Landau-de Gennes' theory for smectic liquid crystals

Paolo Biscari, Politecnico di Milano, Italy

Maria Carme Calderer, University of Minnesota, USA

Eugene M. Terentjev, Cambridge University, UK

Motivation

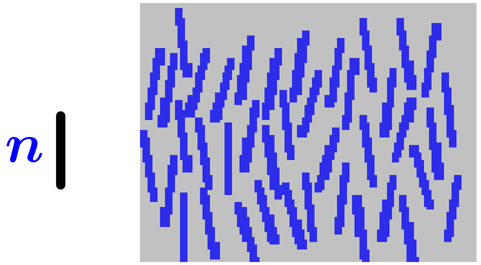
- Telephone-cords instabilities in ferroelectric smectics

- Need for a unified isotropic-nematic-smectic description based on nematic order tensor + smectic complex phase

Telephone-cords instabilities in simplified geometry

(Frank description)

Nematic liquid crystals - Frank energy



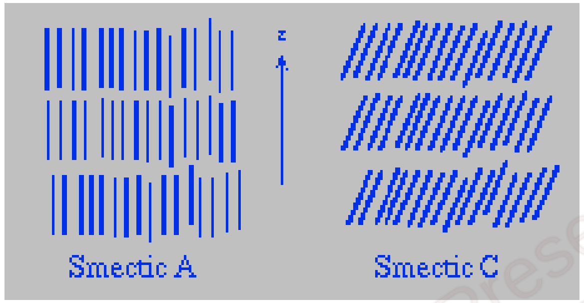
Order parameter: $\boldsymbol{n}$, director

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

q_{ch} : cholesteric pitch

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

Smectic liquid crystals - elastic energy



Order parameter: $\psi = \rho\, e^{i\omega}$ $\quad$ ($\nabla\omega \parallel \boldsymbol{\nu}$, layer normal)

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

q_{sm}: smectic pitch, $\quad C_{\parallel} > 0$

Let $\cos\alpha = \boldsymbol{n} \cdot \boldsymbol{\nu}$

Minimum of σ_{sm} placed at $\alpha = 0$ (Sm-A) when $C_{\perp} \geq 0$

Minimum of σ_{sm} placed at $\alpha > 0$ (Sm-C) when $C_{\perp} < 0$

Spontaneous polarization

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

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

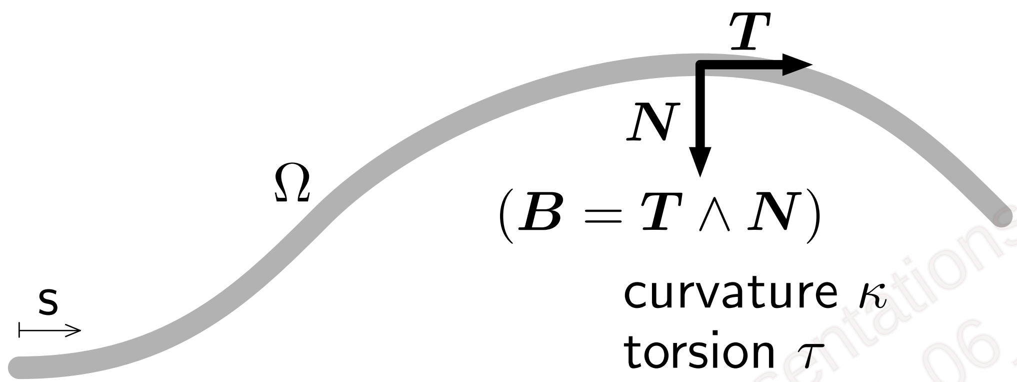
$\mathcal{G}$: scalar potential depending only on P.

