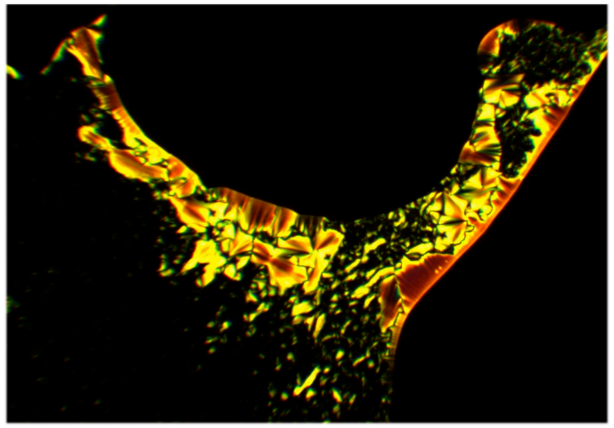
Facets of Order

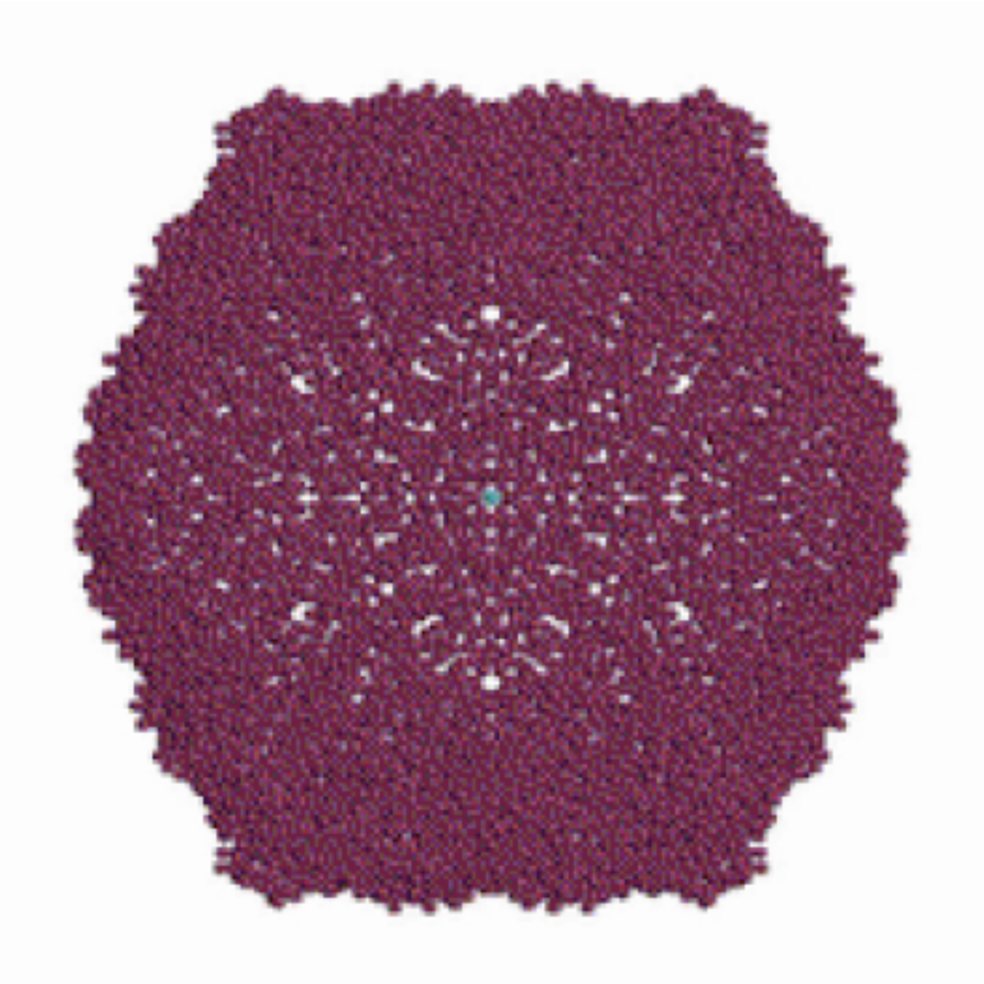


Mark Bowick
Syracuse University

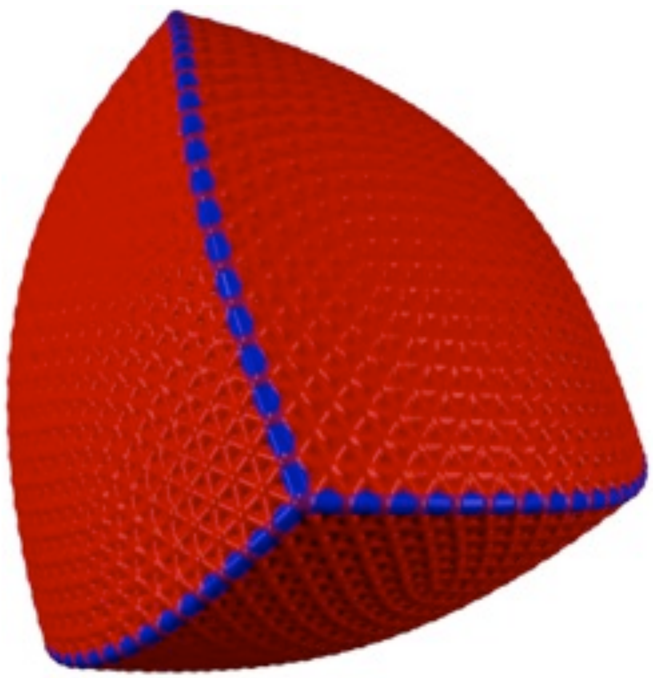
JAKS Bangalore 2012

Art Silverman
Poydras St, New Orleans

Faceting of elastic shells



HK97 Viral Capsid
Lidmar, Mirny, Nelson:
PRE (2003)
Bruinsma & Gelbart



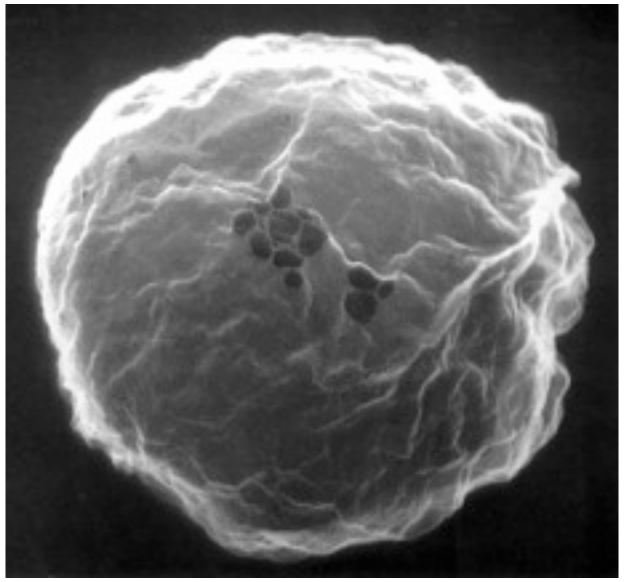
Vernizzi, Sknepnek and Olvera de al Cruz:
PNAS (2011)

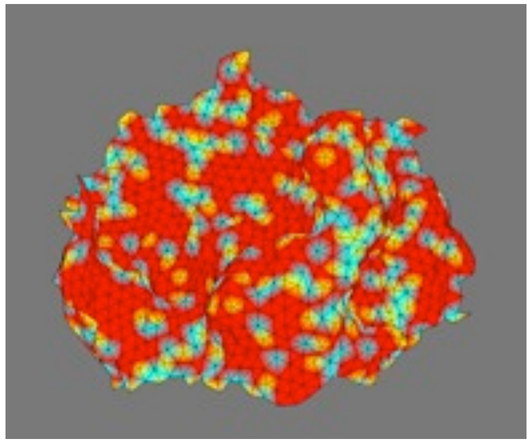
2D Order

Phase	**Order**
Crystalline	Quasi-Long Range Translational Truly Long-Range Bond-Orientational
Nematic	Orientational
Smectic	One-Dim Translational
Hexatic	Quasi-Long Range Bond-Orientational

Membranes

Crystalline (Polymerized)





What about nematic or smectic membranes?

