A Quadratic Elastic Theory for Helical Nematic Phases

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Summary

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- P. J. Barnes, A. G. Douglass, S. K. Heeks & G. R. Luckhurst (1993)
- M. Sepelj, A. Lesac, U. Baumeister, S. Diele, H. L. Nguyen & D. W. Bruce (2007)
- C. T. Imrie & P. A. Henderson (2007)
- V. P. Panov, M. Nagaraj, J. K. Vij, Y. P. Panarin, A. Kohlmeier, M. G. Tamba, R. A. Lewis & G. H. Mehl (2010)

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first characterization

Perhaps, the first complete experimental characterization of this new phase was achieved by

- M. Cestari, S. Diez-Berart, D. A. Dunmur, A. Ferrarini, M. R. de la Fuente, D. J. B. Jackson, D. O. Lopez, G. R. Luckhurst, M. A. Perez-Jubindo, R. M. Richardson, J. Salud, B. A. Timimi & H. Zimmermann (2011)

who employed a number of different methods.

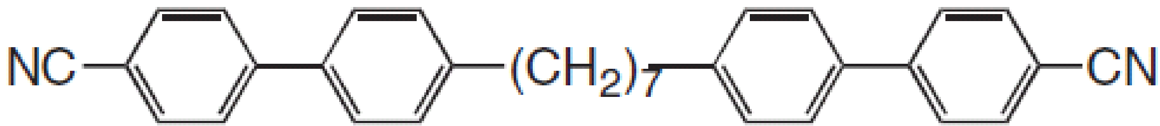
See also

- P. A. Henderson & C. T. Imrie (2011)
- M. Cestari, E. Frezza, A. Ferrarini & G. R. Luckhurst (2011)
- V. P. Panov, R. Balachandran, M. Nagaraj, J. K. Vij, M. G. Tamba, A. Kohlmeier & G. H. Mehl (2011)
- V. P. Panov, R. Balachandran, J. K. Vij, M. G. Tamba, A. Kohlmeier & G. H. Mehl (2012)
- L. Beguin, J. W. Emsley, M. Lelli, A. Lesage, G. R. Luckhurst, B. A. Timimi & H. Zimmermann (2012)

for further, independent experimental confirmations.

material: CB7CB

The simplest molecular structure having core flexibility is a dimer structure in which two semirigid mesogenic groups are connected by a flexible chain.



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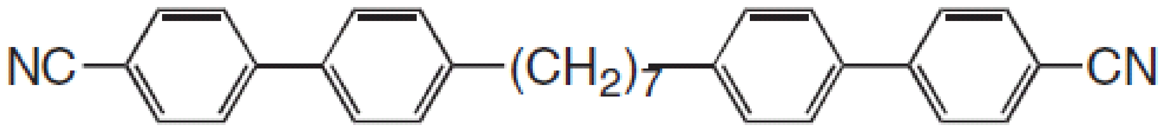
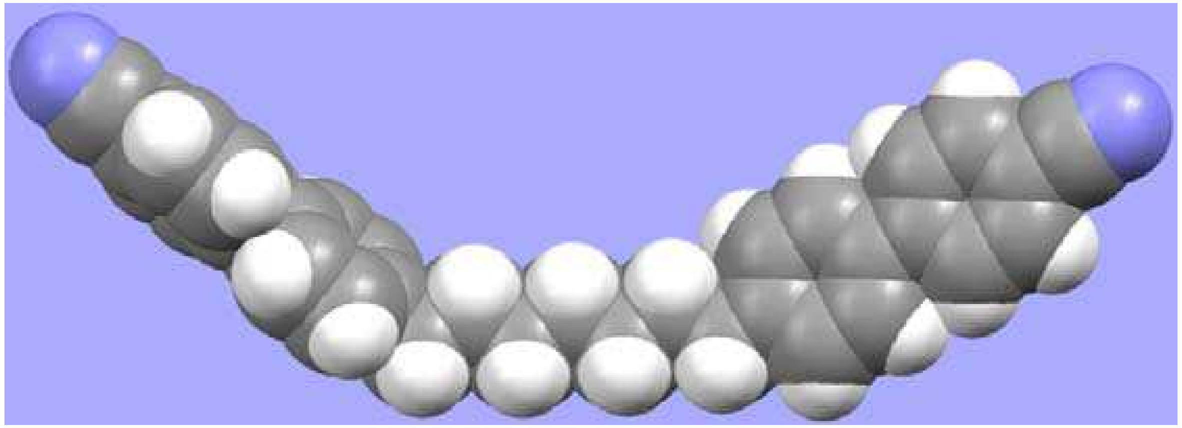


A CB7CB molecule can be viewed as having three parts, each $\approx 1\,\mathrm{nm}$ in length: two rigid end groups connected by a flexible spacer.



transition temperatures

First transition, on cooling, at $T_{\mathrm{NI}} = 116 \pm 1\,^{\circ}\mathrm{C}$, with ***transitional entropy*** $\Delta S_{\mathrm{NI}}/R = 0.34$, where $R \approx 8.31\,\mathrm{J(mol\,K)^{-1}}$ is the gas constant.

