Dynamics of fluctuations in smectic membranes

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1. Introduction to smectic membranes
   Smectic phases
   Dimensionality, ordering and fluctuations
   Smectic membranes studied by x-ray reflectivity

2. Static x-ray scattering
   Displacement correlation function
   Fluctuation profiles

3. Dynamic methods: XPCS and NSE
   Coherent x rays
   X-ray photon correlation spectroscopy
   Neutron spin echo

4. Dynamics of smectic fluctuations
   Theoretical fluctuation modes
   Experimental results

Conclusions
Structure and fluctuations of smectic membranes

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pages 181-235
Contents

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   - Smectic phases
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Issues and outlook
Smectic liquid crystals

Smectic liquid-crystal phase:
- orientationally ordered elongated molecules
- stacked liquid layers
- distribution centers of mass:

\[ f(z) = \frac{2}{d} \sum_{n=0}^{\infty} \tau_n \cos(nq_0 z) \]

- smectic order parameters:

\[ \tau_n = \langle \cos(2\pi nq_0 z) \rangle \]
Smectogenic molecules

K 34 SmA 53.5 N 71.5 I

7AB

K 33 CrB 48.5 SmA 63.5 N 73 I

4O.8

K 72 SmC 79 SmA 129 I

FPP

K 21.5 SmA 33.5 N 40.5 I

8CB
Landau-De Gennes free energy

Bend layers:
\[ K \approx 10^{-11} \text{ N} \]

Compression layers:
\[ B \approx 10^7 \text{ N/m}^2 \]

\[ \langle u^2(r) \rangle = \frac{k_B T}{8 \pi \sqrt{KB}} \ln \left( \frac{L}{d} \right) \]

Fluctuations destroy layer ordering for large \( L \)
Types of order

\[ G(r) \quad I(q) \]

constant \( \propto \delta(q - q_0) \)

\[ r^{-\eta} \]

\[ \propto \frac{1}{(q - q_0)^{2 - n^2 \eta}} \]

\[ e^{-r/\xi} \]

\[ \propto \frac{1}{\xi^2 (q - q_0)^2 + 1} \]
Caillé lineshapes

Full correlation function for a smectic phase:

\[ G(r) = G(r_\perp, z) \propto \exp(-2 \eta \gamma_E) \left( \frac{2d}{r_\perp} \right)^2 \eta \exp \left[ -\eta E_1 \left( \frac{r_\perp^2}{4\lambda z} \right) \right] \]

with \( \eta = \frac{q_0^2 k_B T}{8\pi \sqrt{KB}} \) and \( \gamma_E = 0.5772 \) is Euler’s constant

\( E_1(x) \) is the exponential integral

\( \lambda = \sqrt{K/B} \) is the penetration length

Asymptotic limits:

\[ G(r_\perp, z) \propto z^{-\eta} \quad \text{normal to the layers} \]

\[ G(r_\perp, z) \propto r_\perp^{-2\eta} \quad \text{parallel to the layers} \]
Smectic liquid crystal layering

J. Als-Nielsen et al.

Further examples:

Surfactant membranes
C.R. Safinya et al.

Smectic polymers
E. Nachaliel et al.

Block copolymers
P. Štěpánek et al.
Macromol. 35, 7287 (2002)
Capillary waves

Width of the liquid-vapour interface

\[ \sigma^2 = \sigma_0^2 + \sigma_{cw}^2 \]

\[ = \sigma_0^2 + \frac{k_B T}{2\pi \gamma} \ln \left( \frac{q_{\text{max}}}{q_{\text{min}}} \right) \]

Short-wavelength cut-off: \( q_{\text{max}} = 2\pi / a \)

Long-wavelength cut-off due to gravity: \( q_{\text{min}} = \Delta \rho g / \gamma \)

In practice the long-wavelength cut-off is not reached, and \( q_{\text{min}} \) is determined by the resolution of the x-ray set-up

Other example: Ordering of Langmuir monolayers

Smectic membranes

Typical sizes up to
50 mm
10 × 70 mm²

For neutron work: 50 × 50 mm²
but less control
1. Very well oriented (mosaic < 1 up to 10 mdegree).
2. Centro-symmetric: no substrate!
3. From two to thousands of layers (about 5 nm to 20 μm).
4. Cross-over from bulk behaviour (3D) in thick films to surface-dominated behaviour.
5. In thin films: model for physics of 2D systems.
Experimental situation
X-ray reflectivity

Simple interface:
\( \theta < \theta_c \approx 0.15^\circ \): total reflection
\( \theta > \theta_c \): Fresnel fall-off \( \sim \theta^{-4} \)

