Biaxial mesophase behavior of amphiphilic anisometric colloids: A simulation study

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Supplementary Information

S1. Calculation of the principal axes frame

In order to quantify the orientational order for a given configuration of the molecules within the simulation box, we have calculated the principal axes $\hat{X}_p, \hat{Y}_p, \hat{Z}_p$ that are determined through the diagonalization of the ordering matrix tensors [R1]

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

with $\alpha_i = \hat{x}_i$ or $\hat{y}_i$ or $\hat{z}_i$ the molecular axes of the *i*th molecule and $A,B = \hat{X},\hat{Y},\hat{Z}$ denote the axes of the simulation box. The principal axis $\left(\hat{X}_p \text{ or } \hat{Y}_p \text{ or } \hat{Z}_p\right)$ that corresponds to the maximum positive eigenvalue of the ordering tensors $Q_{AB}^{\alpha\alpha}$, defines the principal director $\hat{n}$ of the phase. The secondary director, $\hat{l}$, is associated with the molecular axis exhibiting the second largest alignment and the third axis of the phase is given by $\hat{m} = \hat{n} \times \hat{l}$.

S2. Phase diagrams for systems with $l^* = 11$, $w^* < 2.4$ and $R^* = 0.5$.

In this section we have examined the phase behavior of anisometric particles (see Fig. 1a main manuscript) with $l^* = 11$, $w^* < 2.4$ and $R^* = 0.5$ using MC-*NpT* simulations. The systems consist of *N*=760 particles. The equation of state for each system is obtained by compression from the isotropic state or by expansion series from the smectic phase (see Fig. S2.1 (left)). The pressure dependence of the order

parameters S^z, $D^{x,y}$ is presented in Fig. S2.1 (right). Representative snapshots of the mesophases are given in Fig. S2.2

The long range positional order has been examined using the usual radial pair correlation functions $g(r)=\left\langle \sum_{i\neq j}\delta\left(r-r_{ij}\right)\right\rangle$ and the corresponding distributions $g_{//}\left(r_{//}\right)=\left\langle \sum_{i\neq j}\delta\left(r_{//}-\left|\vec{r}_{ij}\cdot\hat{n}\right|\right)\right\rangle$ and $g_{\perp}\left(r_{\perp}\right)=\left\langle \sum_{i\neq j}\delta\left(r_{\perp}-r_{ij}^{\perp}\right)\right\rangle$ of the projection of the intermolecular vector $\vec{r}_{ij}$ (of molecules i, j) parallel and vertical to the macroscopic principal director $\hat{n}$ of the *SmA* phase; with $r_{ij}^{\perp}=\sqrt{r_{ij}^2-\left|\vec{r}_{ij}\cdot\hat{n}\right|^2}$. It is evident that the nematic phase lacks long range positional order. A layered structure is shown from the snapshot of the *SmA* phase as well as from the radial correlation function (see Fig. S2.3c).