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The X phase supercools extensively. On ***heating***, the crystal form of CB7CB ***melts*** at $T = 102\,^{\circ}\mathrm{C}$

Theoretical Predictions

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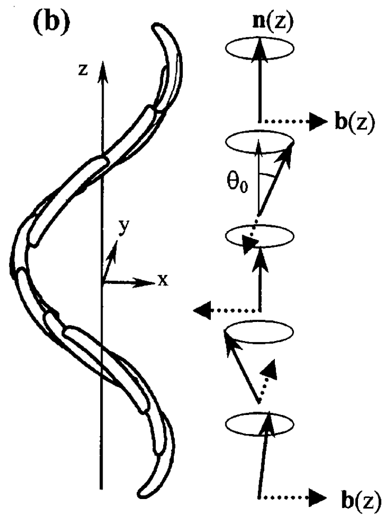
- I. Dozov (2001) arrived independently to the same picture starting from purely static (and steric) considerations.



$$\boldsymbol{b} = \boldsymbol{n} \times \operatorname{curl} \boldsymbol{n}$$

computer simulation

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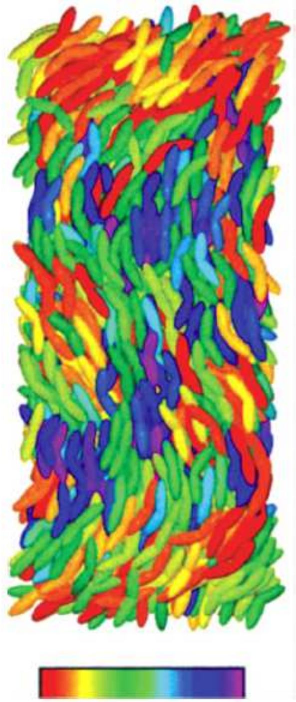

Bent-core Gay-Berne molecules with ***no polar*** interactions.

naming the phase

LUCKHURST ET AL (2011) suggested to call this phase

twist-bend nematic (TBN)

recognizing its ***ground states*** as those envisaged by MEYER and DOZOV.

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The TBN natural states are ***conical*** twists, in which the average molecular orientation $\boldsymbol{n}$ performs uniform precessions, making the angle ϑ with the ***twist*** axis $\boldsymbol{t}$.

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Letting $\boldsymbol{t} = \boldsymbol{e}_z$ in a Cartesian frame $(\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z)$,

$$\boldsymbol{n}_0^{\pm} = \sin\vartheta\cos(\pm qz)\,\boldsymbol{e}_x + \sin\vartheta\sin(\pm qz)\,\boldsymbol{e}_y + \cos\vartheta\,\boldsymbol{e}_z,$$

$$\operatorname{curl}\boldsymbol{n}_0^{\pm}\cdot\boldsymbol{n}_0^{\pm} = \mp q\sin^2\vartheta$$

$q > 0$ twist parameter

$p := \frac{2\pi}{q}$ pitch $\qquad \vartheta$ cone angle

Recent (impressive) Experimental Evidence

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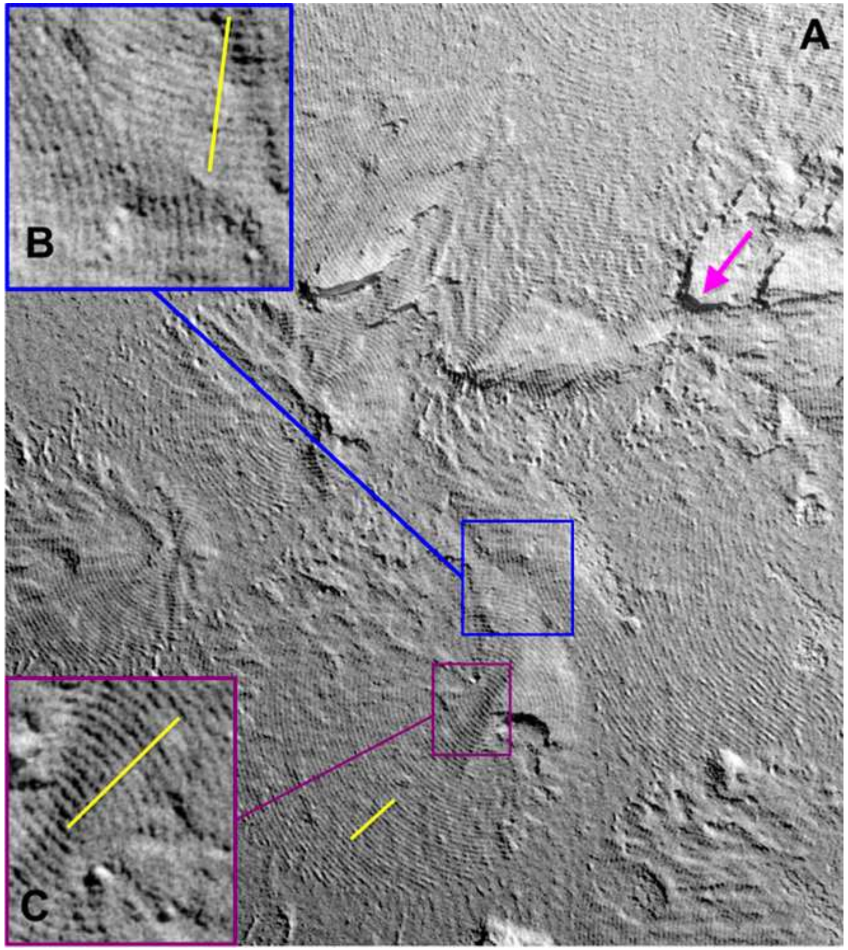
measured pitch and cone angle

$$p \approx 10\,\mathrm{nm} \qquad \vartheta \approx 20^\circ$$

Freeze-Fracture Transmission Electron Microscopy (FFTEM)



