Polyhedra as Ground States

LC Shells

2D systems described by fields $\phi : \Sigma \to \begin{pmatrix}\text{Order}\\ \text{Field}\\ \text{Space}\\ V\end{pmatrix}$

Refs.
PNAS (2012)
PRL (2015)
Xing et al PNAS 109 (2012) 5202
PRL 114 (2015) Manyuhina + MJB 017801

Origin of shape ≡ morphology

Shape change for $\Sigma \hookrightarrow \mathbb{R}^3$ is bend

$$H_{bend} = \frac{\kappa}{2}\int_\Sigma (\sqrt{g}\, d^2x)(\vec{H} - \vec{H}_0)^2 \quad \text{Willmore functional}$$

$$\vec{H} = \frac{1}{2}\mathrm{Tr}\, \underbrace{\vec{K}_{\alpha\beta}}_{\text{2nd fundamental form}} \quad \text{w/} \quad \vec{K}_{\alpha\beta} = D_\alpha \vec{t}_\beta$$

$$\vec{H} = \frac{1}{2}\mathrm{Tr}\, \vec{K}_{\alpha\beta} = \frac{1}{2} g^{\alpha\gamma}\vec{K}_{\gamma\alpha} = \frac{1}{2}\frac{1}{\sqrt{\|g\|}} g_{\alpha\gamma} \vec{K}_{\gamma\alpha}$$

$$\vec{K} = K_{\alpha\beta}\hat{N}$$

$$\vec{H} = H\hat{N}$$

$$H_{bend} = \kappa \int_\Sigma d^2x\, (H - H_0)^2 \qquad (1)$$

where $H = \frac{1}{2}K_\alpha^{\ \alpha}$

Further structure on surface:

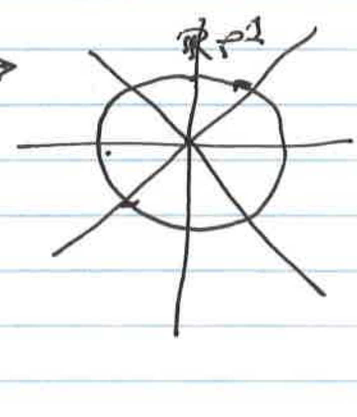
orientational order ≡ director field
≡ line field

$$\overleftrightarrow{n}(x_1, x_2) : \Sigma \to \mathbb{R}P^1$$

$$\overleftrightarrow{n}\cdot\overleftrightarrow{n} = 1$$

3D: $\overleftrightarrow{n} \in \mathbb{R}P^2 \equiv S^2/\mathbb{Z}_2$

2D →



$$H_{LC} = \frac{1}{2}\int_{\Sigma} \sqrt{g}\, d^2x \left[K(\vec{D}\hat{n})^2 \right] \qquad (2)$$

$$\hat{n} = \vec{n}$$

$$H_{total} = H_{LC} + H_{bend}$$

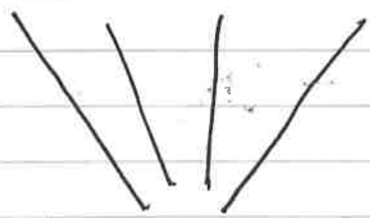
Origin of (2)

More generally invariants are

$$H_{LC} = \frac{1}{2}\int_{\Sigma} \sqrt{g}\, d^2x \Big[K_1 \underbrace{(D\cdot\hat{n})^2}_{\text{splay}} + K_3 \underbrace{(D\times\hat{n})^2}_{\cancel{\text{bend}}} \Big]$$

