Nematic Liquid Crystals: Soft Matter Meets Elasticity and Geometry

Epifanio G. Virga
Department of Mathematics
University of Pavia, Italy
eg.virga@unipv.it

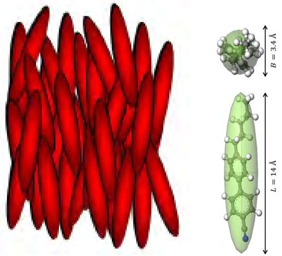
Summary

Nematic Liquid Crystals

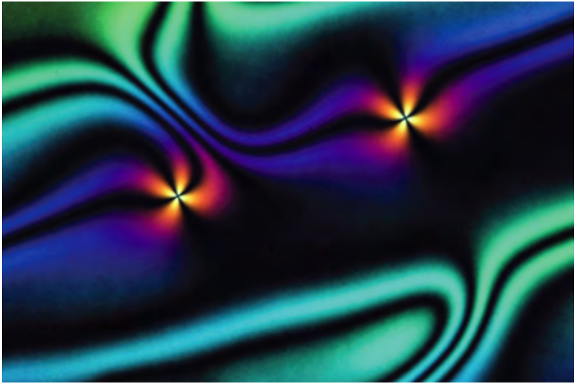
We use the notion of ***uniform distortion*** in the mathematical theory of ***nematic liquid crystals*** to illustrate the interplay between Elasticity and Geometry in Soft Matter.

lexicon

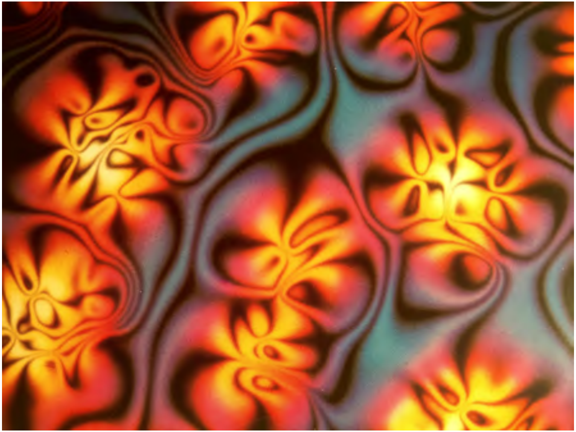
- Liquid crystals are ***anisotropic*** fluids.
- The ***nematic*** phase is ***typically*** produced by the ***ordered*** assembly of elongated, ***rod-like*** molecules, which are on ***average*** aligned along the ***director*** $\boldsymbol{n}$.



- The director $\boldsymbol{n}$ is a unit vector; it resides in the unit sphere $\mathbb{S}^2$.
- Nematic liquid crystals are ***birefringent***; their ***optic axis*** coincides with $\boldsymbol{n}$ and can ***easily*** vary in space.
- For rod-like nematics, a ***natural state*** is any ***uniform*** director field, for which $\nabla\boldsymbol{n} \equiv \mathbf{0}$.
- Nematic liquid crystals are ***not polar***; the theories that describe them must be ***indifferent*** to changing $\boldsymbol{n}$ into $-\boldsymbol{n}$.
- A ***defect*** is a ***singularity*** of $\boldsymbol{n}$.
- Defects are ***optically*** detectable.



Courtesy of O.D. Lavrentovich



Courtesy of O.D. Lavrentovich

early statistical theories

The phase transition from ***isotropic*** to ***nematic***—driven by concentration (***lyotropic***) or temperature (***thermotropic***)—was described by two pioneering theories:

- ONSAGER (1949): purely entropic ***ordering*** forces based on short-range mutual repulsion of molecules.
- MAIER & SAUPE (1958): mean field model based on long-range mutual attractive ***dispersion*** London forces.
- DE GENNES (1969, 1971): Laundau theory based on a ***tensorial*** order parameter.

