Supplementary Information: Defect structures mediate the isotropic-nematic transition in strongly confined liquid crystals

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A. Modified real spherical harmonics

To obtain a suitable basis set for expanding real orientational distributions in our mean field model, we start from the definition of the complex spherical harmonics using the Condon-Shortley normalization [D. M. Brink and G. M. Satchler, *Angular Momentum* Oxford University Press, 1968]

$$C_l^m(\hat{\omega}) = \sqrt{\frac{4\pi}{2l+1}} Y_l^m(\hat{\omega}). \tag{1}$$

Real versions of these functions are then defined through

$$R_l^m(\hat{\omega}) = \begin{cases} C_l^0(\hat{\omega}) & m = 0 \\ \frac{1}{2}\sqrt{2}\left\{C_l^m(\hat{\omega}) + C_l^m(\hat{\omega})^*\right\} & m > 0 \\ \frac{1}{2i}\sqrt{2}\left\{C_l^{|m|}(\hat{\omega}) - C_l^{|m|}(\hat{\omega})^*\right\} & m < 0 \end{cases} \tag{2}$$

The orthogonality relations for these functions are simply

$$\int d\hat{\omega} R_l^m(\hat{\omega}) R_{l'}^{m'}(\hat{\omega}) = \frac{4\pi}{2l+1}\delta_{l,l'}\delta_{m,m'}. \tag{3}$$

and the harmonic addition theorem becomes

$$R_l^0(\hat{\omega}\cdot\hat{\omega}') = \sum_{m=-l}^{l} R_l^m(\hat{\omega}) R_l^m(\hat{\omega}') \tag{4}$$

Parametrizing the unit sphere with the standard spherical angles, $\hat{\omega} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, we list these functions for l, m even, up to $l = 4$

$$R_0^0(\hat{\omega}) = 1 \tag{5}$$

$$R_2^{-2}(\hat{\omega}) = \frac{1}{2}\sqrt{3}\sin^2\theta\sin 2\varphi \tag{6}$$

$$R_2^0(\hat{\omega}) = \frac{1}{2}\left(3\cos^2\theta - 1\right) \tag{7}$$

$$R_2^2(\hat{\omega}) = \frac{1}{2}\sqrt{3}\sin^2\theta\cos 2\varphi \tag{8}$$

$$R_4^{-4}(\hat{\omega}) = \frac{1}{8}\sqrt{35}\sin^4\theta\sin 4\varphi \tag{9}$$

$$R_4^{-2}(\hat{\omega}) = -\frac{1}{4}\sqrt{5}(7\cos^4\theta - 8\cos^2\theta + 1)\sin 2\varphi \tag{10}$$

$$R_4^0(\hat{\omega}) = \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3) \tag{11}$$

$$R_4^2(\hat{\omega}) = -\frac{1}{4}\sqrt{5}(7\cos^4\theta - 8\cos^2\theta + 1)\cos 2\varphi \tag{12}$$

$$R_4^4(\hat{\omega}) = \frac{1}{8}\sqrt{35}\sin^4\theta\cos 4\varphi \tag{13}$$

The standard second rank order parameter tensor $\mathbf{Q}$ can then be expressed in terms of the functions as

$$\mathbf{Q} = \left\langle \frac{1}{2}\left(3\hat{\omega}\otimes\hat{\omega}-\mathbb{I}\right)\right\rangle =$$

$$\begin{pmatrix} -\frac{1}{2}\left\langle R_2^0\right\rangle + \frac{1}{2}\sqrt{3}\left\langle R_2^2\right\rangle & \frac{1}{2}\sqrt{3}\left\langle R_2^{-2}\right\rangle & -\frac{1}{2}\sqrt{3}\left\langle R_2^1\right\rangle \\ \frac{1}{2}\sqrt{3}\left\langle R_2^{-2}\right\rangle & -\frac{1}{2}\left\langle R_2^0\right\rangle - \frac{1}{2}\sqrt{3}\left\langle R_2^2\right\rangle & -\frac{1}{2}\sqrt{3}\left\langle R_2^{-1}\right\rangle \\ -\frac{1}{2}\sqrt{3}\left\langle R_2^1\right\rangle & -\frac{1}{2}\sqrt{3}\left\langle R_2^{-1}\right\rangle & \left\langle R_2^0\right\rangle \end{pmatrix} \quad (14)$$

