CHIRAL SYMMETRY BREAKING IN POLYMER CRYSTALLITES

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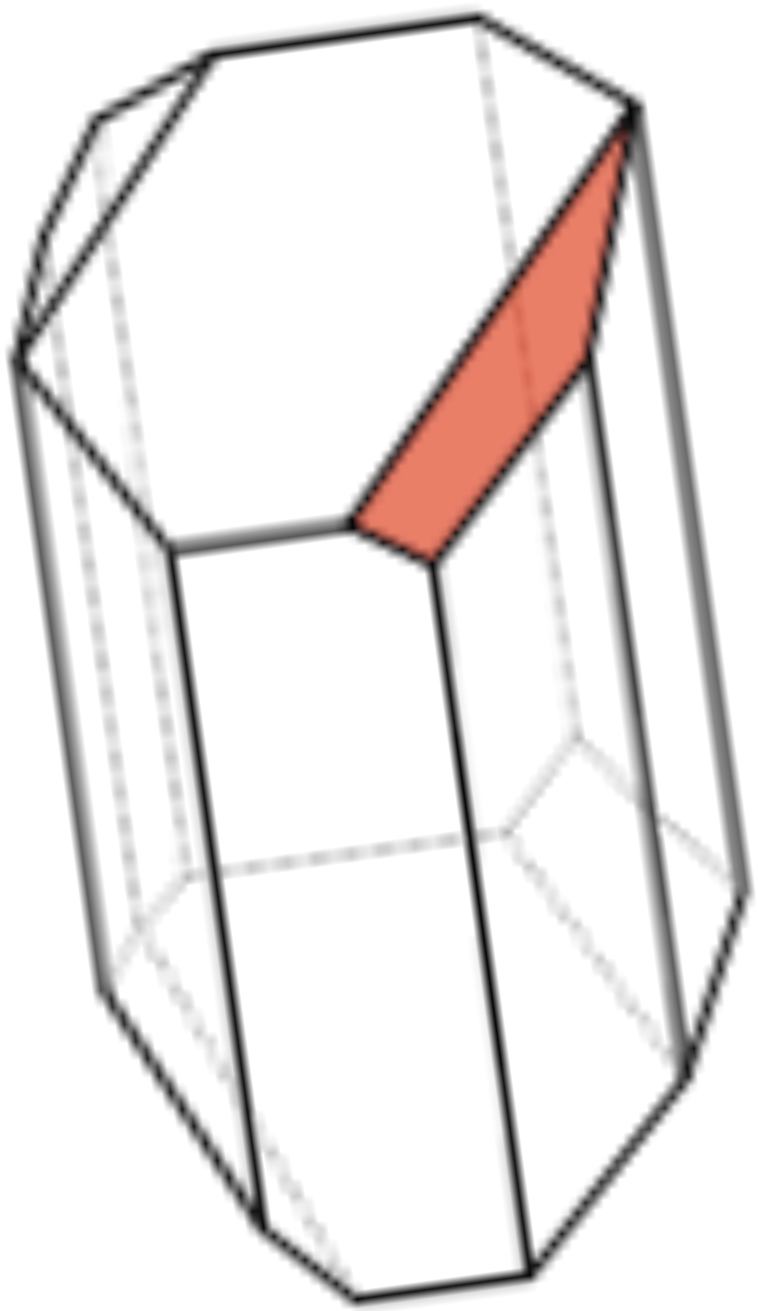
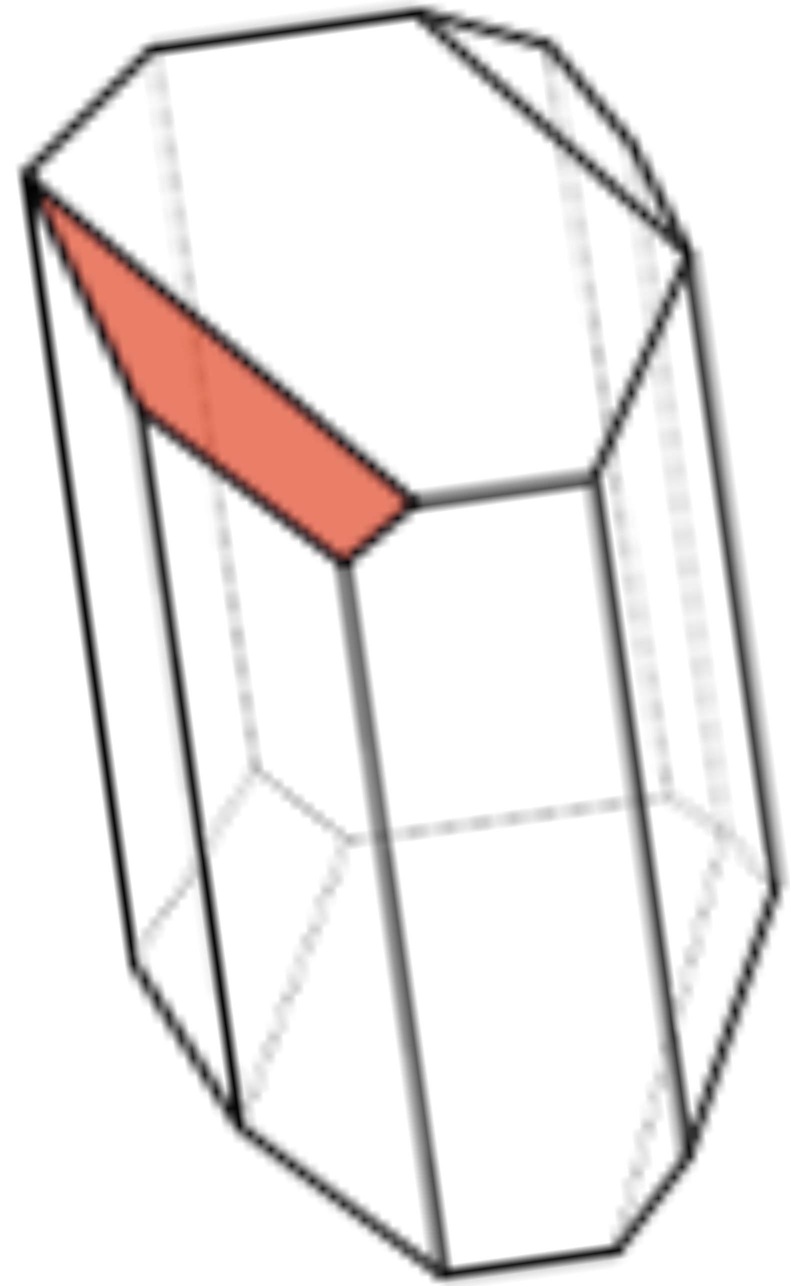
CHIRALITY

