Telephone-cord instabilities in thin smectic capillaries

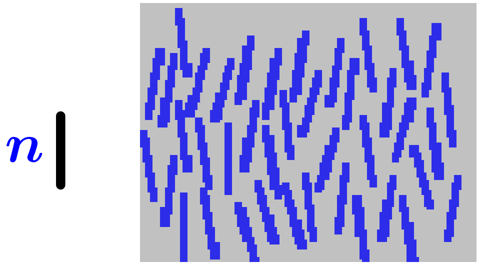
Paolo Biscari, Politecnico di Milano, Italy

Maria Carme Calderer, University of Minnesota, USA

Overview

- Free energy functional and geometry
- Chirality-induced SmA-SmC transition
- Bent SmA*
- Helicoidal SmC*

Nematic liquid crystals - Frank energy



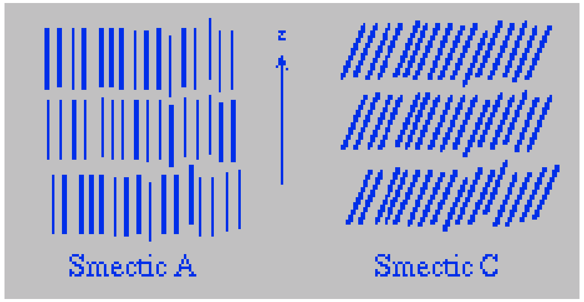
Order parameter: $\boldsymbol{n}$, director

$$\sigma_{\text{nem}} = K_1 \left(\operatorname{div} \boldsymbol{n}\right)^2 + K_2 \left(\boldsymbol{n} \cdot \operatorname{curl} \boldsymbol{n} + q_{\text{ch}}\right)^2 + K_3 \left|\boldsymbol{n} \wedge \operatorname{curl} \boldsymbol{n} + \boldsymbol{v}_0\right|^2$$
$$+ \left(K_2 + K_4\right) \left(\operatorname{tr}(\boldsymbol{\nabla} \boldsymbol{n})^2 - (\operatorname{div} \boldsymbol{n})^2\right)$$

q_{ch} : cholesteric pitch

$\boldsymbol{v}_0$: spontaneous bend (below)

Smectic liquid crystals - elastic energy



Order parameter: $\psi = \rho\, \mathrm{e}^{\mathrm{i}\omega}$,

$$\sigma_{\mathrm{sm}} = C_{\|} \left| \boldsymbol{n} \cdot (\boldsymbol{\nabla}\psi - \mathrm{i}\, q_{\mathrm{sm}} \psi \boldsymbol{n}) \right|^2 + C_{\perp} \left| \boldsymbol{\nabla}\psi - \mathrm{i}\, q_{\mathrm{sm}} \psi \boldsymbol{n} \right|_{\perp}^2 + \zeta(\rho)$$

q_{sm}: smectic pitch

$$\left| \boldsymbol{n} \cdot (\boldsymbol{\nabla}\psi - \mathrm{i}\, q_{\mathrm{sm}} \psi \boldsymbol{n}) \right|^2 = \left(\boldsymbol{n} \cdot \boldsymbol{\nabla}\rho \right)^2 + \rho^2 \left(\boldsymbol{n} \cdot \boldsymbol{\nabla}\omega - q_{\mathrm{sm}} \right)^2$$

$$\left| \boldsymbol{\nabla}\psi - \mathrm{i}\, q_{\mathrm{sm}} \psi \boldsymbol{n} \right|_{\perp}^2 = \left| \boldsymbol{\nabla}\rho \right|_{\perp}^2 + \rho^2 \left| \boldsymbol{\nabla}\omega \right|_{\perp}^2$$

$C_{\perp} \lesseqgtr 0$; σ_{sm} positively defined provided $C_{\|} \cos^2\alpha + C_{\perp} \sin^2\alpha > 0$

$\big(\alpha,$ angle $(\boldsymbol{n}, \boldsymbol{\nabla}\omega)\big)$

Spontaneous polarization

Let $\boldsymbol{P} = P\,\boldsymbol{p}$ be the (spontaneous) polarization vector.

$$\sigma_{\rm pol}\big[\boldsymbol{P}\big] = G_1\,\big(\mathrm{div}\,\boldsymbol{P}\big)^2 + G\,\big|\boldsymbol{\nabla}\boldsymbol{P}\big|^2 + \mathcal{G}\big(P\big)\;.$$