Model calculation of 30 nm membrane.
33-layer 7AB film

Troika beamline, ESRF
Contents

1. Introduction to smectic membranes

2. Static x-ray scattering
   Displacement correlation function
   Fluctuation profiles

3. Dynamic methods: XPCS and NSE

4. Dynamics of smectic fluctuations

Conclusions

Issues and outlook
Static x-ray scattering

Landau-De Gennes-Hołyst theory

\[ F = \frac{1}{2} \int d^3 r \left\{ B \left[ \frac{\partial u(r)}{\partial z} \right]^2 + K [\Delta_1 u(r)]^2 \right\} + \frac{1}{2} \gamma \int d^2 r [\nabla_\perp u(r_\perp, z = \pm \frac{1}{2} L)]^2 \]

Competition between surface \( \gamma \) and bulk \( \sqrt{BK} \)

The x-ray structure factor is the Fourier transform of the density-density correlation function:

\[ S(q) = \int d^3 r \ G(r) \exp(i \mathbf{q} \cdot \mathbf{r}) \]

\[ G(r) = \left\langle \exp \{iq_0 [u(r) - u(0)] \} \right\rangle = \exp \left[ -\frac{1}{2} q_0^2 g(r) \right] \]
Fluctuation profiles

- Hydrodynamic fluctuations depending on \( \nu = \frac{\gamma}{\sqrt{BK}} \)
- Local fluctuations

Calculated profiles for

\( L = 2.94 \text{ nm} \)
\( \gamma = 0.0025 \text{ N/m} \)
\( K = 10^{-11} \text{ N} \)
\( B = 10^9 \text{ N/m}^2 \quad \nu < 1 \)
\( 6.3 \times 10^7 \text{ N/m}^2 \quad \nu = 1 \)
\( 5 \times 10^6 \text{ N/m}^2 \quad \nu > 1 \)
Experimental profiles

Thermal fluctuation profiles for FPP films of various thickness

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2. Static x-ray scattering

3. Dynamic methods: XPCS and NSE
   - Coherent x-rays
   - X-ray photon correlation spectroscopy
   - Neutron spin echo

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Conclusions

Issues and outlook
Young’s experiment

Zero-order is coherent by definition
Transverse coherence length $\xi_t$

As $\Delta \theta$ arises from different points on the source: $\Delta \theta = D/R$

$$2\xi_t \Delta \theta = \lambda \rightarrow \xi_t = \frac{\lambda}{2 \Delta \theta}$$

$$\xi_t = \frac{\lambda}{2D/R}$$
Longitudinal coherence length $\xi_l$

\[ 2\xi_l = N\lambda \]

\[ \lambda \]

A

\[ \lambda - \Delta\lambda \]

B

\[ 2\xi_l = N\lambda = (N + 1)(\lambda - \Delta\lambda) \]

\[ (N + 1)\Delta\lambda = \lambda \]

\[ N \approx N + 1 = \frac{\lambda}{\Delta\lambda} \]

\[ \xi_l = \frac{\lambda}{2\Delta\lambda} \]
Fraunhofer diffraction

Troïka beamline ESRF, $\lambda = 1.05$ Å.
Front pinhole 3.5 μm; back pinhole before detector 5 μm.

Photon correlation spectroscopy

Speckle reflects instantaneous position of scatterers. Motion by analyzing the intensity variation $I(q, t)$.

Intensity autocorrelation function: $\langle I(q, t)I(q, t + \tau) \rangle$

$$g_2(q, \tau) = \frac{\langle I(q, 0)I(q, \tau) \rangle}{\langle I(q, 0) \rangle^2}$$

$g_2(q, \tau)$ can be related to

$$g_1(q, \tau) = \langle E(q, t)E(q, t + \tau) \rangle$$

$\propto S(q, t)$

via the Siegert relation $g_2(q, \tau) = 1 + [g_1(q, \tau)]^2$. 
Experimental situation Troïka beamline

Third/fifth harmonic of set of three undulators.
Source size: $928 \times 23 \ \mu m^2 (s_H \times s_V)$
Mono: Si(111) at $8 - 13$ keV
  $\lambda$ at $1.55 - 0.96 \ \AA$, $\Delta \lambda / \lambda \approx 10^{-4}$
Pinhole: $10 \ \mu m \ \varnothing$ at $R = 44$ m

Coherence lengths:

$$\xi_t = \lambda R / (2s_H) \approx 10 \ \mu m$$
$$\xi_l = \lambda / (\Delta \lambda / \lambda) \approx 1.6 \ \mu m$$

At the Bragg position $\theta \approx 1.5^\circ \rightarrow$
path length difference: $2L \sin \theta = 1.6 \ \mu m \rightarrow L_{\text{max}} \approx 30 \ \mu m$
Storage ring

Bunch structure ESRF:

- 992 bunches, revolution time 2.7 μs
- uniformly distributed in continuous mode: 2.8 ns spacing

Avalanche photo diodes

Time resolution: \( \sim 0.7 \text{ ns risetime} \)

Baron, Hyperfine Interactions 125, 29 (2000)

Correlators

Standard: ALV5000/E correlator, fast extension down to 12.5 ns.