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

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



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

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 1/2

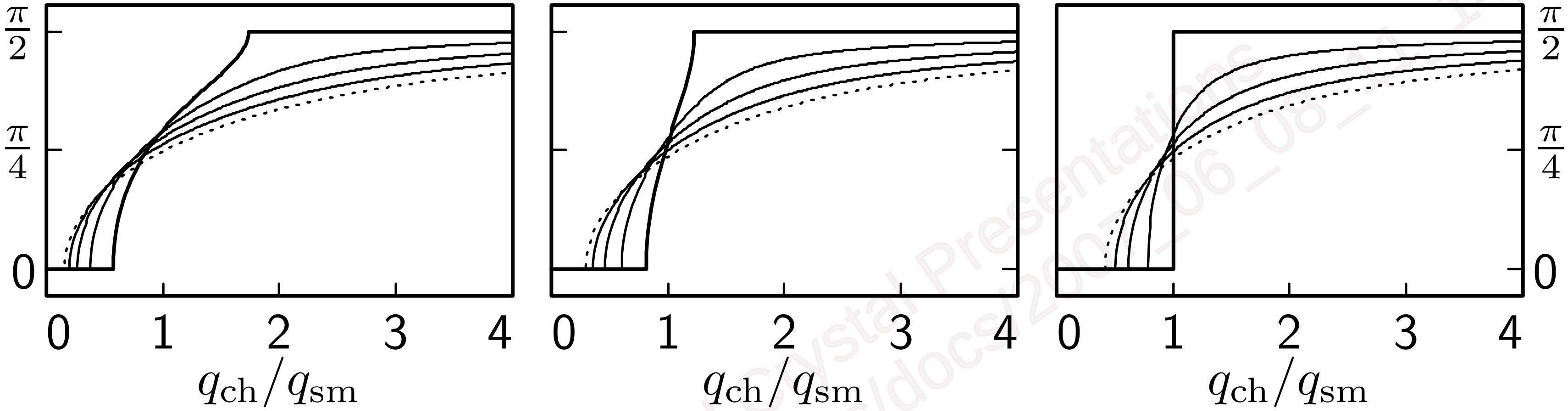
Let $\kappa = \tau \equiv 0$ and $\boldsymbol{P} = \boldsymbol{0}$

A non-zero cholesteric pitch may induce a Sm-A–Sm-C transition even if $C_\perp > 0$.

More precisely, Sm-A unstable even whenever

$$C_\perp q_{\rm sm}^2 \rho_0^2 < \frac{K_2}{K_3}\, q_{\rm ch} \left(K_2 q_{\rm ch} + 2 b_0 K_3\right) .$$

Linear shapes 2/2



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

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

Capillary bending

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

Let $\alpha \equiv 0$ (Sm-A). *Assume* $\rho \equiv \rho_0$, $P \equiv P_0 =: \lambda_0/\lambda$, $([\lambda_0] = L^{-1})$.
Let $\Gamma = GP_0^2$, $\Gamma_1 = G_1 P_0^2$.
Let $\boldsymbol{P} = P_0 \left(\cos\phi\, \boldsymbol{B} + \sin\phi\, \boldsymbol{N} \right)$.

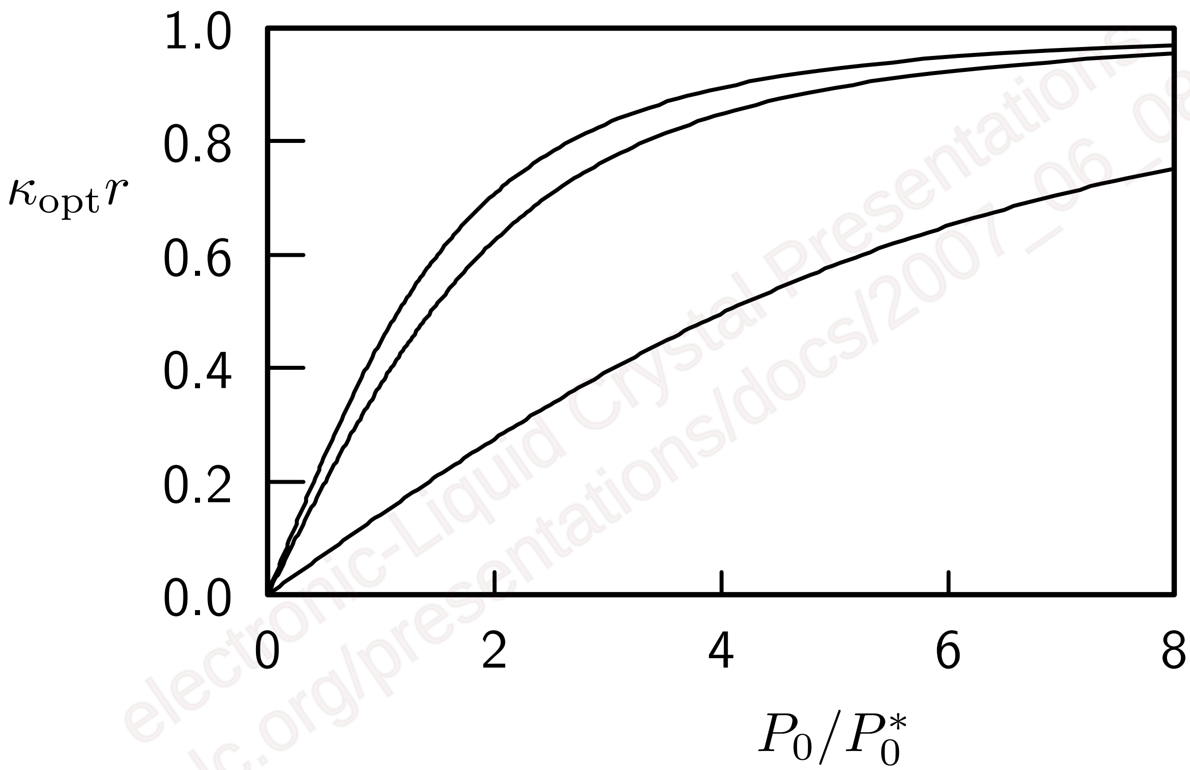
Integrate over the transverse section, insert equilibrium value of ω' ...