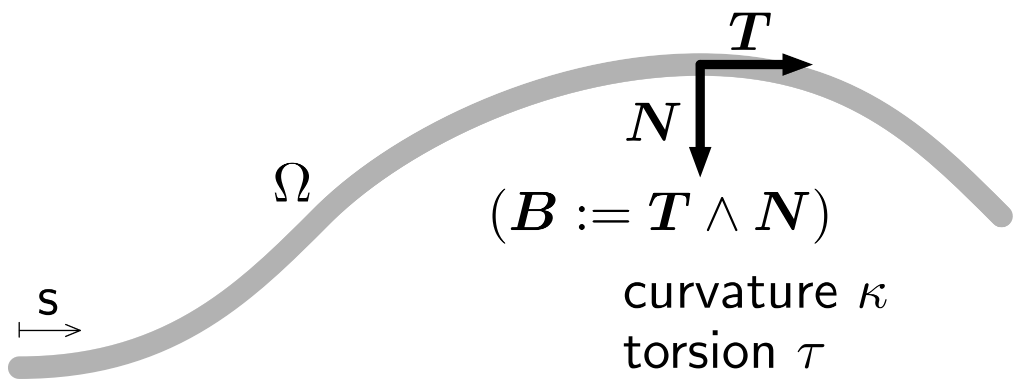
$\mathcal{G}$: scalar potential depending only on P.

Induced charges on the boundary: $\sigma_{\rm anch}[\boldsymbol{P}] = \omega_P\,P\,\big(1 - \boldsymbol{p}\cdot\boldsymbol{\nu}\big)\;.$

The spontaneous bend depends on $\boldsymbol{P}$:

$$\boldsymbol{v}_0 = \begin{cases} \lambda\,\boldsymbol{P} & \text{if } \boldsymbol{P} \neq \boldsymbol{0} \quad \text{(spontaneous-polarization induced bend)} \\ b_0\,\boldsymbol{\nu}\wedge\boldsymbol{n} & \text{if } \boldsymbol{P} = \boldsymbol{0} \quad \text{(flexoelectric; } \boldsymbol{\nu}\text{, layer normal)} \end{cases}$$

Geometry



$$\Omega = \left\{ P \in \mathbb{R}^3 : P = \boldsymbol{c}(s) + \xi\, \boldsymbol{e}\,,\ \text{for } s \in [0,\ell]\,,\ \xi \in [0,r]\,, \quad \boldsymbol{e} = \cos\vartheta\, \boldsymbol{N} + \sin\vartheta\, \boldsymbol{B} \right\}.$$

Free-boundary conditions on nematic and smectic fields

Thin capillary: all fields depend only on s $\quad \big(\ \omega(s) \quad \Rightarrow \quad \boldsymbol{\nu} = \boldsymbol{T}\ \big)$

$$\boldsymbol{n} = \cos\alpha\, \boldsymbol{T} + \sin\alpha\cos\varphi\, \boldsymbol{N} + \sin\alpha\sin\varphi\, \boldsymbol{B}\,.$$

Linear shapes 1/3

Let $\kappa = \tau \equiv 0$ and $\boldsymbol{P} = \boldsymbol{0}$.

A non-zero cholesteric pitch may induce a SmA-SmC transition even if $C_\perp > 0$.

$$\sigma = \sigma_{\rm nem} + \sigma_{\rm sm} = \left(K_1 \sin^2\alpha + K_3 \cos^2\alpha\right)\alpha'^2 + K_2\left(q_{\rm ch} - \varphi' \sin^2\alpha\right)^2$$
$$+ K_3 \sin^2\alpha \left(b_0 - \varphi' \cos\alpha\right)^2 + C_\parallel\left[\rho'^2 \cos^2\alpha + \rho^2\left(\omega'\cos\alpha - q_{\rm sm}\right)^2\right]$$
$$+ C_\perp \sin^2\alpha\left(\rho'^2 + \rho^2\omega'^2\right) + \zeta(\rho)$$

Integrate E.L. eqn's for φ,ω ...

Look for solutions with $\alpha \equiv \alpha_0$ and $\rho \equiv \rho_0$ ...

