

Entropy driven polymorphism in liquids and mesophases consisting of three block amphiphilic molecules

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Supplementary Information

The supplementary information file consists of five sections: In section 1 we define the ordering matrix tensors used in this study to calculate the principal director of the phase. In section 2 we present a set of calculated radial pair correlation functions. In section 3 we present a set of calculated positional two-dimensional pair correlation densities. In section 4 we present the calculated ‘molecular mean square displacement’. In section 5 we briefly describe the methodology for the calculation of the x-ray scattering patterns.

S1. Calculation of the principal director

For a given configuration of the molecules within the simulation box, the principal axes $\hat{X}_p, \hat{Y}_p, \hat{Z}_p$ are determined through the diagonalization of the ordering matrix tensors [R1]

$$Q_{AB}^{\alpha\alpha} = \frac{1}{2N} \sum_{i=1}^N [3(\alpha_i \cdot A)(\alpha_i \cdot B) - \delta_{AB}] \quad (1)$$

with $\alpha_i = \hat{x}_i$ or \hat{y}_i or \hat{z}_i representing the molecular axes of the i th molecule and $A, B = \hat{X}, \hat{Y}, \hat{Z}$ representing the axes of the simulation box. The principal axis (\hat{X}_p or \hat{Y}_p or \hat{Z}_p) that corresponds to the maximum positive eigenvalue of the ordering tensors $Q_{AB}^{\alpha\alpha}$, defines the principal director \hat{n} of the phase.

S2.Radial pair correlation functions

An analysis of the positional order has been performed by the usual radial pair correlation functions $g(r) = \left\langle \sum_{i \neq j} \delta(r - r_{ij}) \right\rangle$ and the corresponding distributions $g_{||}(r_{||})$ of the projection of the intermolecular vector \vec{r}_{ij} (of molecules i, j) parallel to the macroscopic principal director \hat{n} (see section 1) of the columnar phase.

Characteristic calculated $g(r)$ functions for the systems of T-, V- and H- shaped molecules in the isotropic phase are presented in Fig. S1. These systems lack long range positional order. For the systems examined in this study the $g(r)$ function is not appropriate for the detection of the local structure around a molecule; the averaging over spherical shells washes out the local intermolecular correlations. In this case, the description of the local structure can be done by the two dimensional pair correlation densities (see section 3). In the columnar phases, the liquid character along the columns is supported by the $g_{\parallel}(r_{\parallel})$ which is structureless (see Fig. S2).

