Entropy stabilized form chirality in curved rod nematics: structure and symmetries.

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Supplementary Information

S.1 Simulation Details.

We have applied constant pressure Metropolis Monte Carlo simulations of systems composed of N = 4096 particles. Systems of half and/or double size were also simulated at certain pressures to study system size effects. On average, during a MC cycle, a random rotation/translation is attempted for each of the particles, chosen in a random fashion, as well as a random change of the system's volume is attempted. Random particle moves are accepted if they do not result to overlaps between the particles. Similarly, free of overlaps volume changes, $\Delta V = V_n - V_o$, are accepted with probability min $(1, \exp[-P^*\Delta V + N \ln(V_n/V_o)])$. The volume changes are performed allowing the lengths of the simulation box sides to fluctuate independently.

The size of the periodically modulated systems in these simulations should be large enough to ensure that at least one side of the simulation box is an integer multiple of the inherent periodicity length of system. Furthermore, none of the box lengths should be less than twice the cut-off distance of the intermolecular potential. For hard bodies this is given by the distance between the two most distant points on the surface of the particle. Accordingly, the cutoff distance d_c for a

pair of curved hard rods used in the simulations is $d_c / D = 1 + 2 \frac{L}{D} \frac{\sin(\Psi/2)}{\Psi}$. For L/D = 19 and

 $\Psi = 1.31$ one obtains $d_c = 18.67D$. Therefore, none of the simulation box sides can be less than

 $2d_c \approx 37.4D$, otherwise ghost interactions may creep in as a given particle will be allowed to interact simultaneously with a second particle and with the periodic image of that same particle. This in turn introduces fictitious (self-ordering) fields that could bias severely or inhibit the accessible pathways connecting phases with substantially different types of ordering, as is the case in the present systems.

Denoting by $\sigma(\hat{r}_{12}, \omega_{12})$ the contact distance (i.e. the smallest distance before they start to overlap) between two hard particles having relative orientation, ω_{12} and direction of their relative positions along \hat{r}_{12} , d_c is simply the maximum value of $\sigma(\hat{r}_{12}, \omega_{12})$. Under thermodynamic conditions of high orientational ordering of a hard body system, where the orientations of the individual particles exhibit a narrow distribution about a certain direction, d_c may be obtained for interparticle position vectors also narrowly distributed along a given direction. In these cases, a carefully chosen simulation box-size, with only one box-side larger than d_c , could correctly simulate the system under the specific thermodynamic conditions. However, any phase transition resulting in a different distribution of the molecular orientations should be treated very cautiously. The simulations presented here are free of box-size conflicts with d_c and the accompanying fictitious fields.

Several structures of highly packed crystalline states were used as the initial, high-pressure state. Expansion runs from the highly ordered close packed states were performed initially up to the melting point at which the positionally ordered phase melts into a positionally disordered state. This new state is then used as the initial state for further expansion runs to locate other possible phase transitions. The obtained pressure vs packing fraction equation of state, presented in the Figure 3 of the main text, indicates that in the reduced pressure range $P^* = 1-7$ the system exhibits three distinct phases, with isotropic, nematic and smectic-like structures.

Typical snapshots of the three phases are given in Fig. SI.1. We note here that compression runs from the isotropic phase suggest that an ordering transition is taking place at pressures slightly higher than the pressure P_{NI}^* found in the expansion runs. The structure of the first ordered phase during compression runs is highly defective and depends strongly on the size and relative anisotropy of the sides of the simulation box. Similarly, compression runs starting from the



Figure SI.1 Simulation snapshots: (a) Isotropic state at $P^* = 2.15$, (b) Modulated nematic at $P^* = 2.25$ and at $P^* = 4.00$ (c); (d) super compressed fragmented state at $P^* = 5.00$ obtained by continuous compression of a modulated nematic state; (e) Smectic state at $P^* = 5.00$ from expansion runs. The colouring of the particles is associated with different orientations of the molecular y-axis. The RGB colouring scheme has been chosen as $[R, G, B] = 0.5 + [y_x, y_y, y_z]/2$, with, y_A the projection of the polar molecular axis along the sides of the simulation box, 0 < R, G, B < 1. The length, in units of D, of the sides of the simulation box fluctuate slightly about the (L_x, L_y, L_z) values: (a) (50.5, 52.8, 110.2); (b) (49.6, 49.3, 106.5); (c) (42.9, 43.6, 97.2); (d) (41.2, 41.3, 96.3); (e) (42.3, 42.8, 88.5)

modulated nematic phase do not show a sharp phase transition to a smectic phase. Instead, positional correlations develop gradually, and the system organizes into a fragmented phase with a high degree of local positional and orientational order (see Fig SI.1(d)). As this work is focussed on the structure and symmetries of the nematic phase, extensive studies on the structure of the highly ordered states are not presented here.



