X-Ray Lineshape and Order-Disorder in Liquid-Crystalline Elastomers

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1. Introduction
   Liquid-crystalline elastomer systems
   X-ray scattering and types of order
   Experimental

2. Order-disorder in a side-chain siloxane elastomer

3. Disorder and the smectic-nematic transition

Conclusions
Liquid-crystalline phases

Nematic: orientational order

Smectic: orientational order + 1-D layering
Liquid-crystalline polymers

nematic (prolate)  smectic (oblate)
Different organization LC polymers

- **Side chain**
  - end-on
  - side-on

- **Main chain**
Nematic liquid-crystalline elastomers

side-chain end-on

main-chain end-on
Shape change upon stretching LC elastomers

Wermter, Finkelmann
E-Polymers 013 (2001)
Incorporating azobenzenes

\[ R_1 - \begin{array}{c} \text{trans} \\ \text{mesogenic} \end{array} \quad \begin{array}{c} \text{UV} \\ \text{VIS} \end{array} \quad \begin{array}{c} \text{cis} \\ \text{reduces } T_{NI} \end{array} \]

W.H. de Jeu:
*Physical Properties of Liquid Crystalline Materials*
(Gordon and Breach, New York, 1980)
Bending elastomer cantilever

Nematic cantilever bending upon application of a 60 ms light pulse from a 60 mW Ar laser from above

X-ray patterns

nematic

smectic
Order in smectic systems

short range

\[ q = \frac{2\pi}{d} = \frac{4\pi}{\lambda} \sin \theta \]
\[ 2d \sin \theta = \lambda \quad (\text{Bragg - equation}) \]

long range?
Types of order

\[ G(r) \quad \text{constant} \quad \propto \delta(q - q_n) \]

In practice:
Gaussian

\[ I(q) \quad e^{-r/\xi} \quad \propto \frac{1}{\xi^2(q - q_0)^2 + 1} \]

Lorentzian
Finite size and Gaussians

In case of long-range order two contributions to the Gaussian linewidth:
- Domain size of the order
- Instrumental resolution

The linewidth, expressed as full-width-at-half-maximum (FWHM): \( \Delta q \) (nm\(^{-1}\)), gives average domain size

\[
L = \frac{2\pi}{\Delta q} \text{ (nm)}
\]
Short-range order and Lorentzians

In case of short-range order (Lorentzian line shape) \( \xi = 2/\Delta q \) (nm) gives the 1/e value of the exponentially decaying correlation

Fourier transforms:

\[
\begin{align*}
1D & : \quad \frac{2\xi}{1 + \xi^2 q^2} \\
2D & : \quad \frac{2\xi}{(1 + \xi^2 q^2)^{3/2}} \\
3D & : \quad \frac{2\xi}{(1 + \xi^2 q^2)^2}
\end{align*}
\]
Short-range order and Lorentzians

In case of short-range order (Lorentzian line shape)

$$\xi = \frac{2}{\Delta q} \text{ (nm)}$$

gives the 1/e value of the exponentially decaying correlation

A squared Lorentzian or $q^{-4}$ dependence is well known in SAXS of porous materials (Debye-Porod behaviour) and for random Ising magnet systems. These types of system are characterized by scattering from random internal interfaces. There is a parallelism with scattering from a random field of disclinations.
X-ray signature long- and short-range order

Black: Gaussian → finite size
Red: Lorentzian → finite correlation length
**Background correction**

Distinguish

- $q$-dependent background in hutch depending on the incident intensity $I_{\text{MON}}$.
- Dark current of the detector depending on time $t$.

**Procedure:**

1. Measure dark current detector (typically 150 cts/h).
2. Measure $I_0(q)$ for empty sample holder over relevant $q$-range.
   Subtract the dark current scaled to the appropriate time $t$.
   Scale $I_0(q)$ to a reference value $I_{\text{MON}}^{\text{ref}}$.
3. Subtract the dark current (at proper $t$) from the real data $I(q)$.
   Scale the real data $I(q)$ to $I_{\text{MON}}^{\text{ref}}$.
   Subtract the scaled $I_0(q)$. 
Landau-De Gennes free energy smectic

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

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

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

$G(r)$

$\text{constant}$

$I(q)$

$\propto \delta(q - q_n)$

Gaussian

$r^{-\eta}$

$\propto \frac{1}{(q - q_n)^{2-n^2\eta}}$

Caillé lineshape

$e^{-r/\xi}$

$\propto \frac{1}{\xi^2(q - q_0)^2 + 1}$

Lorentzian
Side-chain siloxane with 10% crosslinks

Three orders $n$ of lineshape with scaling of exponent $2-n^2\eta$.