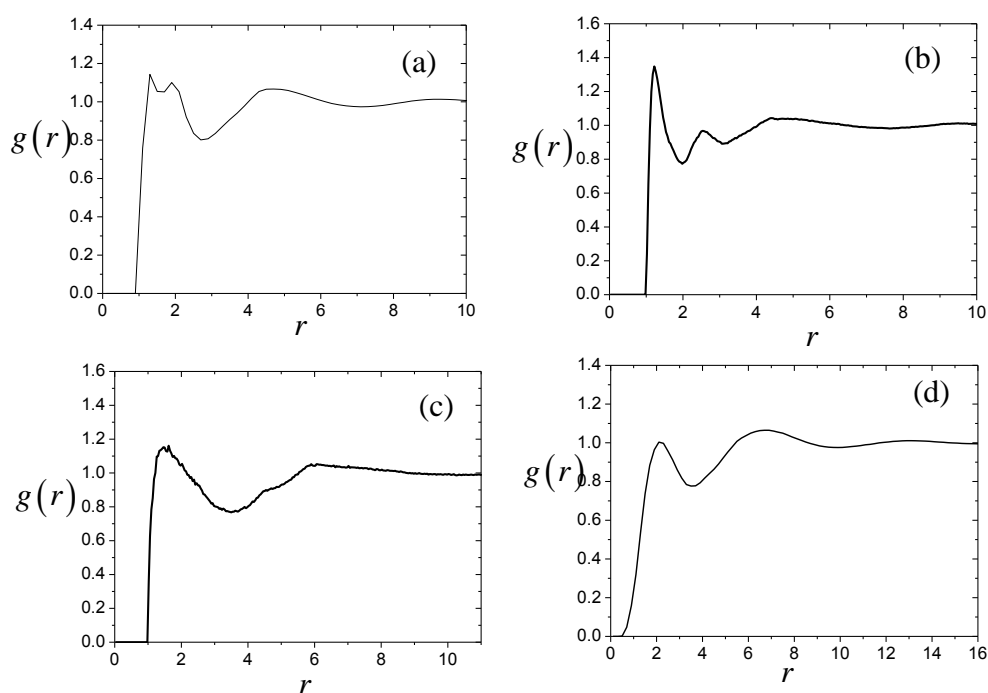


Fig. S1: The radial pair correlation function for the isotropic phase of systems consisting of T-shaped molecules (a) with $R^* = 0.5$ (at $P^* = 0.80$) and (b) with $R^* = 0.75$ (at $P^* = 0.80$), (c) of V-shaped molecules with $R^* = 2.0$ (at $P^* = 0.14$) and (d) H-shaped molecules (at $P^* = 0.16$).

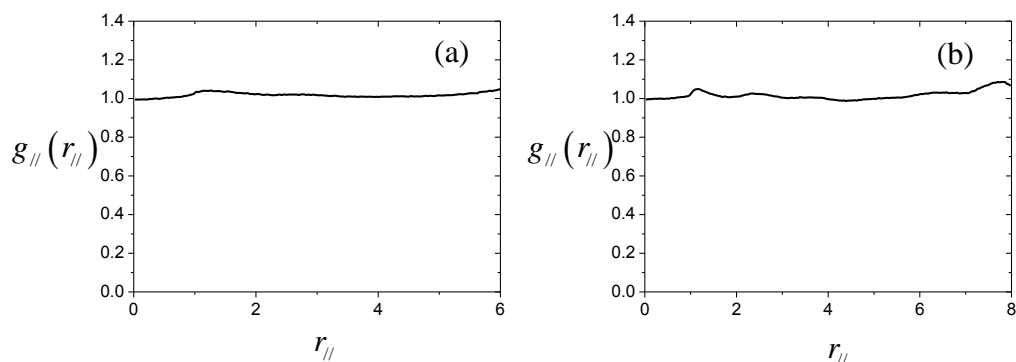


Fig. S2: The projection of the radial pair correlation function $g_{||}(r_{||})$ for the columnar phase of systems consisting of (a) V-shaped molecules with $R^*=2.0$ (at $P^*=0.30$) and (b) T-shaped molecules with $R^*=0.75$ (at $P^*=1.32$).

S3. Two-Dimensional Pair Correlation densities

To analyze the local structure of the phases exhibited, we have calculated a set of positional two-dimensional pair correlation densities defined in the main text of the paper, which refer to molecular axis frames.

S3.1 System of V-shaped molecules ($R^*=2.0$)

In Figs. S3 (left-right) we present the calculated $g_0^{\hat{x},\hat{z}}(x,z)$ and $g_0^{\hat{y},\hat{z}}(y,z)$ functions at different pressures P^* for a system of V-shaped molecules with $R^*=2.0$. In the isotropic phase, well defined maxima are observed (they are indicated by arrows in Fig. S3c); the intensity of the maxima increases by increasing the pressure whereas their position on the pattern does not change. In the columnar phase, long range order is obtained (see Fig. S3f).

S3.2 System of T-shaped molecules ($R^*=0.75$)

In Fig. S4 (left-right) we present the calculated $g_0^{\hat{x},\hat{z}}(x,z)$ and $g_0^{\hat{y},\hat{z}}(y,z)$ functions at various pressures P^* for the system of T-shaped molecules with $R^*=0.75$.