Curvature Elasticity

The curvature elasticity of liquid crystals in ***three dimensions*** is based on a free-energy functional introduced by Frank (1958), which falls within the larger class envisaged by Ericksen (1962).

elastic free energy

The elastic free-energy functional measures the cost associated with producing a ***distortion*** in a natural state.

$$\mathscr{F}[\boldsymbol{n}] = \int_{\mathscr{B}} W(\boldsymbol{n}, \nabla\boldsymbol{n})\,\mathrm{d}V$$

$\mathscr{B}$ domain in space

V volume measure

W elastic free-energy density

W is ***frame-indifferent***

$$W(\mathbf{Q}\boldsymbol{n}, \mathbf{Q}\nabla\boldsymbol{n}\mathbf{Q}^{\mathsf{T}}) = W(\boldsymbol{n}, \nabla\boldsymbol{n}) \quad \forall\ \mathbf{Q} \in \mathsf{O}(3)$$

W is ***even***

$$W(-\boldsymbol{n}, -\nabla\boldsymbol{n}) = W(\boldsymbol{n}, \nabla\boldsymbol{n})$$

Frank's formula

The most general frame-indifferent and even function W that is at most ***quadratic*** in $\nabla\boldsymbol{n}$ was obtained by Frank (1958),

$$W_F(\boldsymbol{n}, \nabla\boldsymbol{n}) = \frac{1}{2}K_1(\operatorname{div}\boldsymbol{n})^2 + \frac{1}{2}K_2(\boldsymbol{n}\cdot\operatorname{curl}\boldsymbol{n})^2 + \frac{1}{2}K_3|\boldsymbol{n}\times\operatorname{curl}\boldsymbol{n}|^2 + K_{24}\left(\operatorname{tr}(\nabla\boldsymbol{n})^2 - (\operatorname{div}\boldsymbol{n})^2\right)$$

K_i Frank's elastic constants

- K_1 splay constant
- K_2 twist constant
- K_3 bend constant
- K_{24} saddle-splay constant

Ericksen's inequalities

$$W_F(\boldsymbol{n}, \nabla\boldsymbol{n}) \geqq 0 \quad \text{a.e. } \forall\ \boldsymbol{n} \in H^1(\mathscr{B}; \mathbb{S}^2) \text{ iff}$$

$$K_3 \geqq 0, \quad K_2 \geqq K_{24}, \quad K_1 \geqq K_{24} \geqq 0$$

Ericksen (1966)

Elementary Distortion Modes

Recently, a fresh look into this established theory has revealed unexpected scenarios.

Machon & Alexander (2016), Selinger (2018)

distortion decomposition

$$\nabla \boldsymbol{n} = -\boldsymbol{b} \otimes \boldsymbol{n} + \frac{1}{2} T \mathbf{W}(\boldsymbol{n}) + \frac{1}{2} S \mathbf{P}(\boldsymbol{n}) + \mathbf{D}$$

$S := \operatorname{div} \boldsymbol{n}$ splay scalar

$T := \boldsymbol{n} \cdot \operatorname{curl} \boldsymbol{n}$ twist pseudoscalar

$\boldsymbol{b} := \boldsymbol{n} \times \operatorname{curl} \boldsymbol{n}$ bend vector

$\mathbf{W}(\boldsymbol{n})$ skew tensor associated with $\boldsymbol{n}$

$\mathbf{P}(\boldsymbol{n}) := \mathbf{I} - \boldsymbol{n} \otimes \boldsymbol{n}$ projector tensor

$\mathbf{D}$ octupolar splay tensor

octupolar splay

$$\mathbf{D} = q(\boldsymbol{n}_1 \otimes \boldsymbol{n}_1 - \boldsymbol{n}_2 \otimes \boldsymbol{n}_2)$$

q ***positive*** eigenvalue of $\mathbf{D}$

identity

$$2q^2 = \operatorname{tr}(\nabla \boldsymbol{n})^2 + \frac{1}{2}T^2 - \frac{1}{2}S^2$$

The four components of $\nabla \boldsymbol{n}$ are ***independent*** from one another.