$\eta = 0.16 \pm 0.02$

Lambreva, Ostrovskii, Finkelmann, de Jeu, PRL 93, 185702 (2004)
High-resolution x-ray set-up

Synchrotron source (X10A, BNL) → Sample → Monochromator → Sample → Analyzer → Detector

Reduction of the tails of the resolution function
Beam properties X10A, NSLS Brookhaven

Double–bounce Ge(111) monochromator
+ triple-pass channel-cut Ge(220) crystal, give tails

\[(q_z - q_n)^{-4.5}\] to \[(q_z - q_n)^{-3}\]

Resolution \( q_z = 0.003 \text{ nm}^{-1} \)

\( q_x = q_n \phi, \phi \text{ is mosaic distribution} \)

\( q_y = 0.02 \text{ nm}^{-1} \)

Beam size: 0.5×1 mm\(^2\) (V×H)

Beam intensity: 5×10\(^9\) cts/s
Sample holder
1. Introduction
2. Order-disorder in a side-chain siloxane elastomer
   Increased domain size
   Disorder and stretched Gaussians
3. Disorder and the smectic-nematic transition
4. Conclusions
Smectic systems

monomer $\rightarrow$ polymer $\rightarrow$ elastomer
Order and disorder by crosslinking

Coupling of Sm-A elastic field to the random rubbery network

Suppression of thermal fluctuations by pinning of smectic layers by crosslinks.

→

Long-range order restored? Order improvement.

Disorder by a random field.

At large enough length scales even weak disorder can destroy translational order.

→

Exponentially decaying positional correlations survive.


Olmsted, Terentjev, PRE 53, 2444 (1996)
Elastomer system

\[\text{Variation nature crosslinker}\]

\[V_1\text{ (flexible)}\]

\[V_8\text{ (stiff)}\]

Different crosslink densities (1)

The graph shows the intensity ratio $I(q)/I_0(q)$ as a function of $q-q_0$ (in nm$^{-1}$) for different crosslink densities: 0%, 5%, and 10%. The y-axis represents the intensity ratio on a logarithmic scale from $10^{-5}$ to $10^0$. The x-axis represents the difference in wavevector $q-q_0$.
Different crosslink densities (2)
Lineshape analysis

$G(z) = \exp\left(-\frac{\beta z^2}{2}\right)$

From inside to outside:
- Sharp boundaries
- Gaussian ($\beta=1.0$)
- Stretched Gaussian ($\beta=0.7$) similar to $\text{Lor}^2$
- Exponential ($\beta=0.5$)

Obraztsov, Muresan, Ostrovskii, de Jeu, PRE 77, 021706 (2008)
Lineshape and crosslink density

Flexible crosslinker $V_1$: $x=0.1, 0.15, 0.2$

Black: Gaussian ($\beta=1.0$)
Blue: stretched Gaussian with $\beta=0.96, 0.66, 0.59$
Red: Lorentzian ($\beta=0.5$)

$\xi = 45$ nm
$\approx 15$ layers
Lineshape and crosslink density (2)

Stiff crosslinker $V_8$: $x=0.1, 0.125, 0.15$

![Graphs showing lineshape and crosslink density](image)

- **Black**: Gaussian ($\beta=1.0$)
- **Blue**: stretched Gaussian with $\beta=0.51, 0.47, 0.44$
- **Red**: Lorentzian ($\beta=0.5$) stretched exponential

$\xi = 53\, \text{nm}$

$\xi = 26\, \text{nm}$

$\xi = 15\, \text{nm}$
Rigid crosslinker V8; $x=12.5\%$

Perfect fit to Lorentzian: short-range order
1. Introduction

2. Order-disorder in a side-chain siloxane elastomer

3. The smectic-nematic transition in LC elastomers
   Phase diagram and thermo-elastic behaviour
   Stress-strain experiments
   X-ray line shapes

Conclusions
Elastomer system

Siloxane polymer backbone with crosslinker V1

Smectogenic sidegroup

Nematogenic sidegroup
Phase diagram

![Phase diagram](image_url)

5% crosslinker V1

R1/R2

- E60/40: SmA 47 N 65 I
- E70/30: SmA 63 N 66 I
Thermo-elastic behaviour

(a) E70/30

(b) E60/40

$L/L_{iso}$ vs. $T$ (°C)

5% and 10% curves for each composition.
Lineshape E60/40 5% around SmN transition

De Jeu, Ostrovskii, Kramer, Finkelmann, PRE 83, 041703 (2011)
Line shape E60/40 at room temperature