$T = 95\,^{\circ}\mathrm{C}$, scale bar: $100\,\mathrm{nm}$

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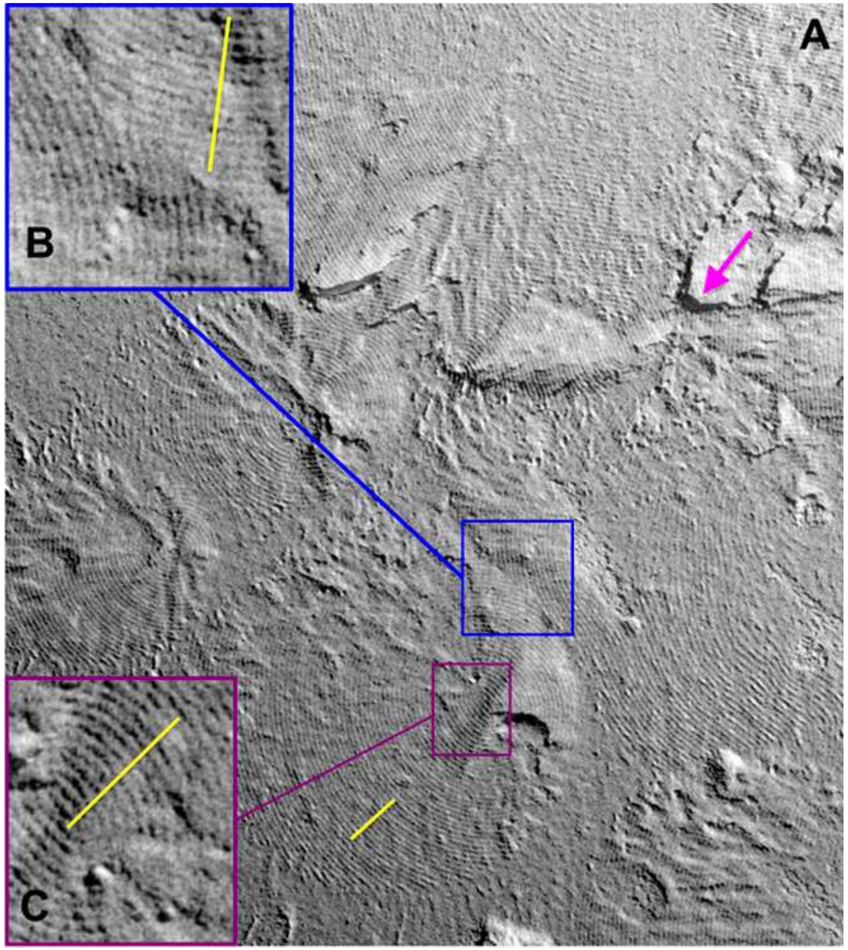

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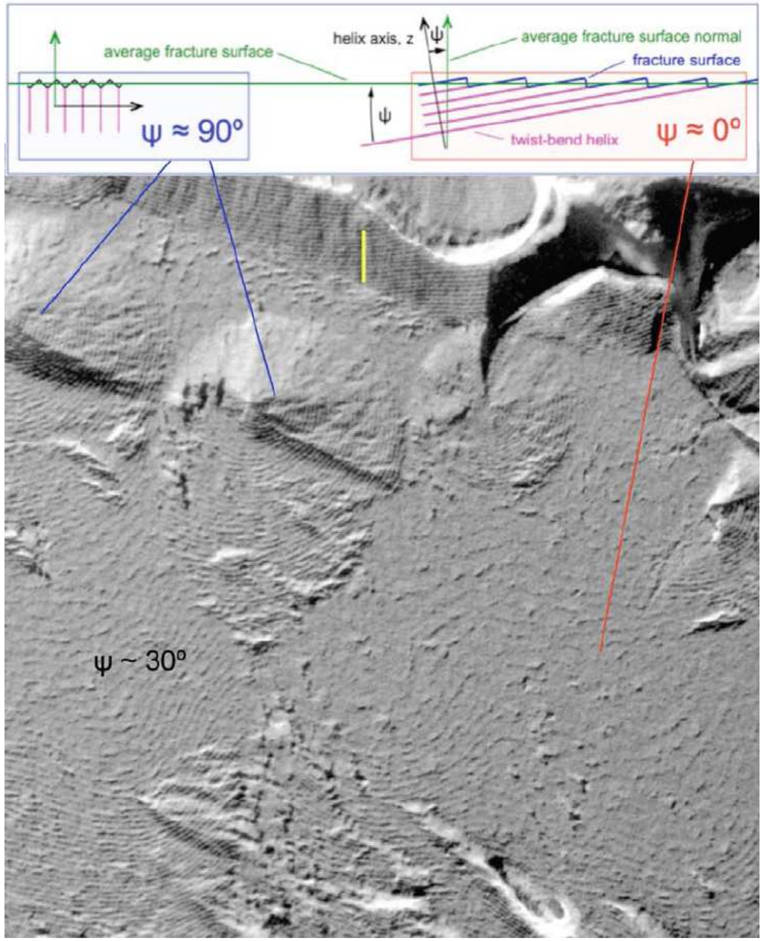