$D\cdot\hat{n} \neq 0$

$D\times\hat{n} = 0$

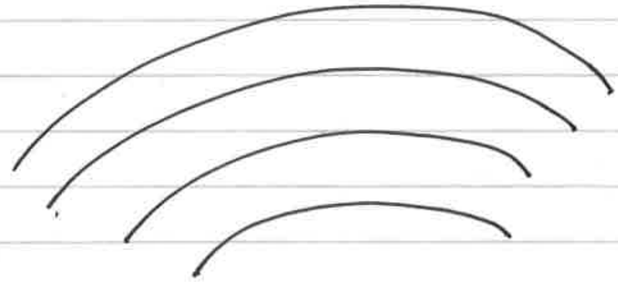


$D = \partial + \Gamma$

N.B $D\times\hat{n}$ is a scalar ϕ in 2D

$D\times\hat{n} \neq 0$

$D\cdot\hat{n} = 0$



In 2D $(\hat{n}\times D\times\hat{n})^2 = (D\times\hat{n})^2$

Twist $\hat{n}\cdot(D\times\hat{n}) = 0$

Case 1 $K_1 = K_3 = K$ $\quad (D\cdot\hat{n})^2 + (D\times\hat{n})^2 = \underbrace{(D\hat{n})^2}_{\text{Non-linear sigma model for projective field}}$

Case 2 $\quad K_3 \to \infty \quad \Rightarrow \quad D \times \hat{n} = 0$ for finite H_m

$$\Rightarrow (\hat{n}\cdot\hat{D})\,\hat{n} = 0 \quad (\Rightarrow \hat{n} \text{ integral curve or equiv. geodesic})$$

Then $\quad H_m = \frac{K_1}{2}\int (D\cdot\hat{n})^2 \quad$ and call K_1 K

Pure splay ≡ a smectic parallel layers w/ const. layer spacing

Now set $\quad H_0 = 0 \quad$ (e.g. symmetric bilayer)

$$H = \frac{K}{2}\int_\Sigma (D\hat{n})^2 + \frac{\kappa}{2}\int_\Sigma H^2$$

Limit 1 $\quad$ Rigid $\quad \frac{\kappa}{K} \to \infty \qquad \kappa \gg K$

$\Rightarrow \quad H = H_{willmore}$ $\quad$ extremized by round sphere $\quad \Sigma = S^2$ (round metric)

$H = 1/R$ const.

$$H = \frac{\kappa}{2}\underbrace{\int_{S^2} d^2x}_{4\pi}\left(\frac{1}{R^2}\right) \qquad H = \frac{1}{2}\left(\frac{1}{R}+\frac{1}{R}\right) = \frac{1}{R}$$

$$= (2\pi\kappa) = \text{const.}$$

$\Rightarrow$ spherical nematic or spherical smectic

Rich novel defect structure (later)

Limit 2 $\quad$ Floppy w/ bend in space

$$K \gg \kappa \qquad \left(\frac{\kappa}{K} \to 0\right)$$

thin-shell $\quad \kappa \sim (\text{thickness})^3$

$K \sim (\text{thickness})$

Extreme case $\kappa = 0$

$$H = \frac{K}{2}\int_{\Sigma} \left(D\hat{n}\right)^2$$

Σ top. homeomorphic to S^2

Extremize for $\{\hat{n}(x_1, x_2)\} = \{\hat{n}(\vec{x})\}$.
and manifold $\Sigma(g_{ab})$

$D^2\hat{n} \to 0$ at extremum (harmonic projective fields)

$\hat{n} \neq$ const. costs energy — spatial inhomogeneity (texture)

$D \neq \partial$ costs energy — geometry not flat
any Gaussian curvature costs energy

$\Rightarrow$ Σ should be developable ($K_{Gauss} = 0$)
but

Impossible since $\frac{1}{2\pi}\int_{\Sigma} K_{Gauss} = 2 = \chi_{S^2}$

$K = \det K_{\alpha\beta} = \frac{1}{R^2}$

Sol^n Σ should be facewise flat

i.e Σ should be the boundary ∂ of
a 3D polyhedron (facets of order)

i.e $K_{Gauss}(\Sigma) = 0$ almost everywhere

$K_{Gauss}(\Sigma) = 0$ except ~~at a discrete # of~~ points x_i
@ which $K_{Gauss}(\vec{x}_i) = c\,\delta(\vec{x}-\vec{x}_i)$ = singular

Fortunately LC (2-fold) order on S^2 possesses zeros of $\hat{n}$ or singularities of $D\hat{n}$.

