

SUPPLEMENTARY INFORMATION

Appendix A: Derivation of Shape Equations

The purpose of this Appendix is to formulate the capillary shape equation for the splay-bend director and the quartic surface energy.

The nematic capillarity vector is defined by the gradient of the scalar field $r\gamma$:

$$\xi(\mathbf{n}, \mathbf{k}) = \nabla[r\gamma(\mathbf{k})] \quad (\text{A1})$$

where r is the magnitude of surface position vector \mathbf{r} : $\mathbf{r} = r\mathbf{k}$. Noting that $d(r\gamma) = \nabla(r\gamma) \cdot d\mathbf{r}$, the gradient of $r\gamma$ yield:

$$\xi(\mathbf{n}, \mathbf{k}) = \nabla[r\gamma(\mathbf{k})] = \gamma \frac{\partial r}{\partial \mathbf{r}} + r \frac{d\gamma}{d\mathbf{k}} = \gamma \mathbf{k} + \mathbf{I}_s \cdot \frac{d\gamma}{d\mathbf{k}} \quad (\text{A2})$$

Thus the normal and tangential components of capillarity vector are:

$$\begin{aligned} \xi_{\perp}(\mathbf{n}, \mathbf{k}) &= \gamma \mathbf{k} \\ \xi_{\parallel}(\mathbf{n}, \mathbf{k}) &= \mathbf{I}_s \cdot \frac{d\gamma}{d\mathbf{k}} = (\mathbf{I}_s \cdot \mathbf{n}) \frac{d\gamma}{d(\mathbf{n} \cdot \mathbf{k})} = \gamma' \mathbf{n}_{\parallel} \end{aligned} \quad (\text{A3})$$

Where $\gamma' = \frac{d\gamma}{d(\mathbf{n} \cdot \mathbf{k})}$ and $\mathbf{n}_{\parallel} = \mathbf{I}_s \cdot \mathbf{n}$ is the tangential component of the surface director field. Noticing that \mathbf{I}_s is the 2×2 unit surface dyadic: $\mathbf{I}_s = \mathbf{I} - \mathbf{k}\mathbf{k}$ where \mathbf{I} is the 3×3 volumetric unit tensor, we have:

$$\xi_{\parallel}(\mathbf{n}, \mathbf{k}) = \mathbf{I}_s \cdot \frac{d\gamma}{d\mathbf{k}} = (\mathbf{I} - \mathbf{k}\mathbf{k}) \cdot \frac{d\gamma}{d\mathbf{k}} = \mathbf{I} \cdot \frac{d\gamma}{d\mathbf{k}} - \mathbf{k}\mathbf{k} \cdot \frac{d\gamma}{d\mathbf{k}} \quad (\text{A4})$$

Replacing the quartic surface free energy $\gamma = \gamma_0 + \mu_2(\mathbf{n} \cdot \mathbf{k})^2 + \mu_4(\mathbf{n} \cdot \mathbf{k})^4$ to eqn (A3) we get:

$$\xi = \xi_{\perp} + \xi_{\parallel} = \left(\gamma_0 + \mu_2(\mathbf{n} \cdot \mathbf{k})^2 + \mu_4(\mathbf{n} \cdot \mathbf{k})^4 \right) \mathbf{k} + \left(2\mu_2(\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{t}) + 4\mu_4(\mathbf{n} \cdot \mathbf{k})^3(\mathbf{n} \cdot \mathbf{t}) \right) \mathbf{t} \quad (\text{A5})$$

Considering the capillary pressure definition, $\Delta P = (\nabla_s \cdot \xi) \equiv \mathbf{t} \cdot \partial \xi / \partial s$ where ΔP represents the pressure difference between the air and N* substrate, and ∇_s is the surface gradient, the case of zero capillary pressure, $\Delta P = 0$ yields $\nabla_s \cdot \xi = 0 \rightarrow \xi = \mathbf{C}_0 = \text{constant}$, where \mathbf{C}_0 is a constant vector:

$$\begin{aligned} (\xi_{\perp})^2 + (\xi_{\parallel})^2 &= \xi \cdot \xi = \mathbf{C}_0^2 \\ \xi_{\perp} \mathbf{k} + \xi_{\parallel} \mathbf{t} &= \mathbf{C}_0 \end{aligned} \quad (\text{A6})$$

