Soft bend elastic constant and transition to a modulated nematic phase

Alenka Mertelj,[1] Martin Čopič,[1],* Geoffrey R. Luckhurst[2], R. P. Tuffin[3], and Owain Parri[3]

[1]Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, Ljubljana 1000, Slovenia

[2]School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

[3]Merck Chemicals Ltd, Chilworth Technical Centre, University Parkway, Southampton SO16 7QD, UK

Outline

- Observation of modulated phase in nematic phase of flexible dimers
- Nematic fluctuations and dynamic light scattering
- Temperature and order parameter dependence of elastic constants
- Conclusions

Modulated nematic phase

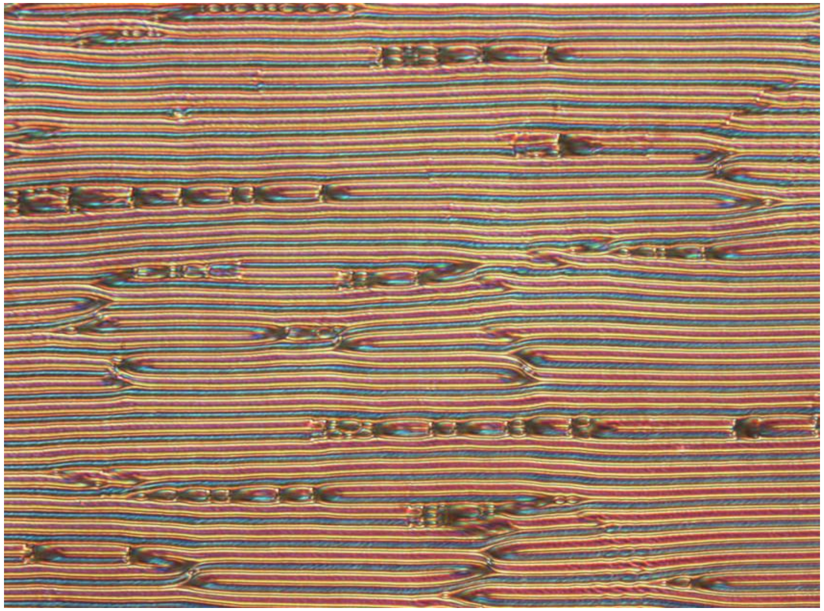
- Observed in flexible dimers of biphenyls like 1,7-bis(4-cyanobiphenyl-4-yl)heptane (CB7CB) and CB9CB [1], or CB11CB[2]
- I.Dozov [3] proposed that a softening of the bend elastic constant could lead to a modulated nematic phase with nematic director forming a twist-bend helix
- In [2] it was suggested that in CB11CB the modulation is due to soft splay elastic constant
- Numerical modeling of A. Ferrarini indicates that bend elastic constant in dimers can become negative

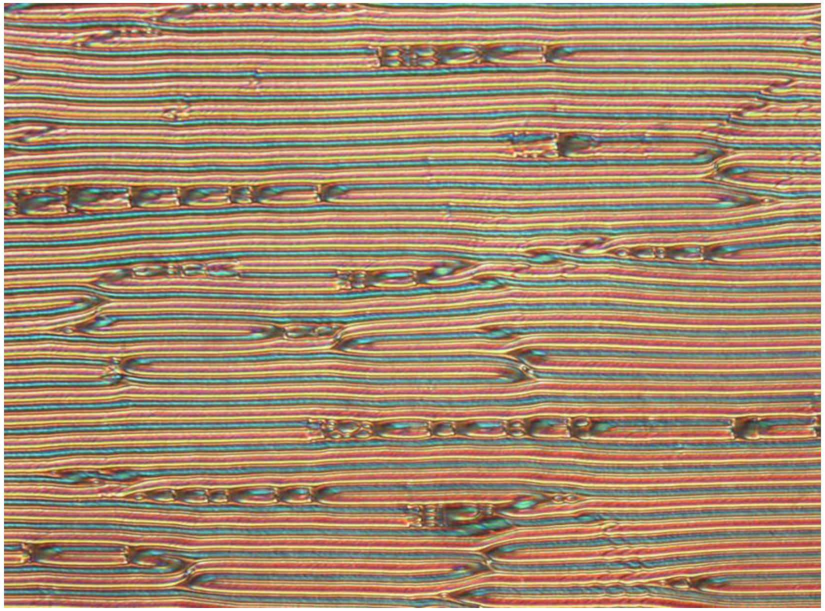
[1] M. Cestari et al., Phys. Rev. E **84**, 031704 (2011)

[2] V. P. Panov et al., Phys. Rev. Lett.**105**, 167801 (2010).