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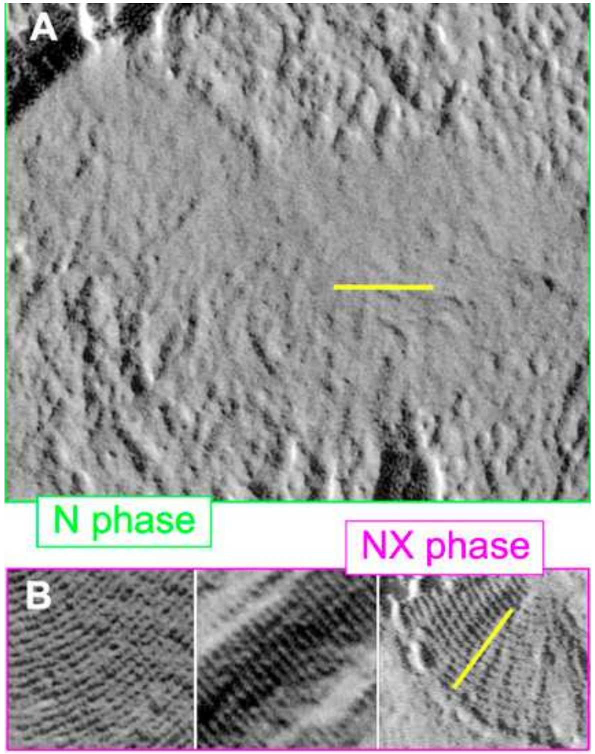
Comparisons

TBN vs N



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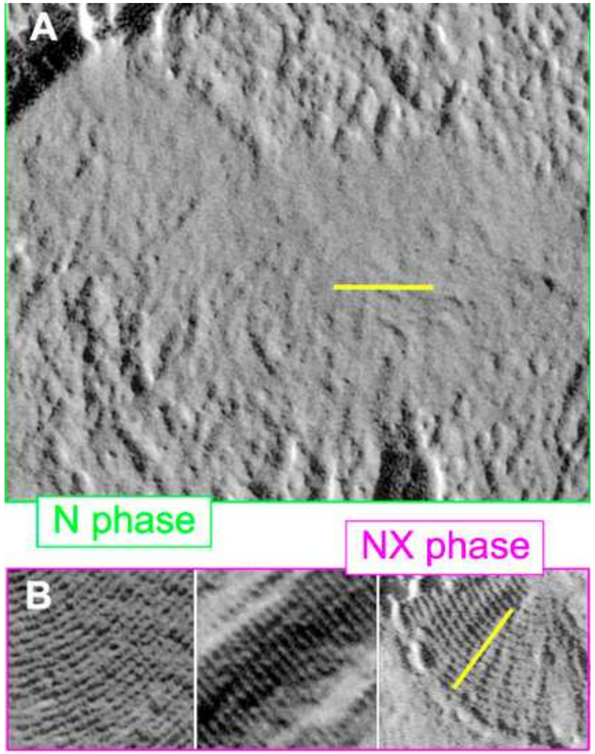

