices $\mathcal{D}_{mn}^l(\Omega)$. For the excluded volume this gives

$$E(\Omega_{12}) = \sum_{l=0}^{\infty} \sum_{m,n=-l}^l E_{mn}^l \mathcal{D}_{mn}^l(\Omega_{12}), \quad (12)$$

where we can use the orthogonality of the Wigner matrices to write the coefficients as

$$E_{mn}^l = \frac{2l+1}{8\pi^2} \int d\Omega E(\Omega) \mathcal{D}_{mn}^l(\Omega)^*. \quad (13)$$

For $\psi(\Omega)$ we expand

$$\psi(\Omega) = \sum_{l=0}^{\infty} \frac{2l+1}{8\pi^2} \sum_{m,n=-l}^l \langle \mathcal{D}_{mn}^l \rangle^* \mathcal{D}_{mn}^l(\Omega), \quad (14)$$

where the coefficients $\langle \mathcal{D}_{mn}^l \rangle$ are order parameters, since they are given by

$$\langle \mathcal{D}_{mn}^l \rangle = \int d\Omega \mathcal{D}_{mn}^l(\Omega) \psi(\Omega). \quad (15)$$

We can also choose to expand the logarithm of the orientation distribution function as

$$\psi(\Omega) = \frac{1}{Z} \exp \left[\sum_{l=0}^{\infty} \sum_{m,n=-l}^l \psi_{mn}^l \mathcal{D}_{mn}^l(\Omega) \right], \quad (16)$$

with the normalization of $\psi(\Omega)$ assured by the factor

$$Z = \int d\Omega \exp \left[\sum_{l=0}^{\infty} \sum_{m,n=-l}^l \psi_{mn}^l \mathcal{D}_{mn}^l(\Omega) \right]. \quad (17)$$

We prefer the expansion Eq. (16), since the coefficients ψ_{mn}^l are unbounded and this expansion is expected to converge faster than Eq. (14). The Euler-Lagrange equation for the second-virial theory is then

$$\psi_{mn}^l = -\rho \sum_{p=-l}^l E_{pn}^l \langle \mathcal{D}_{mp}^l \rangle^* \quad (18)$$

which together with Eq. (15) can be solved for the set of coefficients ψ_{mn}^l , where the expansion in Eq. (16) is truncated at some $l = l_{\text{max}}$. Based on the particle and phase symmetries, the number of ψ_{mn}^l coefficients can be reduced to those with even l, m, n [14] and in addition, since $\psi(\Omega)$ is real we find that $\psi_{mn}^l = (-1)^{m-n} \psi_{-m-n}^l$. Here we focus on the coefficients with $l = 2$, which are the only

ones required by symmetry [14] and also the most important ones close to the dual shape where the isotropic-nematic transition is weakly first order. Of course, at higher densities we expect this approximation to be quantitatively inaccurate and the higher order (even) l coefficients to be important.

For the full-orientation third-virial theory, we also expand

$$\hat{E}(\Omega_{12}, \Omega_{13}) = \sum_{l,m,n} \sum_{l',m',n'} \hat{E}_{mm'nn'}^{ll'} \mathcal{D}_{mn}^l(\Omega_{12}) \mathcal{D}_{m'n'}^{l'}(\Omega_{13}), \quad (19)$$

where for brevity we write $\sum_{lmn} = \sum_{l=0}^{\infty} \sum_{m,n=-l}^l$, and where the coefficients are

$$\hat{E}_{mm'nn'}^{ll'} = \frac{2l+1}{8\pi^2} \frac{2l'+1}{8\pi^2} \int d\Omega_{12} \int d\Omega_{13} \hat{E}(\Omega_{12}, \Omega_{13}) \times \mathcal{D}_{mn}^l(\Omega_{12})^* \mathcal{D}_{m'n'}^{l'}(\Omega_{13})^*. \quad (20)$$