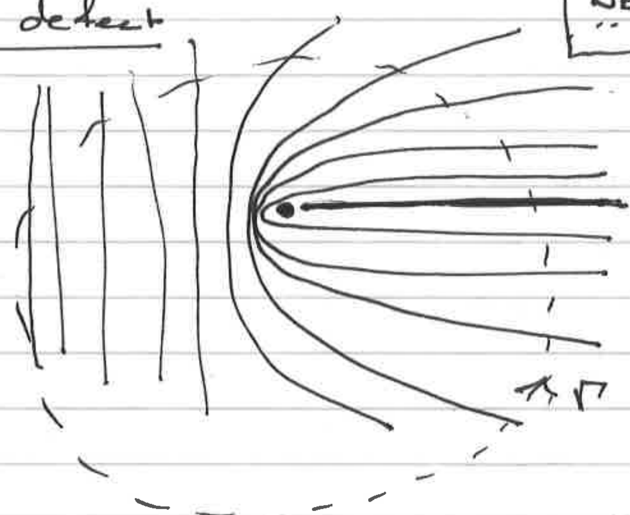
What are the line fields w/ zeros ≡ topological defects

$$\pi_1(\mathbb{RP}^1) = \pi_1(S^1/\mathbb{Z}_2) = \mathbb{Z}$$

$$\left(3D \quad \pi_1(\mathbb{RP}^2) = \pi_1(S^2/\mathbb{Z}_2) = \pi_0(\mathbb{Z}_2) = \mathbb{Z}_2 \right)$$

Simplest defect

NB. Point defects ≡ distinguished points



$\hat{n}$ winds by π as you encircle the defect

⇒ $\hat{n}$ traces closed loop on $\mathbb{RP}^1$

$\Gamma: S^1 \to \mathbb{RP}^1$ and Γ is not contractible

$\Gamma \subset$ non-trivial equivalence class in $\pi_1(\mathbb{RP}^1)$

$$S = \frac{1}{2\pi} \int_\Gamma \hat{n}(dl) = +\frac{1}{2}$$

disclination

s_i = strength of defective line field

$$\sum_i s_i = \chi_{S^2} = 2$$

LC generalization of Poincaré-Hopf theorem ≡ hairy ball theorem

$$\sum_{i} \mathrm{ind}_i = \chi = 2$$

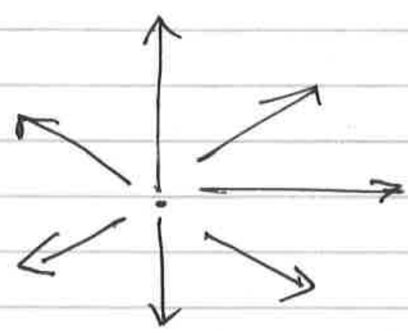
$i \in$ zero of a vector field $\vec{V}$ on S^2

Vector case $\vec{V}$ $\quad \vec{V} : S^2 \to \mathbb{R}^3 \ni \vec{p} \cdot V(\vec{p}) = 0$
vector-valued map $\quad \forall \vec{p} \in S^2$

Thm Any continuous tangent vector field on S^2 must vanish somewhere.
Poincaré (1885)
Brouwer (1912)

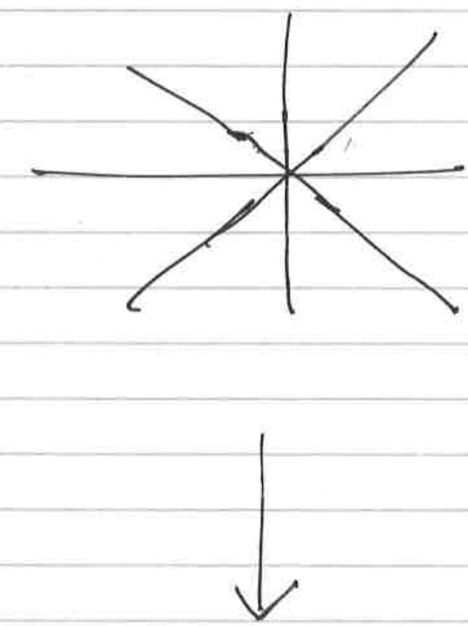
2D/ Poincaré-Hopf: $\sum_{i \in \text{zeros}} \text{ind}_i = \chi$