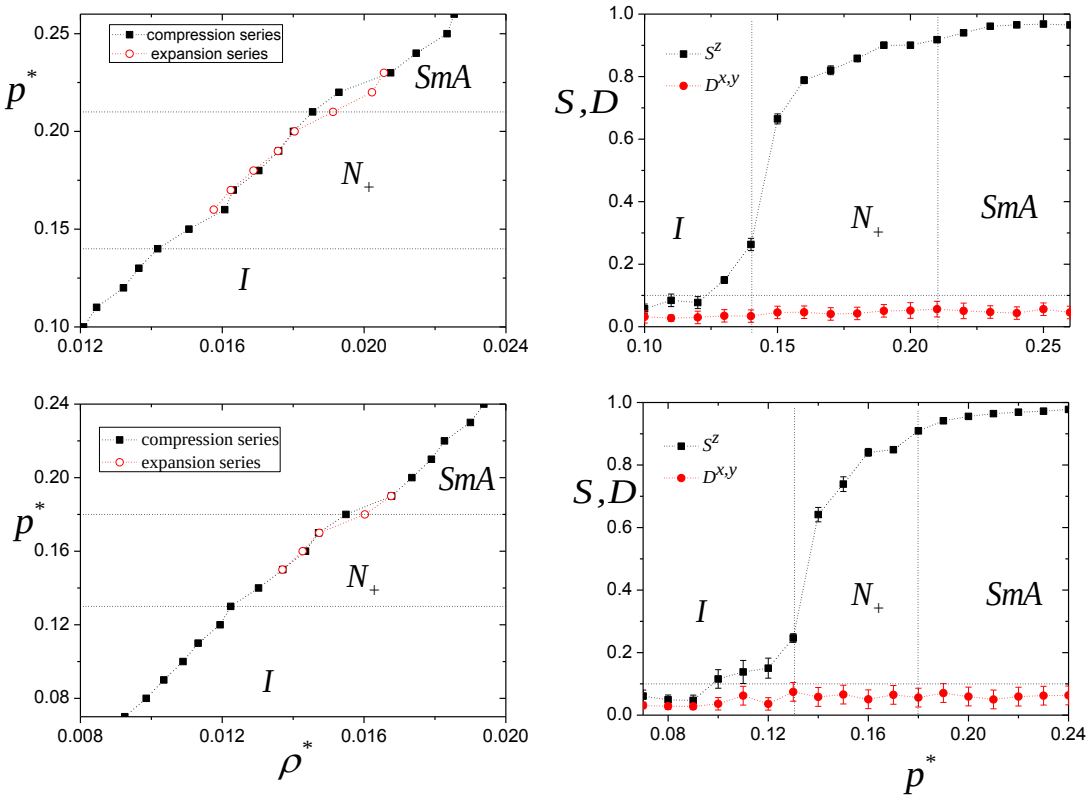
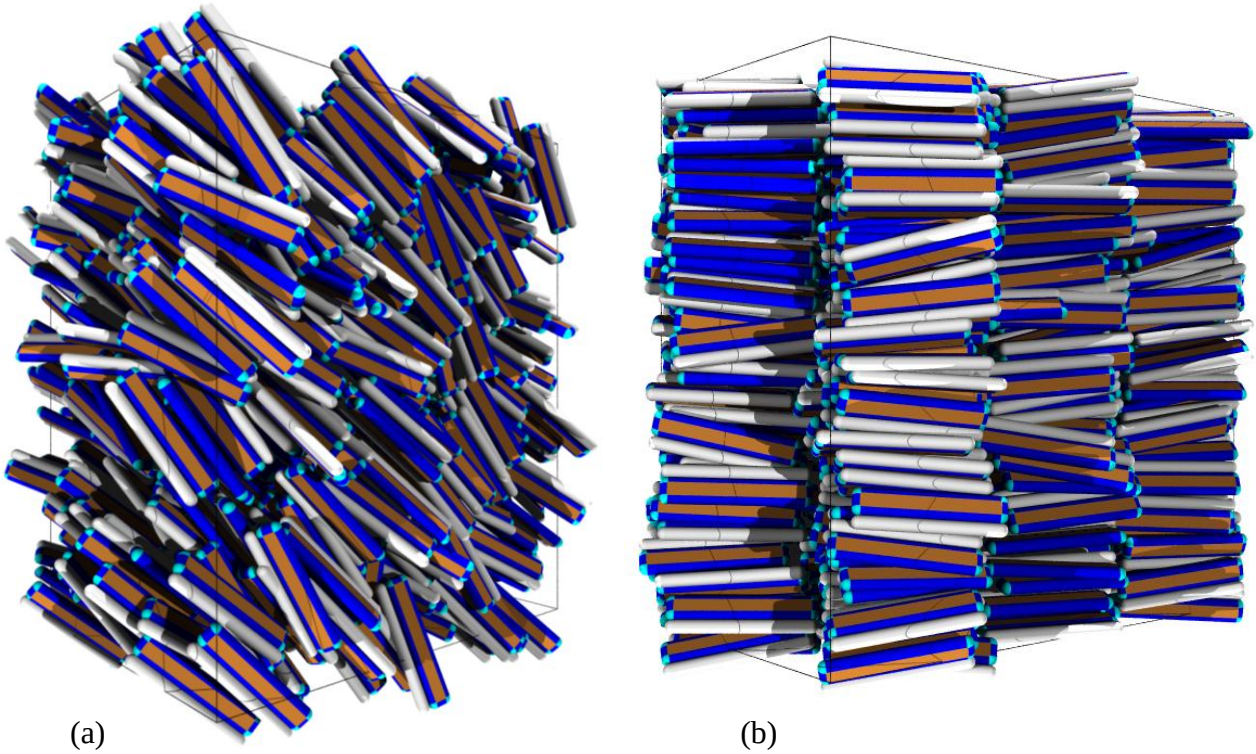