We calculate $\hat{E}_{mm'nn'}^{ll'}$ using Monte Carlo integration, with either 100 or 200 independent runs of with 10^{10} MC steps [15, 16]. The third-virial Euler-Lagrange equation is

$$\psi_{mn}^l = -\rho \sum_{p=-l}^l E_{pn}^l \langle \mathcal{D}_{mp}^l \rangle^* - \frac{\rho^2}{2} \sum_{\tilde{l}\tilde{m}\tilde{n}\tilde{p}} \sum_{l'm'n'p'} \hat{E}_{\tilde{m}\tilde{m}'\tilde{n}\tilde{n}'}^{\tilde{l}\tilde{l}'} (21) \times C(\tilde{l}, \tilde{p}; l', p'; l, m) C(\tilde{l}, \tilde{n}; l', n'; l, n) \langle \mathcal{D}_{\tilde{p}\tilde{m}}^{\tilde{l}} \rangle^* \langle \mathcal{D}_{p'm'}^{l'} \rangle^*,$$

where C is the Clebsch-Gordan coefficient that arises from integrals over three Wigner matrices. Once the second or third-virial Euler-Lagrange equation is solved for the equilibrium $\{\psi_{mn}^l\}$, these can be used to obtain the order parameters [Eq. (15)] and the free energy [Eq. (4)].

Following the convention of Ref. [8], we define four order parameters [which are proportional to those in Eq. (15)], all of which are zero in the isotropic phase. In a uniaxial phase, the order parameters S and U are nonzero and $P = 0 = F$, with $S < 0$ corresponding to an oblate nematic N_- , and $S > 0$ corresponding to a prolate nematic N_+ . In a biaxial nematic, all four of these order parameters are nonzero.

In Fig. 5, we show the free energy differences [(a),(c),(e)] between the phases and the order parameters [(b),(d),(f)] as a function of packing fraction $\eta = \rho v_p$ using the full second-virial theory for three shapes with $M^* = 8$ and: $L^* = 63$ (a-b), $L^* = 64$ (c-d), and $L^* = 65$ (e-f). The plot of the free energy difference between the uniaxial and biaxial phases at $\nu = 0$ ($L^* = 64$) shows that the biaxial phase has a higher free energy than the uniaxial nematic (oblate or prolate, since these have identical free energies) for a small range of packing fractions above the isotropic phase, which corresponds to the dotted line at $\nu = 0$ in Fig. 4(c) of the main text. Note that the order parameters shown in Fig. 5(d) are for both the biaxial nematic N_b , which is metastable in the region $0.1 \lesssim \eta \lesssim 0.17$, and for the prolate nematic N_+ . We

found that there was no direct isotropic-biaxial nematic transition for $M^* = 8$, even if the Wigner matrix expansion was truncated at $l = 4$ or $l = 6$ (not shown). We also note that the isotropic-nematic coexistence region is extremely small for all shapes in the main text phase diagram Fig. 4(c), which is to be expected around the dual shape, though this is perhaps also underestimated by the truncation at $l = 2$.

We make similar plots of the free energy differences between phases as a function of packing fraction η for our full-orientation third-virial theory in Fig. 6, for three shapes from main text Fig. 4(d). Here we see that for the dual shape [Fig. 6(a)], the oblate nematic is always favored over the prolate. For a more rod-like cuboid [Fig. 6(b)], the prolate is favored at low packing fraction and the oblate at higher packing fractions. For an even more rod-like cuboid [Fig. 6(c)], the prolate nematic is favored for a larger range of densities. The free energies in Fig. 6 are typical of all shapes we studied, and in the main text Fig. 4(d) we choose (somewhat arbitrarily) to label the nematic phase sequences up to $\eta = 0.4$ for long particles ($L \geq 50$) and up to $\eta = 0.6$ for short particles ($L < 50$). However, we have not studied the stability of the nematic phases with respect to positionally ordered phases. We also found that the biaxial nematic phase shifts to higher densities (for Fig. 6(a) $\eta \approx 0.3$, not shown) compared to what we found for the second-virial theory, and this phase has very small biaxial order parameters $P, F \sim 0.01$ (not shown). However, we caution that at these high densities our theory is not quantitatively accurate, both because we only take the $l = 2$ term in the Wigner expansion and because the third virial term dominates over the second, and so we focus our attention on the uniaxial nematic behavior close to the isotropic-nematic transition. For all L^* studied, we found that at $\nu = 0$ the oblate nematic is preferred over the prolate within the full third-virial theory.