- ***distortion frame***: the eigenvectors $(\boldsymbol{n}_1, \boldsymbol{n}_2, \boldsymbol{n})$ of $\mathbf{D}$ for $q > 0$.
- ***distortion measures***: the list $(S, T, \boldsymbol{b}, \mathbf{D})$.
- ***distortion characteristics***: the scalars (S, T, b_1, b_2, q).

$$\boldsymbol{b} = b_1 \boldsymbol{n}_1 + b_2 \boldsymbol{n}_2$$

Frank's free energy

$$W_F = \frac{1}{2}(K_{11} - K_{24})S^2 + \frac{1}{2}(K_{22} - K_{24})T^2 + \frac{1}{2}K_{33}B^2 + 2K_{24}q^2$$

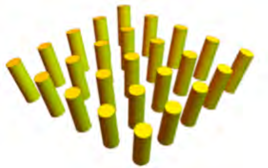
$$B^2 := \boldsymbol{b} \cdot \boldsymbol{b}$$

Modes illustration

The four independent modes can be illustrated pictorially.

Selinger (2021)

splay mode



$S \neq 0 \quad T = 0 \quad B = 0 \quad q = 0$

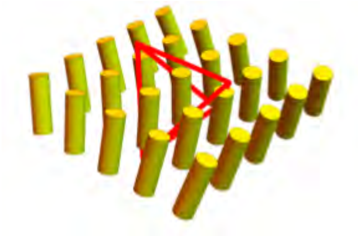
(double) twist mode

$S = 0 \quad T \neq 0 \quad B = 0 \quad q = 0$

bend mode

$S=0 \quad T=0 \quad B\neq 0 \quad q=0$

octupolar splay mode



$S=0 \quad T=0 \quad B=0 \quad q\neq 0$

octupolar representation

An alternative representation, suggested by the octupolar splay mode, is offered for all modes but the (double) twist by an ***octupolar tensor***. Gaeta & Virga (2016, 2019) Pedrini & Virga (2020)

$$\mathbf{A} := \overline{\nabla \boldsymbol{n} \otimes \boldsymbol{n}}$$

$\overline{\cdots}$ irreducible part of a tensor

octupolar potential

$$\Phi(\boldsymbol{x}) := \mathbf{A} \cdot \boldsymbol{x} \otimes \boldsymbol{x} \otimes \boldsymbol{x} = \sum_{i,j,k=1}^{3} A_{ijk} x_i x_j x_k$$

$\boldsymbol{x} = x_1 \boldsymbol{n}_1 + x_2 \boldsymbol{n}_2 + x_3 \boldsymbol{n}$ on the unit sphere $\mathbb{S}^2$

$$\Phi(\boldsymbol{x}) = \left(\frac{S}{2} + q\right) x_1^2 x_3 + \left(\frac{S}{2} - q\right) x_2^2 x_3 - b_1 x_1 x_3^2 - b_2 x_2 x_3^2 + \frac{1}{5}\left(x_1^2 + x_2^2 + x_3^2\right)\left(b_1 x_1 + b_2 x_2 - S x_3\right)$$

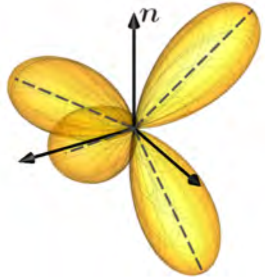
polar plots

splay mode

polar plots

bend mode

polar plots



octupolar splay mode

Uniform Distortions

On a ***smooth*** (not necessarily flat) ***surface*** embedded in 3D ***Euclidean*** space,

$$T \equiv 0 \quad \text{and} \quad \mathbf{D} \equiv \mathbf{0}$$

geometric compatibility

$$K = -S^2 - B^2 - \nabla S \cdot \boldsymbol{n} + \nabla B \cdot \boldsymbol{n}_\perp$$

K Gaussian curvature
∇ covariant derivative
$\boldsymbol{n}_\perp := \mathbf{N}\boldsymbol{n}$ unit vector orthogonal to $\boldsymbol{n}$
$\mathbf{N}$ skew tensor associated with $\boldsymbol{\nu}$
$\boldsymbol{\nu}$ normal to the surface