Fig. S2.1. Left: Equation of state for systems consisting of anisometric particles (see Fig. 1a). The data points obtained by MC-*NpT* simulations: the squares correspond to compression series from an isotropic phase and the circles to expansion series from the *SmA* phase obtained by compression. Right: pressure dependence of the order parameters S^z, $D^{x,y}$. The data points correspond to compression series. Molecular geometry: $l^* = 11$, $R^* = 0.5$ and (a) $w^* = 1.6$ and (b) $w^* = 2.0$.



(a) (b)

Fig. S2.2 Representative snapshots for a system consisting of N=760 anisometric particles with: $l^* = 11$, $w^* = 2.2$, and $R^* = 0.5$: (a) in the N_+ at $p^* = 0.14$ and (b) in the *SmA* phase at $p^* = 0.22$.

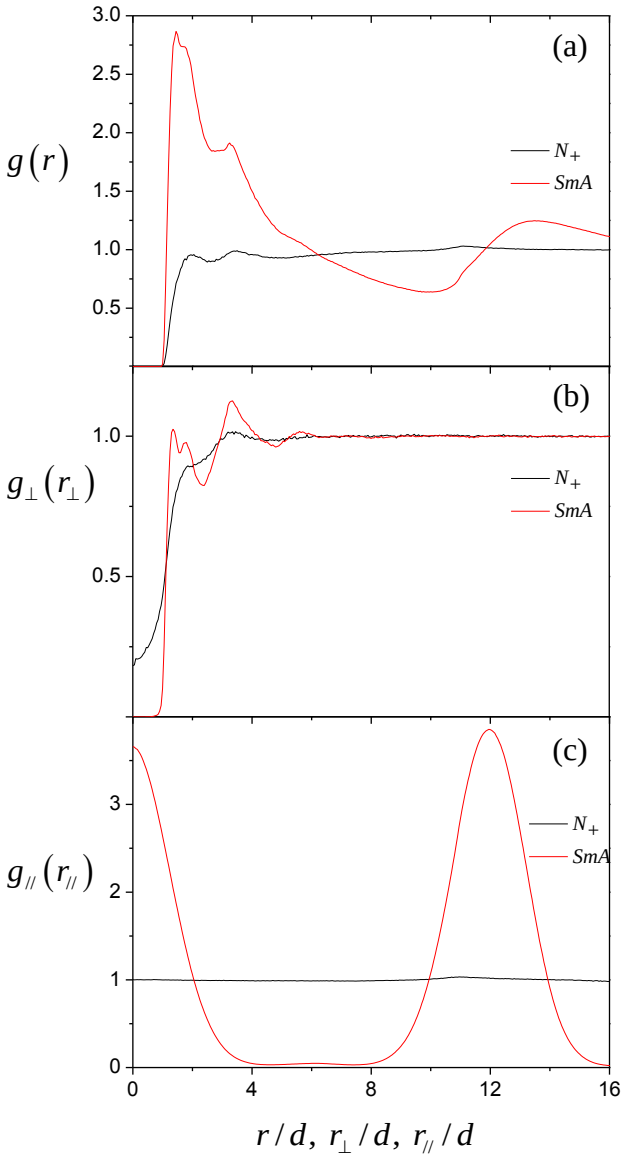