Hexatic

Vesicles (Membrane Sacs)

Amphiphilic Bilayers → Lipid Bilayers

Amphiphilic Bilayers → Block Copolymer Bilayers

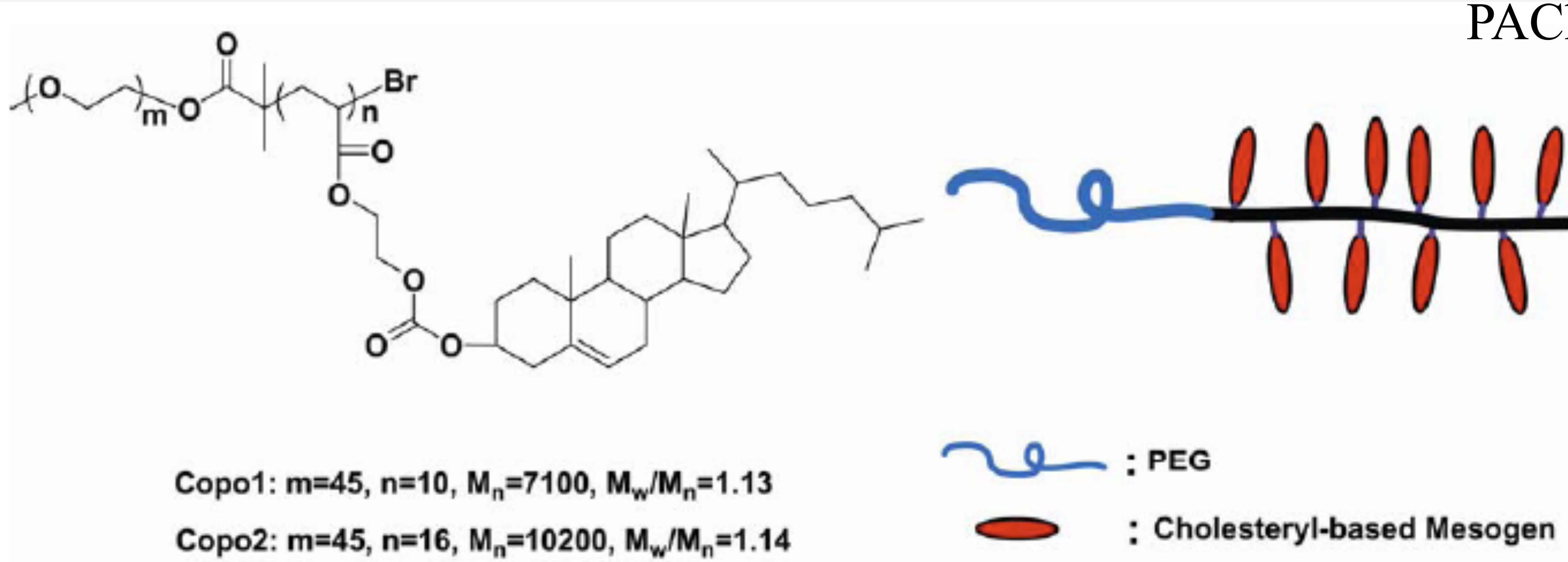
Smectic Polymer Vesicles

Lin Jia,[†,††] Amin Cao,[‡] Daniel Lévy,[†] Bing Xu,[†] Pierre-Antoine Albouy,[$] Xiangjun Xing[#],

Mark J. Bowick[#] and Min-Hui Li[†]*

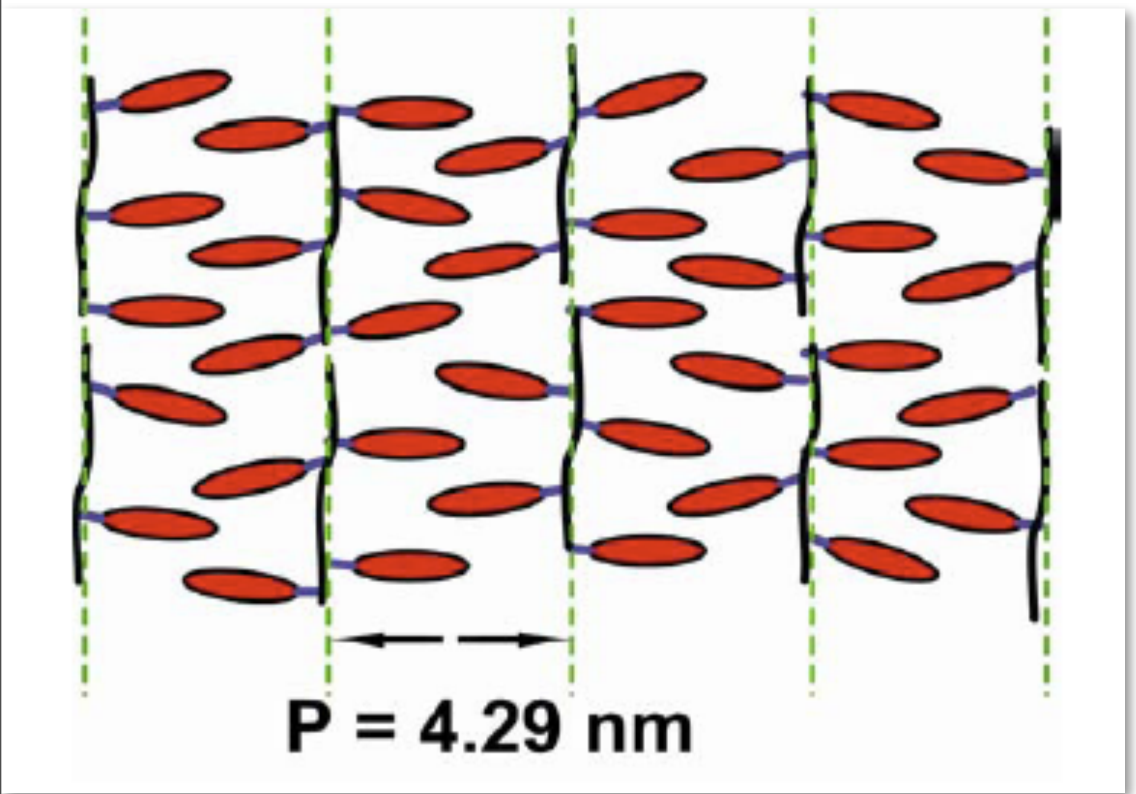
Soft Matter 5, 3446 (2009)