Full line: Lorentzian
Broken line: \((\text{Lorentzian})^2\)
Dottet line: Gaussian

Slopes full lines:
1st order: \(2 - \eta\)
2nd order: \(2 - 4\eta\)

\(\eta = 0.22 \pm 0.02\)
Linewidth E60/40 5%

![Graph](image_url)

**52 °C**

![Graph](image_url)

**51 °C**

![Graph](image_url)
Linewidth E60/40 10%

E60/40 10%

\[ \zeta (\text{nm}) \]

\[ T \left( \text{°C} \right) \]

\[ \text{intensity (cts/10}^6 \text{mon)} \]

\[ q \left( \text{nm}^{-1} \right) \]

\[ 45 \text{ °C} \]

\[ 28 \text{ °C} \]
Effects of quenched disorder in 10\% aerogels on smectic layering in 8CB

\[ \xi = 21.6 \text{ nm} \]

\[ \xi \approx 7 \text{ layers} \]

Clark et al. PRL 71, 3505 (1993)
Lineshape as sum of Lorentzian and square Lorentzian

Radzihovsky & Toner, PRL 79, 4214 (1997); PRB 60, 206 (1999)

Structure factor is sum of ‘classical’ thermal fluctuations and layer displacement disorder (the tendency of the aerogel to force the smectic layers to particular positions)

\[
S(q) \propto \frac{A_{\text{thermal}}}{1 + \xi_\parallel^2 (q_z - q_0)^2 + \xi_\perp^2 q_\perp^2} + \frac{A_{\text{disorder}}}{[1 + \xi_\parallel^2 (q_z - q_0)^2 + \xi_\perp^2 q_\perp^2]^2}.
\]

Similar combination of \( \text{Lor} + \text{Lor}^2 \) found in other cases.
Lineshape as sum of Lorentzian and square Lorentzian (2)

Witkowski & Terentjev, PRE 80, 051701 (2009)

Corrugated potential penalizes deviations of crosslinks from the local layer positions:

\[ F_{\text{random field}} = \gamma \int c(\mathbf{r})|\psi(\mathbf{r})| \cos\{q_0[z - u(\mathbf{r}) + v_z(\mathbf{r})]\} d\mathbf{r} \]

Evaluated for \( |\psi(\mathbf{r})| = 1 \), deep in the smectic phase! Again combination of \( \text{Lor} + \text{Lor}^2 \) but now the induced short-range order is characterized by a correlation length:

\[ \xi = (B / 2\Lambda)^{1/2} \]

with \( \Lambda \propto c \) we arrive at

\[ \xi \propto \left[ \frac{B}{2(c - c_{\text{min}})} \right]^{1/2} \]
Experimental check

\[ \xi \propto \left[ \frac{B}{2(c - c_{\text{min}})} \right]^{1/2} \]

**B-dependence:** \( B_{E60/40} \) about 3 times smaller than \( B_{E70/30} \). At RT for E70/30 we have \( \xi \approx 50 \text{ nm} \rightarrow 50/\sqrt{3} \approx 29 \text{ nm} \). Experimentally for E60/40 we find \( \xi \approx 27 \text{ nm} \).

**c-dependence:** Estimating \( c_{\text{min}} \approx 0.04 \) we should expect \( \xi_{5\%}/\xi_{10\%} \approx \sqrt{6} \approx 2.4 \) (neglecting variations of \( B \)). The experimental ratio’s are (at the SmN transition):
- 4 for E70/30
- 10 for E60/40
Questions, questions, …

1. Intriguing that the combination \( \text{Lor} + \text{Lor}^2 \) returns in many different situations with random disorder.

2. Our Sm-N data can in principle be described by this combination, but…

3. These data are part of the wider set including data deep in the smectic phase, where a transition is found with increasing crosslink concentration

   Gaussian \( \rightarrow \) Stretched Gaussian \( \rightarrow \) Lorentzian

4. Deep in the smectic phase much larger crosslink densities are required (~20%) to reach short-range order than close to the Sm-N transition (~10%).

5. Is this behaviour typical for all smectic elastomers?
Conclusions

1. *Smectic* elastomers show with increasing crosslink density first an increase of the size of the finite-size domains (Gaussians lineshape). Then a gradual transition to short-range correlations at 20% crosslinks (Lorentzian lineshape). For stiffer crosslinks this situation is reached already at 10%.

2. In *smectic-nematic* elastomers the smectic phase disappears at 10% crosslink density, suggesting a shift to a ‘parasmectic’ regime of a first-order smectic-isotropic transition.

3. The interpretation of these result provides a considerable theoretical challenge.
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