Fig. S2.3 Calculated pair correlation functions for a system consisting anisometric particles with $l^* = 11$, $w^* = 2.2$, and $R^* = 0.5$ (see Fig.1a) in the N_+ (black line) phase at $p^* = 0.14$ and in the *SmA* phase (red line) at $p^* = 0.22$. (a) $g(r)$, (b) $g_{\perp}(r_{\perp})$ and (c) $g_{//}(r_{//})$.

S3. Pair Correlation functions for a system with $l^* = 11$, $w^* = 2.4$ and $R^* = 0.5$.

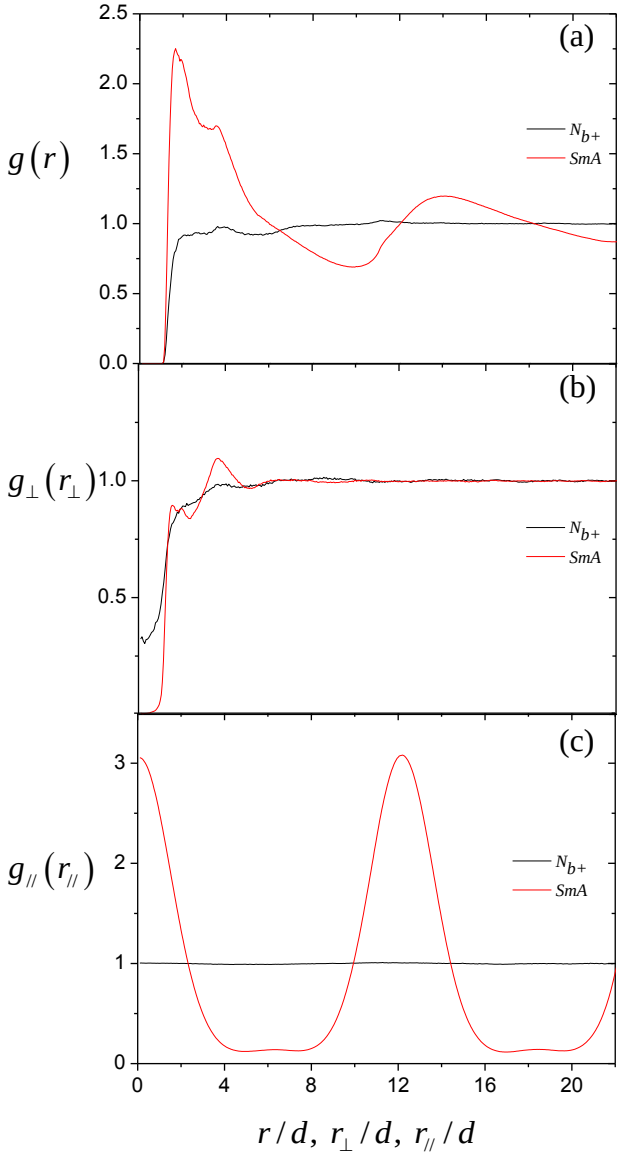


Fig. S3.1 Calculated pair correlation functions for a system consisting anisometric particles with $l^* = 11$, $w^* = 2.4$, and $R^* = 0.5$,(see Fig.1a) in the N_{b+} (black line) phase at $p^* = 0.145$ and in the *SmA* phase (red line) at $p^* = 0.17$. (a) $g(r)$, (b) $g_\perp(r_\perp)$ and (c) $g_{//}(r_{//})$.

S4. System with $l^* = 11$, $w^* = \sqrt{11}$ and $R^* = 0.5$.