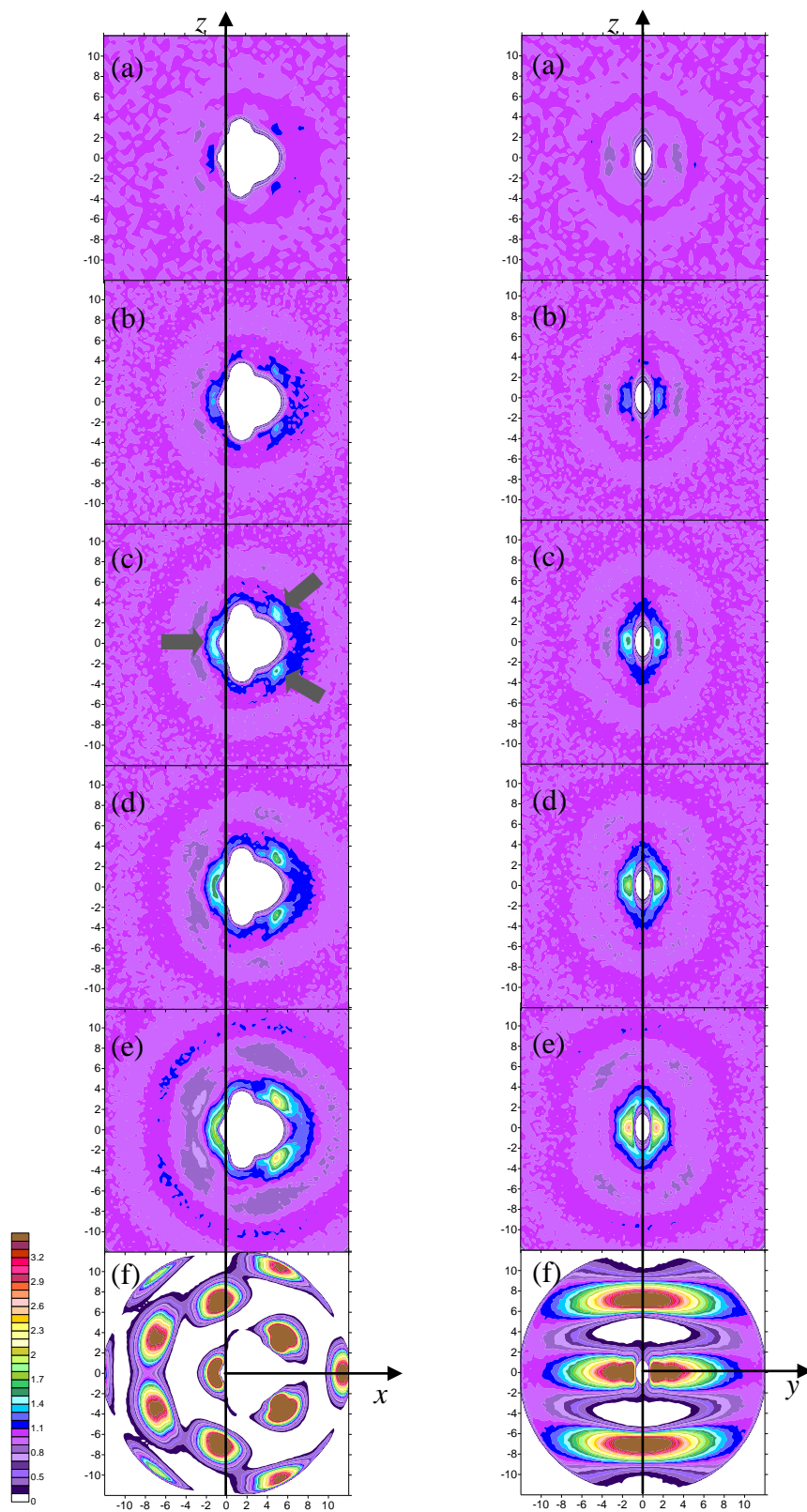


Fig. S3: Calculated two dimensional pair correlation densities $g_o^{\hat{x},\hat{z}}(x,z)$ (left column) and $g_o^{\hat{y},\hat{z}}(y,z)$ (right column) at different pressures, compressing from the isotropic phase for a system of V-shaped molecules with $R^*=2.0$. Isotropic: (a) $P^* = 0.04$, (b) $P^* = 0.06$, (c) $P^* = 0.08$, (d) $P^* = 0.10$, (e) $P^* = 0.16$ and Columnar: (f) $P^* = 0.30$.

