THIN-SHELL MODEL FOR FACETING OF MULTICOMPONENT ELASTIC VESICLES

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In collaboration with:

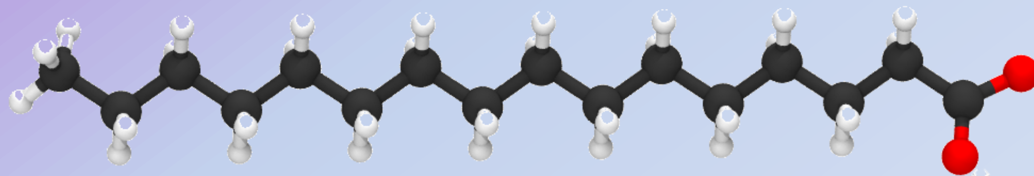
- Monica Olvera de la Cruz (theory)
- Graziano Vernizzi (theory, at Siena College)
- Baofu Qiao (atomistic simulations)
- Cheuk Leung (SAXS/WAXS)
- Michael Bedzyk (SAXS/WAXS)
- Liam Palmer (synthesis, TEM)
- Megan Greenfield (TEM, in consulting)
- Samuel Stupp (synthesis)

NORTHWESTERN UNIVERSITY

Experiments

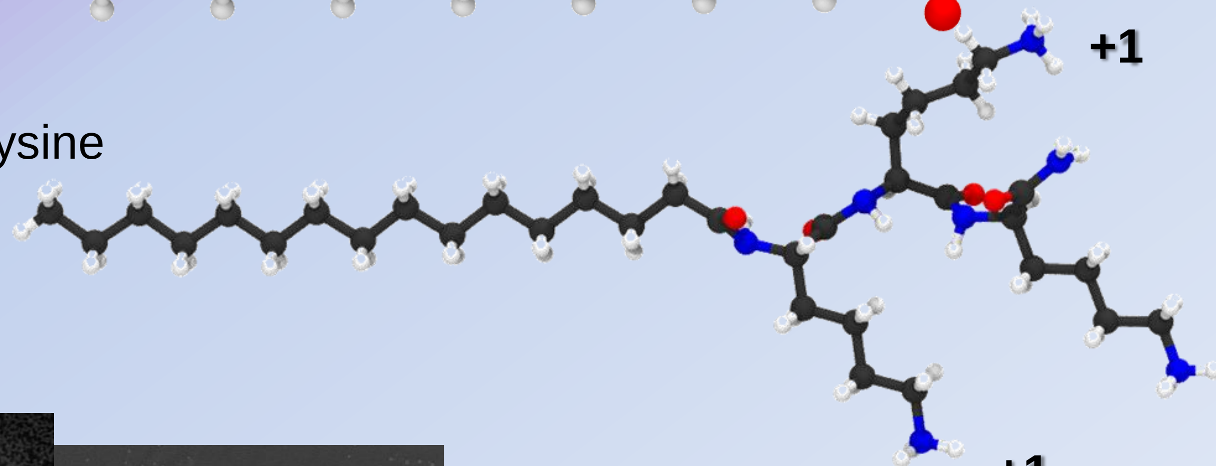
total charge

palmitic acid

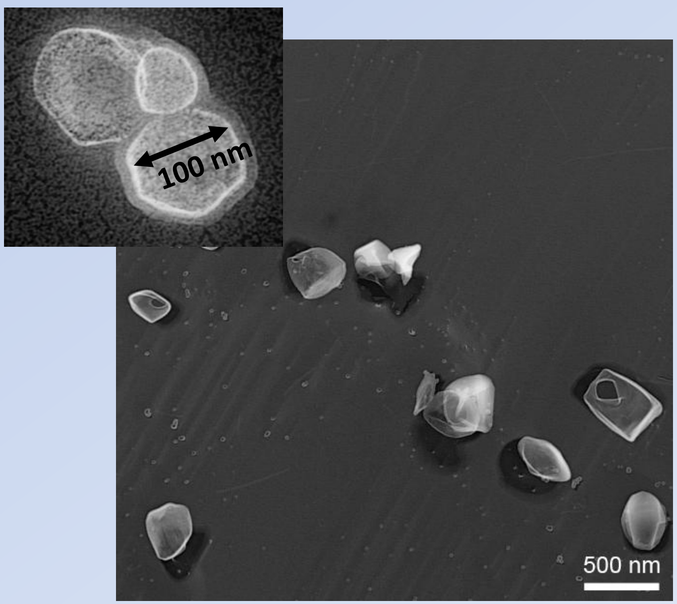


-1

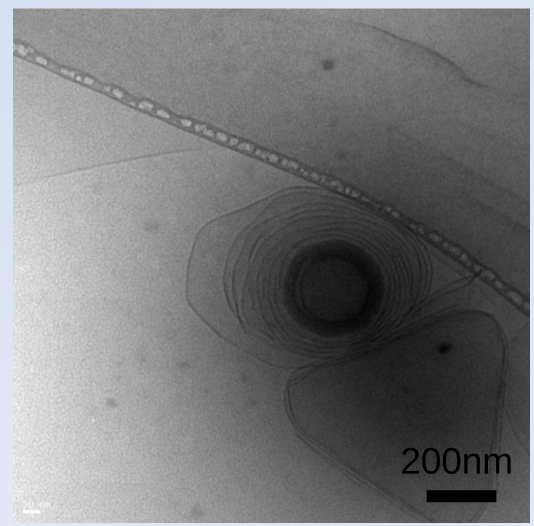
palmitic acid trilysine



+3

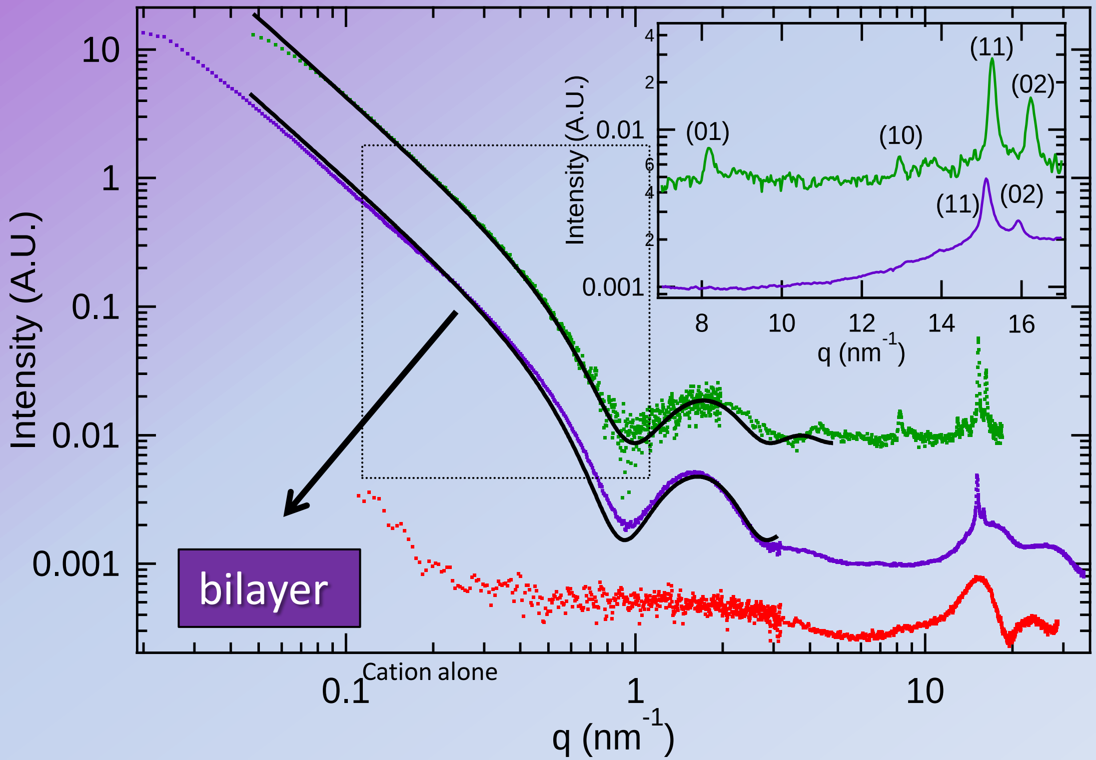


Greenfield, M., et al., JACS (2009)