Niv & Efrati (2018)

consequences

- The field $\boldsymbol{n}$ can be uniquely ***reconstructed*** from the sole knowledge of S and B, provided that $|\nabla S + \mathbf{N}\nabla B| > |S^2 + B^2 + K|$ Pollar & Alexander (2021)
- Only ***hyperbolic*** geometries can host ***uniform*** distortions in 2D.

questions

- How to define ***uniformity*** in 3D?
- Is it possible to fill space with a combination of ***uniform*** modes?

comment

Both questions border on the notion of eligible ***ground states*** meant as the ones suffering ***no*** geometric ***frustration***.

uniform distortion

A field $\boldsymbol{n}$ such that its distortion characteristics (S, T, b_1, b_2, q) are the ***same*** everywhere, although the distortion frame $(\boldsymbol{n}_1, \boldsymbol{n}_2, \boldsymbol{n})$ may not be.

lost in space

For such a field, we could not tell ***where we are*** in space only by sampling the local nematic distortion.

3D Euclidean space

There are only ***two families*** of possible uniform distortions that fill 3D Euclidean space:

$$S = 0, \quad T = 2q, \quad b_1 = b_2 = b$$

$$S = 0, \quad T = -2q, \quad b_1 = -b_2 = b$$

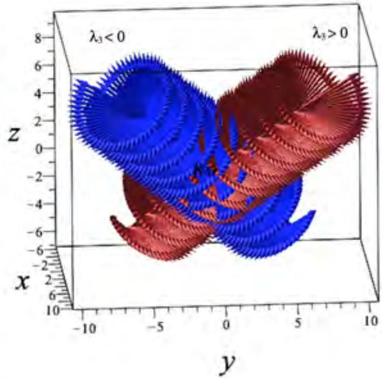
They correspond to ***foliations*** of 3D Euclidean space in ***parallel helices***. Virga (2019)

heliconical fields

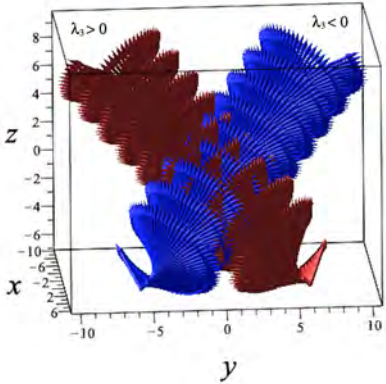
The director $\boldsymbol{n}$ makes a constant ***conical*** angle θ with the ***axis*** of a ***helix*** with ***pitch*** p:

$$\cos\theta = \frac{|b|}{\sqrt{b^2 + 2q^2}}$$

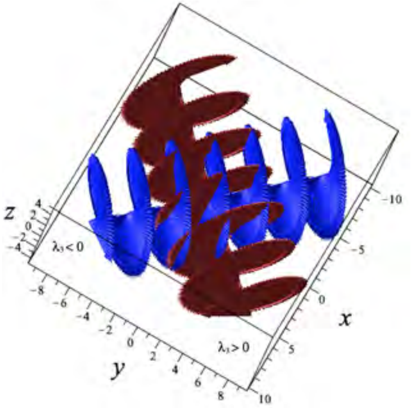
$$p = \frac{2\pi}{|\lambda_3|} \qquad \lambda_3 = \pm\left(2q + \frac{b^2}{q}\right)$$



$b/q = -1$



$b/q = 1$



$b = 0$

Non-Euclidean 3D spaces

The quest for ***uniform distortions*** has recently been also conducted in ***3D Riemannian manifolds*** within Cartan's ***moving frame*** formalism. Pollard & Alexander (2021)
da Silva & Efrati (2021)