We also looked at the importance of the third-virial term as a function of particle aspect ratio. For spherocylinders in the isotropic phase, the ratio of the third-virial term to the second squared $B_{3,\text{iso}}/B_{2,\text{iso}}^2 \approx 0.3$ for short spherocylinders ($L/D = 10$) and less than 0.07 for

long spherocylinders ($L/D = 100$) [17, 18]. For dual-shaped cuboids (with $L^* = M^{*2}$), the same ratio between the virial terms is larger than 0.45 for $L^* = 10$ and about 0.25 for $L^* = 100$. Clearly, for the aspect-ratios studied here the third-virial term cannot be safely neglected, and perhaps even the higher virial terms should be considered.

* m.dijkstra@uu.nl; ³ Present address: Physical Chemistry and Soft Matter, Wageningen University, Stippeneng 4, 6708 WE, Wageningen, The Netherlands; [†] These authors contributed equally to this work.

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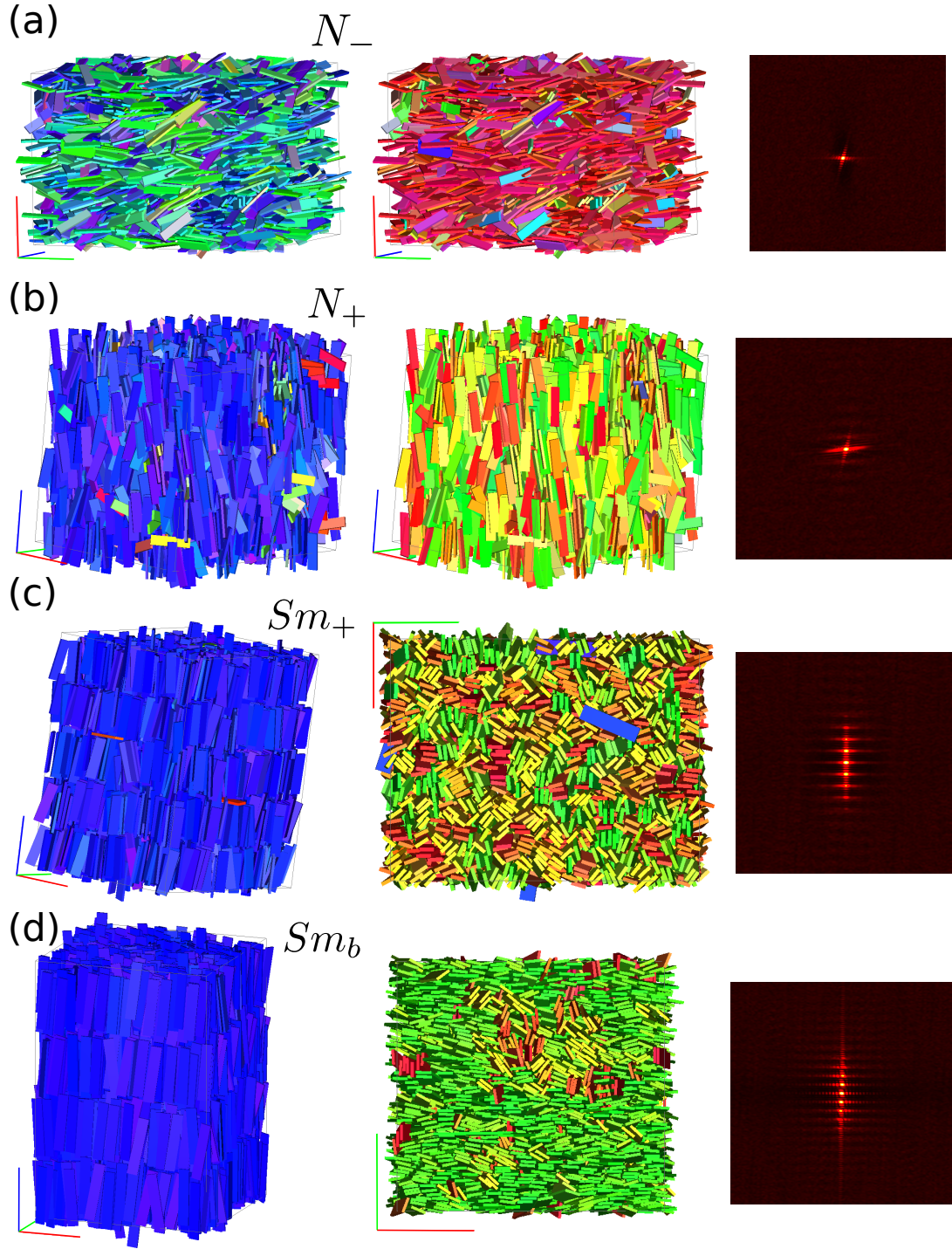