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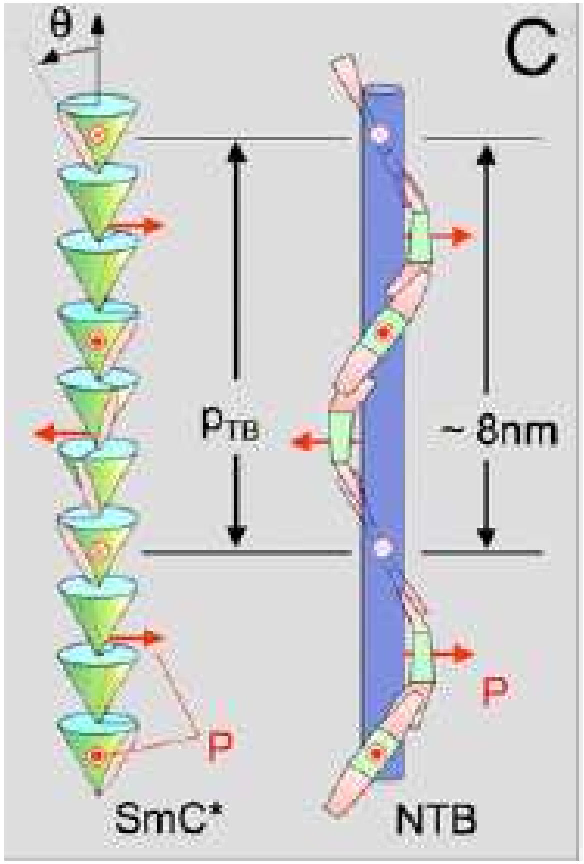
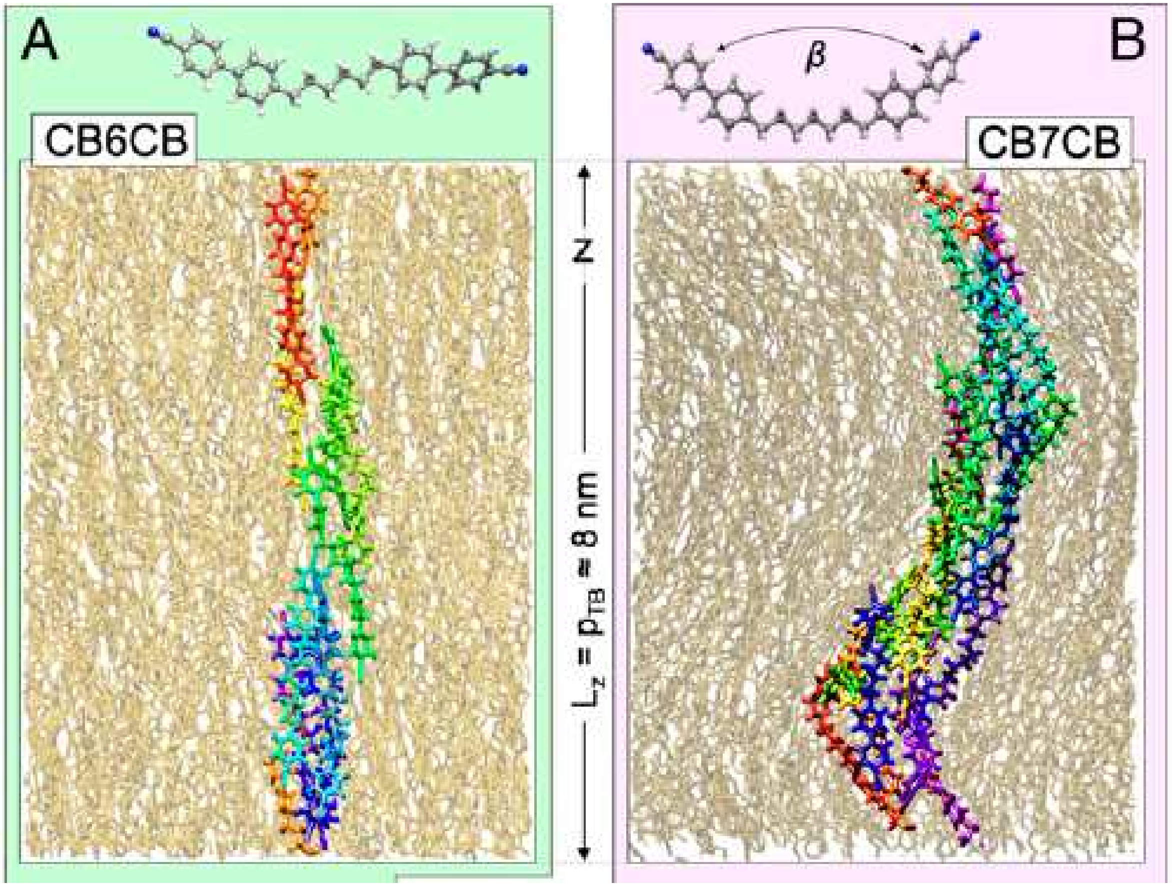
*TBN vs SmC**



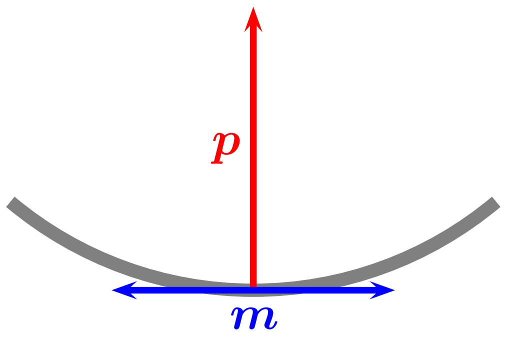
atomistic MD simulations



in periodic box of a nominally $5.6 \times 5.6 \times 8.0\,\text{nm}$

Symmetries

The molecular effective curvature, while inducing ***no*** microscopic ***twist***, allegedly favors a ***chiral*** collective arrangement in which ***bow-shaped*** molecules uniformly precess along an ideal cylindrical ***helix***.