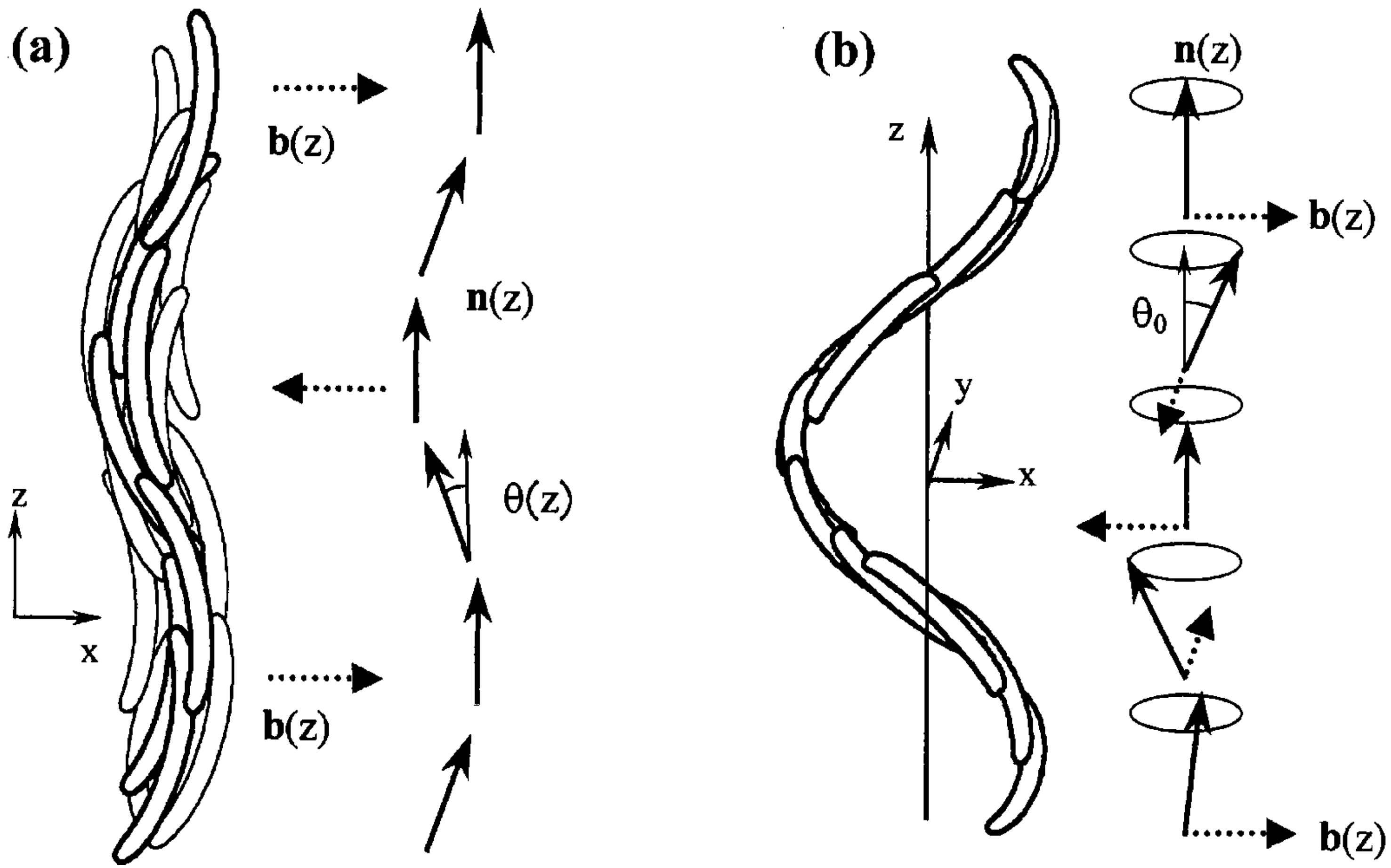
[3] I. Dozov, Europhys. Lett. **56**, 24 (2001).

Observed modulation under polarized microscope





Structures proposed by Dozov



Dozov's model

$$F = \frac{1}{2}\left[K_1\mathbf{s}^2 + K_2\mathbf{t}^2 + K_3\mathbf{b}^2\right] + \frac{1}{4}\left\{C_1\left[\frac{d^2}{dz^2}\left(n_i n_j\right)\right]^2 + C_2\left[\frac{d^2}{dz^2}\left(n_z n_j\right)\right]^2 + C_3\left[\frac{d^2}{dz^2}\left(n_z{}^2\right)\right]^2\right\}$$

Splay-bend phase:

$$\theta_0{}^2 = -\frac{4K_3}{3K_1}, \qquad k^2 = -\frac{K_3}{3C}, \qquad F_{sb} = \frac{K_3{}^3}{27CK_1}$$

If $K_1 > 2K_2$

then twist-bend is the stable phase

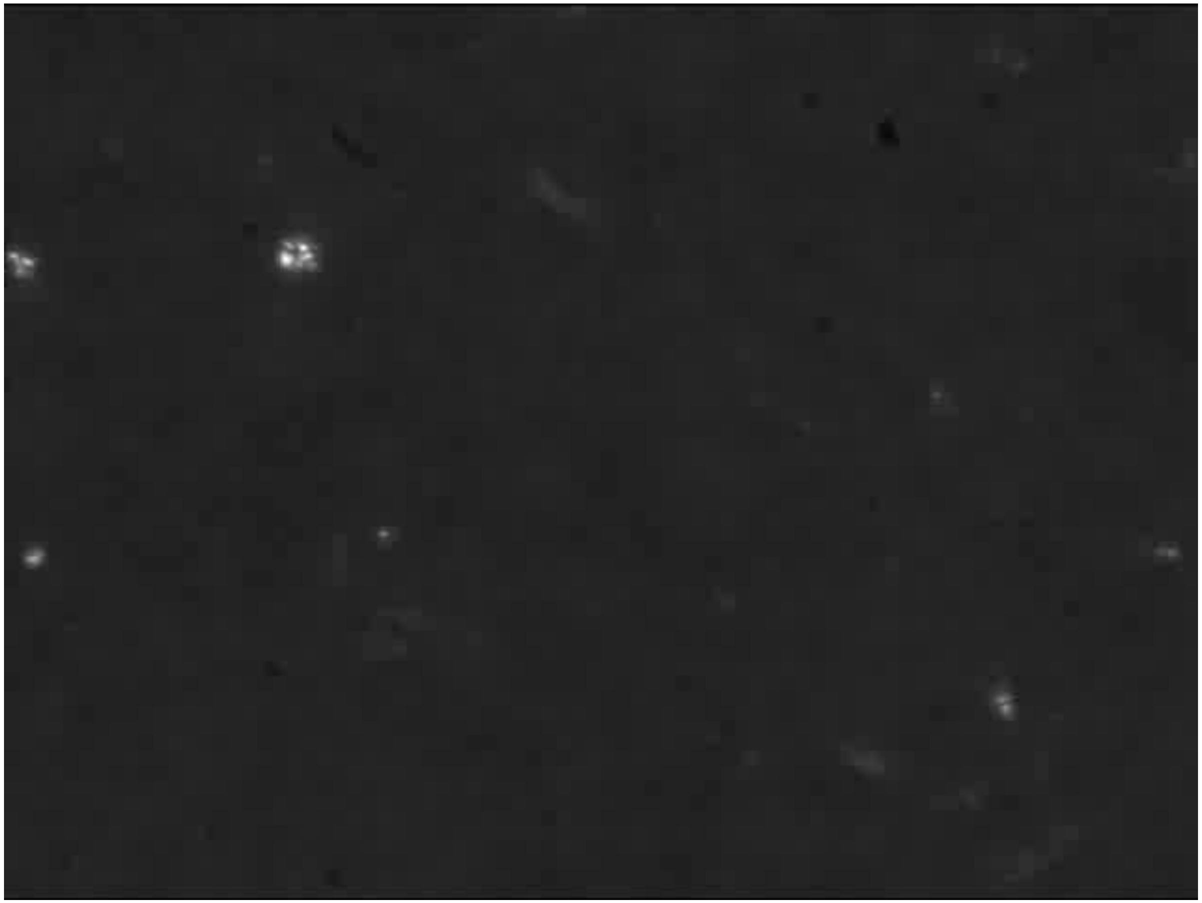
Twist-bend phase:

$$\theta_0{}^2 = -\frac{K_3}{2K_2}, \qquad k^2 = -\frac{K_3}{3C}, \qquad F_{sb} = \frac{K_3{}^3}{54CK_2}$$

Microscope observation - thin cell (8 ❍m)

Microscope observation – thick cell (20 ❍m)

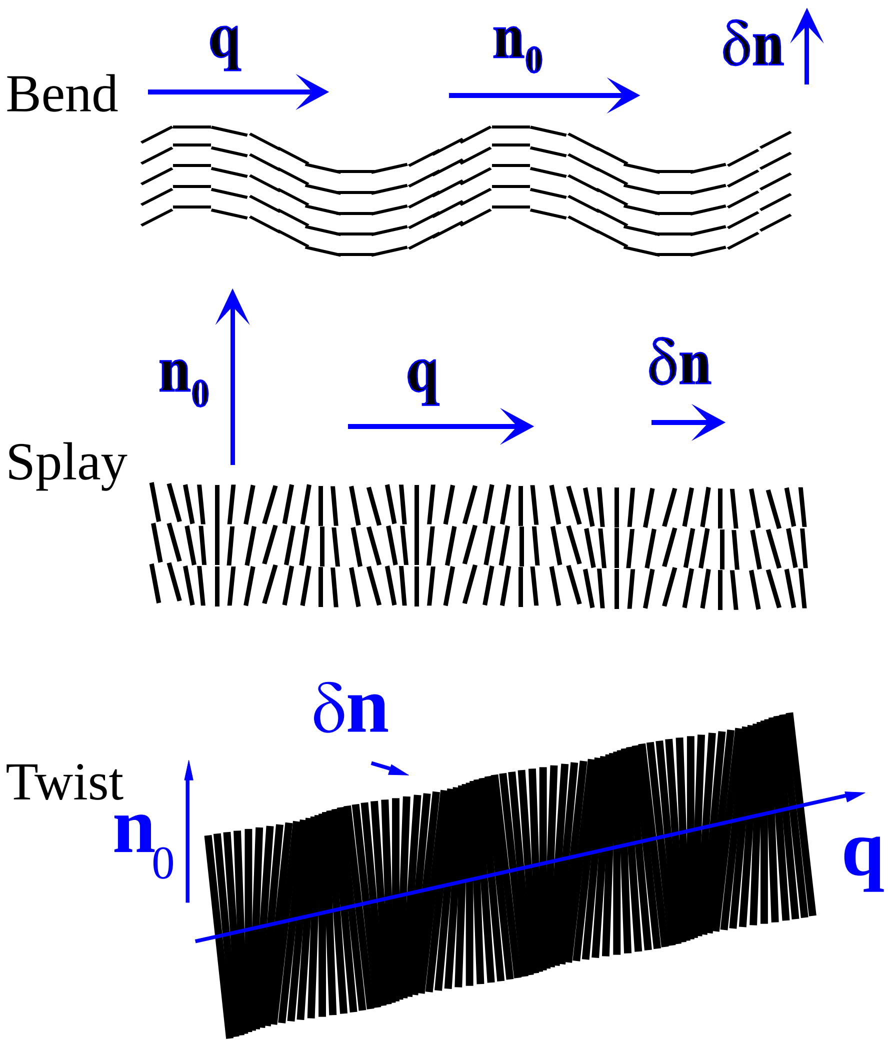
n



Light scattering

- Elastic constants can be measured by observation of thermal director flucutations
- Relaxation rates give ratios K_i/η_i
- Scattering intensity gives (👎ε)$^2/K_i$
- As 👎ε is proportional to S, we get K_i/S^2
- K_i/S^2 are lowest order “bare” elastic coefficients in Landau-deGennes free energy

Nematic fluctuations



$$\delta\mathbf{n_0}(\mathbf{q_n})e^{-i\mathbf{q_n}\cdot\mathbf{r}}e^{-t/\tau_\mathrm{n}}$$

$$\left\langle\left|\delta\mathbf{n_0}(\mathbf{q}_\mathrm{n})\right|^2\right\rangle = \frac{k_\mathrm{B}T}{K\,q_\mathrm{n}^{\;2}}$$

Relaxation rates

Two modes: bend-splay and bend-twist, for ***q*** along ***n*** – pure bend
Relaxation rates:

$$\frac{1}{\tau_i} = \frac{K_i q_\perp{}^2 + K_3 q_z{}^2}{\eta_i}, \quad i = 1,2$$

Effective viscosities:

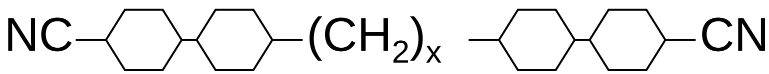
$$\eta_1 = \gamma_1 - \frac{(q_\perp{}^2 \alpha_3 - q_z{}^2 \alpha_2)^2}{q_\perp^4 \eta_b + q_\perp^2 q_z^2 (\alpha_1 + \alpha_3 + \alpha_4 + \alpha_5) + q_z^4 \eta_c}$$

$$\eta_2 = \gamma_1 - \frac{q_z{}^2 \alpha_2}{q_\perp^2 \eta_a + q_z^2 \eta_c}$$

Usually $\alpha_2 >> \alpha_3$, so that bend viscosity is smaller due to backflow