Figure SI.2. Evolution of the Smectic to Nematic and the Nematic to Isotropic phase change as function of the MC-cycles. The initial states are equilibrated at pressures for which the smectic (left) and the nematic state (right) are stable. These pressures are then reduced by $\Delta P^* = 0.05$ and the systems are left to evolve to their equilibrium.

In Fig. SI.2 we present the evolution of the packing fraction, the size of the simulation box and the main orientational order parameters along the smectic to nematic (left panel) and across the nematic to isotropic (right panel) phase transitions. $P^* = 4.40$ is the lowest simulated pressure for which a mechanically stable smectic phase appears, even after very long runs (~10⁸ MC-cycles), having an average packing fraction $\langle \eta \rangle \approx 0.371$. On reducing the pressure to $P^* = 4.35$ the system reduces gradually its packing fraction down to $\langle \eta \rangle \approx 0.368$ while preserving its smectic structure. Below this packing fraction, estimated as the lowest density for which the smectic phase is mechanically stable, the system melts into a modulated nematic phase showing an average packing

fraction $\langle \eta \rangle \simeq 0.363$.

In the smectic phase the box accommodates four smectic layers with layer spacing ~1.22*L*; in the nematic phase it accommodates two helical pitch-lengths with $d \sim 2.55L$. Interestingly the $(\Delta \eta)_{Sm-N} / (\eta)_N \sim 2\%$ change of the packing fraction is a result of an expansion of the system by $(\Delta L_z)_{Sm-N} / (L_z)_N \approx 7\%$ along the direction of the layer normal combined with a lateral contraction by $(\Delta L_{\perp})_{Sm-N} / (L_{\perp})_N \approx -2.4\%$. This inherently very anisotropic change of the volume of the system across the N-Sm transition explains the difficulty in obtaining a direct nematic to smectic phase transition during compression runs. The change of the packing fraction at the transition between the N phase at $P^* = 2.20$ and the isotropic phase at $P^* = 2.15$ is about 10%, a relatively high value that reflects the high compressibility of both phases close their phase transition. However, contrary to the considerably anisotropic expansion of the volume across the Sm-N phase change, $(\Delta L_z)_{N-I} / (L_z)_I \approx (\Delta L_{\perp})_{N-I} / (L_{\perp})_I$.

The graphs at the bottom of Fig. SI.2 show the evolution of the main global orientational order parameters that measure the average (over the entire simulation box) degree of the nematic like orientational order of the long molecular axis $(\overline{S_{\parallel}^{(z)}})$, the biaxiality of the phase $(\overline{\Delta S_{\perp}^{(z)}})$, and its form chirality $(\overline{S^*})$. Apparently, the Sm-N phase transition is a transformation from the high-pressure phase (smectic), which is biaxial and achiral, to a low-pressure phase (nematic) which exhibits form chirality and is globally uniaxial.

S.2 Orientational Order Parameters for Curved Rod Nematics Showing Local C₂ Symmetry.

S2.1 Order Parameters of First Rank.

There are generally 9 order parameters of first rank, $\langle \hat{a} \cdot \hat{A} \rangle$, with the angular brackets indicating ensemble averaging, \hat{a} denoting any one of the three molecular axes, \hat{x} , \hat{y} , \hat{z} and \hat{A} any of the local frame axes \hat{h} , \hat{l} , \hat{m} , with \hat{m} chosen to be the polar director and \hat{h} the direction of the modulation (see also S3.3). As a result of the combination of the local C₂ symmetry of the phase and the C_{2V} symmetry of the bent-rod molecules, the only non-vanishing of the 9 order parameters is $p_{\perp} \equiv \langle \hat{y} \cdot \hat{m} \rangle$.