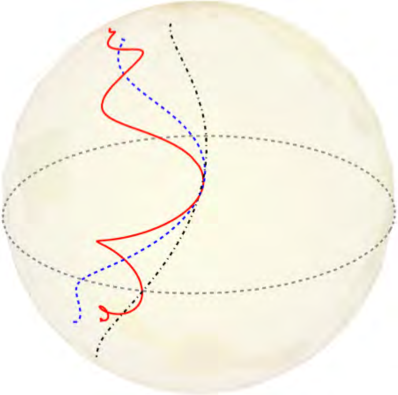
- Each pure distortion mode, characterized by a single non-vanishing component of (S, T, b_1, b_2, q), can ***fill space*** without frustration in at least ***one*** of the eight ***Thurston geometries***. Sadoc, Mosseri & Selinger (2020)
- It had already been shown that the ***double twist*** mode $T \neq 0$, resulting in the ***frustrated*** cholesteric ***blue phases***, can be accommodated in a three-dimensional ***spherical geometry***. Sethna, Wright & Mermin (1983)
- Consider a 3D ***manifold*** with ***Riemannian tensor***

$$R_{ijkl} = R_0(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})$$

If $R_0 > 0$, the ***double twist*** mode is the ***only*** uniform distortion. If $R_0 < 0$, ***all uniform distortions*** provide a ***foliation*** of space by ***non-parallel*** congruent ***helices***.

da Silva & Efrati (2021)

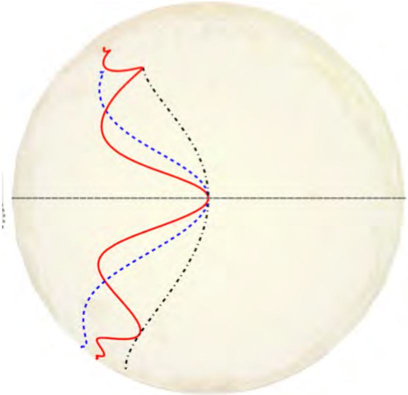
Poincaré ball representation



$B < \sqrt{-R_0}$ $B = \sqrt{-R_0}$ $B > \sqrt{-R_0}$

da Silva & Efrati (2021)

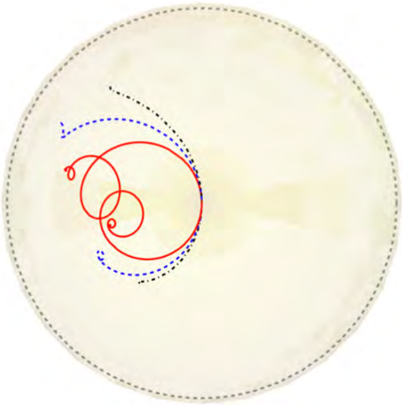
side view



$B < \sqrt{-R_0}$ $B = \sqrt{-R_0}$ $B > \sqrt{-R_0}$

da Silva & Efrati (2021)

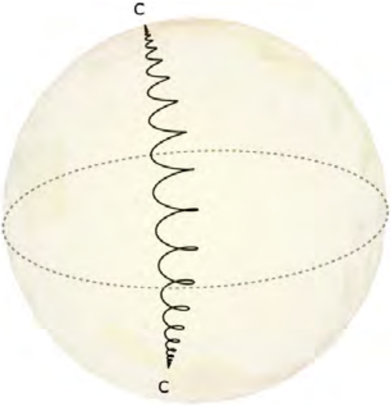
top view



$B < \sqrt{-R_0}$ $B = \sqrt{-R_0}$ $B > \sqrt{-R_0}$

da Silva & Efrati (2021)

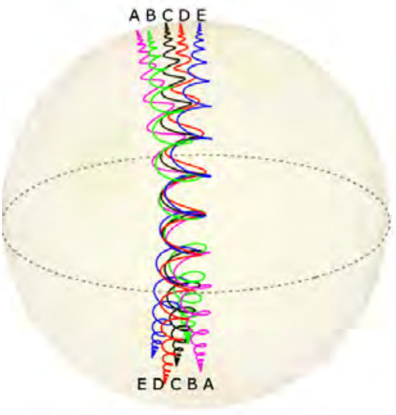
helices foliation



$B > \sqrt{-R_0}$

da Silva & Efrati (2021)

helices foliation



$B > \sqrt{-R_0}$

da Silva & Efrati (2021)

Generalized Elasticity

Uniform distortions are natural ***ground state*** candidates for ***novel phases***, irrespective of the free-energy model in use.

twist-bend phases

The ***heliconical*** distortion was first considered by Meyer (1976) as a possible ground state, in view of its ability to fill space.