- The direction and polarization of the incoming and scattered light and **n** determine which mode is observed

Samples

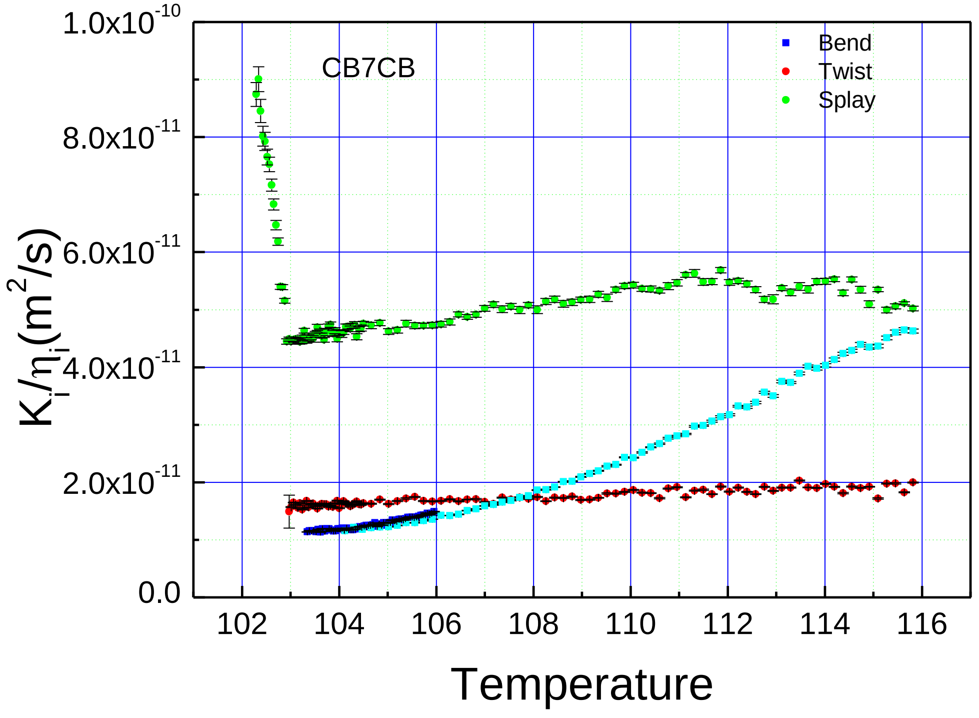


X=7,9 - CB7CB and CB9CB

- CB7CB : T_{NI} = 116 ^oC, T_{NX} = 103 ^oC
- CB9CB : T_{NI} = 124 ^oC, T_{NX} = 109 ^oC

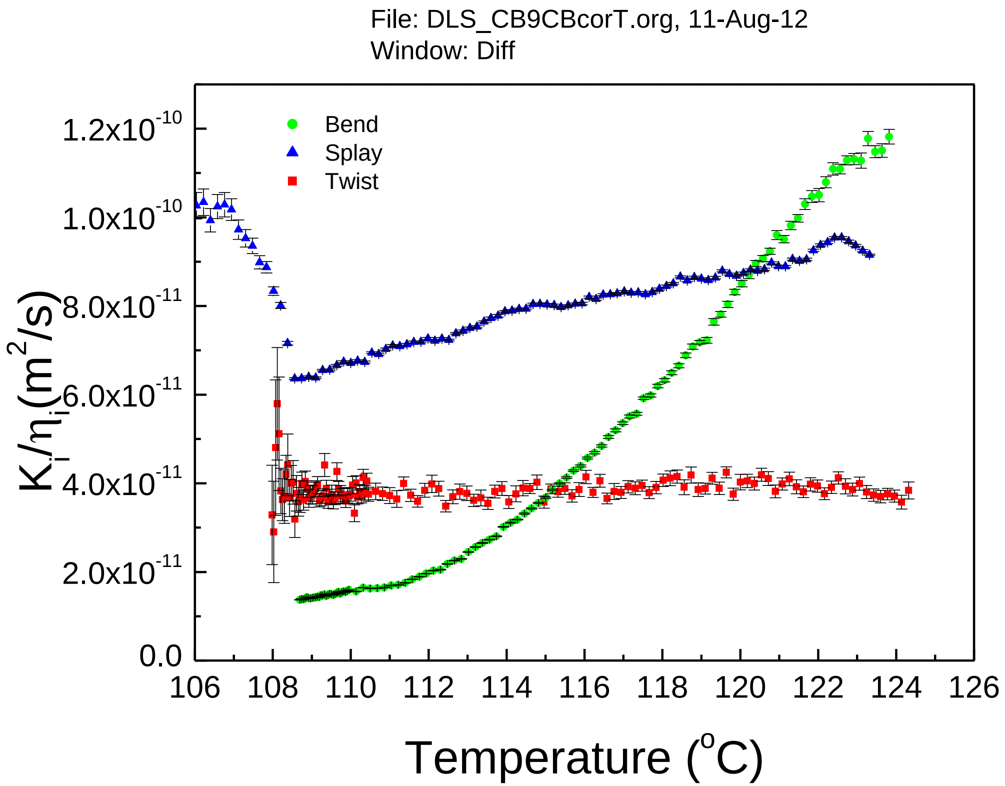
- Planar orientation

CB7CB diffusivities (K/η)



Note increase in the splay diffusivity below T_{NX}

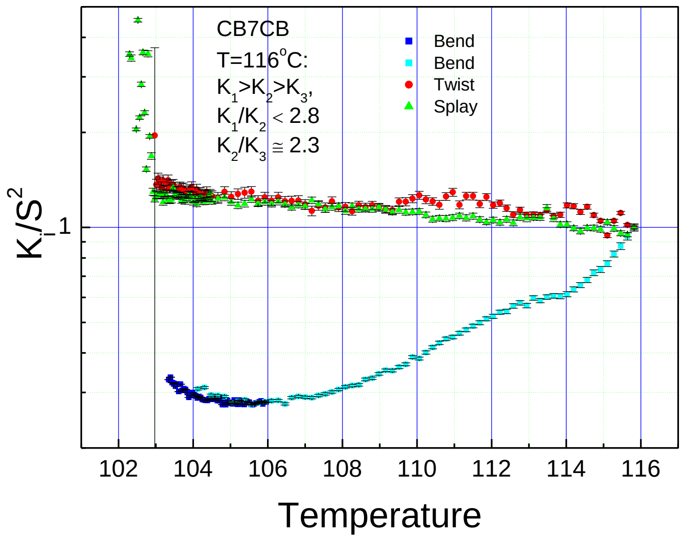
CB9CB diffusivities (K/η)