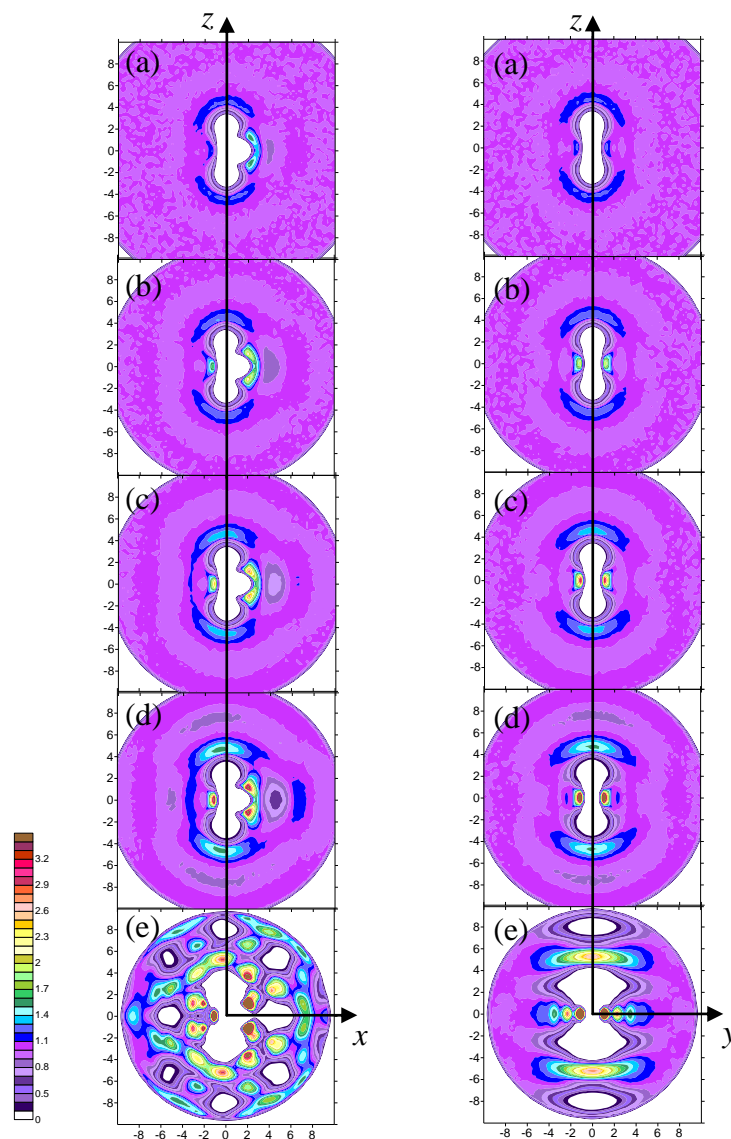


Fig. S4: Calculated two dimensional pair correlation densities $g_o^{\hat{x},\hat{z}}(x,z)$ (left column) and $g_o^{\hat{y},\hat{z}}(y,z)$ (right column) at different pressures, compressing from the isotropic phase for a system of T-shaped molecules with $R^* = 0.75$. Isotropic: (a) $P^* = 0.20$, (b) $P^* = 0.40$, (c) $P^* = 0.60$, (d) $P^* = 0.8$ and Columnar: (e) $P^* = 1.38$.

