Confinement Effects in Two Dimensions on Freely Suspended Liquid Crystal Films

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freely suspended smectic films

- Quantized thicknesses of 1, 2,... layers (each ~3-5 nm thick)
- Low vapor pressure
- Stable fluid structures

8CB - typical film-forming molecule

film holder: 3 – 100 mm in diameter.

reflection microscope image

SmA (no in-plane structure)

~ 60 layers
~ 50 layers
~ 40 layers
~ 25 layers
~ 10 layers
~ 2 layers
islands

side view

island emulsions

(a) 0 min

(b) 20 min

top view in reflection

OASIS Observation and Analysis of Smectic Islands in Space
films with in-plane texture

\[ \Phi(r, \varphi) = s \varphi \]

\( s = +1 \)

\( s = -1 \)
single-layer films - polar smectic A (Sm AP)

highest symmetry polar fluid
**in-plane distortion energy**

\[
U = \frac{1}{2} \int d^2 r [K_s (\nabla \cdot \mathbf{c})^2 + K_b (\nabla \times \mathbf{c})^2] + \frac{1}{2} \int d^2 r \int d^2 r' \frac{\nabla \cdot \mathbf{P}(r) \nabla \cdot \mathbf{P}(r')}{|r - r'|} + \text{Ionic Screening}
\]

elastic

\[
U = \frac{1}{2} \int d^2 r [K_s (\nabla \cdot \mathbf{c})^2 + K_b (\nabla \times \mathbf{c})^2] + (K_b + 4\pi\lambda_{2D}P^2)(\nabla \times \mathbf{c})^2
\]

\[
+ P \cdot E
\]

polarization charge

\[
\text{nonlocal electrostatic interactions, increasing } K_b
\]

\[
\text{screened electrostatic interactions, increasing } K_b
\]

no ions -

\[
\text{with ions -}
\]

\[
\text{chiral SmC}^* \quad P \propto \text{enantiomeric excess (ee)}
\]

\[
\text{SmC}^*
\]

\[
\text{c}
\]

\[
\mathbf{P}
\]

\[
\text{splay} \quad \text{bend}
\]

SmC islands can be left or right handed

left handed island  right handed island

mirror reflection
Dipolar Interaction between Two Islands with Vortices of the Same Handedness
island Brownian motion

Positional fluctuations given by the Diffusion Law

\[ \langle r^2 \rangle = 4Dt \]
3D Diffusion Theory (Stokes-Einstein)

- Einstein’s Relation (1905)

\[ D = \mu k_B T \]

- Stokes’ Law for a sphere in 3D

\[ \mu = \frac{1}{6\pi \eta R} \]

- Stokes’ Law for a disc in a 2D fluid

Stokes' paradox

\[ \mu = \frac{1}{4\pi \eta h \left[ \ln \left( \frac{S}{R} \right) \right]} \]
diffusion of discs on a film (Saffman)

\[ l_{saff} = \frac{h_{film} \eta_{8CB}}{\eta_{air}} \]

\[ \eta_{8CB} = 0.048 \text{ Pa*s} \]
\[ \eta_{air} = 1.78 \times 10^{-5} \text{ Pa*s} \]

\[ D_s = \frac{k_B T}{4\pi \eta h} \left[ \ln \left( \frac{h\eta}{R\eta_a} \right) - \gamma \right] \propto \ln \left( \frac{1}{R} \right) \]

Saffman, (1976)
\[ \ln\left(\frac{2}{\varepsilon}\right) - \gamma \]

\[ \frac{1}{4\pi\eta_{8CB} h_{film}} \left( \ln\left(\frac{2}{\varepsilon}\right) - \gamma + \frac{4\varepsilon}{\pi} - \left(\frac{\varepsilon^2}{2}\right) \ln\left(\frac{2}{\varepsilon}\right) \right) \]

Petrov & Schwille (2008), Hughes, Pailthorpe, and White (1981)
fit to diffusion data (no adjustable parameters)
buckyballs on 2-layer 8CB film

$D \sim 5 \times 10^{-8} \text{ cm}^2/\text{sec}$,  \hspace{1em} \text{cluster size} \sim 50\text{nm}
Dipolar and Quadrupolar Interactions on a Racemic SmC Film
structure vs. handedness

**homochiral dipolar**

**heterochiral quadrupolar**
**island / companion defect interactions**

for an isolated dipole \((K_b=K_s=K)\)

\[
\text{calculated separation} = \sqrt{2} R
\]

Pettley, Lubensky, and Link (1998)

for a dipolar chain \((K_b=K_s=K)\)

\[
\text{calculated separation} = \sqrt{2} R
\]

Equilibrium separation between islands is

\[
D = 2\sqrt{2}R \quad \text{[4]}
\]

heterochiral island lattices
chiral (ee = 100%) MX8068 SmC*
chiral (ee = 100%) MX8068 SmC*
chiral (ee = 100%) MX8068 SmC*
lower marginal dimensionality?
Casimir forces?
why the difference?

\[ \frac{K_s}{K_b} = 0.2 \]
\[ \frac{K_s}{K_b} = 1 \]
\[ \frac{K_s}{K_b} = 20 \]
Link et al. (2005)

-1 defect

high $P$
the focal lines

\[ U \sim \frac{K}{2} L_y \frac{1}{X_0} + \frac{P^2}{4 \pi \varepsilon_0} d^2 L_y \ln(X_0) \quad X_0 = 4\pi \varepsilon_0 \frac{K}{2d^2} \frac{1}{P^2} \]

\[ W \sim (K/B)^{1/2} \]

deGennes
the focal lines
the focal lines

Width (µm) vs. r (µm)

- Fresh film
- Week old film

Slope for fresh film = 0.057
Slope for week old film = 0.007

(struts)
linear variation of wall width with distance

\[
\cos(\phi) - 2 \sin(\phi) = 0
\]

\[
\phi(x) = \arcsin\left(\frac{x + a}{b}\right)
\]

\[
HW = 0.129946 \times L
\]

Width = \(2HW / R_0 = 21^\circ\)
smectic C* film of racemic C7 (ee = 0%)

C7

C7H15O-苯环-苯环-O-CH3


Bahr, Heppke
smectics in 2D

$\nabla \times \mathbf{n} \neq 0$

suppressed by layer elasticity

$\nabla \cdot \rho \neq 0$

suppressed by polarization elasticity

$\nabla \times \mathbf{n} = 0$

$\nabla \cdot \rho = 0$
-1 defect

polarization

2D smectic equivalent
(chevron structure)
parabolic focal conic
variations
chiral C7 (ee = 100%)
the end