S2.2 Order Parameters of Second Rank.

The second rank parameters describing the orientational order of the three molecular axes $\hat{a} = \hat{x}, \hat{y}, \hat{z}$ are generally $S_{AB}^{(a)} = \langle 3(\hat{a} \cdot \hat{A})(\hat{a} \cdot \hat{B}) - \delta_{A,B} \rangle / 2$. These form three sets (one for each molecular axis \hat{a}) of symmetric "ordering matrix" elements. Of those 18 elements in total, when expressed in the frame $\hat{h}, \hat{l}, \hat{m}$, the following 12 survive the implications ($S_{hm}^{(a)} = S_{lm}^{(a)} = 0$) of local phase symmetry: $S_{hh}^{(a)}, S_{ll}^{(a)}, S_{hn}^{(a)}, S_{hl}^{(a)}$ and of those, only 5 are independent, due to the geometrical identities

$$\sum_{a=x,y,z} S_{hh}^{(a)} = \sum_{a=x,y,z} \left(S_{mm}^{(a)} - S_{ll}^{(a)} \right) = \sum_{a=x,y,z} S_{hl}^{(a)} = S_{hh}^{(a)} + S_{ll}^{(a)} + S_{mm}^{(a)} = 0$$
(S1)

Each of the above three ordering matrices, $S_{AB}^{(a)}$, can readily be diagonalized to obtain the principal axes and corresponding principal values : \hat{m} , being the local phase-symmetry axis, automatically constitutes a principal axis of all the second rank tensors; therefore the other two principal axes, say $\hat{h}_{p}^{(a)}, \hat{l}_{p}^{(a)}$ are obtained by a single rotation of \hat{h}, \hat{l} about \hat{m} by an angle $\theta^{(a)}$ satisfying the condition $S_{h_{p}^{(a)}l_{p}^{(a)}}^{(a)} = 0$. The value of this angle is determined from the values of the order parameters in the $\hat{h}, \hat{l}, \hat{m}$ frame according to

$$\tan 2\theta^{(a)} = -4S_{hl}^{(a)} \left[3S_{hh}^{(a)} + S_{mm}^{(a)} - S_{ll}^{(a)} \right]^{-1}.$$
(S2)

Obviously, the values of $S_{mm}^{(a)}$ remain unaffected by this rotation. The principal values corresponding to the axes $\hat{h}_p^{(a)}, \hat{l}_p^{(a)}$ are given by

$$S_{h_{p}h_{p}}^{(a)} = \frac{1}{2} \left[S_{hh}^{(a)} \left(1 + \frac{1}{\cos 2\theta^{(\alpha)}} \right) + S_{ll}^{(a)} \left(1 - \frac{1}{\cos 2\theta^{(\alpha)}} \right) \right]$$

$$S_{l_{p}l_{p}}^{(a)} = \frac{1}{2} \left[S_{ll}^{(a)} \left(1 + \frac{1}{\cos 2\theta^{(\alpha)}} \right) + S_{hh}^{(a)} \left(1 - \frac{1}{\cos 2\theta^{(\alpha)}} \right) \right]$$
(S3)

The three principal values $S_{h_ph_p}^{(a)}, S_{l_pl_p}^{(a)}, S_{mm}^{(a)}$ are not independent as their sum vanishes. Accordingly, the ordering tensor in its principal axes frame is often represented by the largest of the three principal values, defining the ordering $S_{\parallel}^{(a)} \equiv \langle 3(\hat{e}_{\parallel}^{(a)} \cdot \hat{a})^2 - 1 \rangle / 2$ along the major principal axis, $\hat{e}_{\parallel}^{(a)}$, and the difference of the other two, in ascending order, defining the biaxiality $\Delta S_{\perp}^{(a)} \equiv (3/2) \langle (\hat{e}_{\perp'}^{(a)} \cdot \hat{a})^2 - (\hat{e}_{\perp'}^{(a)} \cdot \hat{a})^2 \rangle$ with respect to the principal axes $\hat{e}_{\perp'}^{(a)}, \hat{e}_{\perp'}^{(a)}$. In this representation, the three principal axes $\hat{e}_{\parallel}^{(a)}, \hat{e}_{\perp'}^{(a)}, \hat{e}_{\perp'}^{(a)}$ simply constitute a relabelling of the axes $\hat{h}_{p}^{(a)}, \hat{l}_{p}^{(a)}, \hat{m}$ in ascending sequence of the respective principal values $S_{h_ph_p}^{(a)}, S_{mm}^{(a)}$.