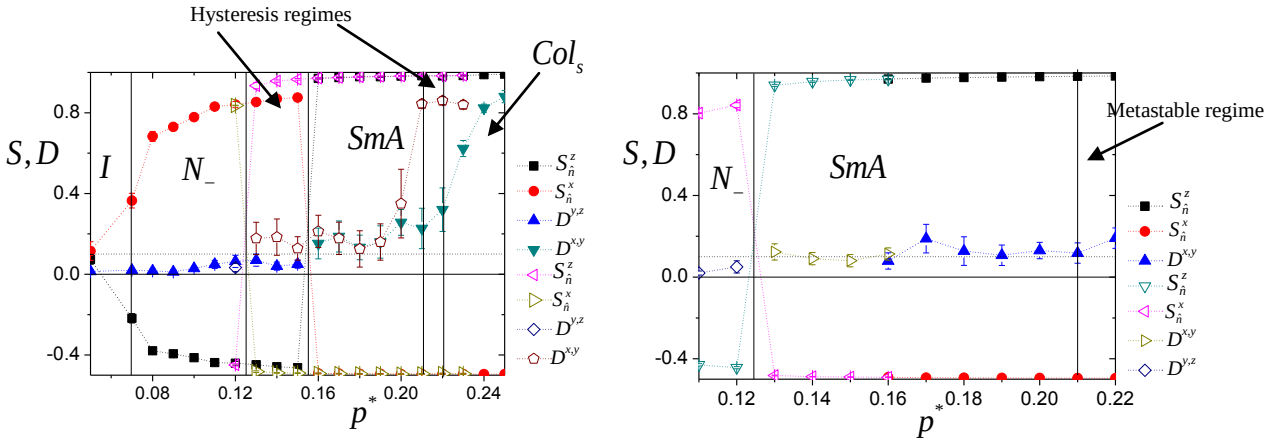


Fig. S4.1. Pressure dependence of the order parameters $S_{\hat{n}}^z$, $S_{\hat{n}}^x$, $D^{y,z}$, $D^{x,y}$ for systems consisting of (a) N=600 particles and (b) N=1500. The closed symbols correspond to compression series and the open symbols to expansion series. The horizontal lines are at 0 (solid) and at 0.1 (dotted) and are used to guide the eye.

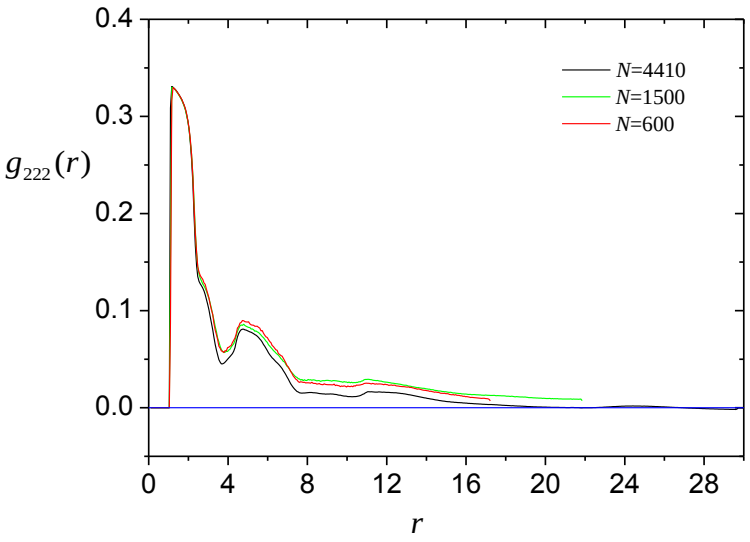


Fig. S4.2. Plot of the $g_{222}(r)$ calculated for systems with $l^* = 11$, $w^* = \sqrt{11}$ and $R^* = 0.5$ (see Fig. 1a), consisting of N=4410 (black line), N=1500 (green line) and N=600 (red line) particles, calculated at the same pressure $p^* = 0.18$. The horizontal blue-line is at 0 and is used to guide the eye.