NO MIRROR PLANE (KELVIN, 1893)

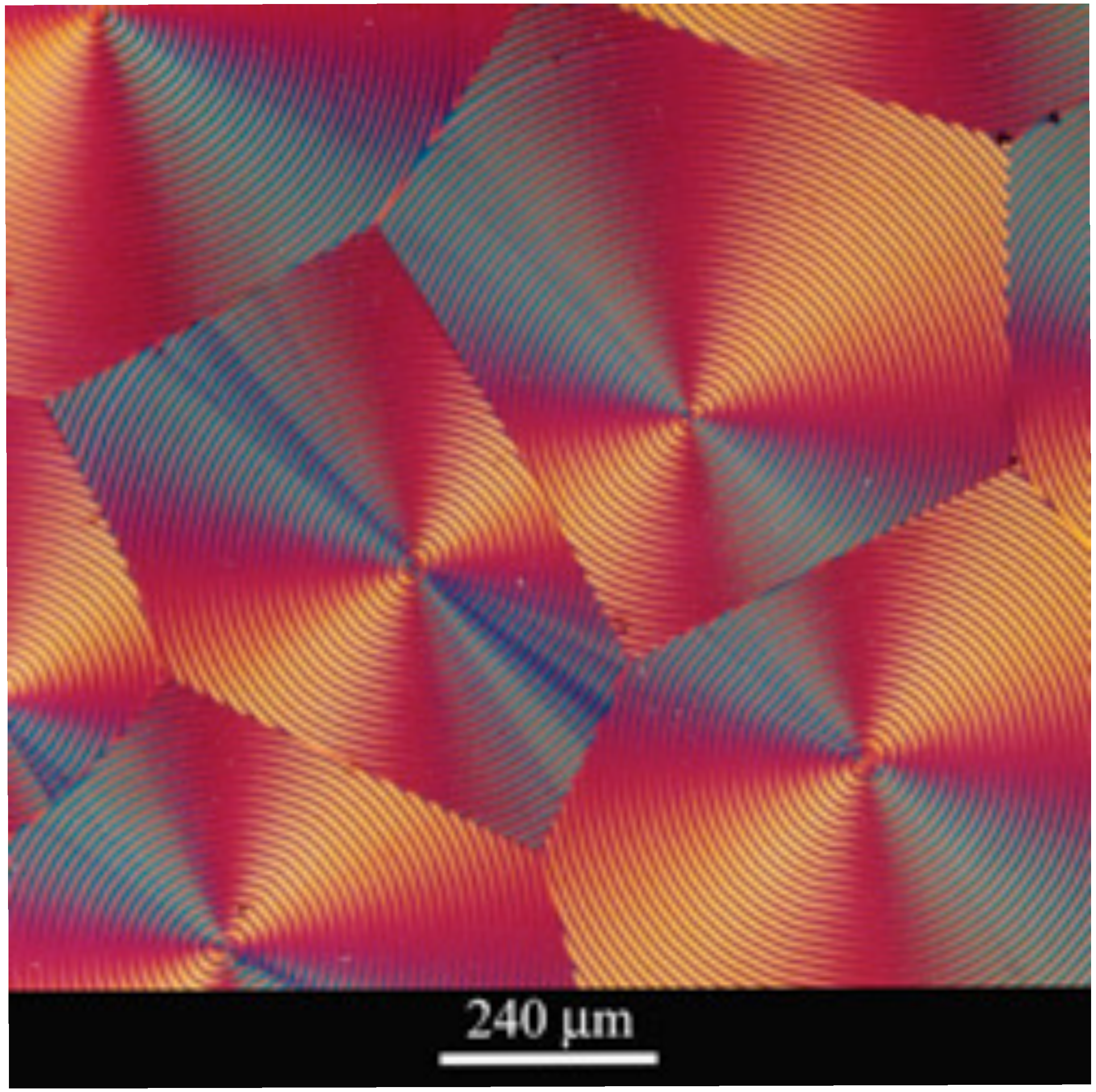


BETA- QUARTZ: ARAGO, 1811

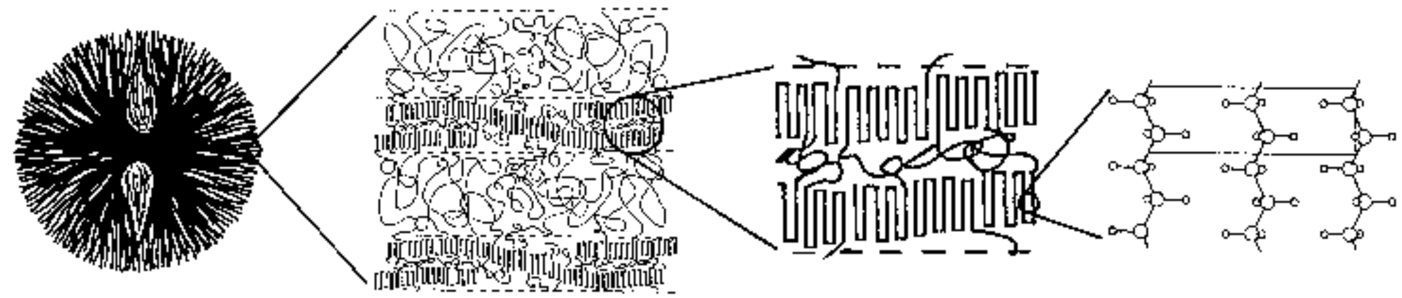


TARTARIC ACID: LOIS PASTEUR, 1849

SOFT MATTER: BLUE PHASE “LIQUID CRYSTAL”: REINITZER, 1888



BANDED SPHERULITES



POLYETHYLENE SPHERULITES
(princeton.edu)

GIGANTIC CHIRAL STRUCTURES FROM ACHIRAL MOLECULES

KELLER (1952)

POLYHYDROXYBUTYRATE SPHERULITES
(UNIV. OF CAMBRIDGE TEACHING AND LEARNING PROGRAMME)

BANDS BECAUSE OF BIREFRINGENCE.

"MALTESE CROSS" PATTERN

CHIRAL SYMMETRY SPONTANEOUSLY BROKEN.

50% LAMELLAE LEFT- (RIGHT-) HANDED.

REMARKABLY UNIFORM PITCH AND WIDTH.

"...A STUBBORN CHALLENGE."

REVIEW BY LOTZ *ET AL.* (2005)

PROPOSE A PHENOMENOLOGICAL, EQUILIBRIUM MODEL.

RESULTS

PHENOMENOLOGICAL THEORY (EQUILIBRIUM).