S2.3 Vector-pseudovector order parameters.

The order parameters $S_{AB}^{(a)}$ fully describe orientational ordering in nonpolar nonchiral LC phases to lowest (2nd) rank; the 1st rank $\langle a_A \rangle$ describe additional features of the polar phases. Order parameters detecting the existence of structural chirality in the phase can be formulated. Thus, the local C₂ phase symmetry combined with the C_{2V} molecular symmetry, give rise to nontrivial values for some components of the vector-pseudovector ordering tensors $S_{AB}^{*(a)}$. With the *y*-axis assigned as the C₂ molecular axis, these are defined as

$$S_{AB}^{*(a)} = \frac{1}{2} \left\langle \left(\hat{a} \cdot \hat{A} \right) \left[\left(\hat{a} \times \hat{y} \right) \cdot \hat{B} \right] + \left(\hat{a} \cdot \hat{B} \right) \left[\left(\hat{a} \times \hat{y} \right) \cdot \hat{A} \right] \right\rangle,$$
(S4)

they are represented by symmetric and traceless matrices and present invariance under improper rotations of the molecule. Clearly $S_{AB}^{*(y)}$ is null and therefore $S_{AB}^{*(z)} = -S_{AB}^{*(x)} \equiv S_{AB}^{*}$. By the C₂ local symmetry of the phase, the only non-vanishing components of the vector-pseudovector ordering tensor in the $\hat{h}, \hat{l}, \hat{m}$ frame are $S_{hh}^*, S_{ll}^*, S_{mm}^*, S_{hl}^*$. Due to the identity $S_{hh}^* + S_{ll}^* + S_{mm}^* = 0$, there are only three independent vector-pseudovector order parameters which can be conveniently chosen to be $S_{hh}^*; S_{mm}^* - S_{ll}^*; S_{hl}^*$. The first two of these components describe correlations between the tilt of the molecular axes \hat{x}, \hat{z} and the polar order of the molecular symmetry axis \hat{y} in the local $\hat{h}, \hat{l}, \hat{m}$ phase axes, while the third includes, in addition, polarity - biaxiality correlations.

Consider S_{hh}^* . With $\vec{t}_h^{(z)} = (\hat{h} \cdot \hat{z})(\hat{h} \times \hat{z})$ denoting the pseudovector describing the angular deviation (instantaneous "tilt") of the molecular axis \hat{z} relative to the phase axis \hat{h} it follows that

$$S_{hh}^{*} = \left\langle \vec{t}_{h}^{(z)} \cdot \hat{y} \right\rangle = \left\langle \left(\vec{t}_{h}^{(z)} \cdot \hat{m} \right) \left(\hat{y} \cdot \hat{m} \right) \right\rangle + \left\langle \left(\vec{t}_{h}^{(z)} \cdot \hat{l} \right) \left(\hat{y} \cdot \hat{l} \right) \right\rangle.$$
(S5)

Accordingly, S_{hh}^* measures the ensemble average of the projection of the molecular symmetry axis \hat{y} along the tilt pseudovector $\vec{t}_h^{(z)}$, or , equivalently, the correlations between the tilt components along the axes normal to \hat{h} (i.e. \hat{l} and \hat{m}) and the respective polar ordering of the molecular symmetry axis along those phase axes. Note that while local phase symmetry implies $\langle (\vec{t}_h^z \cdot \hat{l}) \rangle = 0 = \langle (\hat{y} \cdot \hat{l}) \rangle$, there is no such implication for either of $\langle (\vec{t}_h^{(z)} \cdot \hat{m}) \rangle$ or $\langle (\hat{y} \cdot \hat{m}) \rangle$.