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

Ground state attained at $\tau = 0$ and positive κ.

Bent B_2

Preferred curvature of the axis of a B_2 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 shapes

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

1-constant approximation + thin capillary regime:

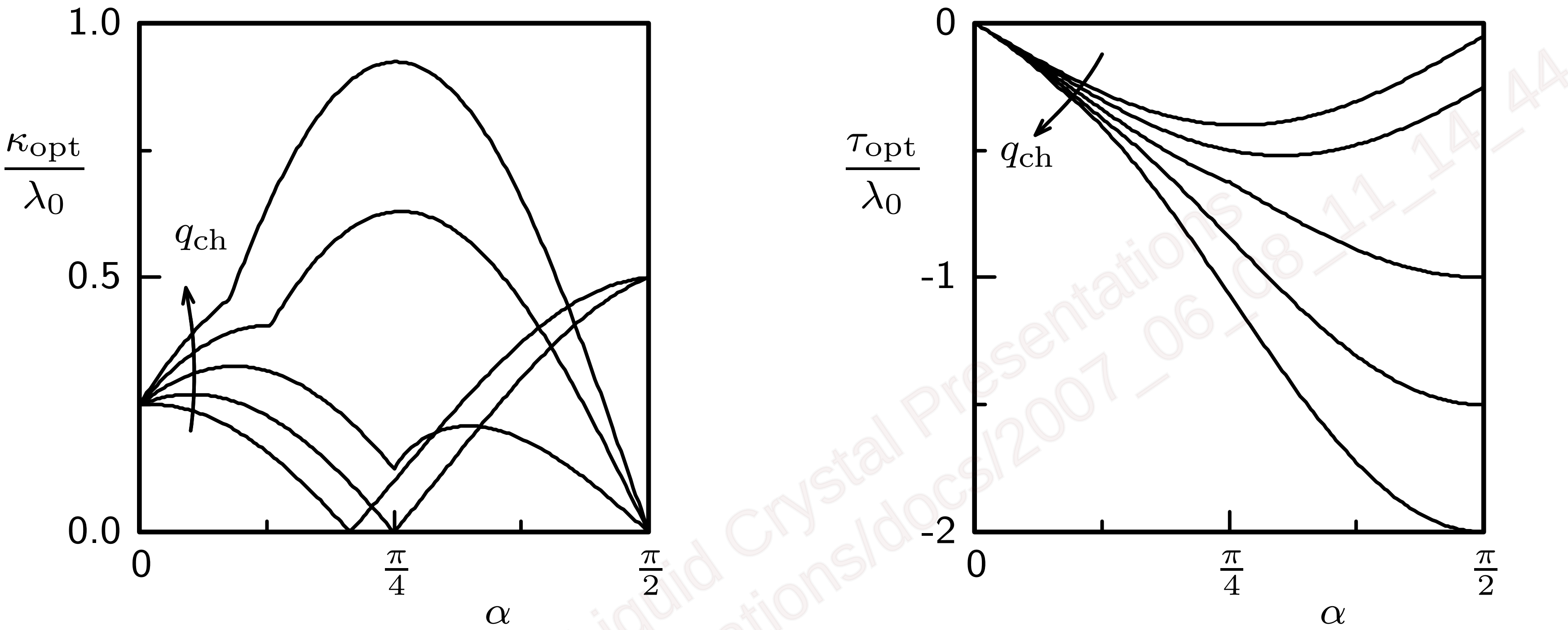
$$K_1 = K_2 = K_3 = \Gamma = \omega_P/\lambda =: K \ ; \qquad \Gamma_1 = 0 \ ; \qquad \lambda_0 r \ll 1 \quad \Longrightarrow$$