A NEW MECHANISM FOR CHIRAL SYMMETRY BREAKING AT A MACROSCOPIC LEVEL.

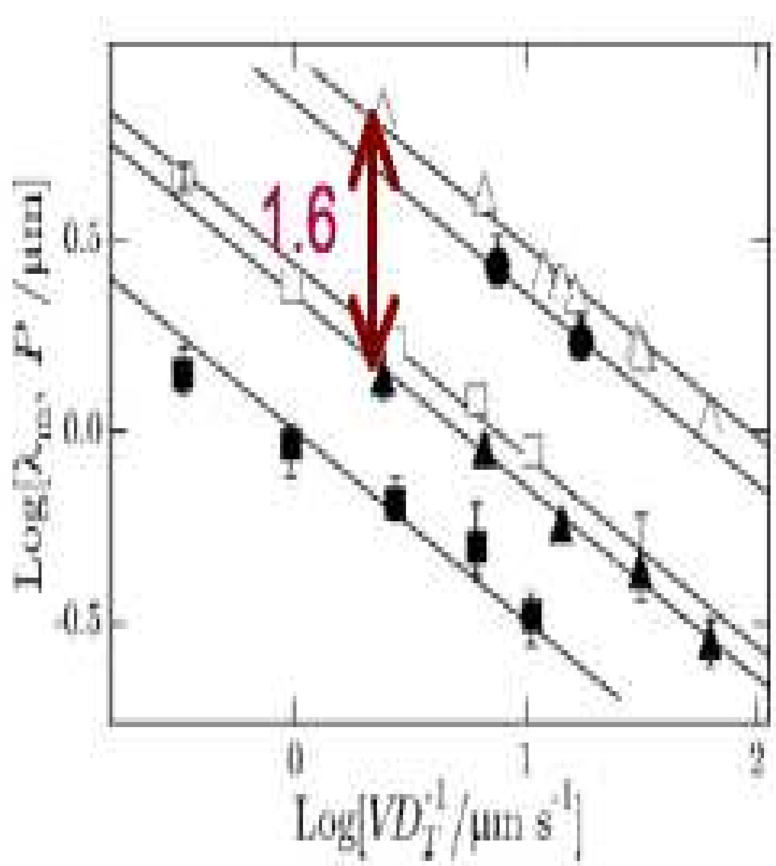
PITCH OF HELICOIDAL LAMELLAE = π WIDTH,

WIDTH = $\sqrt{\kappa_G/\sigma}$.

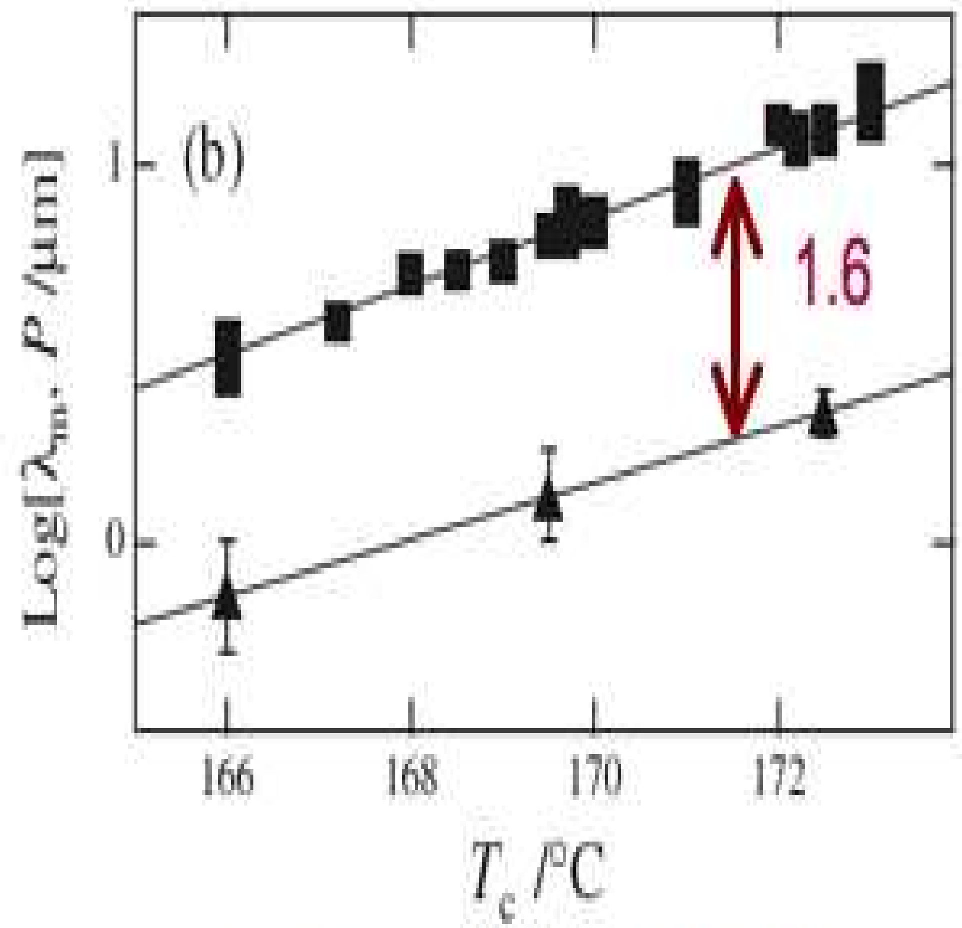
CLAIM: WIDTH AND PITCH OF LAMELLAE SPONTANEOUSLY SELECTED IN EQUILIBRIUM.