Analogously for the order parameters S_{ll}^*, S_{num}^* we obtain

$$S_{mm}^{*} = \left\langle \vec{t}_{m}^{(z)} \cdot \hat{y} \right\rangle = \left\langle \left(\vec{t}_{m}^{(z)} \cdot \hat{h} \right) \left(\hat{y} \cdot \hat{h} \right) \right\rangle + \left\langle \left(\vec{t}_{m}^{(z)} \cdot \hat{l} \right) \left(\hat{y} \cdot \hat{l} \right) \right\rangle$$
(S6)

and

$$S_{ll}^{*} = \left\langle \vec{t}_{l}^{(z)} \cdot \hat{y} \right\rangle = \left\langle \left(\vec{t}_{l}^{(z)} \cdot \hat{h} \right) \left(\hat{y} \cdot \hat{h} \right) \right\rangle + \left\langle \left(\vec{t}_{l}^{(z)} \cdot \hat{m} \right) \left(\hat{y} \cdot \hat{m} \right) \right\rangle, \tag{S7}$$

showing the respective tilt-polarity correlations relative to the appropriate phase axes.

The S_{hl}^* order parameter describes additional correlations,

$$S_{lh}^{*} = \frac{1}{2} \left\langle \left(\hat{z} \cdot \hat{h} \right) \left[\left(\hat{z} \times \hat{y} \right) \cdot \hat{l} \right] + \left(\hat{z} \cdot \hat{l} \right) \left[\left(\hat{z} \times \hat{y} \right) \cdot \hat{h} \right] \right\rangle$$

$$= -\frac{1}{2} \left\langle \left(\hat{y} \cdot \hat{h} \right) \left(\vec{t}_{h}^{z} \cdot \hat{l} \right) + \left(\hat{y} \cdot \hat{l} \right) \left(\vec{t}_{l}^{z} \cdot \hat{h} \right) + \left(\hat{y} \cdot \hat{m} \right) \left[\left(\hat{z} \cdot \hat{h} \right)^{2} - \left(\hat{z} \cdot \hat{l} \right)^{2} \right] \right\rangle$$
 (S8)

that is, polarity-biaxiality correlations, in addition to tilt-polarity correlations referring to crossed

$(\hat{l}, \hat{h} \text{ and } \hat{h}, \hat{l})$ axes.

The matrix associated with the ordering tensor can be diagonalized in analogy to Eqs(S2 and 3) through a rotation about \hat{m} to obtain the principal axes $\hat{h}_{p}^{*}, \hat{l}_{p}^{*}$, the rotation angle θ^{*} and the respective principal values with $S_{h_{p}h_{p}}^{*} + S_{l_{p}l_{p}}^{*} + S_{mm}^{*} = 0$.

S.3 Orientational Pair Correlation Functions for Curved Rod Nematics of Local C₂ Symmetry and Roto-Translational Modulations in One Dimension

The calculation of local order from simulations of periodically modulated phases encounters certain technical ambiguities stemming from the interplay between the periodicity of the modulation and the periodic boundary conditions imposed on the simulated system. Pair correlation functions offer a consistent way to remove such ambiguities from the calculation.

In the case of the one-dimensional modulations of the present systems this can be readily understood: With the modulation taking place along the \hat{Z} -axis, the order parameters $\langle a_A \rangle$, $S_{AB}^{(a)}$, and S_{AB}^* are formed by ensemble averages of various combinations of the projections of the molecular axes *a* along phase axes *A*,*B*, at some slab of fixed *Z*-value. However, the respective correlation functions involve projections of the molecular axes of molecules in a given slab at Z_1 along the molecular axes of other molecules located in a second slab at Z_2 and thus depends on the separation Z_1 - Z_2 , irrespective of the absolute positions of the two slabs.

The pair correlation function associated with the polar order parameter $p_{\perp} \equiv \langle \hat{y} \cdot \hat{m} \rangle$ are presented in the main text. The functions associated with $S_{AB}^{(a)}$, and S_{AB}^{*} are defined as follows.

S3.1 Functions describing the correlation of 2nd rank ordering.