FIG. 1. Representative snapshots and corresponding diffraction patterns for cuboids forming (a) N_- ($L^* = 16$, $M^* = 4$, $\beta P v_p = 2.50$), (b) N_+ ($L^* = 16$, $M^* = 4$, $\beta P v_p = 3.0$), (c) Sm_+ ($L^* = 16$, $M^* = 4$, $\beta P v_p = 4.0$), and (d) Sm_b ($L^* = 30$, $M^* \simeq 5.477$, $\beta P v_p = 4.50$). In the left panels, the particles are colored according to the orientation of their long axis $\hat{\mathbf{u}}$ and in the middle panels according to the orientation of their short axis $\hat{\mathbf{w}}$ (cfr. Fig. 1 of the main text). Colors are defined according to the three axes of the simulation box (red, green, blue segments). Diffraction patterns are calculated in the plane defined by $\frac{2\pi}{\mathbf{n}_u} \simeq \frac{2\pi}{z}$ and $\frac{2\pi}{\mathbf{n}_v} \simeq \frac{2\pi}{x}$ (i.e., the reciprocal of the “blue”-“red” axis shown in the snapshots). In the positionally-ordered smectic phase the sequence of bright dots is along the (reciprocal) main nematic director (corresponding to the reciprocal “blue” axis).