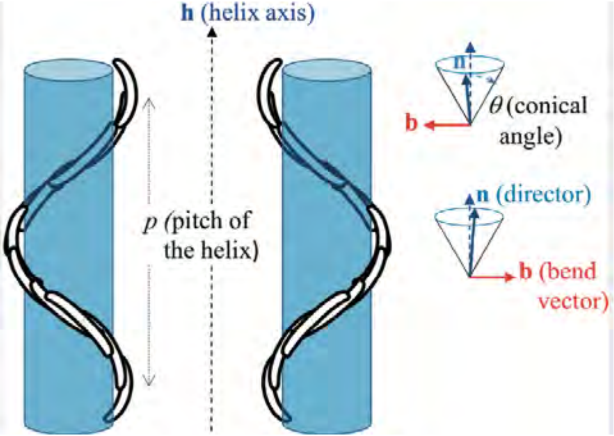
Recently, this phase has been found experimentally in ***bent-core dimers***.

Cestari, Diez-Berart, Dunmur, Ferrarini, de la Fuente, Jackson, Lopez, Luckhurst, Perez-Jubindo, Richardson, Salud, Timimi & Zimmermann (2011)

There is still an active debate on the origin of the phase, but its existence is no longer questioned.

Samulski, Vanakaras & Photinos (2020)
Dozov & Luckhurst (2020)

microscopic picture



Dozov & Luckhurst (2020)

The modulated arrangement in a twist-bend phase is ***not*** accompanied by a ***mass density wave***.

Chen, Porada, Hooper, Klittnick, Shen, Tuchband, Korblova, Bedrov, Walba, Glaser, Maclennan & Clark (2013)

double-well free energy

$$W_{TB}(S,T,b_1,b_2,q) := \frac{1}{2}k_1S^2 + \frac{1}{2}k_2\left(T^2 + (2q)^2\right) + \frac{1}{2}k_3B^2 + \frac{1}{4}k_4\left(T^4 + (2q)^4\right) + \frac{1}{4}k_5B^4 - k_6(2q)Tb_1b_2$$

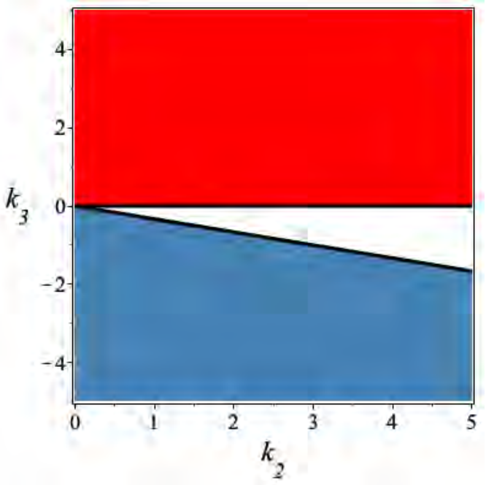
invariance requirements

$$(2q)T \to -(2q)T \qquad b_1b_2 \to -b_1b_2$$

objective form

$$2qb_1b_2 = \operatorname{curl}\boldsymbol{n}\cdot(\nabla\boldsymbol{n})\boldsymbol{b} + \frac{1}{2}TB^2$$

phase diagram



$$k_3 = -2\frac{k_5}{k_6}k_2$$

Uniform constant ***Non-uniform bend*** ***Uniform twist-bend***

Virga (2019)

Conclusions

- The notion of ***uniform distortion*** has been illustrated for liquid crystals, but it is far more general: it can be applied to other ***soft matter*** domains with ***order parameters*** of a different kind.
- The ***lack*** of uniformity in the ***ground state*** entails ***geometric frustration***, which results in ***residual stresses*** and ***super-extensivity*** of the free-energy functional, which may cause ***defects*** to arise. Meiri & Efrati (2021)
- ***Chromonic*** liquid crystals, which are dyes widely used in the food industry, are ***frustrated*** as their ground state is the pure ***double twist*** $T \neq 0$, which is ***not*** uniform.