B. Minimization procedure of the free energy

To obtain the orientational distribution function that minimizes the free energy functional introduced in the main text we consider the stationarity equation

$$\frac{\delta}{\delta\psi\left(\hat{\omega}\right)}\Phi\left[\psi\right] = \beta\mu, \quad (15)$$

where the chemical potential μ serves as a Lagrange multiplier enforcing the normalization of the ODF. Explicitly the stationarity equation becomes

$$\log\psi\left(\hat{\omega}\right) + \eta\int d\hat{\omega}'\sin\gamma\left(\hat{\omega},\hat{\omega}'\right)\psi\left(\hat{\omega}'\right) + \xi_{\parallel}R_2^0\left(\hat{\omega}\right) - \xi_{\perp}R_4^4\left(\hat{\omega}\right) + \xi_d\left\{\frac{\left\langle R_2^2\right\rangle}{\sqrt{\left\langle R_2^2\right\rangle^2+\left\langle R_2^{-2}\right\rangle^2}}R_2^2\left(\hat{\omega}\right) + \frac{\left\langle R_2^{-2}\right\rangle}{\sqrt{\left\langle R_2^2\right\rangle^2+\left\langle R_2^{-2}\right\rangle^2}}R_2^{-2}\left(\hat{\omega}\right)\right\} = \beta\mu \quad (16)$$

We now note that the excluded volume interaction term is symmetric under the inversion of the direction of the particles, as well as all the additional terms, so in the expansion of the ODF

$$\psi\left(\hat{\omega}\right) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\psi_{lm}R_l^m\left(\hat{\omega}\right) \quad (17)$$

we can ignore terms with l odd. Moreover, because of its global rotational invariance the excluded volume term is agnostic about the value of m, and the additional terms only couple to even values of m so without loss of generality we can also restrict ourselves to m even. For numerical purposes, rather than working with the expansion Eq. (17), it is more convenient to work with a cumulant representation

$$\psi\left(\hat{\omega}\right)=\exp\left(\sum_{l=0}^{l_*}{}'\sum_{m=-l}^{l}{}' c_{lm}R_l^m\left(\hat{\omega}\right)\right)=$$
$$\frac{1}{Z\left[c_{lm}\right]}\exp\left(\sum_{l=2}^{l_*}{}'\sum_{m=-l}^{l}{}' c_{lm}R_l^m\left(\hat{\omega}\right)\right)\quad(18)$$

where l_* is a cut-off and the primes denote restriction to even values in the summations and the normalization is simply

$$Z\left[c_{lm}\right]=\int d\hat{\omega}\exp\left(\sum_{l=2}^{l_*}{}'\sum_{m=-l}^{l}{}' c_{lm}R_l^m\left(\hat{\omega}\right)\right)\quad(19)$$

Note that this representation guarantees positivity of the ODF, and requires far fewer terms to describe strongly peaked distributions. Inserting into the stationarity equation Eq. (16) and projecting out the coefficient using the orthogonality relations Eq. (3), we find

$$\frac{4\pi}{2l+1}c_{lm}+\eta\int d\hat{\omega}R_l^m\left(\hat{\omega}\right)\int d\hat{\omega}'\sin\gamma\left(\hat{\omega},\hat{\omega}'\right)\psi\left(\hat{\omega}'\right)+$$
$$\frac{4\pi}{2l+1}\xi_{\parallel}\delta_{l,2}\delta_{m,0}+\frac{4\pi}{2l+1}\xi_{\perp}\delta_{l,4}\delta_{m,4}+$$
$$\frac{4\pi}{2l+1}\xi_d\delta_{l,2}\delta_{m,2}\frac{\left\langle R_2^2\right\rangle}{\sqrt{\left\langle R_2^2\right\rangle^2+\left\langle R_2^{-2}\right\rangle^2}}+$$
$$\frac{4\pi}{2l+1}\xi_d\delta_{l,2}\delta_{m,-2}\frac{\left\langle R_2^{-2}\right\rangle}{\sqrt{\left\langle R_2^2\right\rangle^2+\left\langle R_2^{-2}\right\rangle^2}}=0\quad(20)$$