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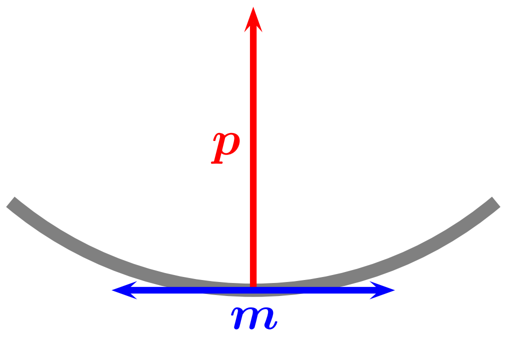

Polar and ***achiral***

Point-group C_{2v}

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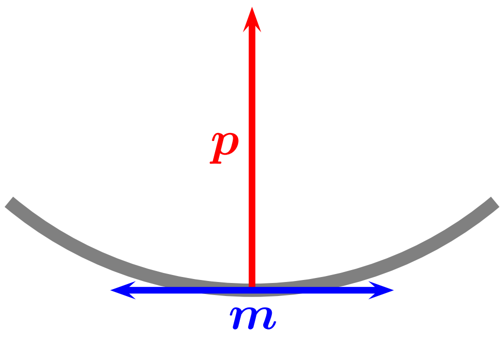

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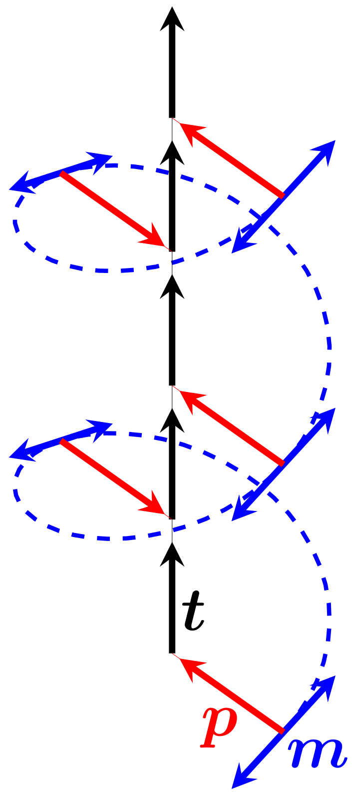

Two symmetries are broken in the ***helical arrangement***:

- the continuous translations ***along*** the twist axis $\boldsymbol{t}$
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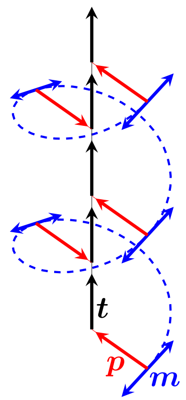

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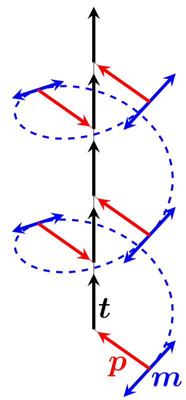

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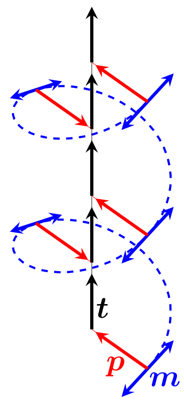

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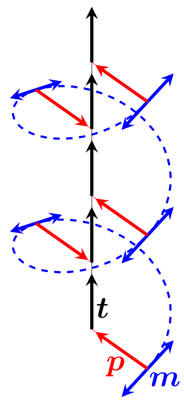
no polarity

While the nematic director $\boldsymbol{n}$ is defined as the ensemble average

$$\boldsymbol{n} := \langle \boldsymbol{m} \rangle$$

no polar order survives in a helical phase, as

$$\langle \boldsymbol{p} \rangle = \boldsymbol{0}$$



Chiral Variants

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Our strategy will be to treat first ***each*** variant separately and then to attempt at ***merging*** them together in a TBN-phase.

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Here we take both the natural pitch $p = 2\pi/q$ and the cone angle ϑ as ***prescribed*** parameters, ***constitutive*** of a certain ***helical phase***.

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(Positive) Natural State

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$$\Downarrow$$

$$\nabla\boldsymbol{n}_0^+ = q\left(\boldsymbol{e}_z \times \boldsymbol{n}_0^+\right) \otimes \boldsymbol{e}_z \qquad \operatorname{curl}\boldsymbol{n}_0^+ \cdot \boldsymbol{n}_0^+ = -q\sin^2\vartheta < 0$$

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twist tensor

More generally, for $\boldsymbol{n}$ prescribed at a point in space, the tensor

$$\mathbf{T}^+ := q(\boldsymbol{t} \times \boldsymbol{n}) \otimes \boldsymbol{t}$$

expresses the ***natural distortion*** associated there with the preferred twisted configuration that agrees with the prescribed nematic director $\boldsymbol{n}$ and has $\boldsymbol{t}$ as twist axis.

natural distortions

We imagine that in the absence of any frustrating cause, given $\boldsymbol{n}$ at a point, the director field would attain in its vicinity a spatial arrangement such that

$$\nabla \boldsymbol{n} = \mathbf{T}^{+}(\boldsymbol{t})$$

with ***any*** $\boldsymbol{t}$ such that

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energy reference

For a generic configuration, the elastic energy that measures locally the ***distortional cost*** should be accounted for ***relative*** to the whole class of ***natural distortions***, vanishing whenever any of the latter is attained.