S4. Calculation of the molecular mean square displacement

The fluidity of the phases obtained has been examined by the calculation of the molecular mean square displacement per monte carlo (mc) cycle M :

$$l(M) = \frac{1}{N} \sum_i [\vec{r}_i(M) - \vec{r}_i(0)]^2, \quad (2)$$

where $\vec{r}_i(0)$ is the initial position of the i th molecule in the simulation box and $\vec{r}_i(M)$ is its position at the M th mc cycle. Note that N is the number of molecules in the

simulation box and one mc cycle consists of N attempted mc moves. Characteristic plots of the $l(M)$ for systems consisting of T-, V- and H- shaped molecules are shown in Fig. S5. These plots confirm that the systems are quite fluid in the liquid crystalline phases since the molecular mean displacement increases linearly mc cycle number.

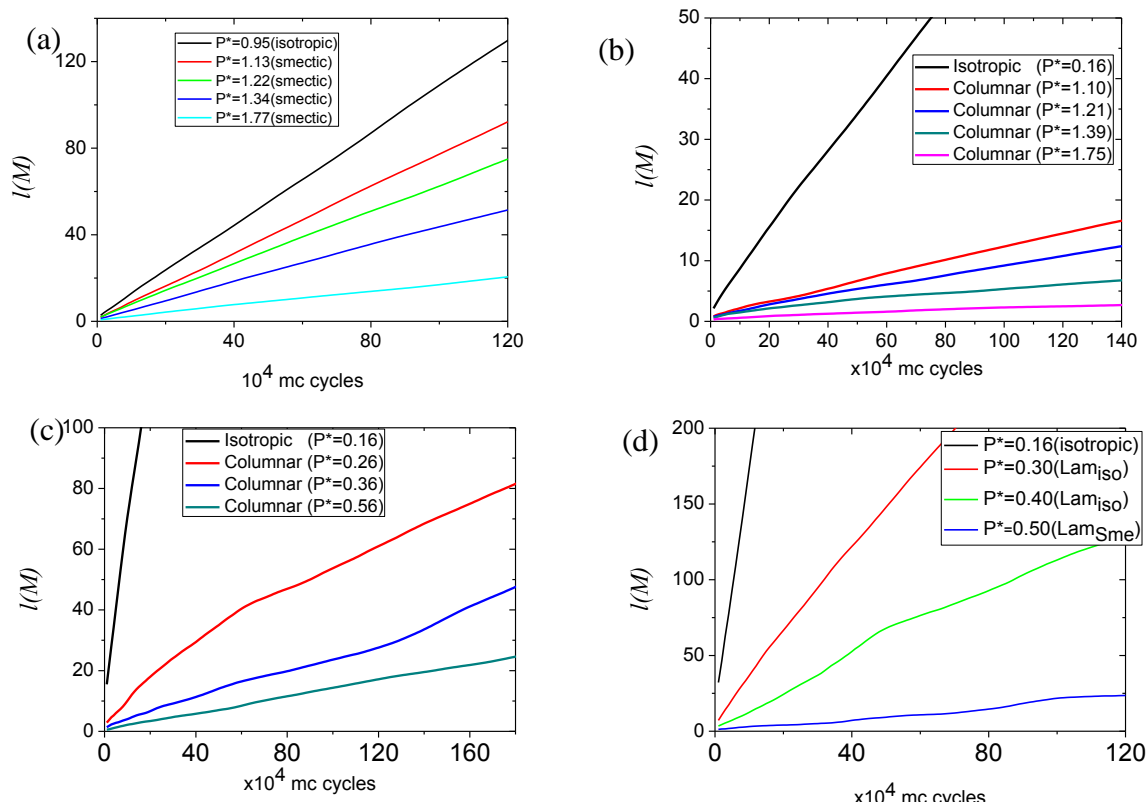


Fig. S5: The molecular mean square displacement $l(M)$ per mc cycle at different pressures for systems of T-shaped molecules (a) with $R^* = 0.5$ and (b) with $R^* = 0.75$, (c) of V-shaped molecules with $R^* = 2.0$ and (d) of H-shaped molecules.