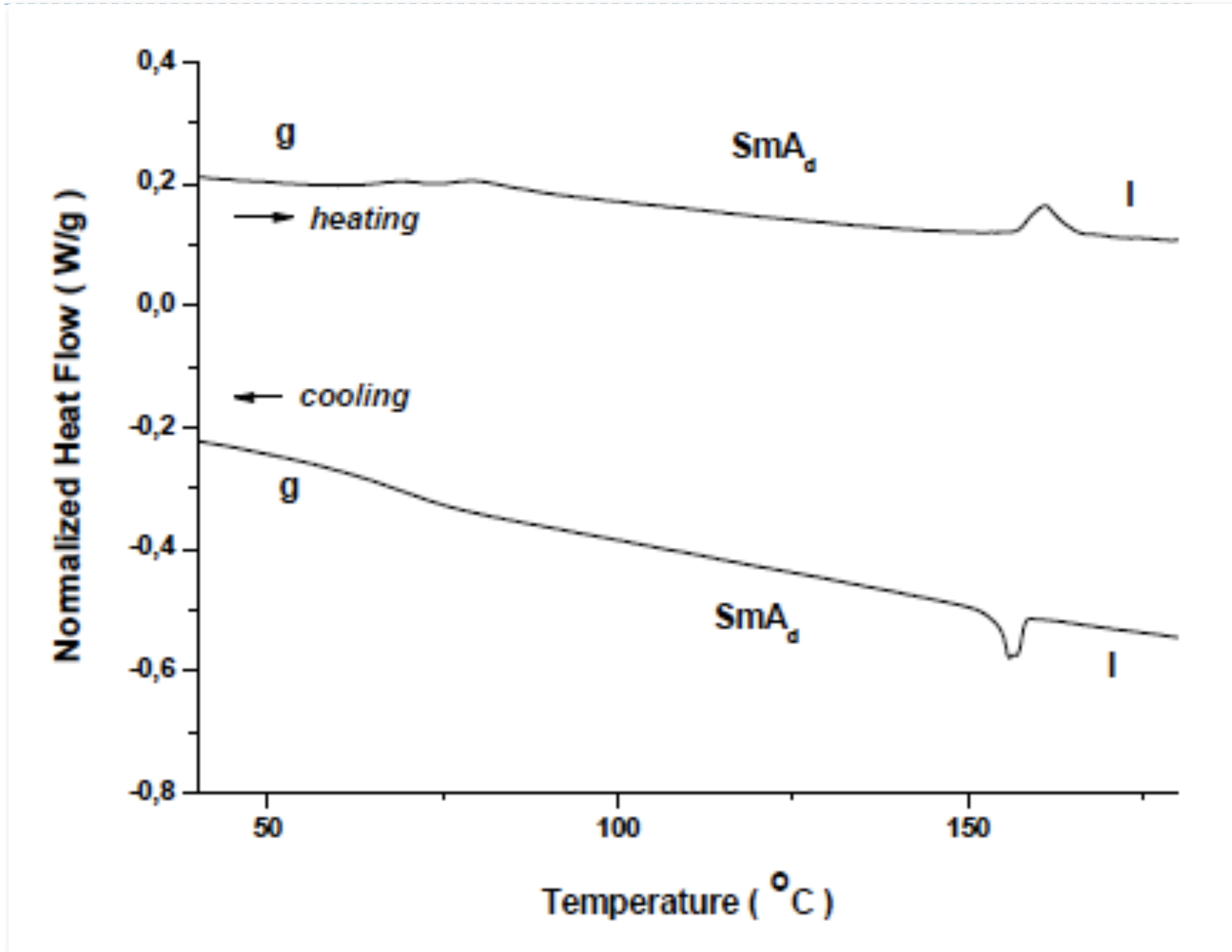
PAChol



PEG: flexible and hydrophilic
PAChol: liquid-crystalline and hydrophobic

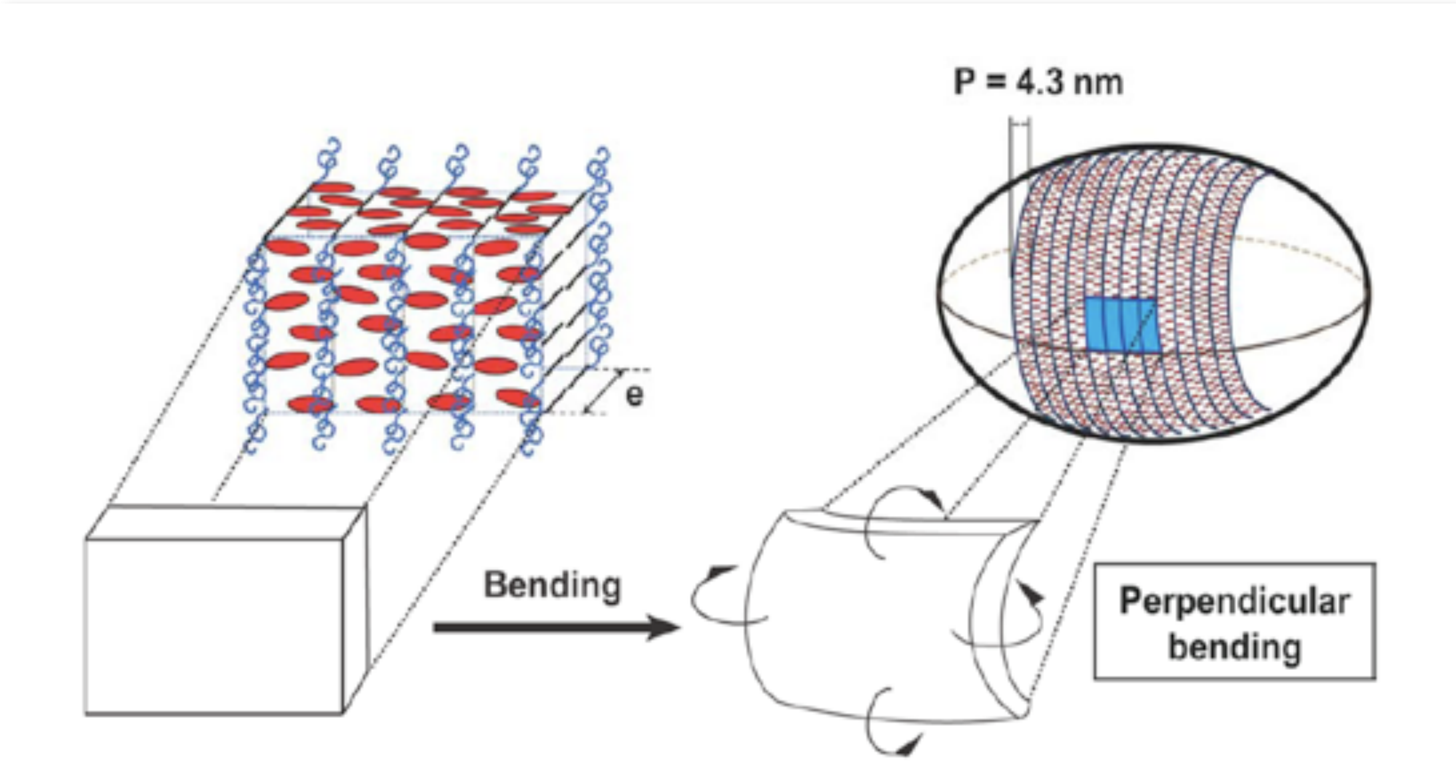
Phase Sequence of PAChol Homopolymer





1. Glassy smectic at room temperature (irrelevant for vesicle formation)
2. Isotropic-Smectic first order transition, no intermediate nematic phase

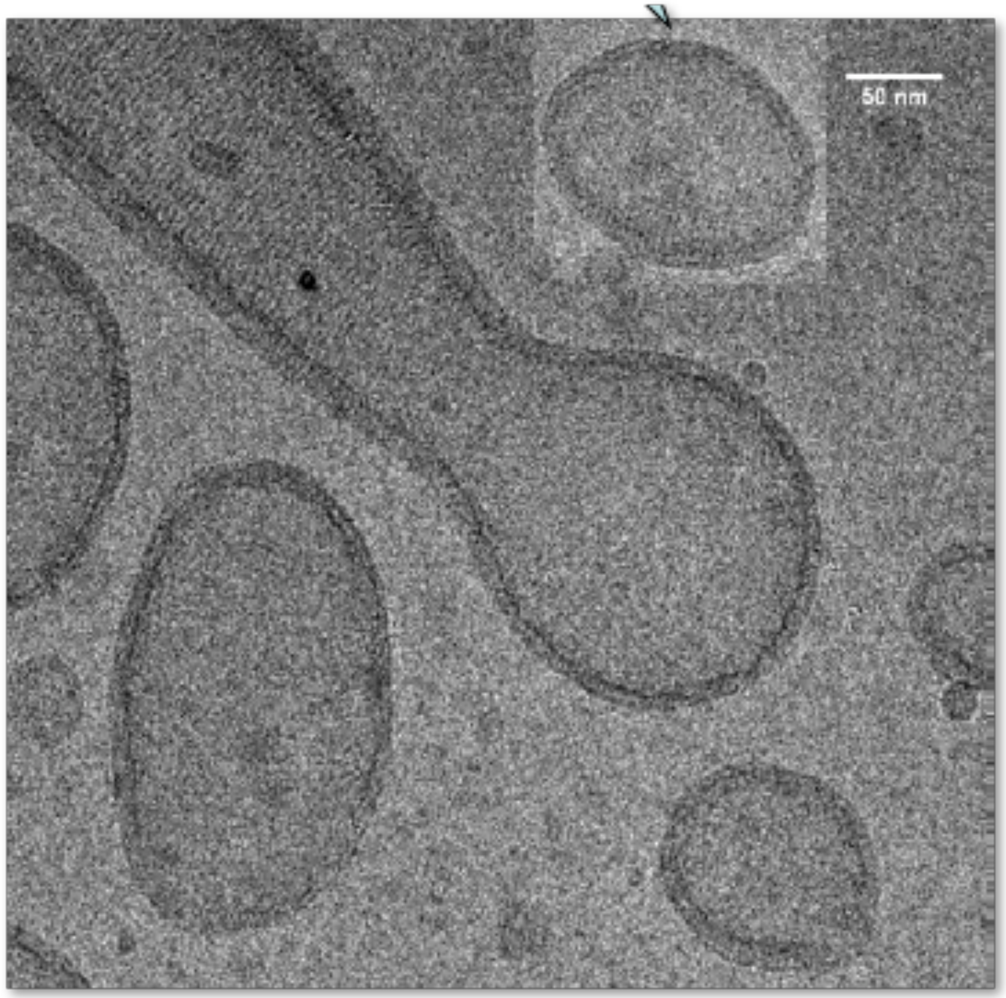
Smectic Polymer Vesicles



Shape change driven by smectic order - defects inevitable

M.-H. Li, *et al*, to be published

Smectic Vesicles



PEG2000-*b*-PAChol (28/72)

Model Free Energy

(MJB, H. Shin, X. Xing and Z. Yao)

$$H_{\mathrm{m}} = \frac{1}{2}\int \sqrt{g}\, d^2x \left[K\,(\vec{D}\hat{n})^2 + \kappa\,(H - H_0)^2 \right]$$