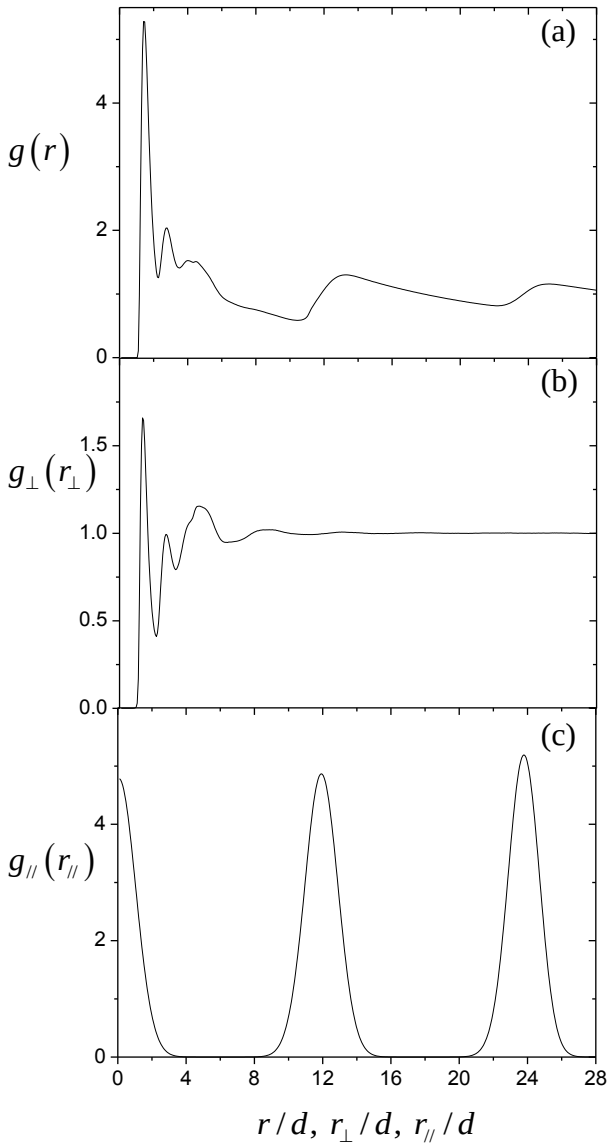


Fig. S4.3 Calculated pair correlation functions for a system consisting anisometric molecules with $l^* = 11$, $w^* = \sqrt{11}$, and $R^* = 0.5$ (see Fig. 1a) in the *SmA* phase at $p^* = 0.18$. (a) $g(r)$, (b) $g_{\perp}(r_{\perp})$ and (c) $g_{//}(r_{//})$.

S5. System with $l^* = 11,\ w^* = \sqrt{11}\ \ R^* = 0.5.$ **(see Fig.1b).**

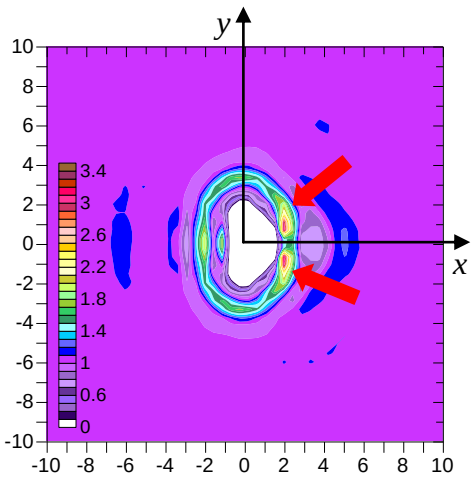


Fig. S5. Contour maps of the calculated correlation function $g_0^{\hat{x},\hat{y}}(x,y)$ at $p^* = 0.18$, in the SmA phase. The maximum (that are shown by red arrows) indicate a tendency for the formation of local triangular supermolecular clusters within the layers.

S6. System with $l^* = 11$, $w^* = \sqrt{11}$ and $R^* = 2.0$ (see Fig. 1c).