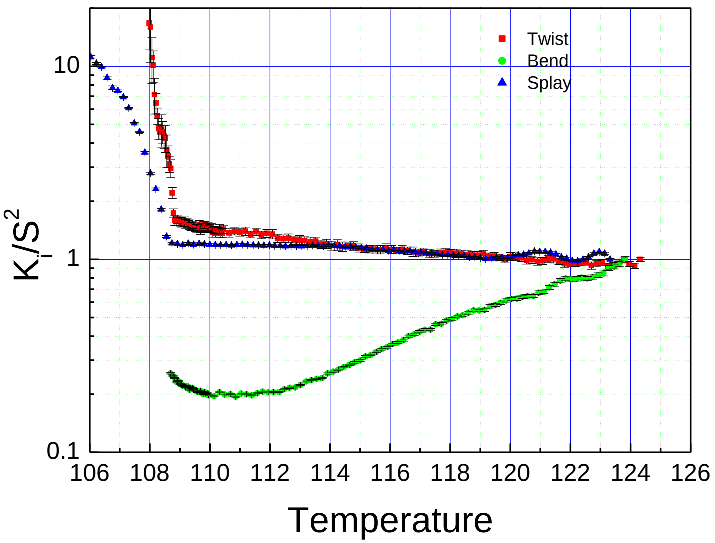
Note increase in the splay diffusivity below T_{NX}

Normalized “bare” elastic constants

CB7CB



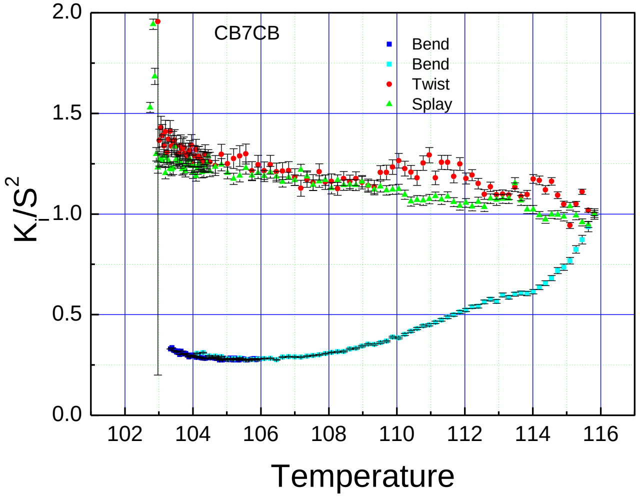
CB9CB



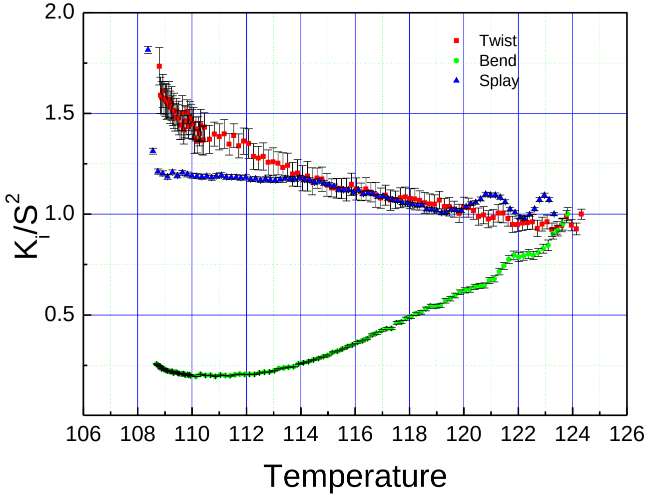
- Absolute scattering cross-sections is difficult to measure, so we obtain only T dependence of K_i relative to the value at T_{NI}
- The bend constant softens, but increases just above T_{NX}
- The splay constant increases below T_{NX} , also seen in diffusivity

“Bare” elastic constants – linear scale

CB7CB

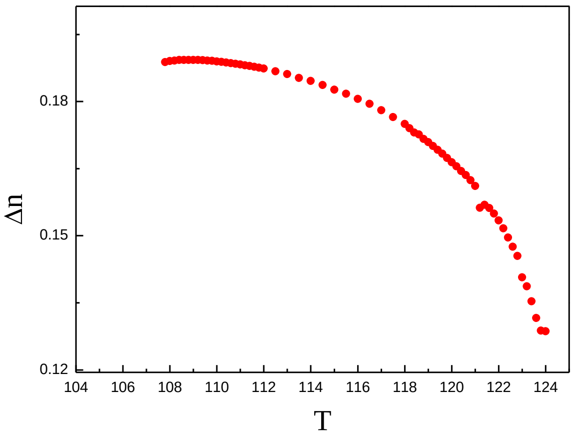


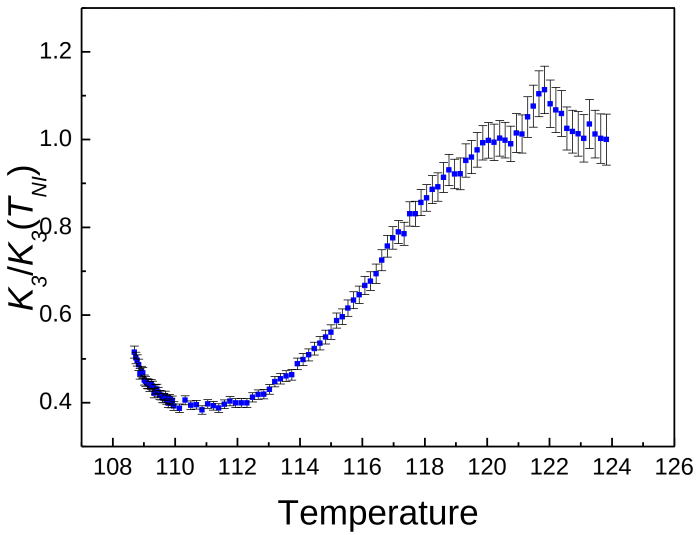
CB9CB



K_i are normalized to 1 at T_{NI}.