These are defined by:

$$g_{2}^{(ac;bd)}(Z) = \frac{\left\langle \sum_{i,j} \left(\frac{3}{2} \left(\hat{a}(\mathbf{r}_{i}) \cdot \hat{b}(\mathbf{r}_{j}) \right) \left(\hat{c}(\mathbf{r}_{i}) \cdot \hat{d}(\mathbf{r}_{j}) \right) - \frac{1}{2} \delta_{ac} \delta_{bd} \right) \delta(Z - \mathbf{r}_{ij} \cdot \hat{Z}) \right\rangle}{\left\langle \sum_{i,j} \delta(Z - \mathbf{r}_{ij} \cdot \hat{Z}) \right\rangle} \quad , \quad (S9)$$

where $\hat{a}, \hat{b}, \hat{c}, \hat{d}$ denote molecular axis directions at the indicated positions. For molecules of C_{2V} symmetry, such as the bent tubes in Figure 2 of the main text, the surviving functions are those with a=c and b=d and therefore there are 9 non-vanishing correlation functions of rank 2. Moreover, as a result of the 6 identities

$$\sum_{a} g_2^{(aa;bb)}(Z) = 0 = \sum_{b} g_2^{(aa;bb)}(Z); \quad a, b = x, y, z, \qquad , \qquad (S10)$$

only three of these non-vanishing functions are independent.

S3.2 Functions describing the correlation of vector-pseudovector ordering.

With \hat{y} chosen to denote the molecular symmetry axis, these are generally defined by

$$g^{*(ac;bd)}(Z) = \frac{3}{2} \frac{\left\langle \sum_{i,j} \left(\hat{a}(\mathbf{r}_{i}) \cdot \hat{b}(\mathbf{r}_{j}) \right) \left((\hat{c}(\mathbf{r}_{i}) \times \hat{y}(\mathbf{r}_{i})) \cdot (\hat{d}(\mathbf{r}_{j}) \times \hat{y}(\mathbf{r}_{j})) \right) + \left(\hat{a}(\mathbf{r}_{i}) \cdot \hat{d}(\mathbf{r}_{j}) \right) \left((\hat{c}(\mathbf{r}_{i}) \times \hat{y}(\mathbf{r}_{i})) \cdot (\hat{b}(\mathbf{r}_{j}) \times \hat{y}(\mathbf{r}_{j})) \right) \right)}{\left\langle \sum_{i,j} \delta(Z - \mathbf{r}_{ij} \cdot \hat{Z}) \right\rangle}, \quad (S11)$$

in the notation of eqs(S9 and 10). Here only the a=c and b=d combinations survive the C₂ molecular symmetry. Clearly $g^{*(yy;aa)}(Z) = g^{*(aa;yy)}(Z) = 0$.

Furthermore, $g^{*(zz;zz)}(Z) = g^{*(xx;xx)}(Z)$ and the identity

$$\sum_{a} g^{*(aa;bb)}(Z) = \sum_{b} g^{*(aa;bb)}(Z) = \frac{2}{3} g_{1}^{(yy)}(Z) , \qquad (S12)$$

imply that, given $g_1^{(yy)}(Z)$, there is essentially just one independent vector-pseudovector correlation function, which, for simplicity, is denoted by $g^*(Z) \equiv g^{*(zz;zz)}(Z)$.

S3.3 The roto-translation model of modulated order.

Briefly, this one-dimensional modulation model, predicted by the molecular theory of the polartwisted nematic phase (N_{PT}) (see refs 11 and 12 of the main text), is formulated by assuming that at each Z position (along the modulation axis \hat{Z}) there is a local frame of axes with respect to which the principal values of the order parameters are the same, independent of Z. What changes on translating along Z is the direction of the respective principal axes, following a simple rotation about \hat{Z} by an angle φ , proportional to the translation, i.e. $\varphi = kZ$, with $k \equiv 2\pi/d$ the wavenumber of the roto-translation modulation and d its periodicity length ("pitch").

With $\hat{m}(Z)$ defining the loacal direction of maximal alignment, and choosing the \hat{h} of the local frame to be parallel to the modulation direction \hat{Z} , in accord with $\hat{m}(Z)$ remaining perpendicular to the modulation direction, the roto-translational modulation implies that, on moving along the modulation axis, (i) the two local axes \hat{m}, \hat{l} rotate about that direction by an angle proportional to the displacement of the modulation, i.e.

$$\hat{m}(Z) = \hat{Y}\cos(kZ) - \hat{X}\sin(kZ) \; ; \; \hat{l}(Z) = \hat{X}\cos(kZ) + \hat{Y}\sin(kZ) \; , \tag{S13}$$

and (ii) the values of the order parameters measuring the degree of orientational ordering of the molecules along the axes $\hat{h}, \hat{l}, \hat{m}$ remain invariant to displacements along $\hat{Z} \parallel \hat{h}$. The choice of the \hat{X}, \hat{Y} axes, to form the orthogonal macroscopic frame $\hat{X}, \hat{Y}, \hat{Z}$, is obviously coupled to the choice of the origin Z = 0.