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

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

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

Helicoidal B_7



Curvature and torsion of an optimal-shaped B_7 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; $q_{ch} = 0$ $\Longrightarrow$

$\alpha_0 \approx 20^\circ$C.

B_2/Sm-A* instability

Small-α_0 limit of the optimal free energy:

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

$$- \frac{2K_2 \big|2K_3\lambda - \omega_P\big| P_0 q_{\rm ch}\alpha_0}{2(K_3+\Gamma+\Gamma_1)} + O(\alpha_0^2) \quad \ldots$$

B_2/Sm-A phase unstable if $q_{\rm ch} \neq 0$!*

Conclusions/flaws

- Chirality may induce a Sm-A*–Sm-C* transition, even when $C_\perp > 0$ (threshold)
- Flexoelectric effects do not induce spontaneous capillary bending
- Spontaneous polarization produces bent Sm-A and helicoidal Sm-C capillaries, even in the absence of chirality
- Spontaneous polarization $+$ chirality induce Sm-A*–Sm-C* transition

but . . .

- No estimate/prediction of the capillary radius
- Observed helices have concentric layers
- Nematic boundary conditions

Landau-de Gennes' phenomenological theory for isotropic/nematic/smectic liquid crystals

Order parameters and phases

- Nematic order tensor $\boldsymbol{Q}$ $\left(\boldsymbol{Q}=\boldsymbol{Q}^T\,,\quad \mathrm{tr}\,\boldsymbol{Q}=0\right)$
- Smectic order parameter $\psi=\rho\,\mathrm{e}^{\mathrm{i}\omega}$ $\left(\boldsymbol{\nabla}\omega\parallel\boldsymbol{\nu}\right)$

Liquid crystal phases (let $\boldsymbol{\chi}=\boldsymbol{Q}\boldsymbol{\nabla}\psi\wedge\boldsymbol{\nabla}\psi$)

isotropic	if	$\boldsymbol{Q}=\mathbf{0}$	and	$\psi=0$
nematic	if	$\boldsymbol{Q}\neq\mathbf{0}$	and	$\psi=0$
smectic-A	if	$\psi\neq 0$	and	$\boldsymbol{\chi}=\mathbf{0}$
smectic-C	if	$\boldsymbol{Q},\psi\neq 0$	and	$\boldsymbol{\chi}\neq\mathbf{0}$.

Free-energy density

$$\sigma = \sigma_{\mathrm{el,n}}(\nabla \boldsymbol{Q}, \boldsymbol{Q}) + \sigma_{\mathrm{LdG}}(\boldsymbol{Q}) + \sigma_{\mathrm{el,sm}}(\nabla \psi) + \sigma_{\mathrm{sm}}(|\psi|) + \sigma_{\mathrm{n,sm}}(\boldsymbol{Q}, \psi)$$

- The (achiral) nematic elastic energy $\sigma_{\mathrm{el,n}}$ is quadratic in $\nabla \boldsymbol{Q}$.
- The Landau-de Gennes potential is given by

$$\sigma_{\mathrm{LdG}}(\boldsymbol{Q}) = a \,\mathrm{tr}\, \boldsymbol{Q}^2 - b \,\mathrm{tr}\, \boldsymbol{Q}^3 + c \,\mathrm{tr}\, \boldsymbol{Q}^4 \,.$$

- The smectic/elastic contribution determines the layer spacing

$$\sigma_{\mathrm{el,sm}}(\nabla \psi) = b_1 \, |\nabla \psi|^2 + b_2 \, |\nabla \psi|^4 \,.$$

- The smectic potential drives the onset of smectic phases:

$$\sigma_{\mathrm{sm}}(|\psi|) = \tilde{a} \, |\psi|^2 + \tilde{c} \, |\psi|^4 \,.$$

Free-energy density (nematic/smectic interaction)