CB9CB: True K_3

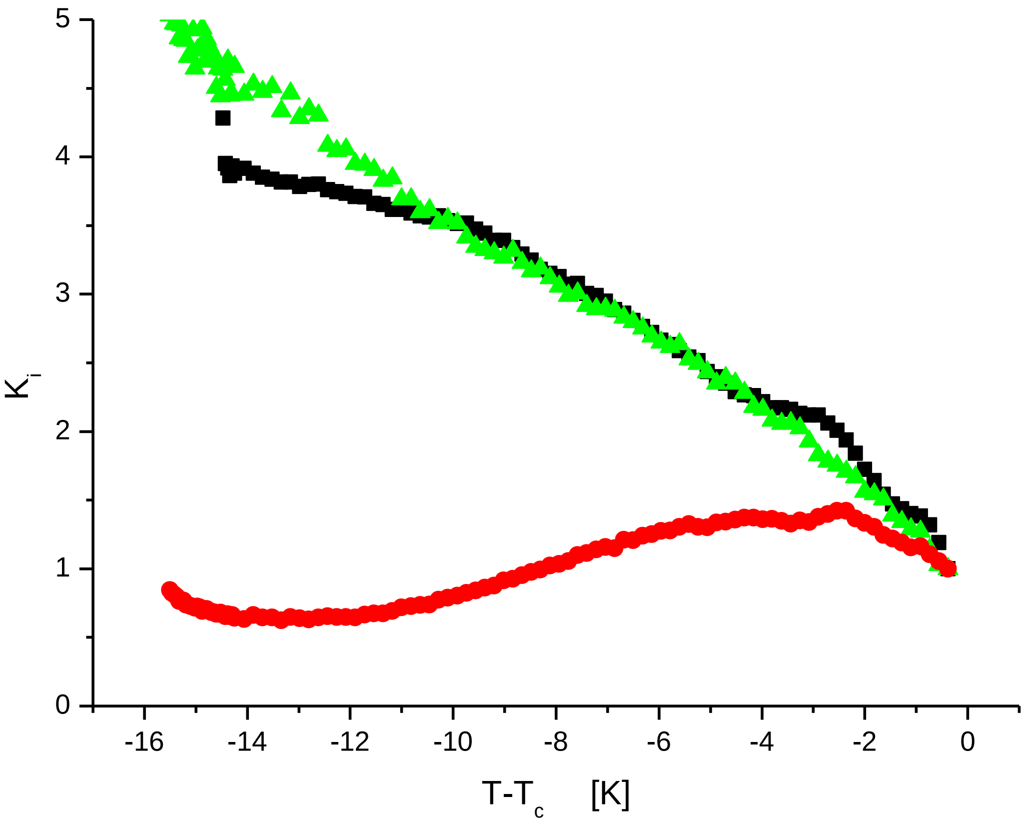




- Δn measured by polarization interference
- Δn is proportional to S

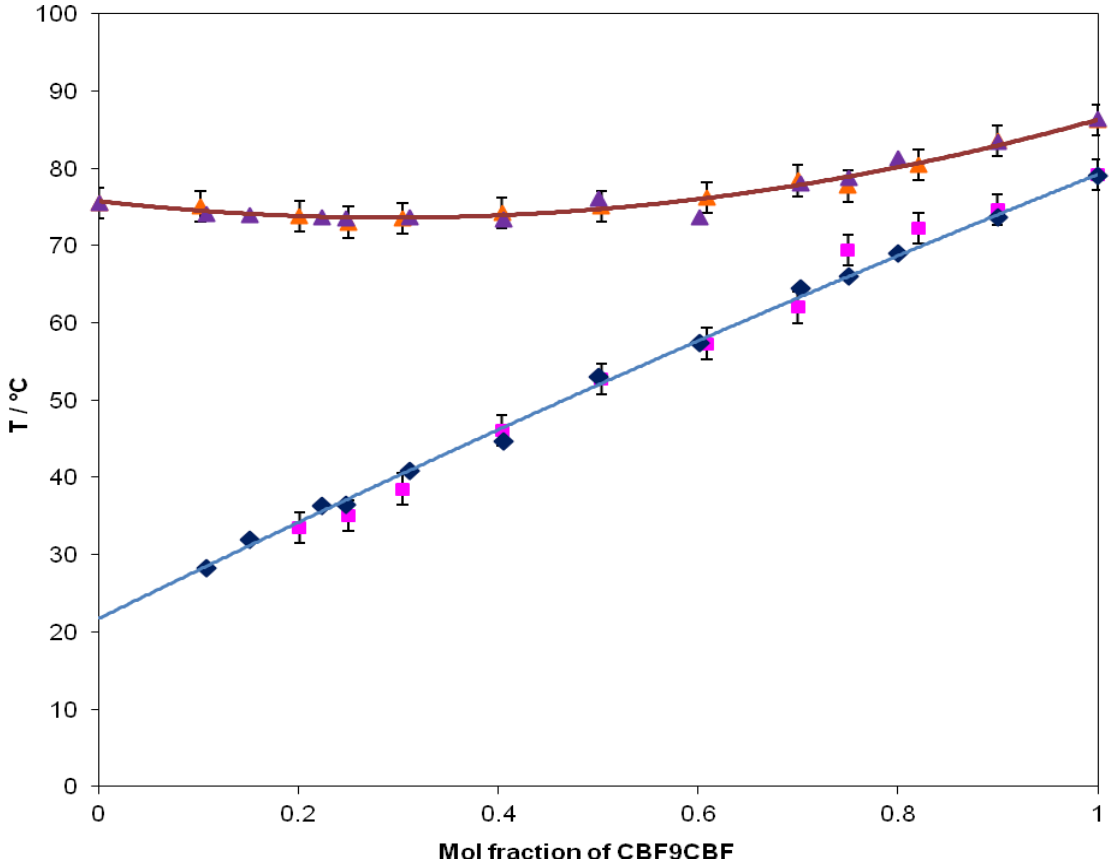
- The increase close to T_{NI} is due to S^2

True elastic constants of CB9CB.