Elastic Energy Density

We write the elastic energy f_e^+ per unit volume as

$$f_e^+(\boldsymbol{t}, \boldsymbol{n}, \nabla\boldsymbol{n}) = \frac{1}{2}[\nabla\boldsymbol{n} - \mathbf{T}^+(\boldsymbol{t})] \cdot \mathbb{K}(\boldsymbol{n})[\nabla\boldsymbol{n} - \mathbf{T}^+(\boldsymbol{t})]$$

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metric interpretation

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If there is no such $\boldsymbol{t}$, then minimizing f_e^+ in $\boldsymbol{t}$ would identify the natural state closest to the nematic distortion represented by $\nabla\boldsymbol{n}$ in the metric induced by $\mathbb{K}(\boldsymbol{n})$.

two-director theory

Here both $\boldsymbol{n}$ and $\boldsymbol{t}$ are to be considered as unknown fields, though ***constrained***: at equilibrium, the free-energy functional that we shall construct is to be ***minimized*** in ***both*** these fields.

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identities

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reduced $\mathbb{K}(\boldsymbol{n})$

$$\mathbb{K}_{ijhk} = k_1 \delta_{ih} \delta_{jk} + k_2 \delta_{ij} \delta_{hk} + k_3 \delta_{ih} n_j n_k + k_4 \delta_{ik} \delta_{jh}$$

k_i elastic moduli

representation formula

$$
\begin{aligned}
f_e^{+}(\boldsymbol{t},\boldsymbol{n},\nabla\boldsymbol{n}) = \frac{1}{2}\Big\{ & K_{11}(\operatorname{div}\boldsymbol{n})^2 + K_{22}(\boldsymbol{n}\cdot\operatorname{curl}\boldsymbol{n} + q|\boldsymbol{t}\times\boldsymbol{n}|^2)^2 \\
& + K_{33}|\boldsymbol{n}\times\operatorname{curl}\boldsymbol{n} + q(\boldsymbol{t}\cdot\boldsymbol{n})\,\boldsymbol{t}\times\boldsymbol{n}|^2 \\
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Ericksen's inequalities

$$2K_{11} \geqq K_{24} \qquad 2K_{22} \geqq K_{24} \qquad K_{33} \geqq 0 \qquad K_{24} \geqq 0$$

Typical Variational Problem

In the absence of other distorting causes, the free-energy functional to be minimized is

$$\mathscr{F}_e^+[\boldsymbol{t}, \boldsymbol{n}] := \int_{\mathscr{B}} f_e^+(\boldsymbol{t}, \boldsymbol{n}, \nabla \boldsymbol{n}) dV$$

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$\mathscr{B}$ region in space

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Remarks

- This theory features two constrained fields, $\boldsymbol{n}$ and $\boldsymbol{t}$.
- Physically, $\boldsymbol{t}$ represents the ***optic axis*** of the medium, likely to be the only optic observable when the pitch p ranges in the nanometric domain.

- Dozov (2001) proposed a ***quartic*** elastic theory, featuring only $\boldsymbol{n}$, but allowing for terms in both $(\nabla \boldsymbol{n})^4$ and $(\nabla^2 \boldsymbol{n})^2$, to counteract a ***negative*** bend constant K_{33} required to ignite the ***twist-bend instability***.

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Merging Opposite Helicities

The natural state of the helical nematic phase with opposite chirality $-q$ is characterized by the ***twist tensor***

$$\mathbf{T}^- := -\mathbf{T}^+ = -q(\boldsymbol{t} \times \boldsymbol{n}) \otimes \boldsymbol{t} \qquad q > 0$$

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Assuming that the elastic response is the same, but about a natural state with opposite helicity, the free energy density f_e^- is obtained from f_e^+ by the formal change $q \mapsto -q$:

$$\begin{aligned} f_e^-(\boldsymbol{t}, \boldsymbol{n}, \nabla\boldsymbol{n}) = \frac{1}{2}\Big\{ & K_{11}(\operatorname{div}\boldsymbol{n})^2 + K_{22}(\boldsymbol{n}\cdot\operatorname{curl}\boldsymbol{n} - q|\boldsymbol{t}\times\boldsymbol{n}|^2)^2 \\ & + K_{33}|\boldsymbol{n}\times\operatorname{curl}\boldsymbol{n} - q(\boldsymbol{t}\cdot\boldsymbol{n})\,\boldsymbol{t}\times\boldsymbol{n}|^2 \\ & + K_{24}[\operatorname{tr}(\nabla\boldsymbol{n})^2 - (\operatorname{div}\boldsymbol{n})^2]\Big\} + K_{24}q\,\boldsymbol{t}\times\boldsymbol{n}\cdot(\nabla\boldsymbol{n})^{\mathsf{T}}\boldsymbol{t} \end{aligned}$$

TBN free energy density

A ***TBN-phase*** can be envisaged as a nematic phase with ***two*** natural states with opposite ***helicities***.