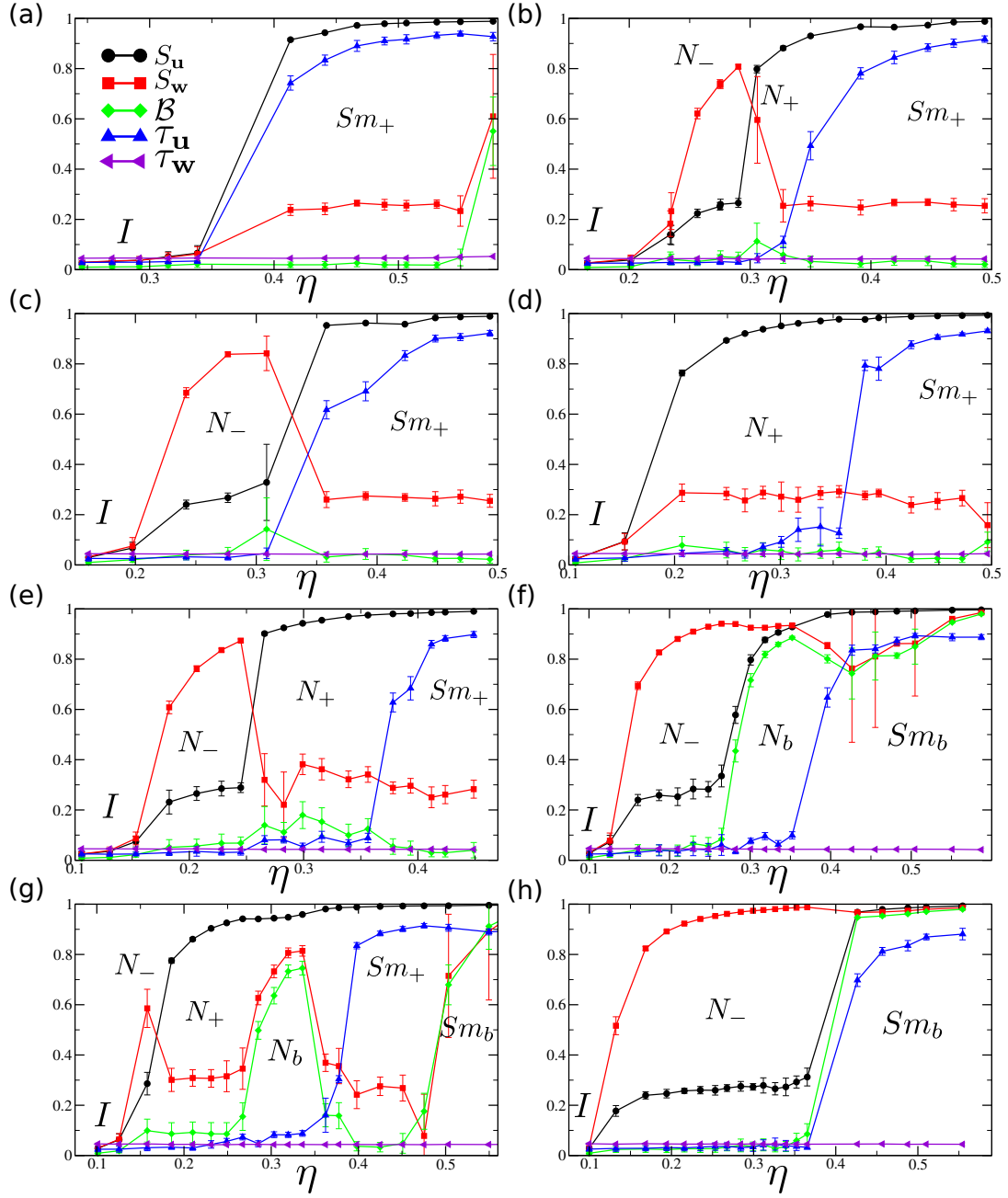


FIG. 2. Order parameters as a function of packing fraction η for hard cuboids obtained by MC-NPT simulations. Symbols correspond to simulation data and bars indicate standard deviation. The keys are the same for all the graphs. (a) $L^* = 10$, $M^* \simeq 3.16$ ($\nu = 0$), (b) $L^* = 16$, $M^* = 4$ ($\nu = 0$), (c) $L^* \simeq 18.06$, $M^* = 4.25$ ($\nu = 0$), (d) $L^* = 25$, $M^* = 4.25$ ($\nu \simeq 0.065$), (e) $L^* = 25$, $M^* = 4.75$ ($\nu \simeq 0.02$), (f) $L^* = 30$, $M^* \simeq 5.47$ ($\nu = 0$), (g) $L^* = 30$, $M^* = 5$ ($\nu \simeq 0.03$), and (h) $L^* = 30$, $M^* = 7$ ($\nu \simeq -0.09$). Notice that we define $\nu = S/M - M/L$.