Frank constant   Bending Rigidity

Generically:

2 Frank constants: K_1 (splay) K_3 (bend)

3 bending rigidities 3 mean spontaneous curvature components

Simplify to above

Nematic Vesicles: $K = K_1 = K_3$ (one Frank constant approx)

Smectic Vesicles: $F = \frac{K_1}{2}\int (D\cdot n)^2 + \frac{K_3}{2}\int (D\times n)^2$

$K_3 \to \infty \quad D\times n = 0 \implies (\vec{n}\cdot\vec{D})\vec{n} = 0$ (Director follows geodesics)

$$K = K_1$$

Minimizing the Free Energy

Minimizing Frank free energy $\Longrightarrow$ $Dn = 0$ $\Longrightarrow$

Gaussian curvature vanishes $\Longrightarrow$ developable surface

e.g. plane, cylinder, cone

Minimizing the bending energy $\Longrightarrow$ $H = H_0$

$\Longrightarrow$ cylindrical monolayer w/ $R = 1/H_0$ Nanofibers

Bilayers

$$H_{\mathrm{m}} = \frac{1}{2}\int \sqrt{g}\, d^2x \left[K\,(\vec{D}\hat{n})^2 + \kappa\, H^2\right]$$ 2 copies

Possibilities:

1. Flat bilayer - contains line energy at boundary
2. Closed vesicle - favored for large system size (Helfrich: 1974)

Closed Bilayer Polymer Vesicles

Assume spherical topology

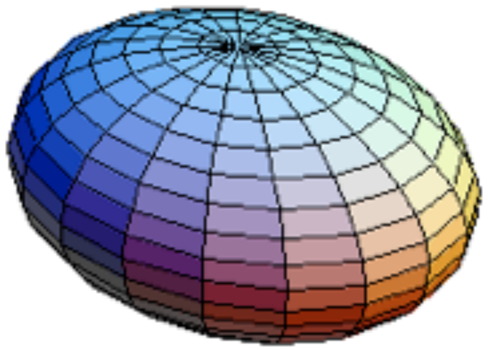
$$\int K(x)d^2x = 4\pi \neq 0$$

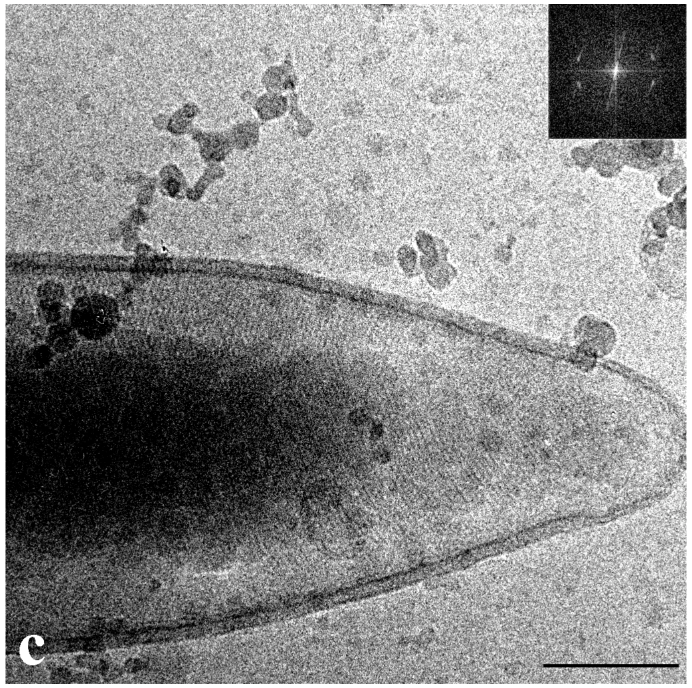
Gaussian curvature

Thus LC Frank free energy (K) competes with bending energy (κ)

$\boxed{\text{Limit 1(stiff)}}$ $K \ll \kappa \implies$ Round sphere

Anisotropic bending rigidity will lead to a deformed sphere

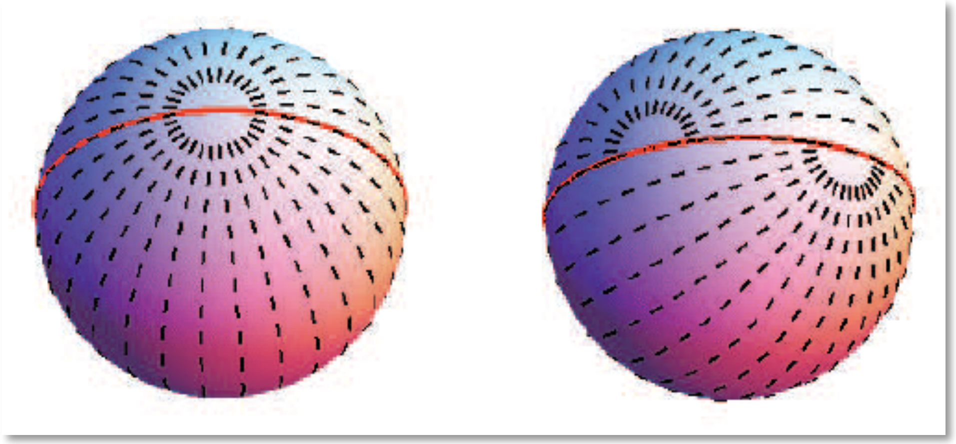




Cryo-TEM of Copo2

100nm scale bar

$$P = 4.3 \pm 0.1\text{nm}$$



Smectic

Limit 2 (floppy) $\kappa \ll K$

Minimizing the (dominant) Frank free energy with non-vanishing integrated Gaussian curvature constraint possible with

faceted polyhedra

Gaussian curvature vanishes ***everywhere*** but at a discrete number of (singular) vertices

Singular sources of curvature ideal sites for *requisite* LC defects:

$$\sum_i s_i = 2 : s_i = 1/2, 1$$

1. 2 (+1) defects
2. 1 (+1), 2 (+½) defects
3. 4 +½ defects

Need at least 4 points to span a non-degenerate polyhedron

$\Longrightarrow$ Ground state shape of a ***liquid crystalline*** vesicle with $\kappa \ll K$ is a faceted tetrahedron with a ½ disclination at each vertex!

The space of all tetrahedral shapes is 5-dimensional but not all tetrahedra support a suitable nematic defect configuration: Covariantly constant director field requires that the sum of the angles at each vertex is 180deg. Gives 3 constraints. Leaves a **two-dimensional manifold** of ground states.