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possible candidates for f_e

- quadratic, but non-smooth

$$f_e(\boldsymbol{t}, \boldsymbol{n}, \nabla \boldsymbol{n}) = \min\{f_e^+(\boldsymbol{t}, \boldsymbol{n}, \nabla \boldsymbol{n}), f_e^-(\boldsymbol{t}, \boldsymbol{n}, \nabla \boldsymbol{n})\}$$

- smooth, but quartic

$$f_e(\boldsymbol{t}, \boldsymbol{n}, \nabla \boldsymbol{n}) = \frac{1}{f_0} f_e^+(\boldsymbol{t}, \boldsymbol{n}, \nabla \boldsymbol{n}) f_e^-(\boldsymbol{t}, \boldsymbol{n}, \nabla \boldsymbol{n})$$
$$f_0 = \frac{1}{2} \sin^2 \vartheta (K_{22} \sin^2 \vartheta + K_{33} \cos^2 \vartheta)$$

Matching opposite helicities

Since f_e^+ is minimized for $\nabla \boldsymbol{n} = \mathbf{T}^+$ and f_e^- is minimized for $\nabla \boldsymbol{n} = \mathbf{T}^-$, possible minimizers for f_e are sequences of ***alternating*** natural states $\mathbf{T}^+$, $\mathbf{T}^-$ matched along appropriate interfaces.

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kinematic compatibility

Letting $\boldsymbol{\nu}$ denote a unit normal to an interface $\mathscr{S}$,

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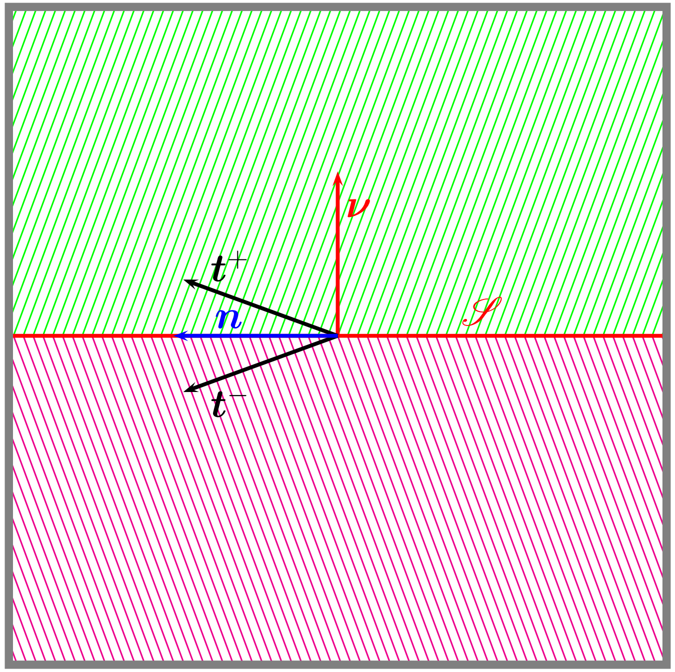
- either ***parallel stacking***
  $\boldsymbol{t}^+ = \boldsymbol{t}^- = \boldsymbol{\nu}$
- or ***wedge laminate***
  $\boldsymbol{t}^+ \times \boldsymbol{n} = -\boldsymbol{t}^- \times \boldsymbol{n} \quad \text{and} \quad \boldsymbol{\nu} = \frac{\boldsymbol{t}^+ - \boldsymbol{t}^-}{|\boldsymbol{t}^+ - \boldsymbol{t}^-|}$

wedge laminate



The trace $\boldsymbol{n}$ on $\mathscr{S}$ should satisfy the compatibility condition

$$\nabla_{\mathrm{s}}\boldsymbol{n} = \kappa \boldsymbol{n}_\perp \otimes \boldsymbol{n} \qquad \boldsymbol{n}_\perp := \boldsymbol{\nu} \times \boldsymbol{n} \qquad \kappa := q \sin\vartheta \cos\vartheta$$

wedge laminate won't work

As a consequence, the integral lines of $\boldsymbol{n}$ on $\mathscr{S}$ should satisfy

$$\kappa_g = \kappa \qquad \text{and} \qquad (\nabla_{\mathrm{s}}\boldsymbol{\nu})\boldsymbol{n} = \mathbf{0}$$

κ_g geodesic curvature

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parallel stacking does work

For $\boldsymbol{t}^+ = \boldsymbol{t}^- = \boldsymbol{\nu}$ and $\boldsymbol{n} \cdot \boldsymbol{\nu} \equiv \cos\vartheta$, the integral lines of $\boldsymbol{n}$ on $\mathscr{S}$ need satisfy

$$(\nabla_{\mathrm{s}}\boldsymbol{\nu})\boldsymbol{n} = \mathbf{0}$$

which only requires $\mathscr{S}$ to be ***developable***

$K = 0$ zero Gaussian curvature

.

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- An ***extra*** field also requires extra ***boundary conditions***. The question is how to set general boundary conditions for both $\boldsymbol{n}$ and $\boldsymbol{t}$ to grant existence of global energy minimizers.
- ***No hydrodynamic*** considerations have entered this study, but the question should already be asked as to whether the ***relaxation*** in time of $\boldsymbol{t}$ represents a further ***source of dissipation***.

Acknowledgements

Discussion

O.D. Lavrentovich
G.R. Luckhurst
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