Linear shapes 2/3

$$\sigma(\alpha_0,\rho_0) = \frac{K_2K_3\,(q_{\rm ch}\cos\alpha_0 - b_0\sin^2\alpha_0)^2}{K_2\sin^2\alpha_0 + K_3\cos^2\alpha_0} + \frac{C_\parallel\,C_\perp\,\rho_0^2 q_{\rm sm}^2\sin^2\alpha_0}{C_\parallel\cos^2\alpha_0 + C_\perp\sin^2\alpha_0} + \zeta(\rho_0)\;.$$

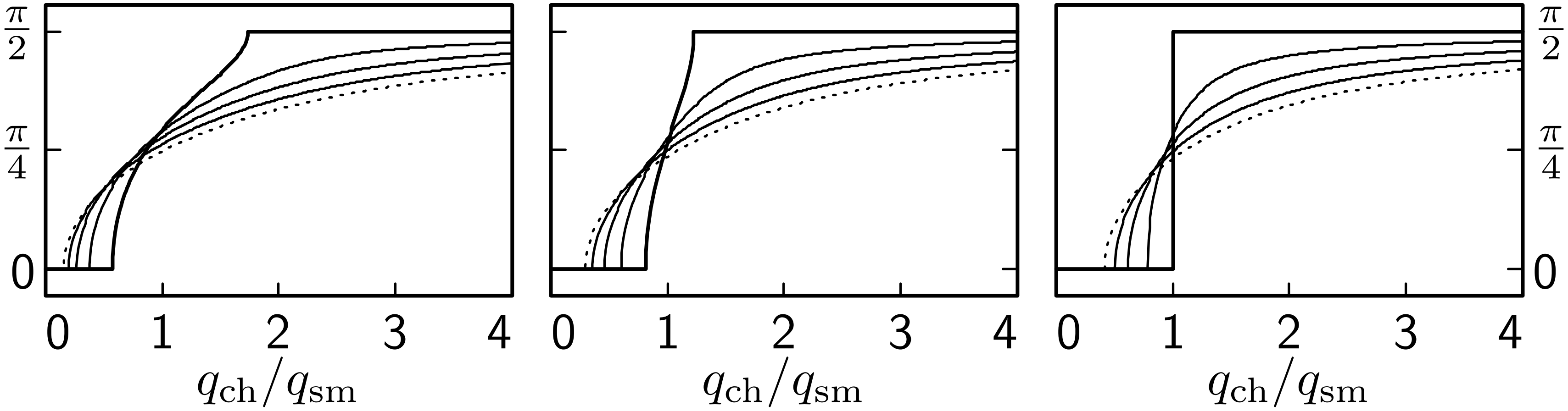
- SmA phase $(\alpha_0 = 0)$ always a stationarity point.
- SmA unstable even when $C_\perp > 0$, provided that

$$C_\perp q_{\rm sm}^2\rho_0^2 < \frac{K_2}{K_3}\,q_{\rm ch}\,\big(K_2 q_{\rm ch} + 2b_0K_3\big)\;,$$

since

$$\sigma(\alpha_0,\rho_0) = \sigma(0,\rho_0) + \left(C_\perp q_{\rm sm}^2\rho_0^2 - \frac{K_2 q_{\rm ch}\,\big(K_2 q_{\rm ch} + 2b_0K_3\big)}{K_3}\right)\alpha_0^2 + O(\alpha_0^4) \qquad \text{as} \quad \alpha_0\to 0.$$

Linear shapes 3/3



$\alpha_0^{\rm opt}$ as a function of $q_{\rm ch}/q_{\rm sm}$ when

$K_2 = K_3 = C_{\|}\rho_0^2$;
$C_\perp = \frac{1}{3}C_{\|}$ (left), $C_\perp = \frac{2}{3}C_{\|}$ (center) or $C_\perp = C_{\|}$ (right), and
$b_0/q_{\rm sm} = 0$ (bold), $\frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1$ (dotted).

Flexoelectric bending?