We can expand

$$\sin\gamma\left(\hat{\omega},\hat{\omega}'\right)=\sum_{l=0}^{\infty}{}' s_l R_l^0\left(\hat{\omega},\hat{\omega}'\right)\quad(21)$$

where following Kayser and Raveché [Phys. Rev. A 17, 2067–2072 (1978), see also Gradshteyn & Ryzhik, *Table of Integrals, Series, and Products*, Academic Press, entry 7.132]

$$\frac{4\pi}{(4n+1)}s_{2n}=\int d\hat{\omega}\sin\gamma\left(\hat{\omega},\hat{\omega}'\right)P_{2n}\left(\hat{\omega}\cdot\hat{\omega}'\right)$$
$$=2\pi\int_{-1}^{1}dx\sqrt{1-x^2}P_{2n}\left(x\right)$$
$$=-2\pi\frac{\pi}{4}4^{1-2n}\frac{1}{n}\begin{pmatrix}2n-2\\n-1\end{pmatrix}\frac{1}{n+1}\begin{pmatrix}2n\\n\end{pmatrix}\quad(22)$$

so that

$$s_{2n} = -2\pi \frac{4n+1}{n(n+1)} 4^{-(2n+1)} \begin{pmatrix} 2n-2 \\ n-1 \end{pmatrix} \begin{pmatrix} 2n \\ n \end{pmatrix} \tag{23}$$

We now note that (see Eq. (4))

$$\int d\hat{\omega} R_l^m(\hat{\omega}) R_{l'}^0(\hat{\omega}, \hat{\omega}') = \frac{4\pi}{2l+1} \delta_{l,l'} R_l^m(\hat{\omega}') \tag{24}$$

so that for l even

$$\begin{aligned} \int d\hat{\omega} R_l^m(\hat{\omega}) \int d\hat{\omega}' \sin\gamma(\hat{\omega}, \hat{\omega}') \psi(\hat{\omega}') &= \\ \sum_{l' \text{ even}} s_l \int d\hat{\omega}' \int d\hat{\omega} R_l^m(\hat{\omega}) R_{l'}^0(\hat{\omega}, \hat{\omega}') \psi(\hat{\omega}') &= \\ \frac{4\pi}{2l+1} s_l \int d\hat{\omega}' R_l^m(\hat{\omega}') \psi(\hat{\omega}') \equiv \frac{4\pi}{2l+1} s_l \langle R_l^m \rangle \end{aligned} \tag{25}$$

so that for $l \geq 2$

$$\begin{aligned} c_{lm} + \eta s_l \langle R_l^m \rangle + \xi_{\|} \delta_{l,2} \delta_{m,0} - \xi_{\perp} \delta_{l,4} \delta_{m,4} \\ + \xi_d \left\{ \delta_{l,2} \delta_{m,2} \frac{\langle R_2^2 \rangle}{\sqrt{\langle R_2^2 \rangle^2 + \langle R_2^{-2} \rangle^2}} + \delta_{l,2} \delta_{m,-2} \frac{\langle R_2^{-2} \rangle}{\sqrt{\langle R_2^2 \rangle^2 + \langle R_2^{-2} \rangle^2}} \right\} = 0 \end{aligned} \tag{26}$$

We can determine fairly accurate solutions to this functional equation by making a cumulant expansion of $\psi(\hat{\omega})$ in terms of real spherical harmonics up to rank $l = 4$.