Correlator.com lag time 8 ns.
Dynamic methods

Length scale [Å]

Energy [eV]

Scattering vector q [Å⁻¹]

- Raman
- Brillouin
- IXS
- Spin-Echo
- INS
- XPCS
- NFS

Frequency [Hz]
Neutron Spin Echo

For an angular displacement \((\delta, \varphi)\)

\[
q_{\perp} = \frac{2\pi}{\lambda} \sqrt{(\cos(\varphi) \cos(\theta + \delta - \omega) - \cos(\theta + \omega))^2 + \sin^2(\varphi)}
\]
Neutron Spin-Echo Spectrometer

IN15 at the ILL (Grenoble)
# Contents

1. Introduction to smectic membranes  
2. Static x-ray scattering and conformality  
3. Dynamic methods: XPCS and NSE  
4. **Dynamics of smectic fluctuations**  
   - Theoretical fluctuation modes  
   - Experimental results  

Conclusions  

Issues and outlook
Fundamental relaxation time

Starting point: Landau-de Gennes-Holyst theory.

Calculate the time-dependent correlation function

\[ C(q_\perp, z, z', t) = \langle u(q_\perp, z, 0) u(q_\perp, z', t) \rangle. \]

From the equation of motion involving viscous forces and restoring elastic force:

\[
\rho_0 \frac{\partial^2 u}{\partial t^2} = \eta_3 \frac{\partial}{\partial t} \nabla^2 u + (B \nabla^2_z - K q^4 \Delta^2_{\perp}) u
\]

Lowest root solution for \( q^2 \ll B / (\gamma L) \)

\[
\tau_1 = \eta_3 \left[ \frac{2\gamma}{L} + \left(1 - \frac{\gamma^2}{3KB} \right)Kq^2_{\perp} \right]^{-1}
\]

For \( q_{\perp} = 0 \) we find

\[
\tau_1 = \frac{\eta_3 L}{2\gamma}
\]
Exponential relaxations

Price, Sorensen et al., PRL 82, 755 (1999)

Thick films
soft x-rays
4O.8 membranes

1. $L=0.23 \, \mu m$ ($N=105$)
2. $L=3.1 \, \mu m$ ($N=1430$)
3. $L=5.5 \, \mu m$ ($N=2500$)

Sikharulidze, Dolbnya, Fera, Madsen, Ostrovskii, de Jeu, PRL 88, 115503 (2002)
Full solution including inertia

Incompressible membranes \((B \to \infty)\): undulations only

\[
C(q_\perp, t) = \left\langle u(q_\perp, t)u^*(q_\perp, 0) \right\rangle = \frac{k_B T \tau_s \tau_f}{L \rho_0 (\tau_s - \tau_f)} \left[ \tau_s \exp \left( -\frac{t}{\tau_s} \right) - \tau_f \exp \left( -\frac{t}{\tau_f} \right) \right].
\]

With values for the fast and slow relaxation:

\[
\tau_{s,f} \approx \frac{2 \rho_0}{\eta_3 q_\perp^2} \left( 1 + \sqrt{1 - \frac{4 \rho_0}{\eta_3^2 q_\perp^4} \left( Kq_{\perp}^4 + \frac{2 \gamma}{L} q_\perp^2 \right)} \right)^{-1}.
\]

For small \(q_\perp\) critical wavelength fluctuations: \(q_{\perp c} = \frac{2}{\eta_3} \sqrt{\frac{2 \rho_0 \gamma}{L}}\).