No spontaneous bending if $\boldsymbol{v}_0$ is of flexoelectric origin.

$$\int_{\xi,\vartheta} \sigma = f(\kappa r) K_{13} A^2 + \big(f(\kappa r) - 1\big) K_{23} \Phi^2 + \varpi^2 \, \frac{f(\kappa r) - 1}{f(\kappa r)}$$

$$+ K_{23} \left(\Phi - q_1\right)^2 + \frac{K_2 K_3}{K_{23}} \left(q_{\rm ch} \cos\alpha - b_0 \sin^2\alpha\right)^2 + \frac{C_\parallel C_\perp \rho_0^2 q_{\rm sm}^2 \sin^2\alpha}{C_\parallel \cos^2\alpha + C_\perp \sin^2\alpha}$$

with

$$A := \alpha' + \kappa \cos\varphi \qquad K_{13} := K_1 \sin^2\alpha + K_3 \cos^2\alpha$$

$$\Phi := (\varphi' - \tau) \sin\alpha - \kappa \cos\alpha \sin\varphi \qquad K_{23} := K_2 \sin^2\alpha + K_3 \cos^2\alpha$$

$$q_1 := \frac{(K_2 q_{\rm ch} + K_3 b_0 \cos\alpha) \sin\alpha}{K_{23}} \qquad \varpi^2 := \frac{C_\parallel^2 \rho_0^4 q_{\rm sm}^2 \cos^2\alpha}{C_\parallel \cos^2\alpha + C_\perp \sin^2\alpha}$$

$$f(x) := \begin{cases} 2\left(1 - \sqrt{1 - x^2}\right) \Big/ x^2 & \text{if } x \in (0, 1] \\ 1 & \text{if } x = 0 \,, \end{cases}$$

Bent SmA* 1/4

Let $\alpha \equiv 0$. *Assume $\rho \equiv \rho_0$, $P \equiv P_0 =: \lambda_0/\lambda$,* $([\lambda_0] = L^{-1})$.

Let $\Gamma := G P_0^2$, $\Gamma_1 := G_1 P_0^2$.

Let $\boldsymbol{P} = P_0 \left(\cos\phi\, \boldsymbol{B} + \sin\phi\, \boldsymbol{N} \right)$.

Bulk free-energy density $\sigma_{\rm b} = \sigma_{\rm nem} + \sigma_{\rm sm} + \sigma_{\rm pol}$

$$\sigma_{\rm b} = K_2 q_{\rm ch}^2 + K_3 \left[\left(\lambda_0 - \frac{\kappa}{1 - \kappa\xi\cos\vartheta} \right)^2 + \frac{2\kappa\lambda_0 \left(1 - \sin\phi\right)}{1 - \kappa\xi\cos\vartheta} \right]$$

$$+ C_{\|} \rho_0^2 \left(\frac{\omega'}{1 - \kappa\xi\cos\vartheta} - q_{\rm sm} \right)^2 + \frac{\Gamma_1\, \kappa^2 \sin^2\phi}{(1 - \kappa\xi\cos\vartheta)^2}$$

$$+ \Gamma\, \frac{\kappa^2 \sin^2\phi + (\phi' + \tau)^2}{(1 - \kappa\xi\cos\vartheta)^2} \; .$$

Anchoring: $\sigma_{\rm anch} = \omega_P\, P_0 \left(1 - \sin(\vartheta + \phi)\right)$.

Bent SmA* 2/4

Integrate over the transverse section, insert equilibrium value of $\omega' \ldots$

$$\frac{1}{\pi r^2}\int_{\xi,\vartheta}\sigma = K_2 q_{\rm ch}^2 + K_3\big(\lambda_0^2 - 2\kappa\lambda_0\sin\phi + \kappa^2 f(\kappa r)\big) + C_{\|}\rho_0^2 q_{\rm sm}^2\,\frac{f(\kappa r)-1}{f(\kappa r)} + (\Gamma+\Gamma_1)\,\kappa^2\sin^2\phi\, f(\kappa r) + \Gamma\,(\phi'+\tau)^2 f(\kappa r) + \frac{\omega_P\lambda_0\,\big(2+\kappa r\,\sin\phi\big)}{\lambda r}$$

Optimal polarization direction for K_3-term: $\boldsymbol{P} = P_0\,\boldsymbol{N}$.