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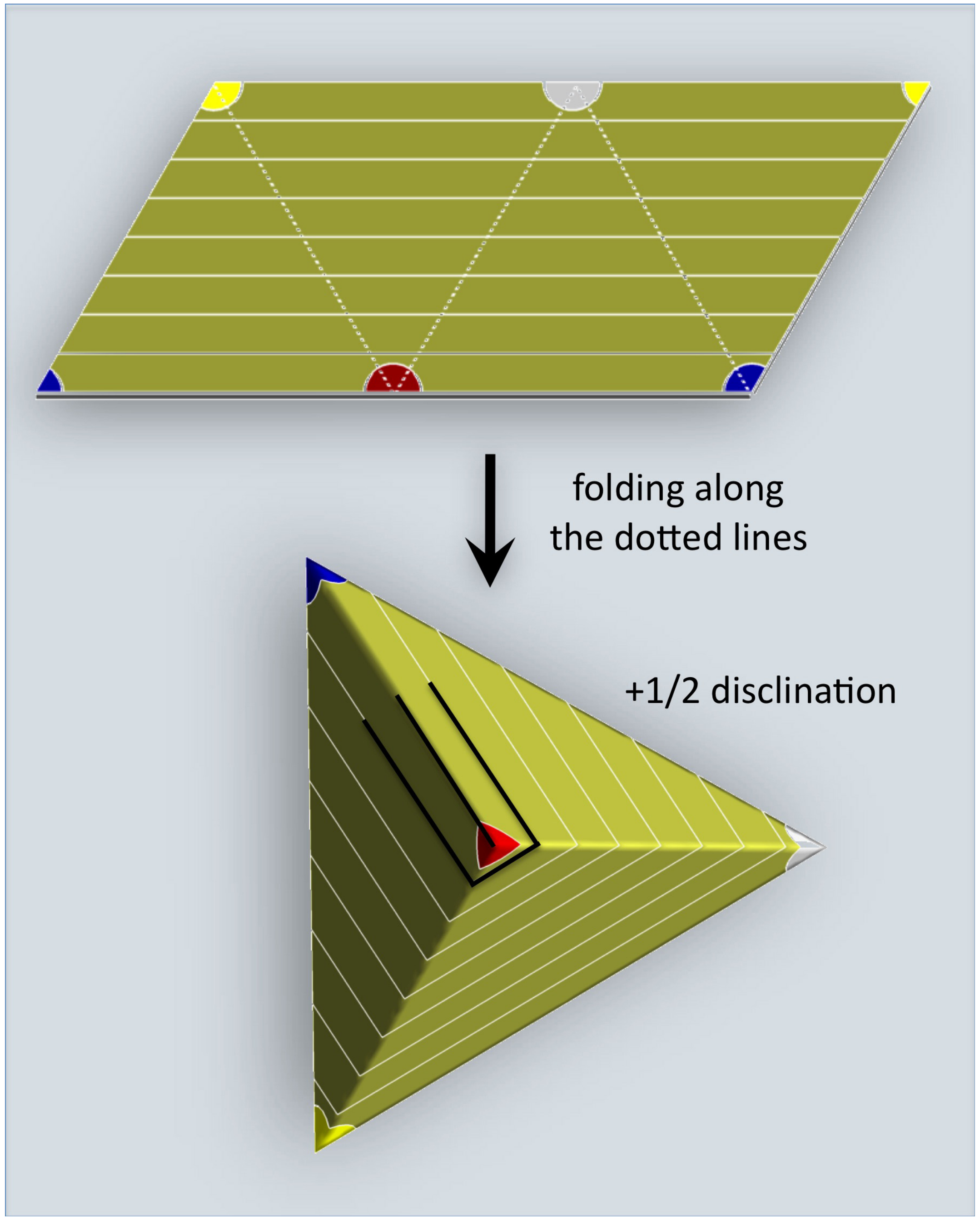
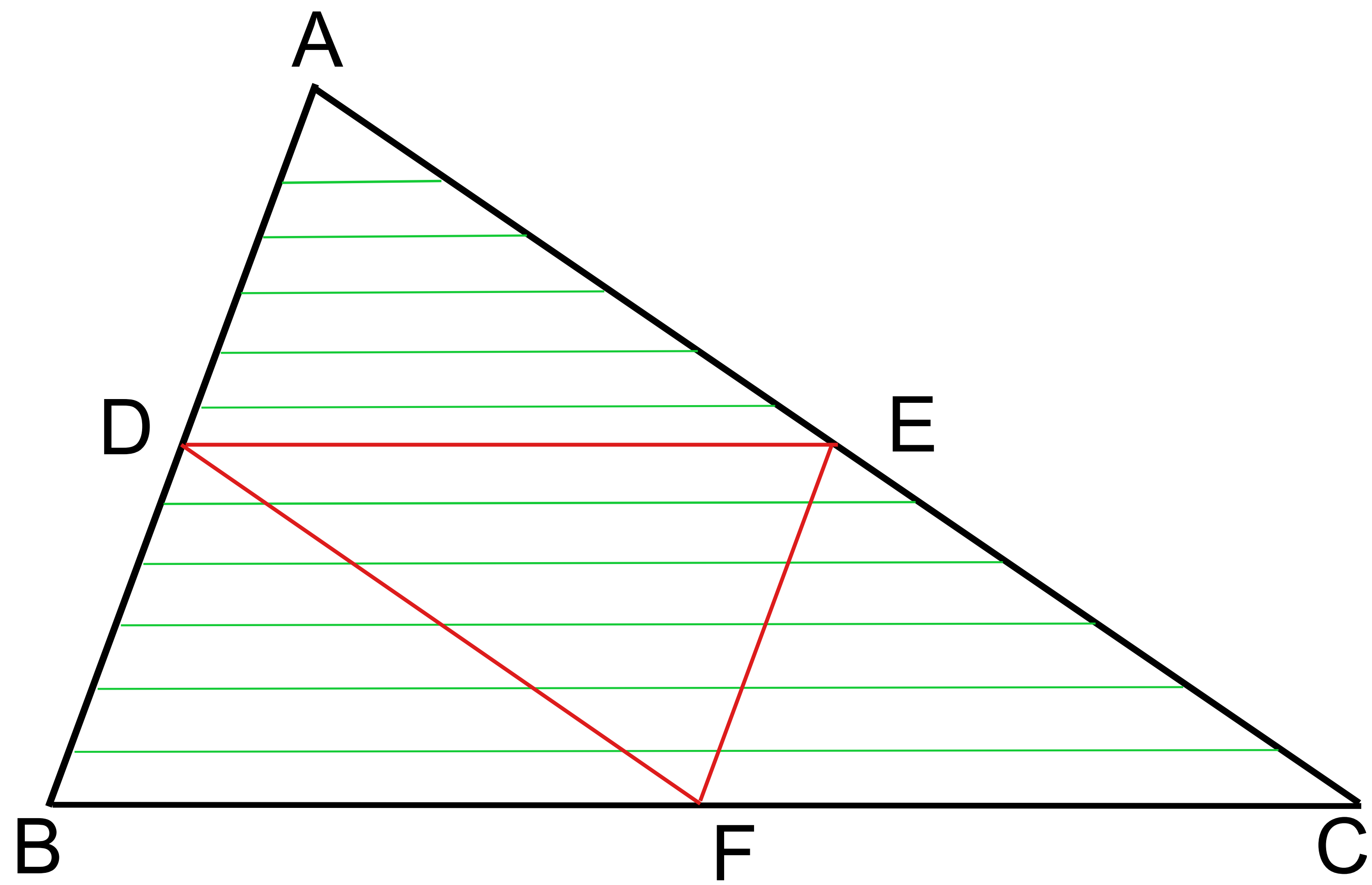
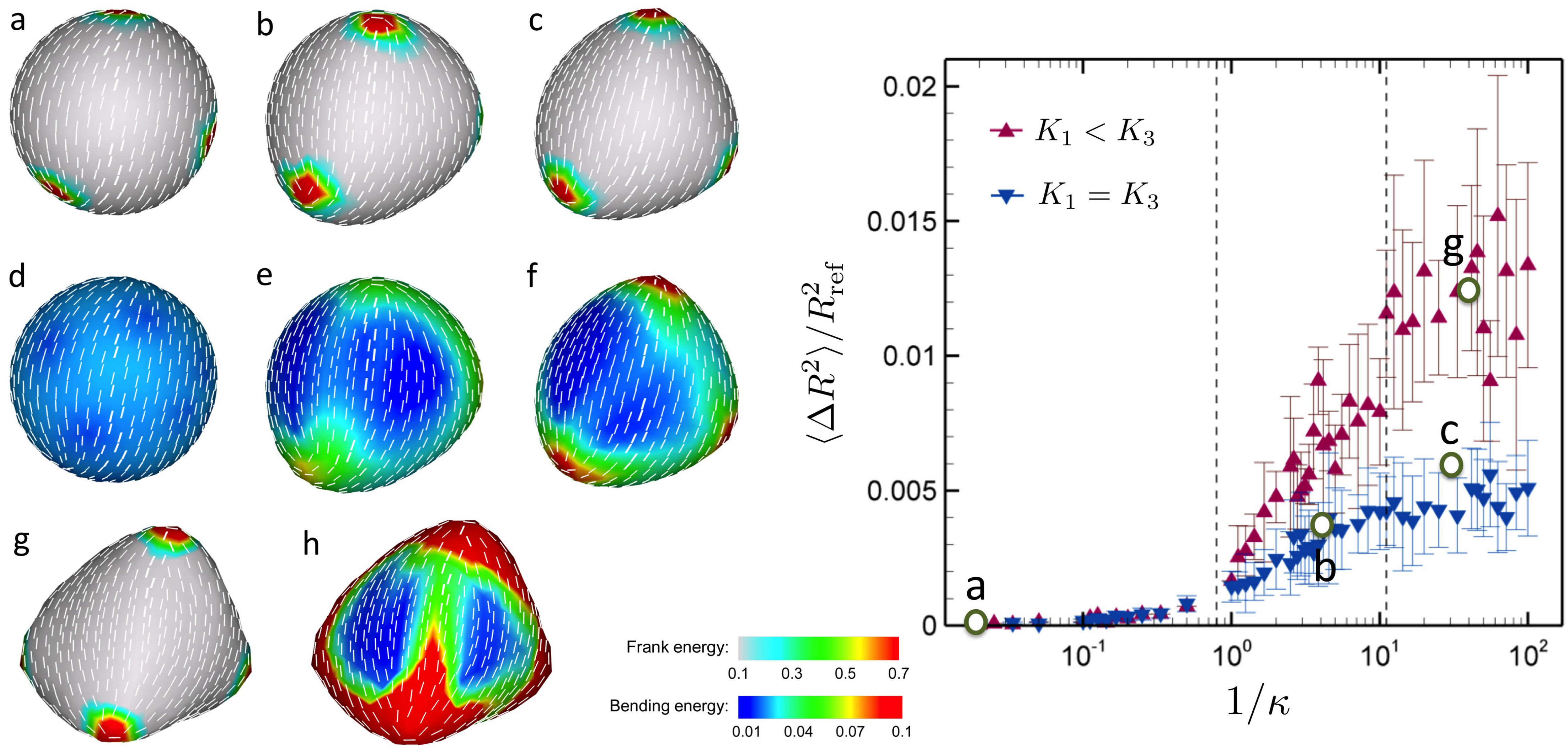