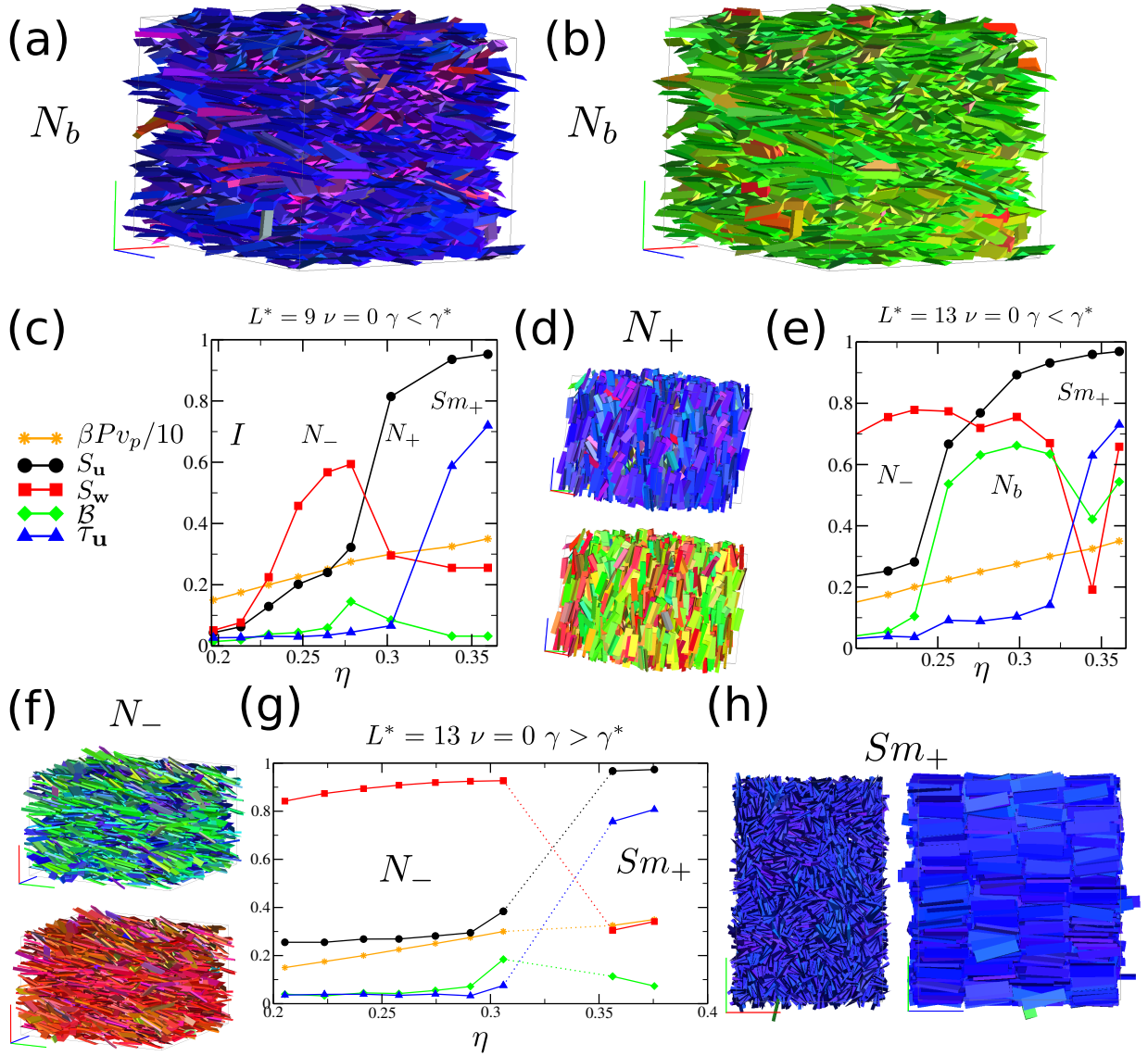


FIG. 3. (a-b) Representative snapshots of N_b formed by triangular rods with $L^* = 13$, $\nu = 0$ and $\gamma < \gamma^* = \pi/3$. Same configuration is shown with particles colored according to the orientation of the long axis (a) or short axis (b). (c) Order parameters and equation of state ($\beta P v_p$, with $\beta = 1/k_B T$ and v_p the single-particle volume, as a function of packing fraction η), for triangular rods with $L^* = 9$, $\nu = 0$ and $\gamma < \gamma^*$. (d) Representative configuration of N_+ formed by triangular rods ($L^* = 9$, $\nu = 0$, $\gamma < \gamma^*$, $\beta P v_p = 3.00$), color-coded according with orientation of the long (top) and short (bottom) axis. (e) Same as in (c) for $L^* = 13$. (f) Same as in (d) for N_- ($L^* = 13$, $\nu = 0$, $\gamma > \gamma^*$, $\beta P v_p = 1.50$). (g) Same as in (e) for $\gamma > \gamma^*$. The first-order $N_- - Sm_+$ transition is indicated with dotted lines. (h) Representative configuration of Sm_+ formed by triangular rods with $L^* = 13$, $\nu = 0$, $\gamma > \gamma^*$, $\beta P v_p = 3.50$; particles are colored according to the orientation of the long axis, two cross-sections are shown.