Bent SmA* 3/4

With above choices

$$\frac{\mathcal{F}_{\rm opt}(\kappa,\tau)}{\pi r^2\ell} = A_0 - A_1\kappa r + A_2\,(\kappa r)^2\, f(\kappa r) - \frac{A_3}{f(\kappa r)} + B_1\, f(\kappa r)\,(\tau r)^2\ ,$$

where A's and B's are non-negative:

$$A_0 = K_2 q_{\rm ch}^2 + K_3\lambda_0^2 + C_\| \rho_0^2 q_{\rm sm}^2 + 2\omega_P P_0/r$$

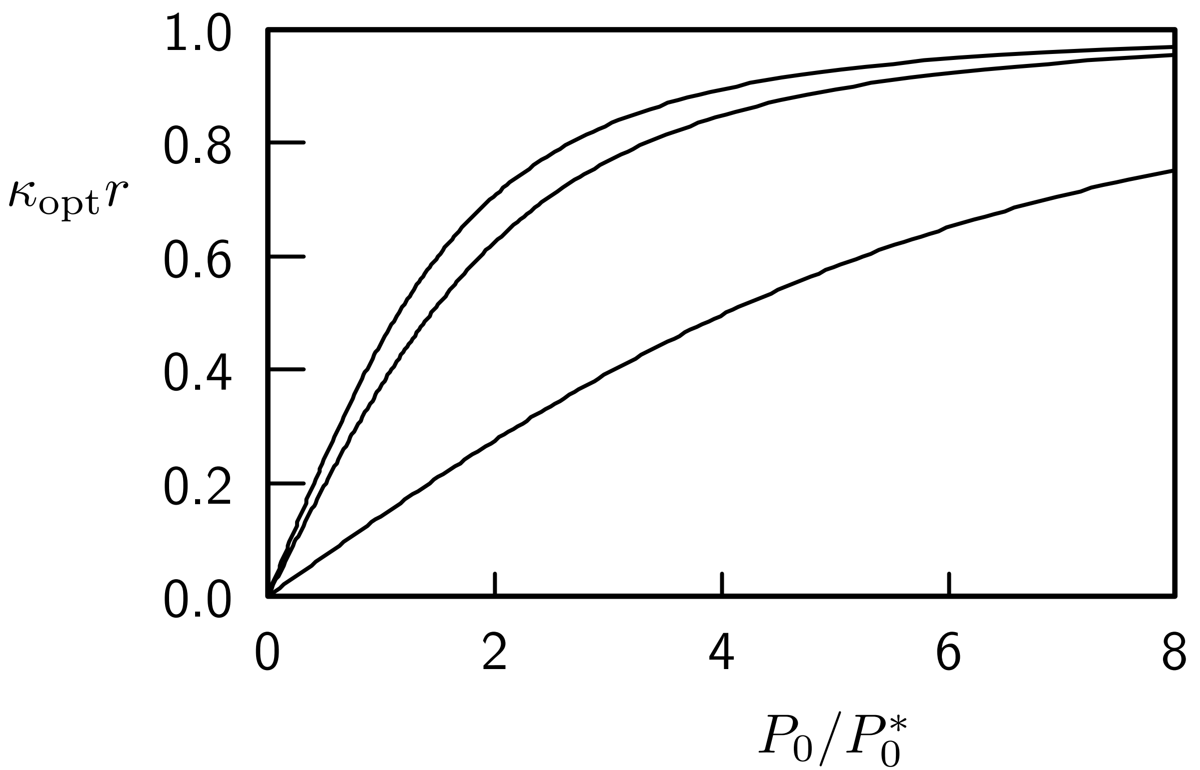
$$A_1 = (2K_3\lambda - \omega_P)\,\frac{P_0}{r} \qquad\qquad A_3 = C_\|\rho_0^2 q_{\rm sm}^2$$

$$A_2 = \big(K_3 + \Gamma + \Gamma_1\big)\,/\,r^2 \qquad\qquad B_1 = \Gamma/r^2\ .$$

Minimum attained at $\tau = 0$ and positive κ:

$$\frac{\mathcal{F}_{\rm opt}(\kappa,0)}{\pi r^2\ell} = (A_0 - A_3) - A_1\kappa r + \left(A_2 + \frac{A_3}{3}\right)(\kappa r)^2 + O(\kappa r)^4 \quad (\kappa r \to 0)$$

Preferred curvature of the axis of a SmA capillary*



$$\left(P_0^* := \frac{K_3 + \Gamma + \Gamma_1}{(2K_3\lambda - \omega_P)r} \right).$$

Top to bottom, $\dfrac{C_{\|}\rho_0^2 q_{\rm sm}^2}{K_3 + \Gamma + \Gamma_1} = 0, 1, 10.$