S3.4 The form of the correlation functions according to the roto-translation model.

The detailed information obtained directly from the simulations for the correlation functions, regarding the structure of the modulated nematic and the local order parameters of the phase, is used to test the predictions of the roto-translation model. Perfect agreement is found for all the correlation functions computed.

Consider, for example, $g_1^{(yy)}(Z)$. It can be calculated theoretically assuming roto-translational symmetry of the polar axis \hat{m} along \hat{h} . Expressing the molecular axes \hat{y}_i, \hat{y}_j in the local axes associated with two planes perpendicular to \hat{h} and positioned at $Z = Z_1$ and $Z = Z_2$ we have $\hat{y}_i \cdot \hat{y}_j = \left[(\hat{y}_i \cdot \hat{m}(Z_1)) (\hat{y}_j \cdot \hat{m}(Z_2)) + (\hat{y}_i \cdot \hat{l}(Z_1)) (\hat{y}_j \cdot \hat{l}(Z_2)) \right] \cos k (Z_2 - Z_1) + (\hat{y}_i \cdot \hat{h}) (\hat{y}_j \cdot \hat{h}).$ Taking then into account the C₂ symmetry about \hat{m} we obtain upon averaging

 $\left\langle \sum_{i,j} \hat{y}_i \cdot \hat{y}_j \right\rangle / \left\langle \sum_{i,j} \right\rangle = \left\langle \hat{y} \cdot \hat{m} \right\rangle^2 \cos k \left(Z_2 - Z_1 \right)$. Therefore, with the notation introduced in S2.1 for

the polar order parameter we have

$$g_1^{(yy)}(Z) = p_{\perp}^2 \cos kZ$$
 (S14)

Theoretical expressions, within the roto-translation model, for the three independent correlation functions $g_2^{(xx)}(Z)$, $g_2^{(yy)}(Z)$ and $g_2^{(zz)}(Z)$ can be obtained by an analogous procedure. Consider for example $g_2^{(xx)}(Z)$. On expressing the orientations of \hat{x}_i, \hat{x}_j in local axes associated with planes at $Z = Z_1$ and $Z = Z_2$ we have, taking into account the local C₂ symmetry about \hat{m} ,

$$\left\langle \left[\sum_{i,j} \left(\frac{3}{2} \left(\hat{x}_i \cdot \hat{x}_j \right)^2 - \frac{1}{2} \right) \right] / \left(\sum_{i,j} \right) \right\rangle = \\ = \left\langle \frac{3}{2} \left(\hat{x} \cdot \hat{h} \right)^2 - \frac{1}{2} \right\rangle^2 + 3 \left\langle \left(\hat{x} \cdot \hat{h} \right) \left(\hat{x} \cdot \hat{l} \right) \right\rangle^2 \cos k \left(Z_2 - Z_1 \right) + \frac{3}{4} \left(\left\langle \left(\hat{x} \cdot \hat{m} \right)^2 \right\rangle - \left\langle \left(\hat{x} \cdot \hat{l} \right)^2 \right\rangle \right)^2 \cos 2k \left(Z_2 - Z_1 \right) \right) \right\rangle^2 \right\rangle$$

and similarly for the \hat{y}, \hat{z} axes. Therefore, we have the final expressions

$$g_{2}^{(aa)}(Z) = \left(S_{hh}^{(a)}\right)^{2} + \frac{4}{3}\left(S_{lh}^{(a)}\right)^{2}\cos kZ + \frac{1}{3}\left(S_{mm}^{(a)} - S_{ll}^{(a)}\right)^{2}\cos 2kZ, \text{ for } a = x, y, z.$$
(S15)

This relates the correlation functions to the values of all the second rank orientational order parameters that describe the C₂ local orientational order, and verifies that the order parameter values are indeed consistent with the constraints in Eq(S1). Note that opposite signs of the order parameter $S_{lh}^{(a)}$ correspond to domains of opposite chirality.