The nematic-smectic interaction consists in two terms:

- The onset of an ordered phase promotes further order formation

$$\sigma^{(1)}_{\mathrm{n,sm}}(\boldsymbol{Q}\,, |\psi|) = -\tilde{b}\,|\psi|^2\,\mathrm{tr}\,\boldsymbol{Q}^2$$

- The layer normal interacts with the eigendirections of $\boldsymbol{Q}$

$$\sigma^{(2)}_{\mathrm{n,sm}}(\boldsymbol{Q}\,, \nabla\psi) = e\,\boldsymbol{Q}\nabla\psi\cdot\nabla\psi^* + f\,\boldsymbol{\chi}\cdot\boldsymbol{\chi}^*$$

Sm-A Sm-C

$$(\boldsymbol{\chi} = \boldsymbol{Q}\nabla\psi \wedge \nabla\psi)$$

I-N, I-A phase transitions

Uniform configurations: $\boldsymbol{Q} \equiv \boldsymbol{Q}_0, \quad \psi(\boldsymbol{x}) = \rho_0 \, e^{i\mathbf{q}_0 \cdot \mathbf{x}}$.

Close to the isotropic phase, both ρ_0 and $|\boldsymbol{Q}_0|$ are small.

Isotropic-nematic transitions

The usual first-order I-N transition arises at the nematic-isotropic temperature $T_{\rm NI}$ at which $a = \frac{1}{12}\frac{b^2}{c}$.

Isotropic–Smectic-A transitions

A direct I-A transition may arise at the temperature $T_{\rm AI}$ at which both b_1 and $\tilde{a}$ change sign (provided that $T_{\rm AI} \geq T_{\rm NI}$). In such a case

$$\rho_0^2 = -\frac{\tilde{a}}{2\tilde{c}} \qquad \text{and} \qquad q_0^2 = \frac{b_1}{\tilde{a}} \frac{\tilde{c}}{b_2} \, .$$

Direct I-C phase transitions

Assume that $T_{\rm AI} = T_{\rm NI}$.

The Sm-*A* state $\boldsymbol{\chi} = \mathbf{0}$ becomes unstable if

$$f < f_{\rm cr} = \frac{e}{\rho_0^2 q_0^2 s_+} .$$

If the coupling constant f lies below the threshold $f_{\rm cr}$, the *I*–Sm-*A* transition becomes a direct *I*–Sm-*C* phase transition.

No direct I–*Sm-*C *transition may arise if the e-term is explicitly promoting the Sm-*A *phase.*

Nematic-smectic phase transitions / parameters

Consider a uniaxial nematic with degree of orientation $s = s_0$.

Define the critical temperature $T_{\rm NA}$ such that

$$\tilde{a} - \frac{2}{3}\,\tilde{b}s_0^2 = \hat{a}\big(T - T_{\rm NA}\big) \quad \text{and} \quad b_1 + \frac{2}{3} e s_0 = \hat{b}\,\big(T - T_{\rm NA}\big),$$

where $\hat{a}$ and $\hat{b}$ are positive.

We further introduce the following notations:

$$q_{\rm sm}^2 = \frac{\hat{b}\tilde{c}}{\hat{a}b_2}\,, \qquad \rho_{\rm M}^2 = \frac{\hat{a}\,T_{\rm NA}}{2\tilde{c}}\,, \qquad T_{\rm AC} = T_{\rm NA}\left(1 - \frac{e}{f\,s_0 q_{\rm sm}^2 \rho_{\rm M}^2}\right).$$

$T_{\rm AC} < T_{\rm NA}$ if $e, f < 0$; $\quad T_{\rm AC} > 0$ if $f < \dfrac{e}{s_0 q_{\rm sm}^2 \rho_{\rm M}^2}$.

$$\mu = -\frac{4b_2}{f s_0^2} > 1 \quad \text{(dimensionless)}.$$

Nematic-smectic phase transitions / minimizers

(N) $T \geq T_{\rm NA} \quad \Longrightarrow \quad \psi_{\rm opt} = 0$: nematic

(Sm-A) $T_{\rm AC} \leq T \leq T_{\rm NA} \quad \Longrightarrow$

$$\rho_{0,\rm opt} = \rho_{\rm M}\sqrt{1 - \frac{T}{T_{\rm NA}}}\,, \qquad q_{0,\rm opt} = q_{\rm sm}\,, \qquad \theta_{\rm opt} = 0\,.$$