Substituting eqn (A5) to eqn (A6) yields:

$$\left(\gamma_0 + \mu_2(\mathbf{n} \cdot \mathbf{k})^2 + \mu_4(\mathbf{n} \cdot \mathbf{k})^4 \right)^2 + \left(2\mu_2(\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{t}) + 4\mu_4(\mathbf{n} \cdot \mathbf{k})^3(\mathbf{n} \cdot \mathbf{t}) \right)^2 = \mathbf{C}_0^2 \quad (\text{A7})$$

Replacing the unit tangent, \mathbf{t} unit normal, \mathbf{k} in terms of the tangent angle ϕ : $\mathbf{t}(x) = (\sin\phi(x), \cos\phi(x), 0)$
 $\mathbf{n}(x) = (\cos\theta, \sin\theta, 0)$, and the director field, \mathbf{n} in terms of the director angle, θ : $\theta = qx$; $q = \frac{2\pi}{P_0}$:
 $\mathbf{n}(x) = (\cos\theta, \sin\theta, 0)$ and following the parametrization: at $s=0$, $d\kappa(s=0)/ds=0$; $\kappa(s=0) = \kappa_0$; $\phi(s=0) = \pi/2$;
 $(\mathbf{n} \cdot \mathbf{k})=0$, we obtain the constant \mathbf{C}_0 :

$$(\gamma_0) \delta_y = \mathbf{C}_0 \quad (\text{A8})$$

The dot product of the capillary vector, eqn (A6) with the unit vectors δ_y and δ_x respectively, gives:

$$\left(\gamma_o + \mu_2 (\mathbf{n} \cdot \mathbf{k})^2 + \mu_4 (\mathbf{n} \cdot \mathbf{k})^4 \right) \sin \varphi - \left(2\mu_2 (\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{t}) + 4\mu_4 (\mathbf{n} \cdot \mathbf{k})^3 (\mathbf{n} \cdot \mathbf{t}) \right) \cos \varphi = \gamma_o \quad (\text{A9-a})$$

$$\left(\gamma_o + \mu_2 (\mathbf{n} \cdot \mathbf{k})^2 + \mu_4 (\mathbf{n} \cdot \mathbf{k})^4 \right) \cos \varphi + \left(2\mu_2 (\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{t}) + 4\mu_4 (\mathbf{n} \cdot \mathbf{k})^3 (\mathbf{n} \cdot \mathbf{t}) \right) \sin \varphi = 0 \quad (\text{A9-b})$$

Multiplying eqn (A9-a) and eqn (A9-b) by $\cos \varphi$ and $\sin \varphi$ respectively, we get:

$$\left(\gamma_o + \mu_2 (\mathbf{n} \cdot \mathbf{k})^2 + \mu_4 (\mathbf{n} \cdot \mathbf{k})^4 \right) \sin \varphi \cos \varphi - \left(2\mu_2 (\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{t}) + 4\mu_4 (\mathbf{n} \cdot \mathbf{k})^3 (\mathbf{n} \cdot \mathbf{t}) \right) \cos^2 \varphi = \gamma_o \cos \varphi \quad (\text{A10-a})$$

$$\left(\gamma_o + \mu_2 (\mathbf{n} \cdot \mathbf{k})^2 + \mu_4 (\mathbf{n} \cdot \mathbf{k})^4 \right) \cos \varphi \sin \varphi + \left(2\mu_2 (\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{t}) + 4\mu_4 (\mathbf{n} \cdot \mathbf{k})^3 (\mathbf{n} \cdot \mathbf{t}) \right) \sin^2 \varphi = 0 \quad (\text{A10-b})$$