ROLE OF ELASTICITY, TOPOLOGICAL DEFECTS IN DETERMINING CRYSTALLITE MORPHOLOGY.

EXPERIMENTS



(Polyethylene)



Poly(vinylidine fluoride)

DIFFERENT CONDITIONS LEAD TO DIFFERENT WIDTH AND RING PERIOD, BUT

RATIO OF RING PERIOD TO LAMELLAR WIDTH APPROX. 1.6.

RING PERIOD IS HALF THE PITCH, POLARISING MICROSCOPE.

PROFESSOR A. TODA'S GROUP, HIROSHIMA UNIVERSITY.
PLOTS COURTESY M. MUTHUKUMAR.

BASIC IDEA

STRESS MITIGATION VIA IMBIBITION OF DEFECTS.

SHOW THAT HOOKIAN STRESS VANISHES IF DEFECT DENSITY MATCHES GAUSSIAN CURVATURE.

DRIVING MECHANISM: POSITIVITY OF THE COEFFICIENT OF GAUSSIAN CURVATURE TERM IN THE BENDING ENERGY.

STRATEGY

COMPARE THE ENERGETICS OF TWO SHAPES: PLANAR, AND HELICOIDAL.

SHOW THAT THE APPARENTLY “DISTORTED” HELICOIDAL SHAPE HAS LOWER ENERGY. FURTHER, THAT IT IS A STABLE SOLUTION.

ORIGAMI 101

CUT AWAY A WEDGE FROM A PIECE OF PAPER,

JOIN THE LIPS OF THE CUT.

PAPER BUCKLES INTO A CONE.

POSITIVE GAUSSIAN CURVATURE AT THE APEX, NONZERO MEAN CURVATURE EVERYWHERE.

INSERT THE WEDGE INTO A SLIT CUT IN THE PAPER,

JOIN THE LIPS OF THE SLIT WITH THOSE OF THE WEDGE.

PAPER BUCKLES INTO A SADDLE.

NEGATIVE GAUSSIAN CURVATURE EVERYWHERE, NONZERO MEAN CURVATURE.

HELICOIDS: NEGATIVE GAUSSIAN CURVATURE, ZERO MEAN CURVATURE.

STRETCHING ELASTICITY OF A RIBBON

$$(t << w < l)$$

EASY TO STRETCH WITHOUT BENDING,
DIFFICULT TO COMPRESS WITHOUT BENDING.

HOOKE'S LAW: $$\sigma_{ij} = E\, u_{kk}\, \delta_{ij} + \mu\, (u_{ij} - \frac{1}{2} u_{kk}\, \delta_{ij})$$

E AND μ : EFFECTIVE 2- DIMENSIONAL ELASTIC MODULI.

LINEARISED LAGRANGIAN STRAIN TENSOR:

$$u_{ij} \simeq \frac{1}{2}(\partial_i u_j + \partial_j u_i)$$

$\mathbf{u}$: DISPLACEMENT FIELD

ELASTIC FREE ENERGY: $$F_H = \int \sigma_{ij}\, u_{ij}\, d^2x,$$

WITH INTEGRATION OVER UNDISTORTED RIBBON.

DISCLINATIONS

VOLTERRA CONSTRUCTION

VOLTERRA (1907)

$$\oint d\theta = \oint \partial_i \theta dx_i = \frac{s}{2\pi}$$

MULTIVALUED

WHERE θ IS THE BOND-ANGLE.