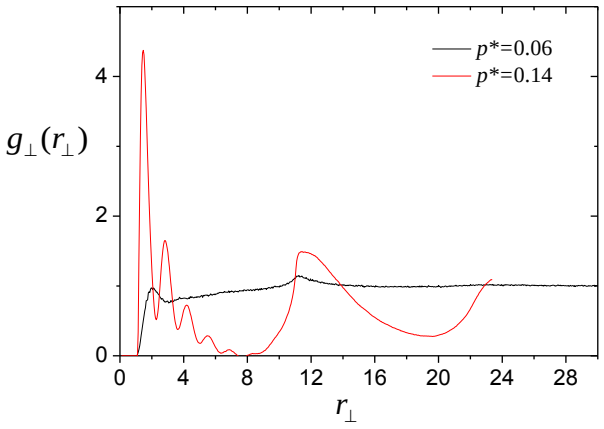


Fig. S6.1 Calculated pair correlation function $g_\perp(r_\perp)$ in the Lam_{Nb} phase at $P^* = 0.06$. (black line) and in the Col_s phase at $P^* = 0.14$ (red line).

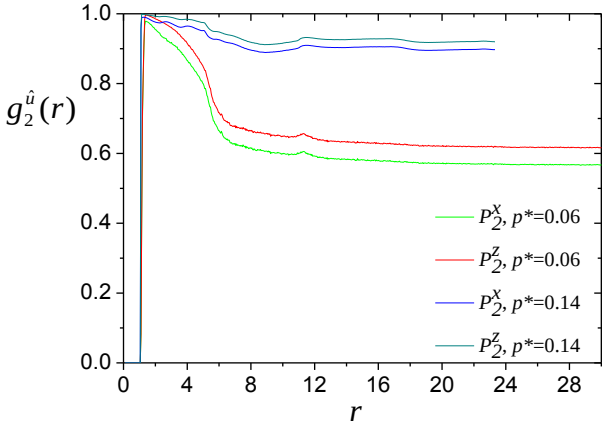


Fig. S6.2. Calculated pair correlation functions $g_2^{\hat{u}}(r) = \left\langle \sum_{i,j} P_2\left(\hat{u}_i \cdot \hat{u}_j\right)(r) \right\rangle$ with $u = x$ *or* z in the Lam_{Nb} phase at $p^* = 0.06$ and in the Col_s phase at $p^* = 0.14$.

S7. Systems with $l^* = 11$, $w^* \geq 8$ and $R^* = 2.0$.

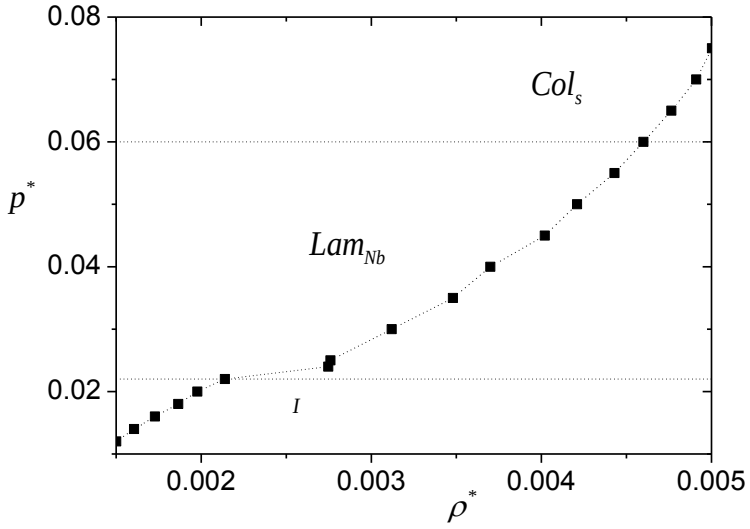


Fig. S7.1 Equation of state for a system consisting of N=686 anisometric particles with $l^* = 11$, $w^* = 8$, and $R^* = 2.0$ (see Fig. 1d). The data points obtained by MC-*NpT* simulations and correspond to compression from an isotropic phase.