Subtracting eqn (A10-a) from eqn (A10-b) gives:

$$\left(2\mu_2 (\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{t}) + 4\mu_4 (\mathbf{n} \cdot \mathbf{k})^3 (\mathbf{n} \cdot \mathbf{t}) \right) \cos^2 \varphi + \left(2\mu_2 (\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{t}) + 4\mu_4 (\mathbf{n} \cdot \mathbf{k})^3 (\mathbf{n} \cdot \mathbf{t}) \right) \sin^2 \varphi = -\gamma_o \cos \varphi \quad (\text{A11})$$

$$2\mu_2 (\mathbf{n} \cdot \mathbf{k})(\mathbf{n} \cdot \mathbf{t}) + 4\mu_4 (\mathbf{n} \cdot \mathbf{k})^3 (\mathbf{n} \cdot \mathbf{t}) + \gamma_o \cos \varphi = 0$$

Replacing $\mathbf{t}(x)$, $\mathbf{k}(x)$, and $\mathbf{n}(x)$ in terms of the normal angle φ and the director angle θ yields the algebraic shape equation for the normal angle $\varphi(x, \mu_2/\gamma_o, \mu_4/\gamma_o, P_0)$:

$$\frac{2\mu_2}{\gamma_o} \cos(\varphi - \theta) \sin(\varphi - \theta) + \frac{4\mu_4}{\gamma_o} \cos^3(\varphi - \theta) \sin(\varphi - \theta) + \cos \varphi = 0 \quad (\text{A12})$$

Appendix B: Linear Model

The purpose of this Appendix is to formulate the linear model corresponding to the capillary shape equation for the splay-bend director and the quartic surface energy.

The dot product of the capillary vector, eqn (A5) with the unit tangent, \mathbf{t} , gives:

$$\left(2\mu_2 (\mathbf{n} \cdot \mathbf{k}) + 4\mu_4 (\mathbf{n} \cdot \mathbf{k})^3 \right) (\mathbf{n} \cdot \mathbf{t}) = \gamma_o \delta_y \cdot \mathbf{t} \quad (\text{B1})$$

Expressing the unit tangent, \mathbf{t} and unit normal, \mathbf{k} in terms of the surface amplitude, h_x gives:

$$\mathbf{t} = \frac{1}{\sqrt{1+h_x^2}} \begin{pmatrix} 1 \\ -h_x \end{pmatrix}; \quad \mathbf{k} = \frac{1}{\sqrt{1+h_x^2}} \begin{pmatrix} h_x \\ 1 \end{pmatrix} \quad (\text{B2})$$

As we focus on the surface nano-wrinkling, $h_x \ll 1$, the linear approximation of \mathbf{t} and \mathbf{k} is valid: $\mathbf{t} = \delta_x$; $\mathbf{k} = \delta_y$.

Replacing the unit tangent, \mathbf{t} and unit normal, \mathbf{k} into eqn (B1) gives:

$$2\mu_2 n_y n_x + 4\mu_4 n_y^3 n_x = -\gamma_o h_x \quad (\text{B3})$$

Rearranging eqn (B3) yields:

$$\left(2\mu_2 (\mathbf{n} \cdot \delta_y) + 4\mu_4 (\mathbf{n} \cdot \delta_y)^3 \right) (\mathbf{n} \cdot \delta_x) = -\gamma_o h_x \quad (\text{B4})$$

Since $n_x dx = \frac{1}{q} dn_y$, the eqn (B4) becomes:

$$-\frac{1}{q} \left(\mu_2 (\mathbf{n} \cdot \delta_y)^2 + \mu_4 (\mathbf{n} \cdot \delta_y)^4 \right) = \gamma_o h \quad (\text{B5})$$