Helicoidal SmC* 1/4

Assume $\alpha \equiv \alpha_0$, $\phi \equiv \phi_0$. Then:

$$\sigma_{\rm b} = \sigma_{\rm sm}(\alpha_0) + K_1 \frac{\kappa^2 \cos^2\varphi \sin^2\alpha_0}{(1-\kappa\xi\cos\vartheta)^2}$$

$$+ K_2 \left(q_{\rm ch} - \frac{\sin\alpha_0}{1-\kappa\xi\cos\vartheta} \big((\varphi' - \tau)\sin\alpha_0 - \kappa\cos\alpha_0\sin\varphi \big) \right)^2$$

$$+ K_3 \Bigg[\left(\lambda_0 \sin\phi_0 - \frac{\kappa\cos\varphi\cos\alpha_0}{1-\kappa\xi\cos\vartheta} \right)^2$$

$$+ \left(\lambda_0 \cos\phi_0 - \frac{(\varphi'-\tau)\sin\alpha_0 - \kappa\cos\alpha_0\sin\varphi}{1-\kappa\xi\cos\vartheta} \cos\alpha_0 \right)^2 \Bigg]$$

$$+ \frac{\Gamma_1}{(1-\kappa\xi\cos\vartheta)^2} \Big[\big((\varphi'-\tau)\cos\alpha_0 + \kappa\sin\alpha_0\sin\varphi \big) \cos\phi_0 \sin\alpha_0$$

$$- \big((\varphi'-\tau)\sin\alpha_0\cos\phi_0 + \kappa\cos\varphi\sin\phi_0 - \kappa\cos\alpha_0\sin\varphi\cos\phi_0 \big) \cos\alpha_0 \Big]^2$$

$$+ \frac{\Gamma}{(1-\kappa\xi\cos\vartheta)^2} \Big[\big((\varphi'-\tau)\cos\alpha_0 + \kappa\sin\alpha_0\sin\varphi \big)^2$$

$$+ \big((\varphi'-\tau)\sin\alpha_0\cos\phi_0 + \kappa\cos\varphi\sin\phi_0 - \kappa\cos\alpha_0\sin\varphi\cos\phi_0 \big)^2 \Big]$$

Helicoidal SmC* 2/4

1-constant approximation + thin capillary regime:

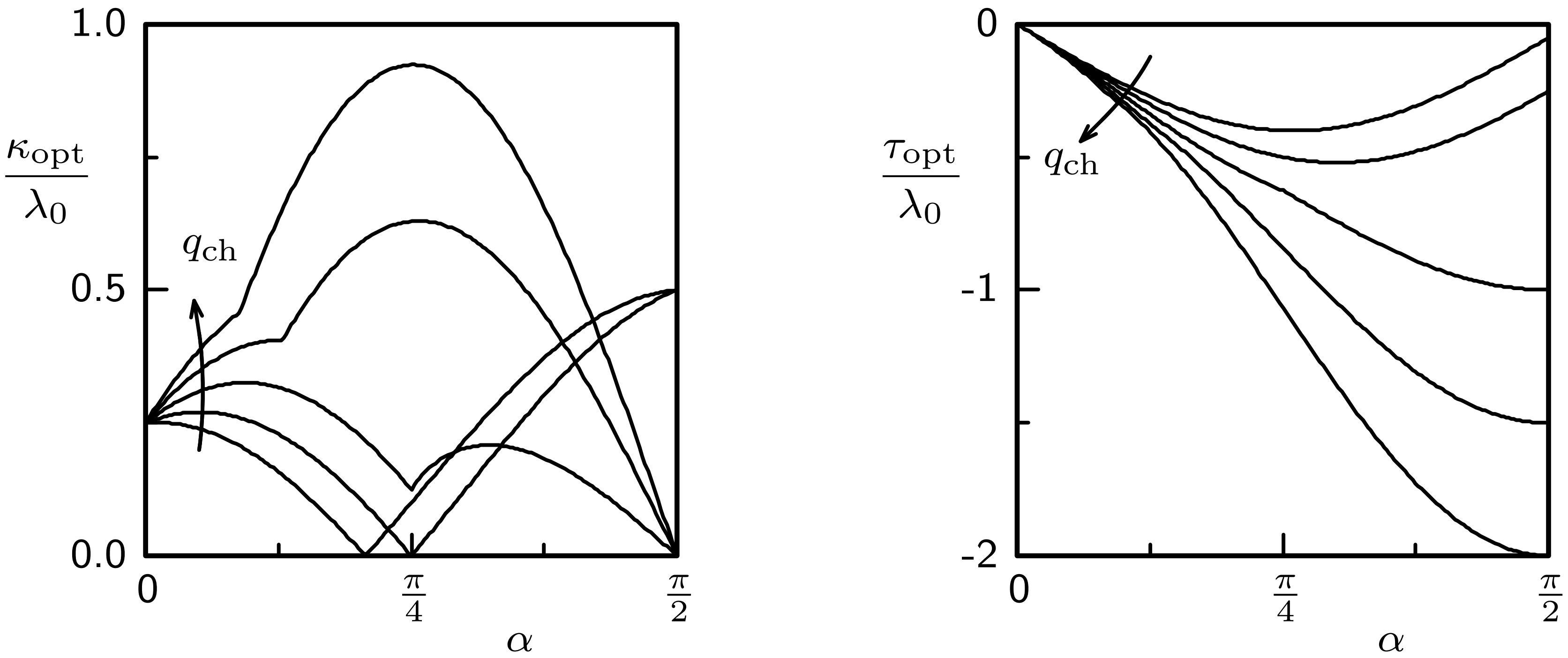
$$K_1 = K_2 = K_3 = \Gamma = \omega_P/\lambda =: K \; ; \qquad \Gamma_1 = 0 \; ; \qquad \lambda_0 r \ll 1 \quad \Longrightarrow$$