Similarly, the vector-pseudovector correlation function $g^*(Z)$ has the following theoretical expression within the roto-translation model

$$g^{*}(Z) = \left(S_{hh}^{*}\right)^{2} + \left[\frac{4}{3}\left(S_{hl}^{*}\right)^{2} + \frac{3}{4}\left\langle\hat{y}\cdot\hat{m}\right\rangle^{2}\right]\cos kZ + \frac{1}{3}\left(S_{mm}^{*} - S_{ll}^{*}\right)^{2}\cos 2kZ \qquad .$$
(S16)

S.4 Modulated and Global Orientational Order

In view of the eqs(S13), describing the transformation of the local axes implied by the rototranslation symmetry, the order parameters of section S.2 can be expressed in the phase-fixed macroscopic frame $\hat{X}, \hat{Y}, \hat{Z}$ as follows:

$$p_x = p_\perp \sin(kZ); \ p_y = p_\perp \cos(kZ); \ p_z = 0,$$
 (S17)

for the polar order parameter in S2.1.

$$S_{AB}^{(a)}(Z) = \begin{pmatrix} -\frac{1}{2}S_{hh}^{(a)} + \frac{1}{2}(S_{ll}^{(a)} - S_{mm}^{(a)})\cos 2kZ & \frac{1}{2}(S_{ll}^{(a)} - S_{mm}^{(a)})\sin 2kZ & S_{lh}^{(a)}\cos kZ \\ \frac{1}{2}(S_{ll}^{(a)} - S_{mm}^{(a)})\sin 2kZ & -\frac{1}{2}S_{hh}^{(a)} - \frac{1}{2}(S_{ll}^{(a)} - S_{mm}^{(a)})\cos 2kZ & S_{lh}^{(a)}\sin kZ \\ S_{lh}^{(a)}\cos kZ & S_{lh}^{(a)}\sin kZ & S_{lh}^{(a)}\sin kZ \end{pmatrix}$$
(S18)

for the 2nd rank ordering tensors in section S2.2, with A, B = X, Y, Z, and similarly for the vectorpaseudovector order parameters in section S2.3, only with the superscript (a) = (x), (y), (z)replaced by *.

On averaging Eq(S17) over the Z-variable within a full pitch length $d = 2\pi / k$, both alternating components of the polar order parameter yield vanishing average values, i.e. $\overline{p_X} = \overline{p_Y} = 0$, with the bar indicating Z-averaging. The same averaging of the expression in Eq (S18) yields the uniaxial ordering tensors

$$\overline{S_{AB}^{(a)}} = S_{hh}^{(a)} \begin{pmatrix} -\frac{1}{2} & 0 & 0\\ 0 & -\frac{1}{2} & 0\\ 0 & 0 & 1 \end{pmatrix}; \quad \overline{S_{AB}^{*}} = S_{hh}^{*} \begin{pmatrix} -\frac{1}{2} & 0 & 0\\ 0 & -\frac{1}{2} & 0\\ 0 & 0 & 1 \end{pmatrix} \quad , \quad (S19)$$

with principal axis along \hat{Z} .

The components of the Z-averaged tensors can be independently calculated from the simulations by sampling within the entire simulation box. For example, the average ordering tensor $\overline{S_{AB}^{(a)}}$ of the MC generated configurations of the systems is calculated as the average over MC cycles of $\frac{1}{N}\sum_{i=1}^{N} (3a_{i,A}a_{i,B} - \delta_{A,B})/2$, where N is the number of particles and i runs over all the particles.

The eigenvalues, and the corresponding eigenvectors, of the resulting $\overline{S_{AB}^{(a)}}$ are calculated and sorted out in descending order.

Direct spatial averaging of the orientational correlation functions yields, according to Eqs(S15 and 16) $\overline{g_2^{(aa)}} = \left(S_{hh}^{(a)}\right)^2$ and $\overline{g_2^*} = \left(S_{hh}^*\right)^2$. These relations are reproduced consistently with those in Eq (S19) by direct calculation from the simulations at various pressures.