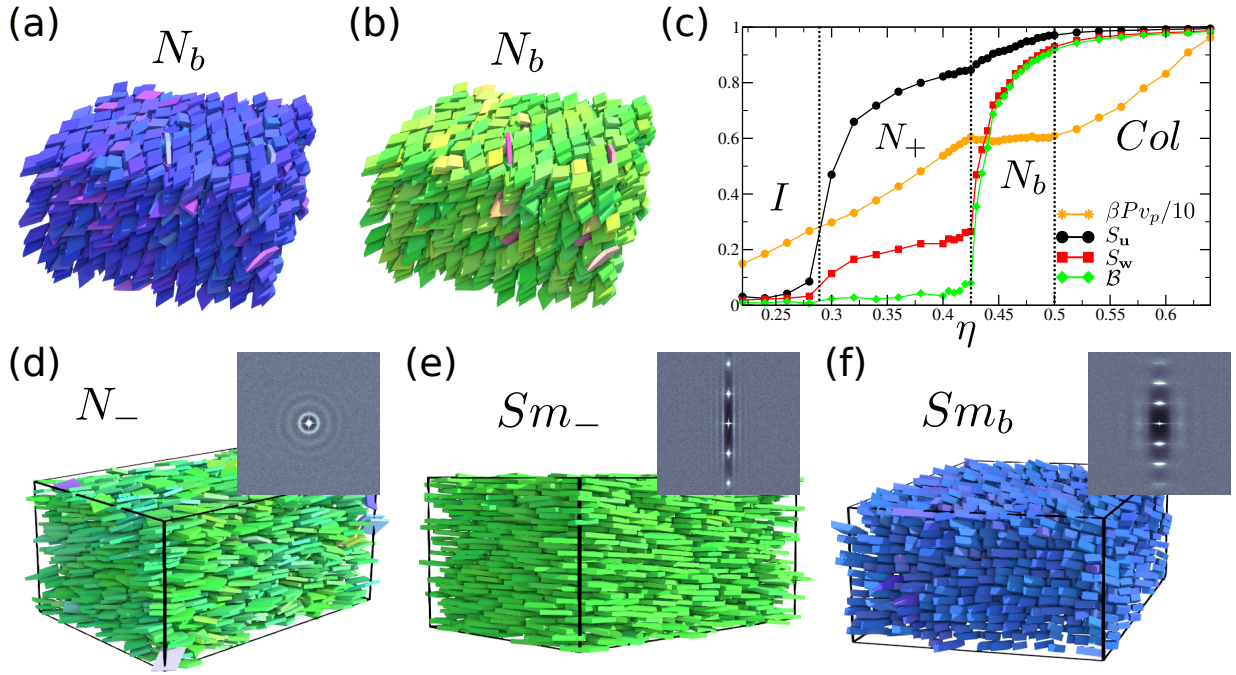


FIG. 4. (a-b) Representative snapshots of N_b phase formed by rhombic particles with $L^* = 11$ and $M^* = 4$. The same configuration is shown with particles colored according to the orientation of their long axis (a) and their short axis (b). (c) Order parameters as a function of packing fraction η and equation of state for rhombic platelets with $L^* = 11$ and $M^* = 4$ as obtained from EDMD simulations. An isotropic to prolate nematic to biaxial nematic to columnar phase sequence is observed. Approximate boundaries are shown as dotted lines. (d) Representative configuration and corresponding diffraction pattern of N_- phase of rhombic platelets with $L^* = 11$ and $W^* = 7$ ($\eta = 0.42$). (e) Sm_- phase for $L^* = 11$ and $W^* = 7$ ($\eta = 0.52$). (f) Sm_b for $L^* = 11$ and $W^* = 2$ ($\eta = 0.52$).