Generic Tetrahedral Smectic Vesicle



For $\kappa \neq 0$ total energy proportional to sum of edge lengths (plus defect energy) $\Longrightarrow$ regular tetrahedron is the ground state

Simulations



a-c local Frank energy
d-f bending energy

a & d: $\kappa = 100$

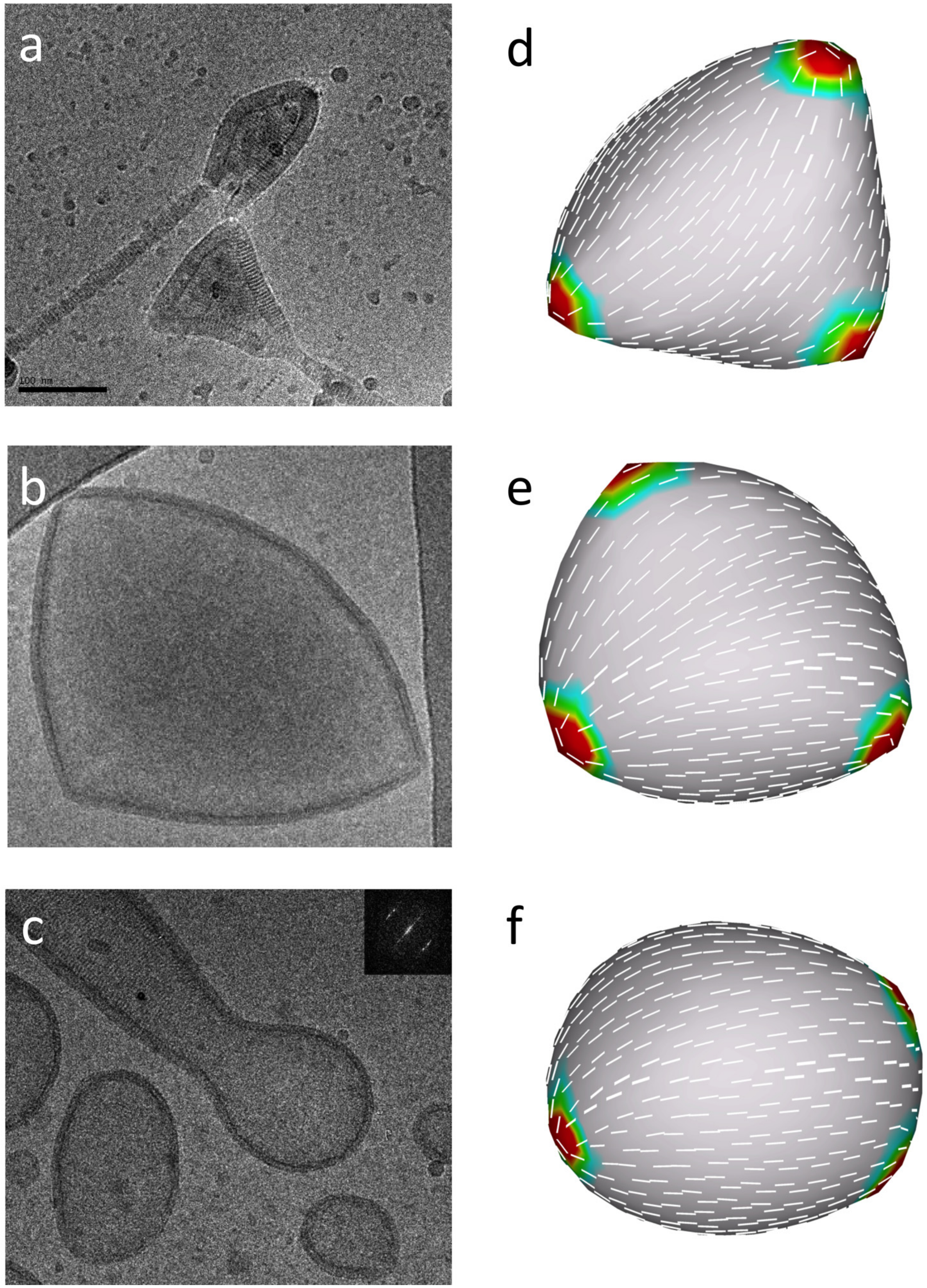
b & e: $\kappa = 0.3$

c & f: $\kappa = 0.05$

g & h: $K_3/K_1 \approx 2$

$\kappa = 0.04$

Comparison with experiments $K_3/K_1 \approx 2$



$$\kappa = 0.04$$

$$\kappa = 0.1$$

$$\kappa = 0.5$$

Nanotube vs Tetrahedron

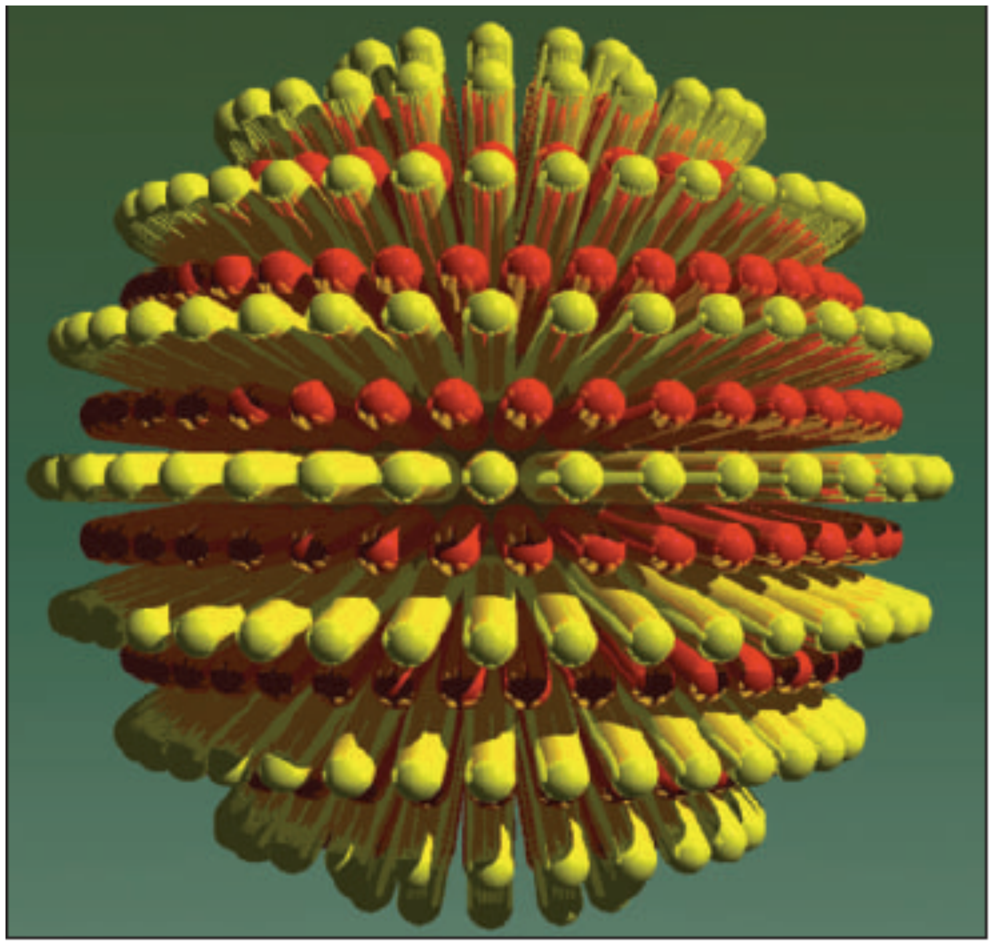
Nanotube: $$H_{nt} = \kappa \frac{A}{a^2} \propto \kappa A$$ (*a* = nanotube radius)