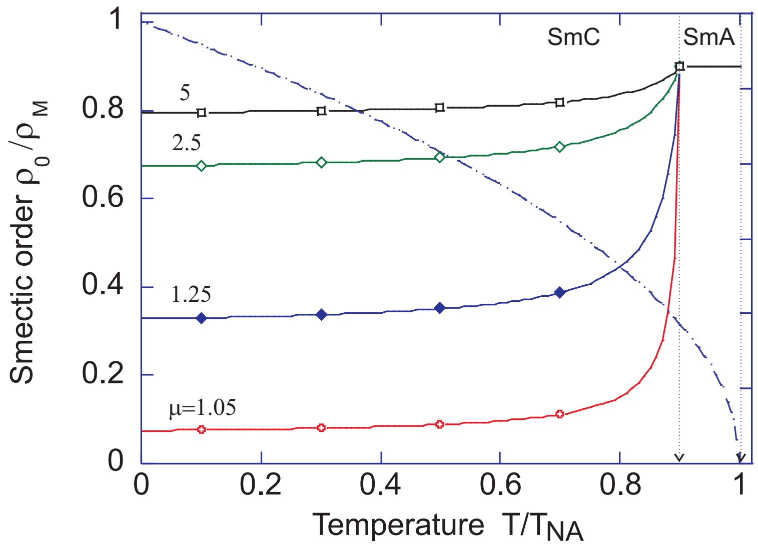
(N–Sm-A transition is 2nd order)

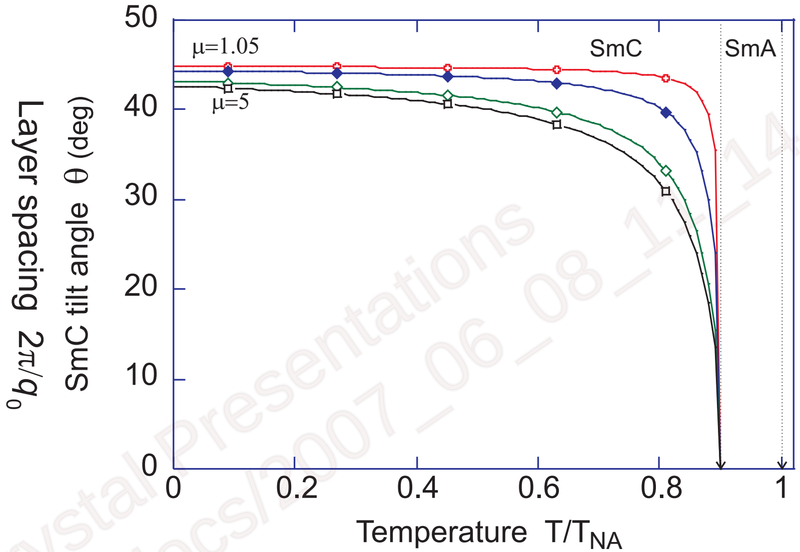
(Sm-C) $T \leq T_{\rm AC} \quad \Longrightarrow$

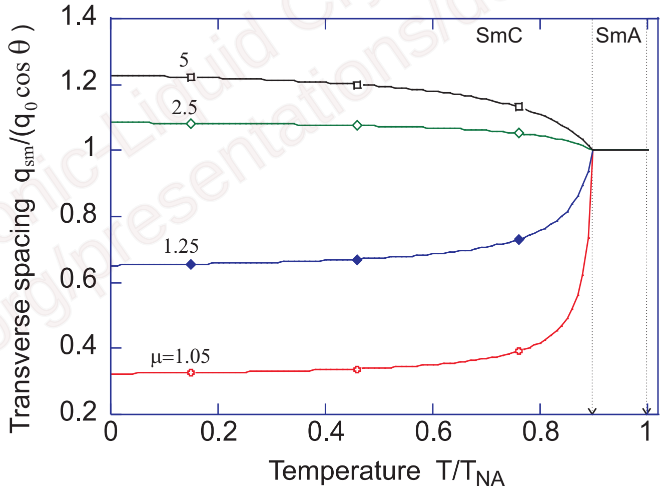
$$\rho_{0,\rm opt} = \rho_{\rm M}\sqrt{1 - \frac{T}{T_{\rm NA}}}\,, \qquad q_{0,\rm opt} = q_{\rm sm}\sqrt{1 + \frac{T_{\rm AC} - T}{(T_{\rm NA} - T)(\mu - 1)}}$$

$$\cos 2\theta_{\rm opt} = \frac{(T_{\rm NA} - T_{\rm AC})(\mu - 1)}{T_{\rm AC} - T + (T_{\rm NA} - T)(\mu - 1)}\,.$$