S5. Calculation of x-ray scattering patterns from computer simulation

X-ray diffraction provides a useful technique for the study of the translational order of liquids and liquid crystals. In computer simulations, the calculation of the x-ray scattering patterns can be performed directly knowing the positions of the electron scatterers [R2]. Here we follow the methodology that has been introduced by Bates and Luckhurst in [R2]. The basic equations of the scattering intensity have been written considering the case of multi scatterers per molecule. The total scattering intensity, for a system of N molecules with K scatterers per molecule, is given by

$$I_{tot}(\vec{Q}) = \sum_{j=1}^N \sum_{n=1}^K F_{j,n}(\hat{u}_{j,n}, \vec{Q}) \exp(i\vec{Q}\vec{r}_{j,n}) \times \sum_{j=1}^N \sum_{n=1}^K F_{j,n}(\hat{u}_{j,n}, \vec{Q}) \exp(-i\vec{Q}\vec{r}_{j,n}) \quad (3)$$

where \vec{Q} is the scattering vector, $F_{j,n}(\hat{u}_{j,n}, \vec{Q})$ is the scattering factor of the n th scatterer of the j th molecule, $\vec{r}_{j,n}$ is its position and $\hat{u}_{j,n}$ is its orientation.

For a uniaxial ellipsoidal scattering factor of length σ_l and breadth σ_b (with $\kappa = \sigma_l/\sigma_b$) we have

$$F_{j,n}(\hat{u}_{j,n}, \vec{Q}) = \frac{3(\sin \gamma_{j,n} - \gamma_{j,n} \cos \gamma_{j,n})}{\gamma_{j,n}^3} \quad (4)$$

with $\gamma_{j,n} = \frac{1}{2}|\vec{Q}|\sigma_b(\kappa^2 \cos^2 \varphi_{j,n} - \sin^2 \varphi_{j,n})^{\frac{1}{2}}$ and $\cos \varphi_{j,n} = (\vec{Q}\hat{u}_{j,n})/|\vec{Q}|$. In the case of scattering spheres $\kappa = 1$.

The intermolecular scattering intensity $I_{inter}(\vec{Q})$ reported in this study is given by subtracting the single molecular intensity $I_{mol}(\vec{Q})$ from the total intensity $I_{tot}(\vec{Q})$,

$$I_{inter}(\vec{Q}) = I_{tot}(\vec{Q}) - I_{mol}(\vec{Q}) \quad (5)$$

$$\text{with } I_{mol}(\vec{Q}) = \sum_{j=1}^N \sum_{n=1}^K \sum_{m=1}^K F_{j,n}(\hat{u}_{j,n}, \vec{Q}) F_{j,m}(\hat{u}_{j,m}, \vec{Q}) \exp[i\vec{Q}(\vec{r}_{j,n} - \vec{r}_{j,m})].$$

Here, for simplicity, we have assigned a single scattering sphere ($\kappa = 1$) or an ellipsoid ($\kappa = \sigma_l/\sigma_b$) at the origin of the molecular axes frame (see Fig. 1 in the main text). In this case, the intermolecular distances indicated by the theoretically calculated scattering pattern can be compared directly with those of the pair correlation densities.

The theoretically calculated scattering patterns ($Q_{\perp x}, Q_{\perp z}$) for the columnar phases correspond to those obtained for real columnar phases with the ‘incident beam’ parallel to the column axis. The discretization of the scattering pattern is taken to be $q = 0.02$; for example, a scattering pattern between Q_x and $Q_z = -2\pi \dots + 2\pi$ is calculated on a grid of 314×314 points. For a given equilibrium configuration of the system, a random vector generator produces a number of vectors \vec{Q} (comparable to the number of points of the grid), and for each vector \vec{Q} the intensity from eq.5 is

calculated. The total $I_{\text{inter}}(\vec{Q})$ is obtained as an ensemble average over equilibrium configurations, typically for 10^5 mc cycles.

References of the supplementary file

[R1] P. J. Camp, M. P. Allen and A. J. Masters, *J. Chem. Phys.*, 1999, **111**, 9871.

[R2] M. A. Bates and G. R. Luckhurst, *J. Chem. Phys.*, 2003, **118**, 6605.