Tetrahedron: $$H_{tet} = 4\kappa L/b \propto \kappa\sqrt{A}$$

radius of curvature of ridges

Tetrahedron favored for large system size $L > L_c \sim a^2/b$

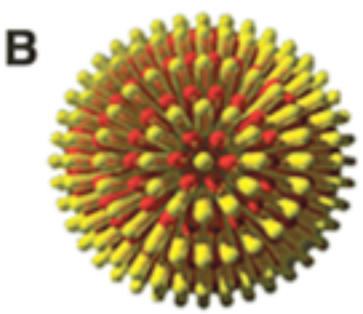
Tilt & Smectic Order on NPs



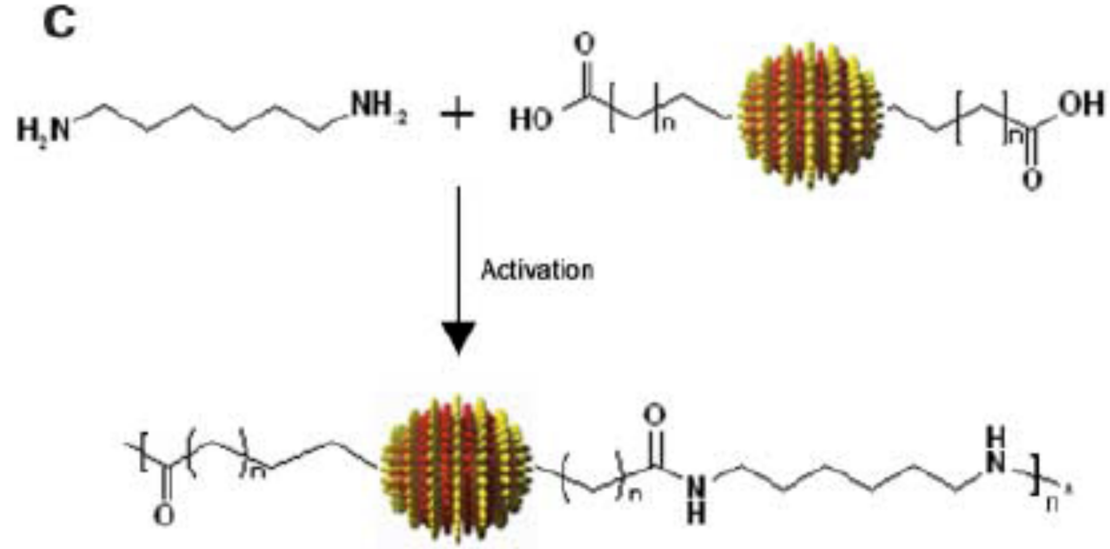
SAM consisting of 2 types of thiol-terminated ligands (1-nonanethiol and 4-methybenzenethiol) on Au

DeVries et al (Stellacci): Science (2007)

B



C

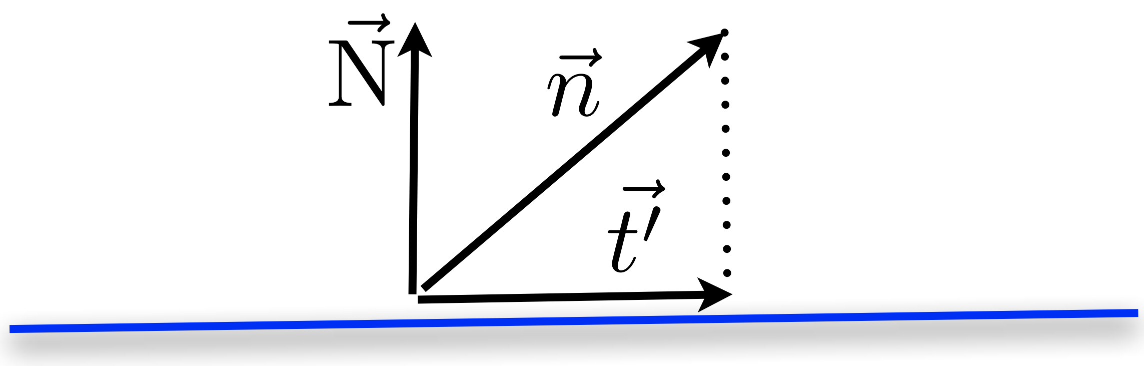


Functionalization by MUA

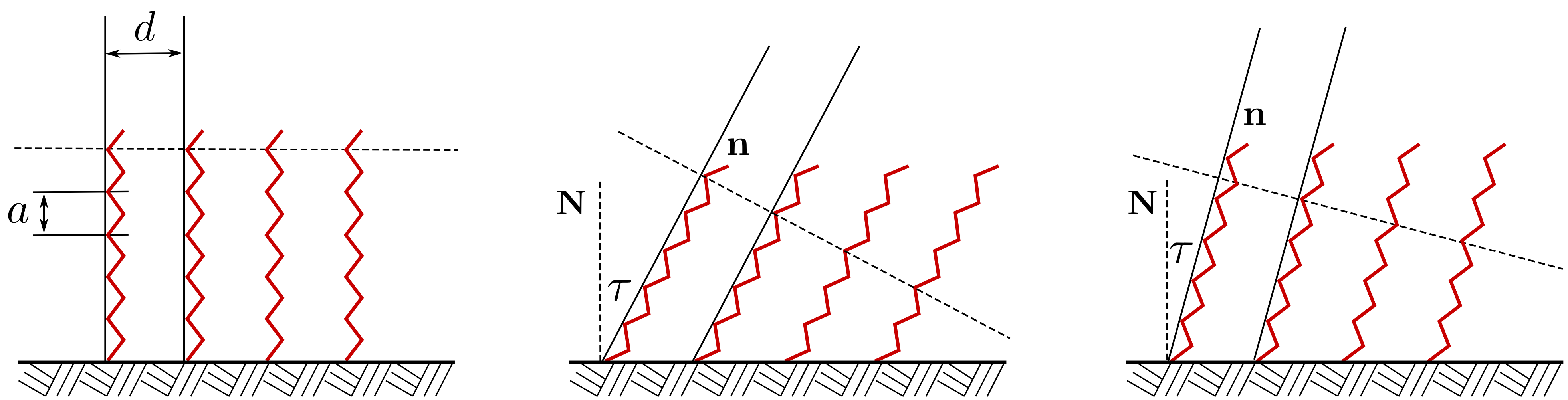
Single-Species Thiols on Gold/Silver (SAMs)

L. Giomi, X. Ma, A. Majumdar, MJB

Preferred tilt angle of thiols projects to a vector field on the nanoparticle surface



$$\mathbf{t} = \frac{\mathbf{n}}{\mathbf{n}\cdot\mathbf{N}} - \mathbf{N}$$



(a) (b) (c)

$$t = |\vec{t}| = \tan\tau \qquad t_0 = a/d$$

Landau-Ginzburg free-energy

$$E = \int dA \left[\tfrac{1}{2} K_A \nabla_i t_j \nabla^i t^j + \tfrac{1}{4}\lambda (t^2 - t_0^2)^2\right]$$

In frame $(\mathbf{e_1}, \mathbf{e_2})$ $\quad \mathbf{t} = \cos\alpha\, \mathbf{e}_1 + \sin\alpha\, \mathbf{e}_2$

$A_i = \mathbf{e}_1 \cdot \partial_i \mathbf{e}_2$ *(spin connection)*

$$\Delta t + \left(\frac{\lambda}{K_A} t_0^2 - |\nabla\alpha - \mathbf{A}|^2 \right) t - \frac{\lambda}{K_A} t^3 = 0$$

$$\nabla \cdot \left[t^2 (\nabla\alpha - \mathbf{A}) \right] = 0$$

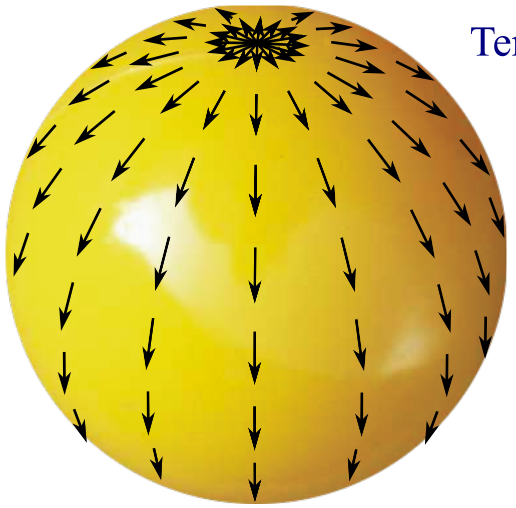
$\equiv$ LG equations for superconductors