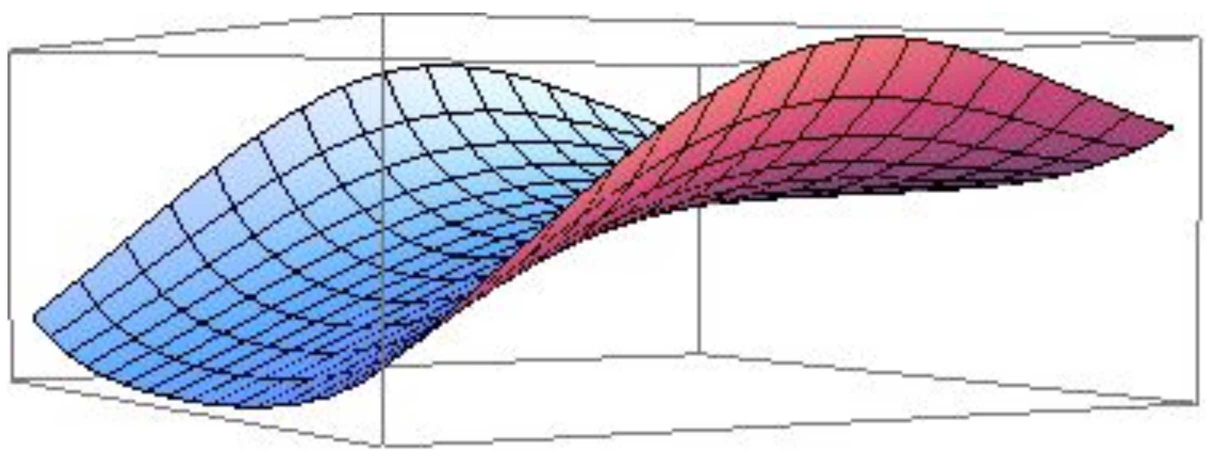
$$\theta = \frac{1}{2}\epsilon_{ij}\partial_i u_j \, .$$

$$\epsilon_{ij}\partial_i\partial_j\theta = \frac{s}{2\pi}\delta(\mathbf{x} - \mathbf{x_0}).$$

CAN FORMALLY CONSIDER A CONTINUOUS DISTRIBUTION OF DISCLINATIONS.

BENDING ENERGY OF A RIBBON (I)

IMAGINE A VERY THIN RIBBON; PLANAR IN EQUILIBRIUM.



$$\mathbf{R} = (x, y, h(x, y))$$

MONGE REPRESENTATION

$\partial_x h,\ \partial_y h$ CONSTANT → RIGIDLY ROTATED PLANE

BENDING → NONZERO SECOND DERIVATIVES

BENDING ENERGY OF A RIBBON (II)

CURVATURE TENSOR $K_{ij}(x,y) \simeq \partial_i \partial_j h(x,y)$

$$\mathbf{K} = \begin{pmatrix} 1/R_1 & 0 \\ 0 & 1/R_2 \end{pmatrix}$$

MEAN CURVATURE $H = \frac{1}{2}(\frac{1}{R_1} + \frac{1}{R_2})$

GAUSSIAN CURVATURE $K = \frac{1}{R_1 R_2}$

BENDING ENERGY $F_b \simeq \int (\frac{\kappa}{2} H^2 + \tilde{\kappa}_G K) dx dy$

FÖPPL - VON KÁRMÁN THEORY (I)

ROTATIONALLY INVARIANT STRAIN TENSOR:

$$u_{ij} = \frac{1}{2}(\partial_i u_j + \partial_j u_i + \partial_i u_k \, \partial_j u_k + \partial_i h \, \partial_j h)$$

$$\simeq \frac{1}{2}(\partial_i u_j + \partial_j u_i + \partial_i h \, \partial_j h)$$

EFFECTIVE ELASTIC CONSTANTS:

E AND μ ~ THICKNESS,

κ AND κ_g ~ (THICKNESS)^3 .

SEE, FOR EXAMPLE L & L, TE

STABILITY CONDITIONS

κ > 0.

NO RESTRICTION ON THE SIGN OF κ_G.

FOR SURFACES WITHOUT HOLES AND EDGES,

$$\int_S K dS + \int_{\partial S} k_g dl = 0,$$

GAUSS*
BONNET (1848)

WHERE k_g : GEODESIC CURVATURE OF THE BOUNDARY.