Vector field $\pi_1(S^1) = \mathbb{Z}$



monopole/aster
ind = +1

Nematic/Smectic



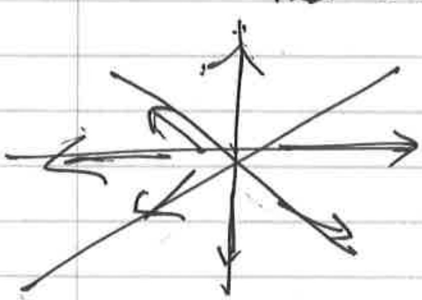
vortex
ind = +1

$E_{(+1)} = (+1)^2 E_0$

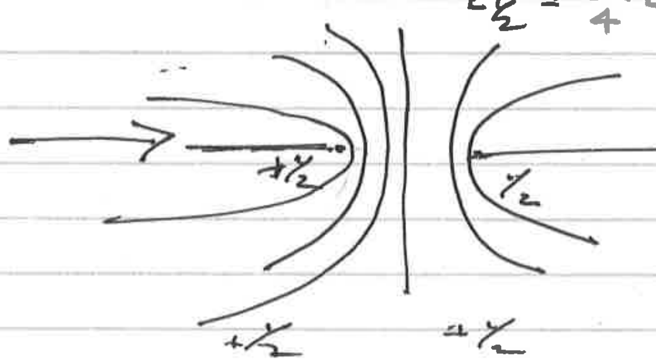
$E_{1/2} = \frac{1}{4} E_0$

$E_{+1} = 2(E_{+1/2} + E_{+1/2})$

$= 2 E_{+1/2}$ pair



+1 $\longrightarrow$



+1/2 $\quad$ +1/2

for line field

LC case — nematic / smectic

$$\sum_{i \in \{\text{defects}\}} s_i = 2 = \mathcal{X}(S^2)$$

$s_i = \pm\frac{1}{2}, \pm 1, \pm\frac{3}{2}, \pm 2, \ldots = n\left(\frac{1}{2}\right) \quad n \in \mathbb{Z}$

Sol^ns 1 strength +2 defect
2 +1 defects
1 (+1) 2 (+½)
4 (½)

Set of defects	Nematic Energy	$E_i = s_i^2 E_0$, $K\ln(R/a)$
+2	$4 E_0$	
+1, +1	$2 E_0$	
+1, +½, +½	$\frac{3}{2} E_0$	
$\boxed{4\left(+\frac{1}{2}\right)_s}$	$\boxed{E_0}$	

Smectic case $E_{+1} = 2 E_{1/2} \quad (K_3 \to \infty)$

* $E_{+2}, \ 2 E_1 = 4 E_{1/2}$

+2	$4 E_0$
+1, +1	$4 E_0$
$+1, 2\left(+\frac{1}{2}\right)_s$	$4 E_0$
$4\left(\frac{1}{2}\right)_s$	$4 E_0$

Degenerate

Now one needs at least four points to span a non-degenerate polyhedral boundary.

Minimal case $\Rightarrow$ tetrahedron

Vertices $\pm \frac{1}{2}$ defects

Thus $K \gg \kappa$, the ground state morphology of a LC vesicle w/ spherical topology is a faceted tetrahedral shell $= \partial(\underbrace{\text{solid tetrahedron}}_{T})$

N.B. Faceting has a completely different origin to the well-known buckling of elastic shells where buckling occurs above a critical size $R \sim \sqrt{\frac{\kappa}{Y}}$ Y = Young's modulus

Elastic YR^2 Bend κ

Buckling $\kappa < YR^2$

$\Rightarrow R > R_c = \sqrt{\frac{\kappa}{Y}}$

Here H is scale free. The faceting is not size dependent. Depends only on K/κ

Which tetrahedra support a suitable nematic defect configuration?