If $q_{\text{ch}} = 0$,

$$\kappa_{\text{opt}}\Big|_{q_{\text{ch}}=0} = \frac{|3\cos 2\alpha_0 - 1|}{8}\,\lambda_0 \quad \text{and} \quad \tau_{\text{opt}}\Big|_{q_{\text{ch}}=0} = -\frac{3}{8}\sin 2\alpha_0\,\lambda_0 \; .$$

In general, $\kappa_{\text{opt}}, \tau_{\text{opt}}$ are different from zero.

Helicoidal SmC* 3/4



Curvature and torsion of an optimal-shaped SmC* capillary.
The plots correspond to $q_{ch}/\lambda_0 = 0.1, 0.5, 1.0, 1.5, 2.$

Exp obs: $r = 0.85\mu$m, $r_{hel} = 2.25\mu$m, $p_{hel} = 6.7\mu$m; $q_{ch} = 0$ $\Longrightarrow$

$$\alpha_0 \approx 20^\circ\text{C}.$$

Small-α_0 limit:

$$\kappa_{\rm opt} = \frac{2K_3\lambda - \omega_P}{2(K_3+\Gamma+\Gamma_1)} P_0 + O(\alpha_0)\,,$$

$$\tau_{\rm opt} = -\frac{K_3\big(2(\Gamma+\Gamma_1)\lambda + \omega_P\big)}{2\Gamma(K_3+\Gamma+\Gamma_1)} P_0\alpha_0 + O(\alpha_0^2) \quad \text{as } \alpha_0 \to 0\,.$$

Optimal free energy:

$$\frac{\mathcal{F}_{\rm opt}}{\pi r^2 \ell} = \sigma_{\rm sm}(\alpha_0) + \left[K_3\lambda_0^2 - \frac{\big(2K_3\lambda - \omega_P\big)^2 P_0^2}{4(K_3+\Gamma+\Gamma_1)} + K_2 q_{\rm ch}^2 + \frac{2\omega_P P_0}{r}\right]$$
$$- \frac{2K_2\big(2K_3\lambda - \omega_P\big)P_0 q_{\rm ch}\alpha_0}{2(K_3+\Gamma+\Gamma_1)} + O(\alpha_0^2) \quad \ldots$$

SmA phase unstable if $q_{\rm ch} \neq 0$!*

Conclusions

- A non-null cholesteric pitch may induce a SmA-SmC transition, even when $C_\perp > 0$
- Flexoelectric effects do not lead to a spontaneous capillary bending
- $\kappa > 0$ in a SmA* capillary
- Telephone-cord instabilities arise in SmC*
- Cholesteric pitch not a direct ingredient for the tel-cord instability, but it induces also a SmA*-SmC* transition.