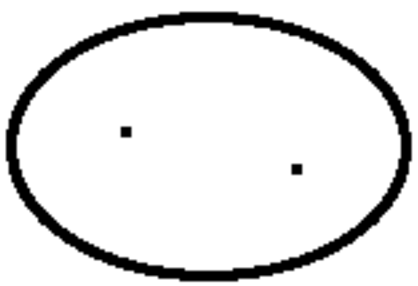
* "PAUCA, SED MATURA.": FEW, BUT RIPE.

FÖPPL - VON KÁRMÁN THEORY (II)

AIM: SEEK MECHANICAL EQUILIBRIUM.

BALANCE FORCES AND TORQUES; BULK & BOUNDARY.

STRATEGY: AVOID TENSORS!



VOLUME ELEMENT

STRESS → EQUILIBRIUM MOLECULAR SEPARATION CHANGES.

ELASTICITY THEORY: MACROSCOPIC, RANGE OF MOLECULAR FORCES VERY SMALL.

FORCES ACT ONLY ON THE SURFACE OF THE VOLUME ELEMENT

FORCE DENSITY $$f_i = \partial_i \sigma_{ij} = 0.$$

AIRY STRESS FUNCTION $$\sigma_{ij} = \epsilon_{ik}\epsilon_{jl}\partial_k\partial_l\chi.$$ AIRY (1862)

FÖPPL - VON KÁRMÁN THEORY (III)

COMPATIBILITY CONDITIONS:

1. NO TOPOLOGICAL DEFECTS: FÖPPL (1907) , VON KÁRMÁN (1910)

u_{ij} SHOULD LEAD TO A SINGLE - VALUED DISPLACEMENT FIELD $\mathbf{u}$.

$$\frac{1}{Y}\nabla^4\chi = K.$$

2. ALLOW TOPOLOGICAL DEFECTS: SEUNG AND NELSON (1988)

$\mathbf{u}$ IS NOT SINGLE-VALUED.

$$\frac{1}{Y}\ \nabla^4\chi = s - K,$$

s IS THE DEFECT DENSITY,

K THE GAUSSIAN CURVATURE.

Y IS YOUNG'S MODULUS, RELATED TO E AND μ

FÖPPL - VON KÁRMÁN THEORY (IV)

TOTAL ELASTIC ENERGY

$$F_{el}[\mathbf{u}, h] = F_H[\mathbf{u}, h] + F_b[h].$$

HEIGHT EQUATION FOR MINIMAL SURFACES

$$\frac{\delta F_{el}}{\delta h} = K_{ij}\sigma_{ij} = 0,$$

WITH

$$\sigma_{ij} = \epsilon_{ik}\epsilon_{jl}\partial_k\partial_l\chi.$$

COMPATIBILITY CONDITION

$$\nabla^4\chi = Y(s - K).$$

+ BOUNDARY CONDITIONS

“THESE EQUATIONS ARE VERY COMPLICATED, AND CANNOT BE SOLVED EXACTLY EVEN IN VERY SIMPLE CASES.” L AND L, TE.

OTHER TERMS IN THE FREE ENERGY:

SURFACE TENSION:

$$F_S = \sigma \int dS$$

LINE TENSION:

$$F_L = \gamma \oint dl$$

GEODESIC CURVATURE OF THE BOUNDARY:

$$F_{GC} = k \oint k_g dl$$

MERELY RENORMALISES

$\tilde{\kappa}_g$ TO κ_g

FREE BOUNDARY CONDITIONS

I. $$\sigma_{ij} N_j = 0,$$ CAUCHY (1820)

N_j : OUTWARD NORMAL AT THE RIBBON EDGE.

II. FOR ZERO MEAN CURVATURE,

FORCE BALANCE AT THE EDGE:

$$\kappa_G K + \gamma k_g + \sigma = 0,$$

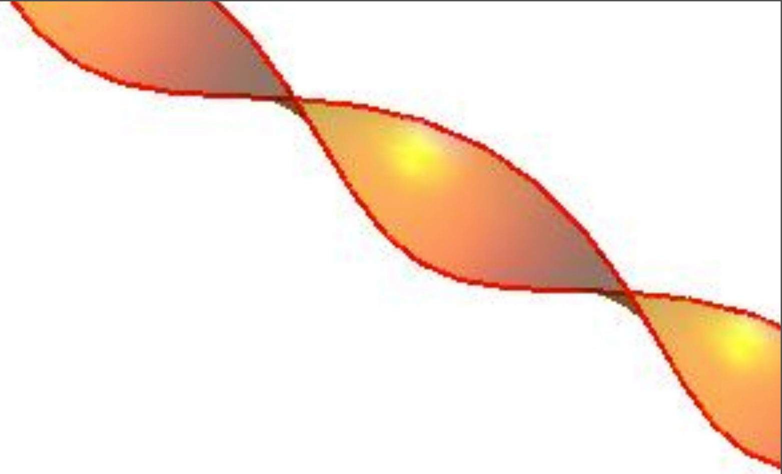
BOAL AND RAO (1992)
CAPOVILLA *ET AL.* (2002)