  Paparini & Virga (2021)

Acknowledgements

Collaboration

G. Gaeta
S. Paparini
A. Pedrini

Discussion

J. V. Selinger

UNIVERSITÀ DI PAVIA

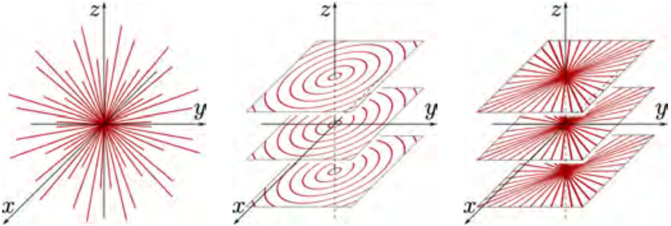
Soft Matter Mathematical Modelling
Department of Mathematics
University of Pavia, Italy

Addendum: Quasi-uniform distortions

A distortion is ***quasi-uniform*** if its characteristics are in ***constant*** ratio to one another. PEDRINI & VIRGA (2020)

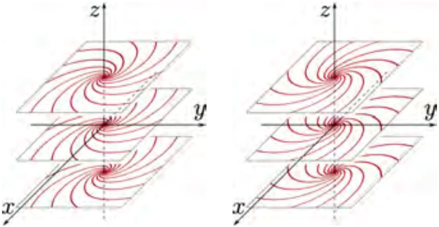
The distortion landscape is the same everywhere, to within a ***scaling*** factor depending on ***position***.

simple examples



These distortions are all ***universal solutions*** according to ERICKSEN (1967).

non-universal ones



more generally

Any unit vector field which is a constant combination of

$$\boldsymbol{e}_1 = \cos g(z)\boldsymbol{e}_x + \sin g(z)\boldsymbol{e}_y, \quad \boldsymbol{e}_2 = -\sin g(z)\boldsymbol{e}_x + \cos g(z)\boldsymbol{e}_y, \quad \boldsymbol{e}_3 = \boldsymbol{e}_z$$

$g(z)$ antiderivative of the scaling function

quasi-uniform heliconical

$$\cos\theta\boldsymbol{e}_z + \sin\theta(\cos g(z)\boldsymbol{e}_x \pm \sin g(z)\boldsymbol{e}_y)$$

Pollar & Alexander (2021)

Sources

Books

- P. de Gennes & J. Prost, *The Physics of Liquid Crystals*, Oxford University Press, Oxford, 1993.
- M. Kleman & O. D. Lavrentovich, *Soft Matter Physics: An Introduction*, Springer, New-York, 2003.
- E. G. Virga, *Variational Theories for Liquid Crystals*, Chapman & Hall, London, 1994.

Articles

- D. Chen, J. H. Porada, J. B. Hooper, A. Klittnick, Y. Shen, M. R. Tuchband, E. Korblova, D. Bedrov, D. M. Walba, M. A. Glaser, J. E. Maclennan & N. A. Clark, Chiral heliconical ground state of nanoscale pitch in a nematic liquid crystal of achiral molecular dimers, *Proc. Natl. Acad. Sci. USA*, **110**, 2013, 15931.