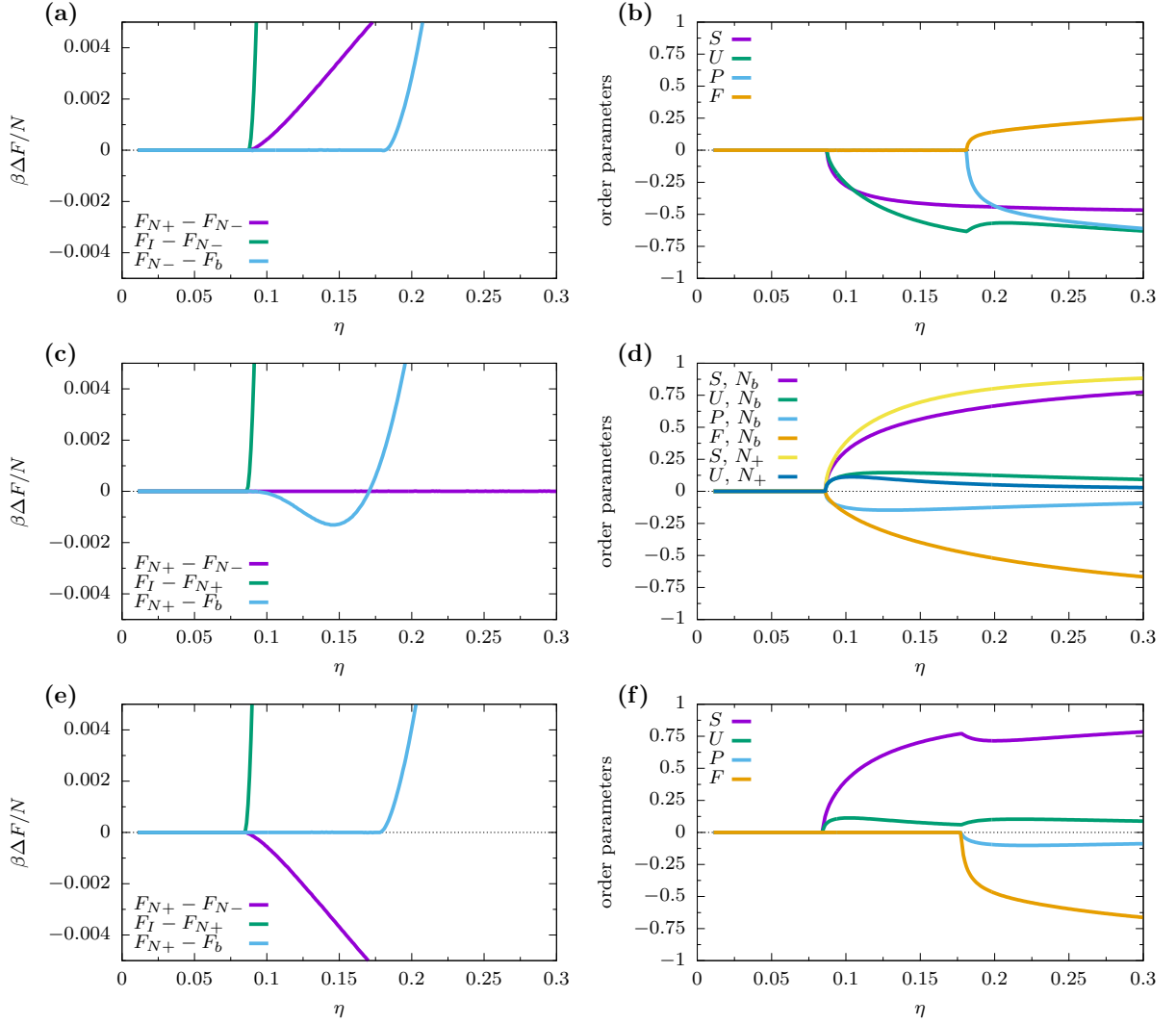


FIG. 5. Full-orientation second-virial theory results for cuboids with $M^* = 8$ and $L^* = 63$ (a-b), $L^* = 64$ (c-d), and $L^* = 65$ (e-f). The left column (a,c,e) shows the free energy difference ΔF between the different phases as a function of packing fraction η . The right column (b,d,f) shows the order parameters as a function of η for the (possibly metastable) biaxial phase (order parameters S, U, P, F are nonzero), oblate nematic ($P = 0 = F, S < 0$), or prolate nematic ($P = 0 = F, S > 0$).

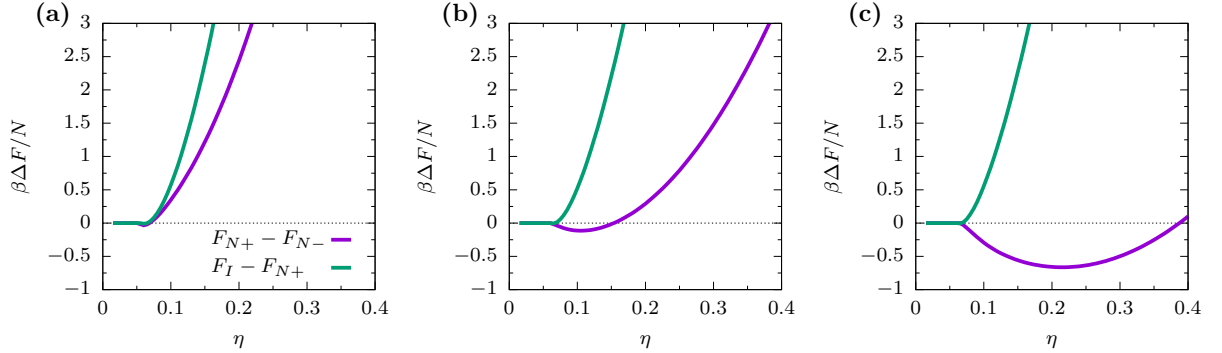


FIG. 6. Full-orientation third-virial theory results for cuboids with $L^* = 64$. The free energy difference ΔF between the different phases as a function of packing fraction η is shown for (a) $M^* = 8$ ($\nu = 0$), (b) $M^* = 4.2$, and (c) $M^* = 3.2$. Key applies to (a-c).