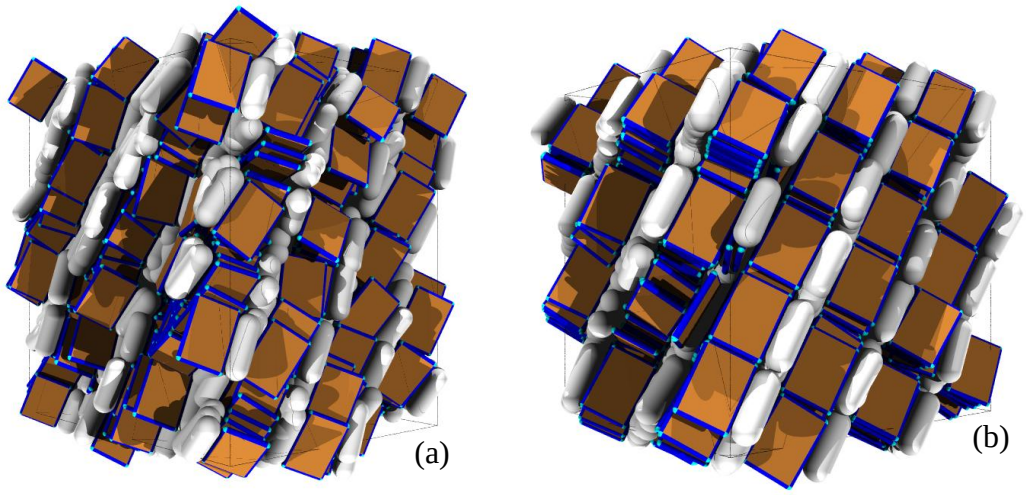


Fig. S7.2 Representative snapshots for a system consisting of N=686 anisometric particles with: $l^* = 11$, $w^* = 8$, and $R^* = 2.0$. (a) in the Lam_{Nb} at $p^* = 0.30$ and (b) in the *Col* phase at $p^* = 0.75$.

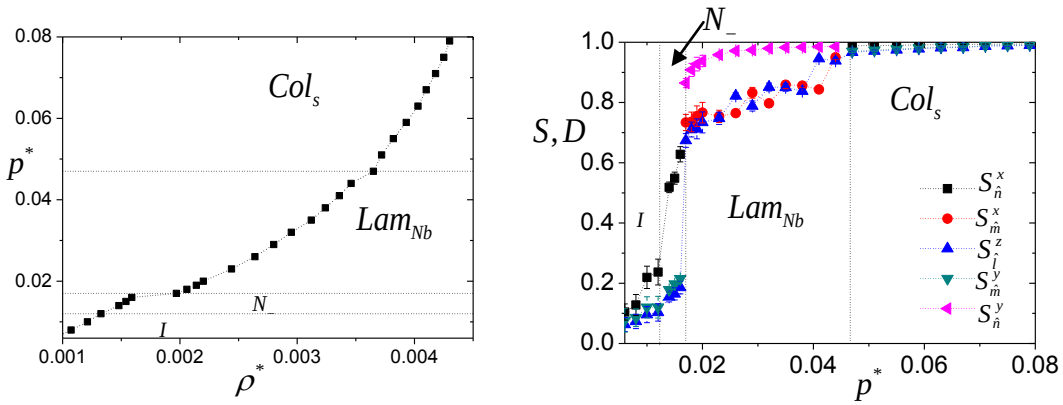


Fig. S7.3 Left: Equation of state for a system consisting of N=588 anisometric particles with $l^* = 11$, $w^* = 11$, and $R^* = 2.0$ (see Fig. 1d). The data points obtained by MC-*NpT* simulations and correspond to compression from an isotropic phase. Right: pressure dependence of the order parameters.

References of the supplementary file

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