- 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, Phase behavior and properties of the liquid-crystal dimer 1”, 7” -bis(4-cyanobiphenyl-4’-yl) heptane: A twist-bend nematic liquid crystal, *Phys. Rev. E*, **84**, 2011, 031704.
- I. Dozov & G. R. Luckhurst, Setting things straight in “The twist-bend nematic: a case of mistaken identity”, *Liq. Cryst.*, 2020, DOI: 10.1080/02678292.2020.1795944.
- J. L. Ericksen, Nilpotent energies in liquid crystal theory, *Arch. Rational Mech. Anal.*, **10**, 1962, 189.
- J. L. Ericksen, Inequalities in liquid crystal theory, *Phys. Fluids*, **9**, 1966, 1205.
- J. L. Ericksen, General solutions in the hydrostatic theory of liquid crystals, *Trans. Soc. Rheol.*, **11**, 1967, 5.
- F. C. Frank, On the theory of liquid crystals, *Discuss. Faraday Soc.*, **25**, 1958, 19.
- G. Gaeta & E. G. Virga, Octupolar order in three dimensions, *Eur. Phys. J. E*, **39**, 2016, 113.

- G. Gaeta & E. G. Virga, The symmetries of octupolar tensors, *J. Elast.*, **135**, 2019, 295.
- P. G. de Gennes, Short range order effects in the isotropic phase of nematics and cholesterics, *Mol. Cryst. Liq. Cryst.*, **12**, 1971, 193.
- P. G. de Gennes, Phenomenology of short-range-order effects in the isotropic phase of nematic materials, *Phys. Lett. A*, **30**, 1969, 454.
- T. Machon & G. P. Alexander, Umbilic lines in orientational order, *Phys. Rev. X*, **6**, 2016, 011033.
- W. Maier & A. Saupe, Eine einfache molekulare Theorie des nematischen kristallinflüssigen Zustandes, *Z. Naturforsch.*, **13a**, 1958, 564.
- S. Meiri & E. Efrati, Cumulative geometric frustration in physical assemblies, *arXiv:2101.09816*, 2021.
- R. B. Meyer, Structural problems in liquid crystal physics In: *Les Houches Summer School in Theoretical Physics*, vol. XXV, pp. 273–373, Gordon & Breach, New York, 1976.

- I. Niv I & E. Efrati, Geometric frustration and compatibility conditions for two-dimensional director fields, *Soft Matter*, **14**, 2018, 424.
- L. Onsager, The effects of shape on the interaction of colloidal particles, *Ann. N. Y. Acad. Sci.*, **51**, 1949, 627.
- S. Paparini & E. G. Virga, Nematic tactoid population, *Phys. Rev. E*, **103**, 2021, 022707.
- A. Pedrini & E. G. Virga, Liquid crystal distortions revealed by an octupolar tensor, *Phys. Rev. E*, **101**, 2020, 012703.
- J. Pollard J & G. P. Alexander, Intrinsic geometry and director reconstruction for three-dimensional liquid crystals, *arXiv:2102.00232*, 2021, to appear in *New J. Phys.*
- J. F. Sadoc, R. Mosseri & J. V. Selinger, Liquid crystal director fields in three-dimensional non-Euclidean geometries, *New J. Phys.*, **22**, 2020, 093036.
- E. T. Samulski, A. G. Vanakaras & D. J. Photinos, The twist bend nematic: a case of mistaken identity, *Liq. Cryst.*, 2020, DOI: 10.1080/02678292.2020.1795943.

- J. P. Sethna, D. C. Wright & N. D. Mermin, Relieving cholesteric frustration: The blue phase in a curved space, *Phys. Rev. Lett.*, **51**, 1983, 467.
- J. V. Selinger, Director deformations, geometric frustration, and modulated phases in liquid crystals, *arXiv:2103.03803*, 2021.
- J. V. Selinger, Interpretation of saddle-splay and the Oseen-Frank free energy in liquid crystals, *Liq. Cryst. Rev.*, **6**, 2018, 129.
- L. C. B. da Silva & E. Efrati, Moving frames and compatibility conditions for three-dimensional director fields, *arXiv:2102.07907*, 2021, to appear in *New J. Phys.*
- E. G. Virga, Uniform distortions and generalized elasticity of liquid crystals, *Phys. Rev. E*, **100**, 2019, 052701.