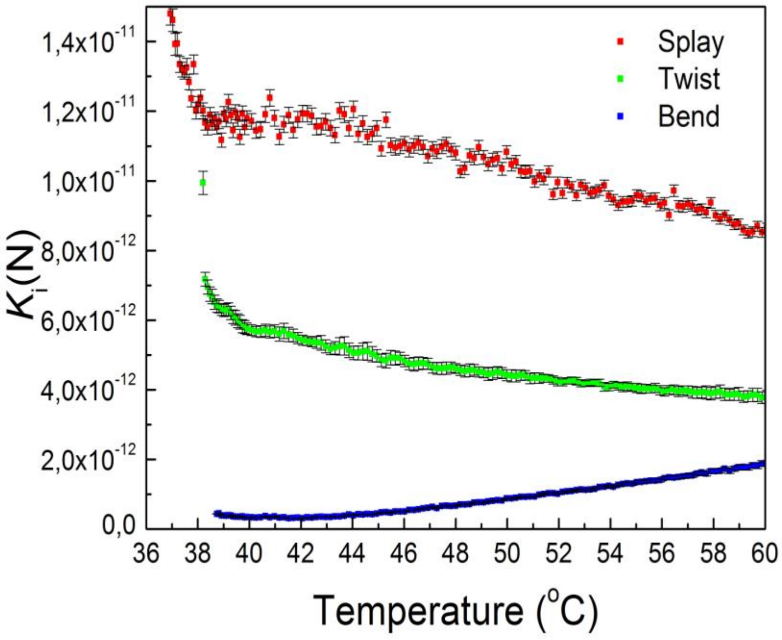
Values are relative to the values at TNI. Black squares - splay, green triangles – twist, red circles – bend.

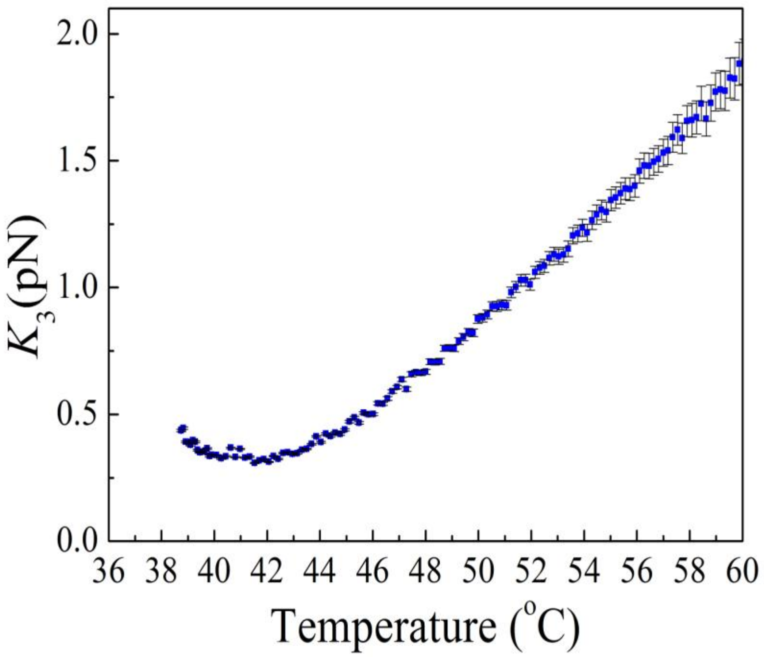
Mixture of dimers



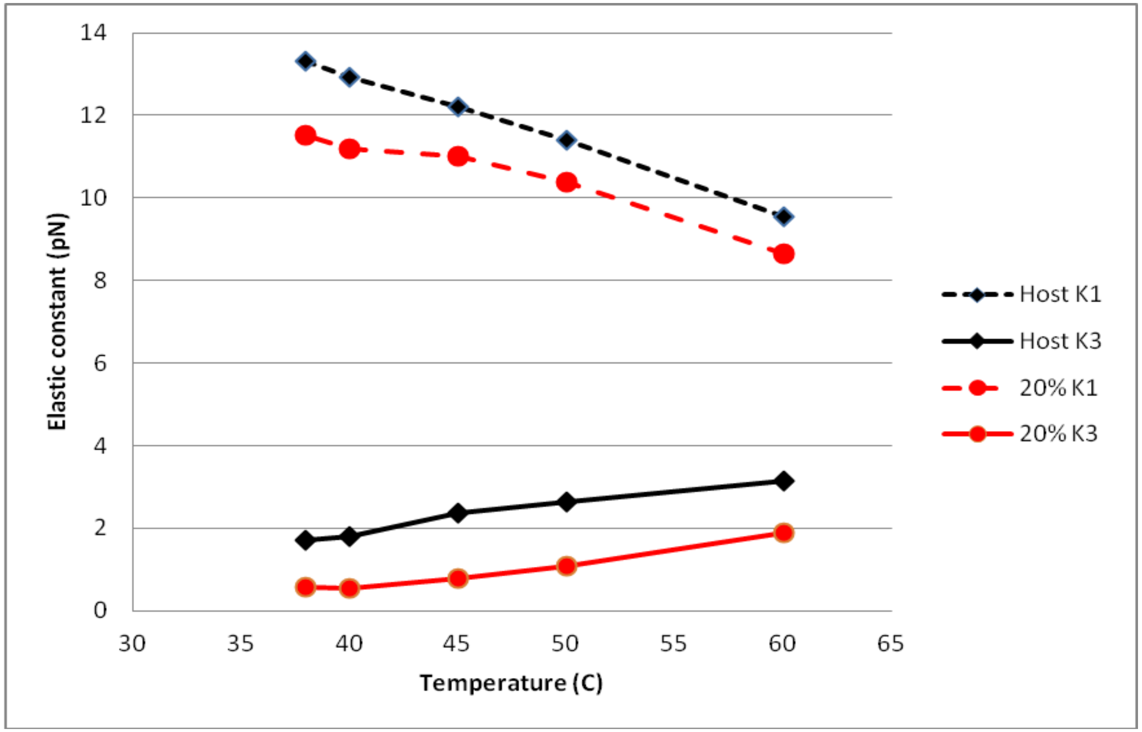
The phase diagram for a mixture of KA and the liquid crystal dimer, CBF9CBF