Rearranging eqn (B5) gives the surface profile, $h(x)$ as the ratio of anisotropic anchoring energy to isotropic surface tension (divided by wave vector, q):

$$h(x) = -\frac{\gamma_{\text{anc}}}{\gamma_o q} = -\frac{1}{\gamma_o q} \left(\mu_2 (\mathbf{n} \cdot \boldsymbol{\delta}_y)^2 + \mu_4 (\mathbf{n} \cdot \boldsymbol{\delta}_y)^4 \right) = -\frac{1}{\gamma_o q} \left(\mu_2 (\sin qx)^2 + \mu_4 (\sin qx)^4 \right) \quad (\text{B6})$$

The surface curvature h_{xx} then can be obtained from:

$$h_{xx} = -2 \frac{\mu_2}{\gamma_o} q \left(\cos qx^2 - \sin qx^2 \right) - 4 \frac{\mu_4}{\gamma_o} q \left(3 \sin qx^2 \cos qx^2 - (\sin qx)^4 \right) \quad (\text{B7})$$

Appendix C: Multiple Scales

The purpose of this Appendix is to formulate the surface amplitudes for the planar, h_{\parallel} , homeotropic, h_{\perp} and oblique, h_o orientations as a function of $r = \mu_2 / 2\mu_4$; $-1 \leq r \leq 0$.

Considering eqn (B6), we can find the planar, h_{\parallel} homeotropic, h_{\perp} and oblique, h_o amplitudes as follows:

(a) Planar

$$n_x = 1, \sin qx = 0 \rightarrow h_{\parallel} = 0 \quad (\text{C1})$$

(b) Homeotropic

$$n_y = 1, \cos qx = 0 (\mathbf{n} \text{ along } y) \rightarrow h_{\perp} = -\frac{1}{\gamma_o q} (\mu_2 + \mu_4) = -\frac{\mu_4}{\gamma_o q} \left(2 \frac{\mu_2}{2\mu_4} + 1 \right) = -\frac{\mu_4}{\gamma_o q} (2r + 1) \quad (\text{C2})$$

(c) Oblique

for $-1 < \mu_2 / 2\mu_4 < 0$, $\mu_2 < 0$

$$\sin qx^2 = -\frac{\mu_2}{2\mu_4}, \cos qx^2 = 1 + \frac{\mu_2}{2\mu_4} \rightarrow h_o = -\frac{1}{\gamma_o q} \left(-\mu_2 \left(\frac{\mu_2}{2\mu_4} \right) + \mu_4 \left(\frac{\mu_2}{2\mu_4} \right)^2 \right) = \frac{\mu_4}{\gamma_o q} \left(\left(\frac{\mu_2}{2\mu_4} \right)^2 \right) = \frac{\mu_4}{\gamma_o q} (r^2) \quad (\text{C3})$$

Appendix D: Scaling Laws

The purpose of this Appendix is to formulate the two-scale ratio $SR = h_o / h_2$ as a function of $r = \mu_2 / 2\mu_4$. Using straight algebra, the distance h_2 (shown in Fig 8) can be expressed in terms of amplitudes for the homeotropic, h_{\perp} and oblique, h_o orientations:

$$h_2 = h_o - \text{sign}(h_{\perp}) \times |h_{\perp}| = \frac{\mu_4}{\gamma_o q} \left(\left(\frac{\mu_2}{2\mu_4} \right)^2 + 2 \frac{\mu_2}{2\mu_4} + 1 \right) = \frac{\mu_4}{\gamma_o q} (r^2 + 2r + 1) > 0 \quad (\text{D1})$$

Using the oblique amplitude, h_o , eqn (C3) gives the following linear scaling law:

$$\frac{h_o}{h_2} = \frac{\frac{\mu_4}{\gamma_o q} \left(\left(\frac{\mu_2}{2\mu_4} \right)^2 \right)}{\frac{\mu_4}{\gamma_o q} \left(\left(\frac{\mu_2}{2\mu_4} \right)^2 + 2 \frac{\mu_2}{2\mu_4} + 1 \right)} = \frac{r^2}{r^2 + 2r + 1} = \frac{r^2}{(1+r)^2} \quad (\text{D2})$$

We note that the same scaling law (D2) are obtained for the H^+ / P_{12} modes.