Dispersion curves

\[ [\text{Re}(1/\tau_{1,2})] (\mu s) \]

\[ q_{\perp,c} \quad q_{\perp} (\text{nm}^{-1}) \]

Oscillations  Exponential decay

Complex mode  Slow mode

Fast (inertial) mode

Points 2 and 3 indicate transitions between oscillatory and exponential decay regimes.
FPP off-specular

Sikharulidze, Dolbnya, Fera, Madsen, Ostrovskii, de Jeu, PRL 88, 115503 (2002)
Various regimes

\[ \tau_{s,f} \approx \frac{2\rho_0}{\eta_3 q_\perp^2} \left( 1 \mp \sqrt{1 - \frac{4\rho_0}{\eta_3^2 q_\perp^4} \left( Kq_\perp^4 + \frac{2\gamma}{L} q_\perp^2 \right)} \right)^{-1} \]

Small \( q_\perp \):

\[ \tau_{s,f} \approx \frac{2\rho_0}{\eta_3 q_\perp^2} \left( 1 \mp \sqrt{1 - \frac{8\rho_0\gamma}{\eta_3^2 Lq_\perp^2}} \right)^{-1} \]

transition at

\[ q_{\perp,c} = \frac{2}{\eta_3} \sqrt{\frac{2\rho_0\gamma}{L}} \]

\( q < q_{\perp,c} \)

\( q > q_{\perp,c} \)

Complex mode (oscillations):

\[ \tau_s = \frac{\eta_3}{2\gamma / L + Kq_\perp^2} \]

\[ \tau_s = \frac{\eta_3 L}{2\gamma} \]

\[ \tau_s = \frac{\eta_3}{Kq_\perp^2} \]

\[ \tau_s = \tau_f^* \]
Dispersion curves

\[ \tau_1 = \frac{\eta_3}{2\gamma / L + Kq_{\perp}^2} \]
XPCS: 8CB

Specular \( q_\perp = 0 \)

\[ q_\perp = 3.5 \times 10^{-3} \text{ nm}^{-1} \]
8CB: NSE results

Fit to stretched exponential: \[ S(q_\perp, t) = \exp\left\{-\left(\frac{t}{\tau}\right)^{0.59}\right\} \]

\[ \langle \tau \rangle = \int_0^\infty S(\mathbf{q}, t)dt = \frac{\Gamma(1/\beta)}{\beta} \tau'. \]
8CB: XPCS and NSE

Sikharulidze, Farago, Dolbnya, Madsen, de Jeu, PRL 91, 165504 (2003)
Homodyne/heterodyne detection

40.8 membrane, thickness 3.8 μm

Off-specular: \( \tau = 3.3 \, \mu s \rightarrow \) homodyne detection scheme
Specular: \( \tau = 6.2 \, \mu s \rightarrow \) heterodyne detection scheme.

Crystalline-B membranes

Start from the Landau-De Gennes-Hołyst theory to which solid-like elasticity is added.

**Easy-shear approximation:** $C_{44}$ associated with shear of the layers is much smaller than the other constants:

\[
F_{\text{uniax}} = \frac{1}{8} \int d^3 r C_{44} [\nabla_\perp u(r)]^2.
\]

The effect of $C_{44}$ is to renormalize the surface tension, as can be seen from the undulation part of the free energy:

\[
F_{\text{undul}} = \frac{1}{2} \int dxdy \left[ LK (\Delta_\perp u)^2 + (2\gamma + \frac{1}{4} LC_{44}) (\nabla_\perp u)^2 \right]
\]

Hence Cr-B membranes fluctuate essentially as Sm-A ones, with an effective damping by $\gamma_{\text{eff}} = \gamma + \frac{1}{8} LC_{44}$.

Cr-B experiments in 4O.8

Fera, Dolbnya, Optiz, Ostrovskii, de Jeu, Phys. Rev. E 63, 020601 (2001)
Conclusions

1. Thanks to the high degree of control, smectic membranes provide excellent model systems to study low-dimensional physics.
2. XPCS can be done on smectic membranes at energies up to 13 keV and down to time scales of 10 ns.
3. A complex fundamental surface relaxation mode is observed, combining exponential decay with oscillatory behaviour.
4. Transitions from complex behaviour to exponential decay occur as a function of film thickness and of $q_\perp$, in agreement with theory.
5. Combination with neutron spin echo shows a transition from surface-tension damped modes to bulk elastic ones.
6. Both heterodyne (at the specular ridge) and homodyne (off-specular) detection schemes have been realized.
7. Thin crystalline-B films fluctuate essentially in the same way as smectic-A membranes, due to the easy shear associated with $C_{44}$. 
THANKS

Liesbeth Mol
Andrea Fera
Irakli Sikharulidze PhD students

Joe Schindler
Ricarda Optitz
Daniel Sentenac post-docs

Boris Ostrovskii
Vladimir Kaganer
Arcadi Shalaginov guests

Gerhard Grübel/Anders Madsen
Igor Dolbnya ESRF

Bela Farago ILL
Thanks for your attention

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