Elastic constants of mixture





Elastic constants of mixture by Frederiks transition



Minimum K_3 =0.63 pN – by light scattering 0.3 pN

Relation to cubic invariants

- To quadratic order in gradient of **Q** splay and bend constants are equal.
- Cubic invariants that contribute to the elastic constants are

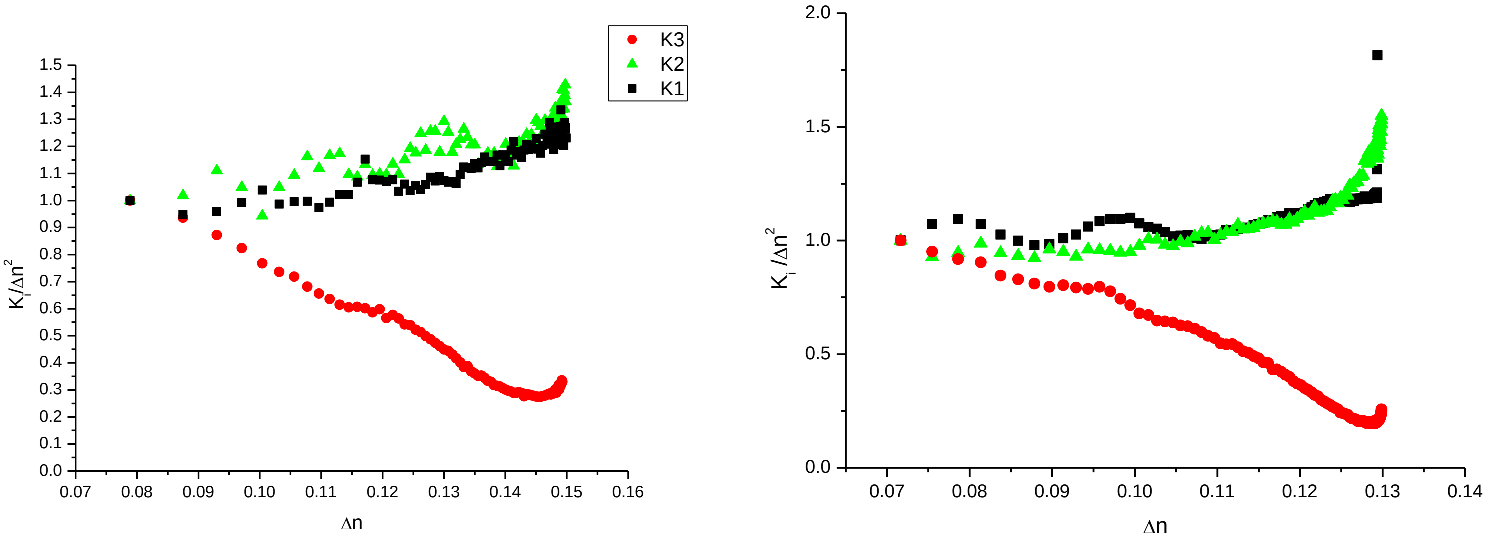
$$C_1 Q_{ij} Q_{kl,i} Q_{kl,j} \qquad C_2 Q_{ij} Q_{ik,k} Q_{jl,l} \qquad C_3 Q_{ij} Q_{ik,l} Q_{jk,l}$$

$$K_1^{(3)} = 1/3(-2C_1 + 2C_2 + C_3)$$

$$K_2^{(3)} = 1/3(-2C_1 + C_3)$$

$$K_3^{(3)} = 1/3(4C_1 - C_2 + C_3)$$

Values of third order coefficients



Ki/S2 as functions of *Δn* for CB7CB (left) and CB9CB (right).

C_1 negative, C_2 and C_3 about 0

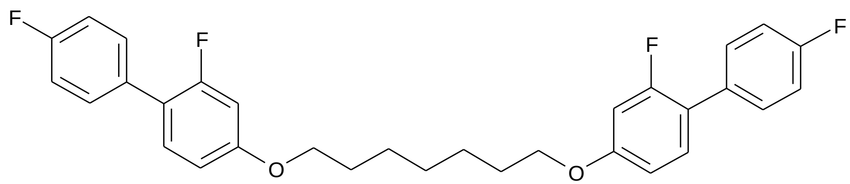
- Transition seems to be driven by increase in S

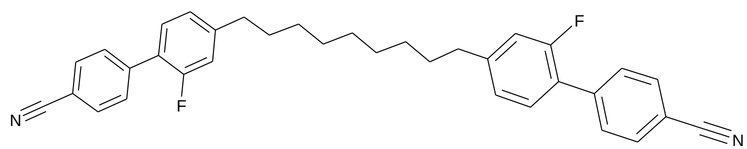
Problems

- Bend constant increases just before the transition to Nx phase
  - Bent core molecules also have small bend constant, but go to Sm phase – perhaps the increase of K_3 due to competition with smectic order
- Standard methods based on Frederiks transition give smaller decrease of the bend constant

Conclusions

- Bend elastic constant in the nematic phase of flexible dimers dramatically decreases with T and is probably the cause of an instability resulting in the modulated phase
- Just above the transition K_3 slightly increases – effect of pretransitional fluctuations?
- Below the transition light scattering corresponding to splay fluctuations strongly decreases – analogy with SmA phase?


F
F
O
O
F
F


N
F
F
N