At each vertex i $\quad \sum \theta_{int} = \pi \quad$ 3 constraints $\quad$ 4 vertices but 3 independent constraints

$\#$d.o.f $\quad$ 4 vertices $\times$ 3 coords $= 12$

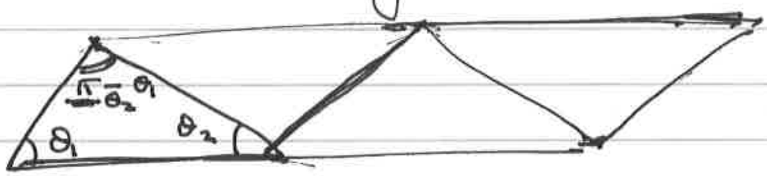
$-$ (3 translations + 3 rotations) $\quad 6$

$-$ scale invariance $\quad 5$

3 constraints

2-dimensional moduli space of ground states $\quad 2$

Moduli Space of ground states $\equiv$ scalene triangle (θ_1, θ_2)



Two parameter family of ground states for
$\kappa = 0$

$\kappa = 0^+$
$H_{LC} \equiv 0$ for these structures

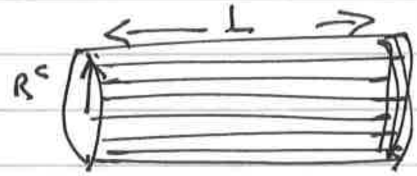
$H_{bend} \propto \sum$ edge lengths

$H = H_{bend}$ minimized by regular tetrahedra
(NB/ A fixed)

Ground state morphology is a regular tetrahedra when the bending rigidity is vanishingly small but non-zero

Other structures

Cylinder $\equiv$ Nanotube



$H^c_{LC} = 0$

$H^c_{bend} = \frac{\kappa}{8} \frac{A}{(R^c)^2}$

$H = \frac{1}{2}\left(\frac{1}{R^c}\right)$

$H^c_{bend} = \frac{\kappa}{2}\int d^2x \left(\frac{1}{4}\frac{1}{R^{c\,2}}\right)$

$= \frac{\kappa}{8R_c^2} \cdot \underbrace{(2\pi R^c L)}_{A}$

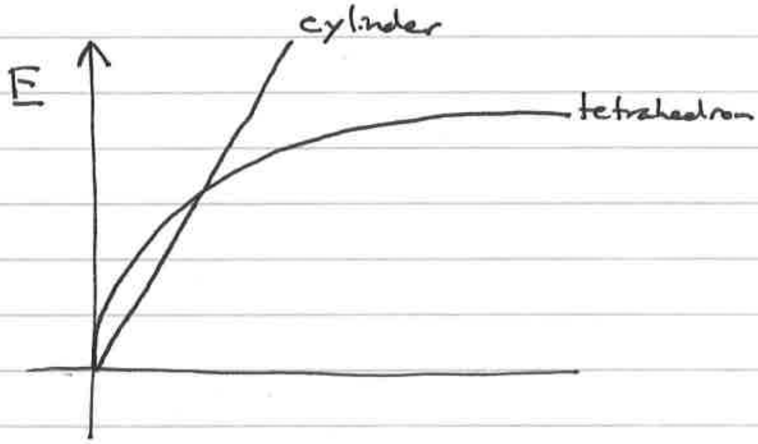
$= \frac{\kappa A}{8 R_c^2}$

$H^{tetra} = 4\kappa \frac{L}{b}$

$= \frac{4}{3^{1/4}} \kappa \frac{\sqrt{A}}{b}$

$L =$ edge length
$b =$ radius of curvature of ridge

$A = \sqrt{3} L^2$
$L = \left(\frac{A}{\sqrt{3}}\right)^{1/2}$



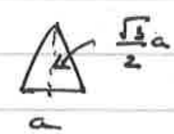
i.e. Tetrahedron wins for $\quad \frac{4}{(3)^{1/4}} \frac{\cancel{K}\sqrt{A}}{b} < \frac{\cancel{K}}{8} \frac{A}{R_c^2}$

$$\frac{16}{\sqrt{3}} \frac{\cancel{A}}{b^2} < \frac{A^{\cancel{2}}}{64 R_c^4}$$

$$\Rightarrow \quad A > \frac{2^{10}}{\sqrt{3}} \left(\frac{R_c^2}{b}\right)^2$$

$$\frac{A}{R_c^2} > \frac{1024}{\sqrt{3}} \left(\frac{R_c}{b}\right)^2$$

Cylinder wins for a Nanotube $\quad \frac{A}{R_c^2} < \frac{1024}{\sqrt{3}} \left(\frac{R_c}{b}\right)^2$