γ : LINE TENSION, σ : SURFACE TENSION,

k_g : GEODESIC CURVATURE OF THE RIBBON EDGE.

BOUNDARY CONDITIONS FOR A SURFACE WITH NON-ZERO MEAN CURVATURE ARE EXTREMELY COMPLICATED.

THE DERIVATION OF FREE BOUNDARY CONDITIONS IN L AND L, TE, IS MISLEADING.



HELICOIDS

$$\mathbf{R} = (\rho\cos\phi, \rho\sin\phi, b\phi), \ \mid \rho \mid \leq r,$$

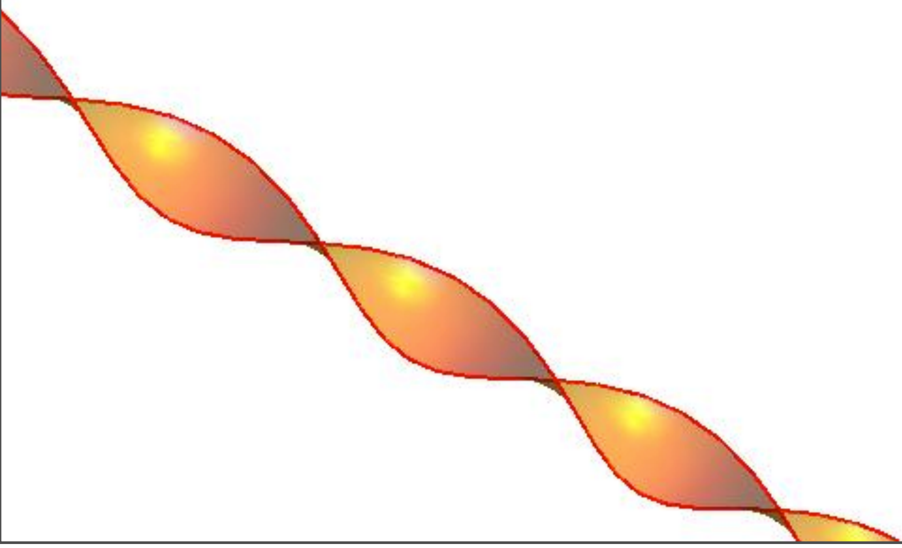
PITCH $p = 2\pi|b|$, WIDTH $2r$.

$b > 0$, RIGHT- HANDED; $b < 0$, LEFT- HANDED.

$$H = 0,$$ MEAN CURVATURE
MINIMAL SURFACE

$$K = -b^2/(\rho^2 + b^2)^2,$$ GAUSSIAN CURVATURE

$$k_g = r/(r^2 + b^2),$$ GEODESIC CURVATURE



SOLUTION

POSSIBLE BECAUSE

THE HELICOID IS A MINIMAL SURFACE,

USED A CONTINUOUS DISTRIBUTION OF DISCLINATIONS.

MINIMISED ELASTIC ENERGY OF THE RIBBON.

CHECKED THAT THE LINE TENSION TERM DOES NOT AFFECT THE RESULTS MUCH, EVEN QUANTITATIVELY.

OPEN ISSUES:

THE SIGN OF κ_g .

THE ROLE OF "CILIA". "HOMOGENEOUS, ISOTROPIC" BODIES CAN'T HAVE THE RIGHT SIGN.

EFFECTIVE ELASTICITY THEORY FOR "ORTHORHOMBIC RIBBONS".

RESIDUAL STRESS BECAUSE OF DISCRETE NATURE OF DEFECTS.

BANDED SPHERULITES OF CHIRAL POLYMERS.

TENTS AND CHAIRS, SCROLLS.

TENT- AND CHAIR MORPHOLOGIES
(WITH JAYA KUMAR A., M. MUTHUKUMAR).

THANK MADAN RAO FOR DISCUSSIONS, COMMENTS.