Nematic-smectic phase transitions / minimizers

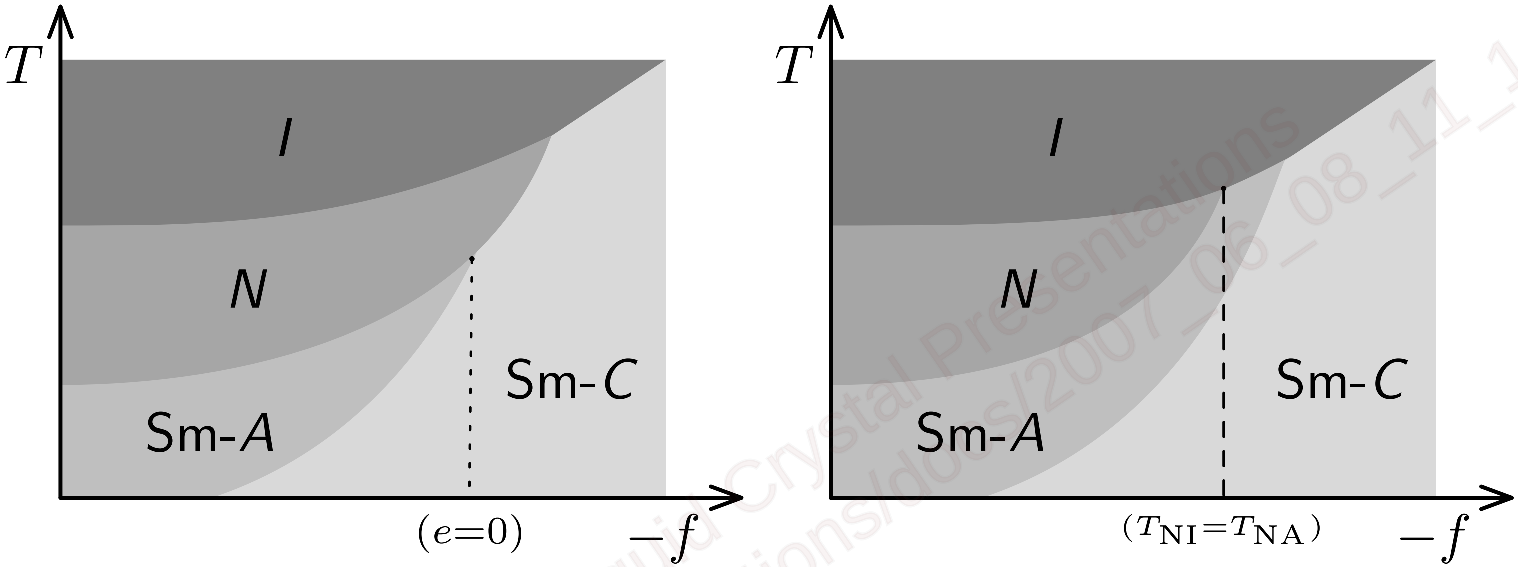






$\left(T_{\rm AC} = 0.9 T_{\rm NA};\ \mu = 1.05, 1.25, 2.5, 5.0\right)$; $\mu = 2$: de Vries' Sm-C

Phase diagrams



No Sm-C phase can be identified if f is not sufficiently negative.

A tricritical point N–Sm-A–Sm-C arises if $T_{\rm NA} < T_{NI}$ when e vanishes.

A tricritical point I–N–Sm-A occurs if $T_{\rm NA} = T_{NI}$ when the parameter e is still negative.

References

P.B., M.C. Calderer: *Telephone-cord instabilities in thin smectic capillaries*, Phys. Rev. E **71**, #051701 (2005).

P.B., M.C. Calderer, E.M. Terentjev: *Landau-de Gennes theory of isotropic-nematic-smectic liquid crystal transitions*. Phys. Rev. E **75**, #051707 (2007).

Comments? Reprints?

`paolo.biscari@polimi.it`

`mcc@math.umn.edu`

`emt1000@cam.ac.uk`