$A_{face} = \frac{\sqrt{3}}{4} a^2$

$A_{tetra} = \sqrt{3} a^2$

Other topologies

Disk — Planar w/ edge: contains $H_{edge} \propto \tau L$ L = length of perimeter

$$H = H_{LC} + H_{bend} + H_{edge}$$

For large system sizes Hedge is costly and vesicles spontaneously close holes (surgery) to form closed S^2 rather than disk
(Helfrich 1974)

Nanofibres

Nano-size cylindrical micelles

Ellipsoidal polymersomes/vesicles : $\bar{\kappa}/\kappa \sim 1$

Tori

Without topological constraint vanishing Gaussian curvature $\Rightarrow$ developable surfaces

Limit $K \gg k$

Geometry – round sphere

$K = K_1 = K_3$: Defects $(4 (+\frac{1}{2})s)$ repel :

- Spherical Nematic

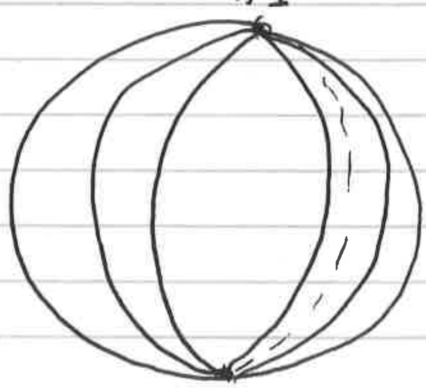
$$H_{def} = \frac{-\pi K}{8} \sum_{i \neq j} n_i n_j \ln(1 - \cos \beta_{ij}) + E(R) \sum_j n_j^2$$

$$\beta_{ij} = d_{ij}/R$$

Extremum: 4 defects at the vertices of an inscribed tetrahedron

- $K_3 = 0$ $K = K_1$ Spherical Smectic

+1



+1

$E_{+1} = 2 E_{1/2}$

Cut along the great circle corresponding to any given meridean and slide along director by an arbitrary angle α $\Leftrightarrow$ zero mode

$\Rightarrow$ One parameter family of ground states w/ 4 $\frac{1}{2}$ defects on a single great circle w/ arbitrary separation b/w 2 sets w/ angle α

α

Functionalization of defects: # defects / defective regions = valence

Geometrical distribution of defects = type of directional bonding

Types of Order

Order/ Symmetry Z_p	Field	Physical Model	Defects	Valence	Directional Bonding
1	Vector	X-Y ferromagnet on S^2 Tilt order	Dipoles Vortices Monopoles Index +2, +1	1 or 2	Bipolar
2	$\mathbb{R}P^1$	Nematic or Smectic LCs	strength $\mathbb{Z} = \{\frac{1}{2} n\}$ strength +2, +1, +½ disclinations strength ½	1, 2, 3 or 4	Bipolar sp^2, sp^3 $K_3 \to \infty$ planar Valence 4
3	triatic	Triskelion proteins	$2\pi/3$ defects strength ⅓	6	Octahedra
4	tetratic	Cubic colloidosomes made w/ cubic NPs	$\pi/2$ defects strength ¼	8	cube
6	crystalline/ hexatic	2d crystal	$\pi/3$ disclination strength ⅙	12	icosahedral

Appendix

$$D \times \hat{n} = 0 \qquad \text{(pure splay)}$$

$$\Rightarrow \quad \epsilon_{ab} D_a \hat{n}_b = 0$$

$$\Rightarrow \quad D_a \hat{n}_b = D_b \hat{n}_a$$

Thus $(\hat{n}_a D_a)\hat{n}_b = \hat{n}_a D_b \hat{n}_a = 0$ since $\hat{n}\cdot\hat{n} = 1$, $\vec{n}\cdot D\vec{n} = 0$

Thus $(\hat{n}\cdot D)\hat{n} = 0$

$\Rightarrow \hat{n}$ Integral curve or geodesic