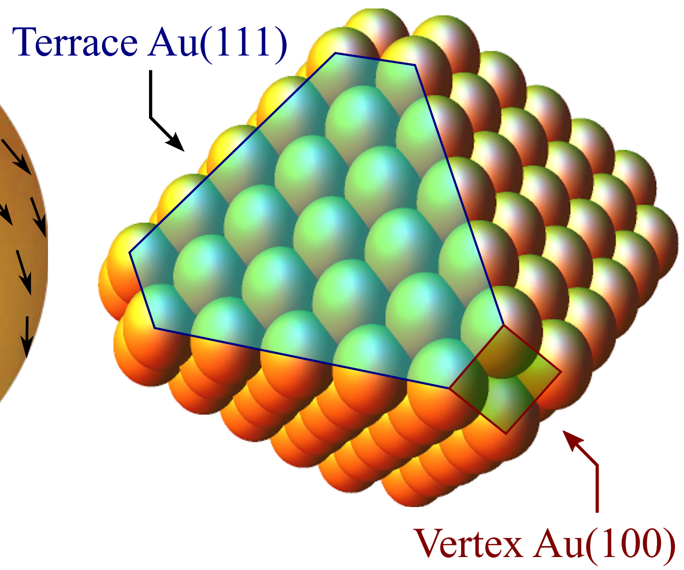
Gaussian curvature $\longleftrightarrow$ External magnetic field

High Curvature/Small R $\longleftrightarrow$ Normal phase

Low curvature/Large R $\longleftrightarrow$ Superconducting

Simplest Solution

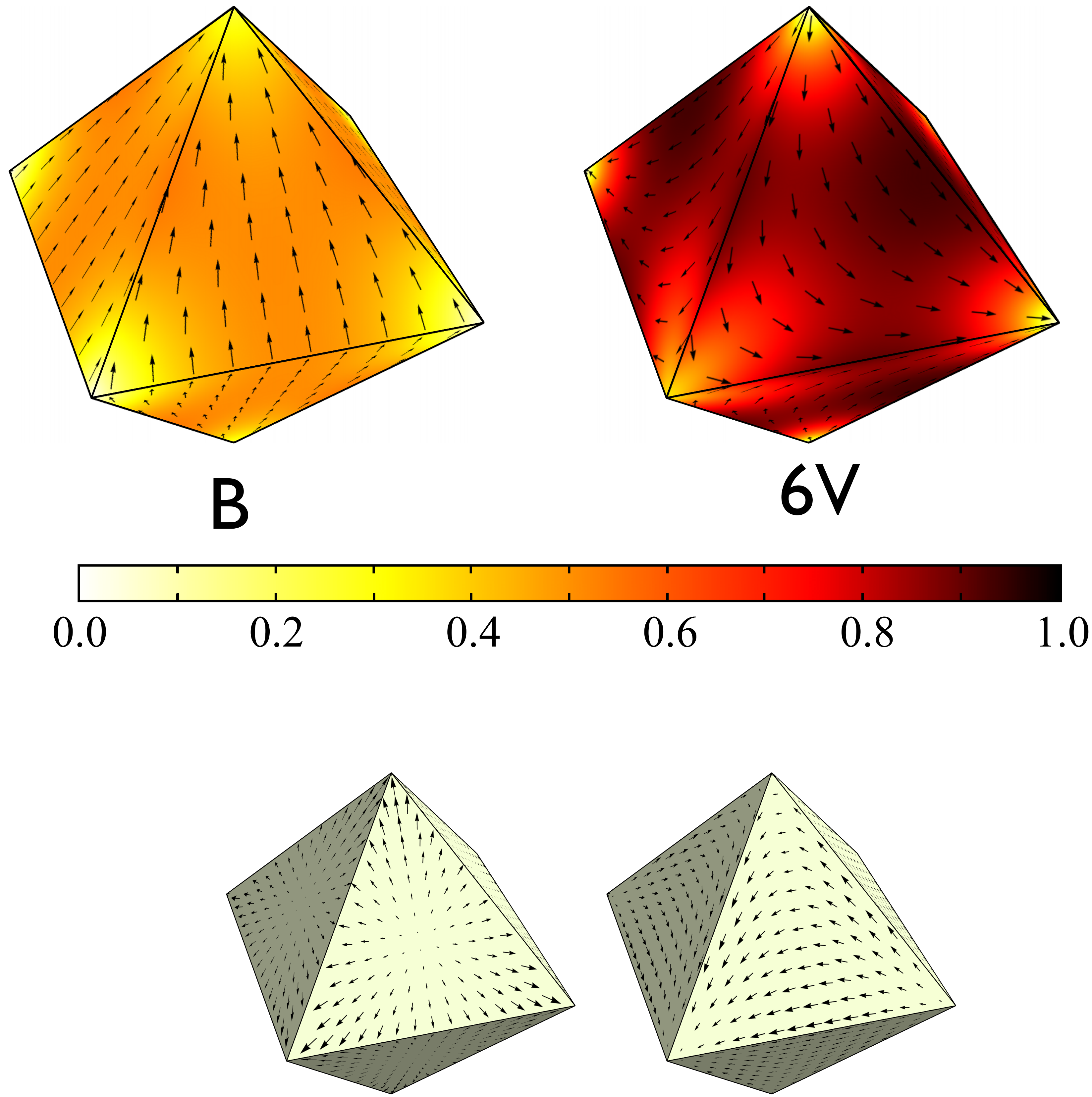




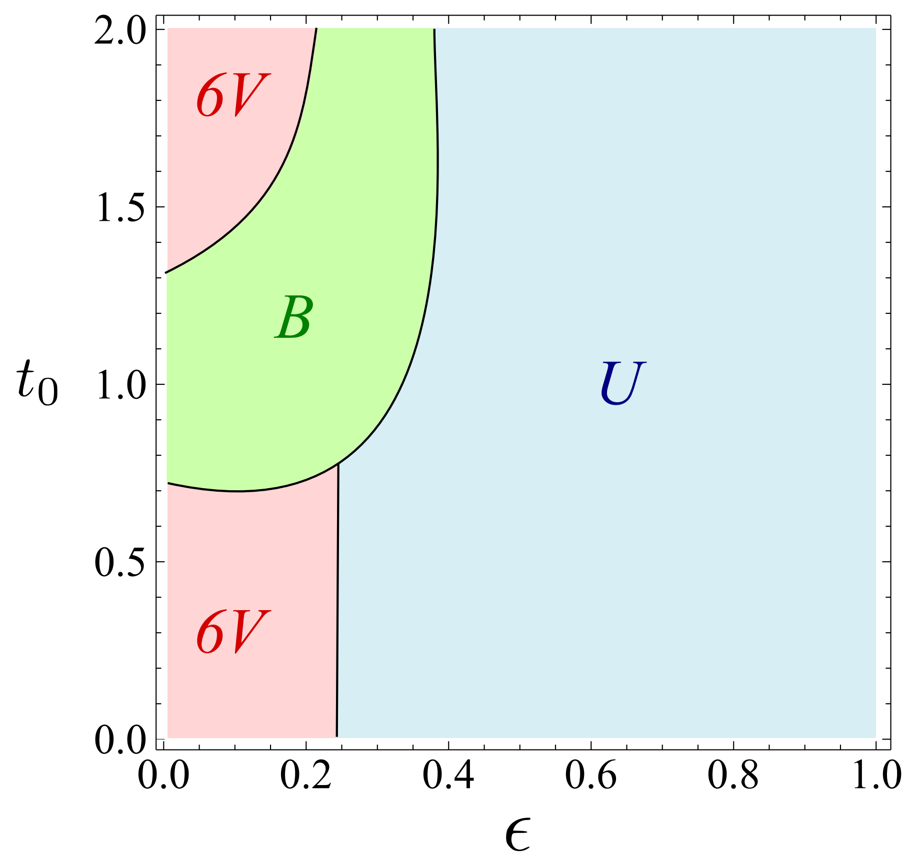
$$\alpha = \text{constant} \; ; \mathbf{A} = A_\phi \hat{\phi} \; ; A_\phi = -\cos\theta$$

$$\partial_\theta^2 u + \cot\theta \, \partial_\theta u + (2/\epsilon^2 - \cot^2\theta) u - (2/\epsilon^2) \, u^3 = 0$$

$$u = t/t_0 \; ; \epsilon^2 = 2K_A/\lambda t_0^2 R^2$$


B
6V
0.0
0.2
0.4
0.6
0.8
1.0

Phase Diagram



Conclusions: Facets of Order

Block Copolymer Vesicles

Order Drives Faceting

LC order drives faceting for floppy vesicles:
Faceted Liquids

Coated Nanoparticles

Shape Drives Order