Courtesy L.C. Palmer (2012)

SAXS/WAXS analysis (C. Leung and M. Bedzyk, Northwestern)



+2/-1 vesicles at pH8.5

+3/-1 vesicles at pH8.5

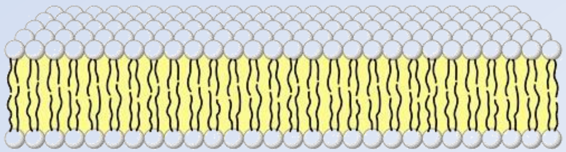
+3 cation alone

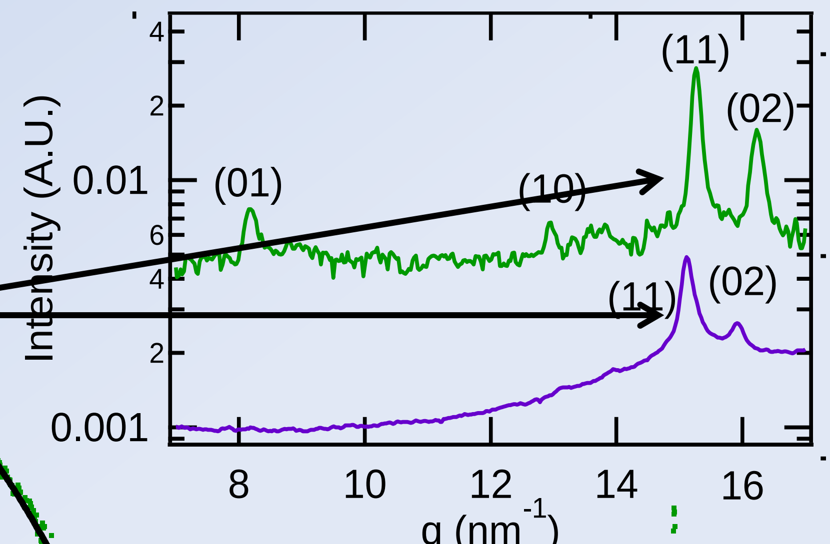
SAXS region

Porod Power law: $I(q) \sim q^{-\alpha}$

α~2 → 2D structure → bilayer

Thickness ~4nm.





WAXS region:

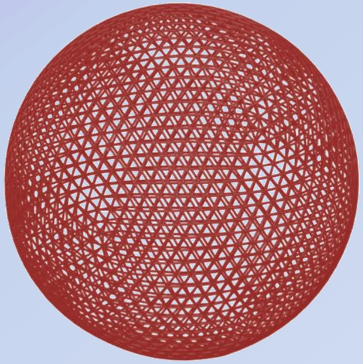
- Peaks indicate that there is crystalline order.
- Peak width tell us there are domains ~25nm in diameter.

Palmer, et al., submitted

How about topological defects?

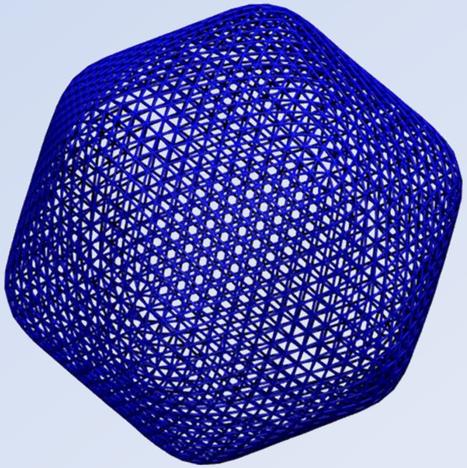
As a consequence of spherical topology, defects are always present.

$$N_5 - N_7 = 12$$ → At least 12 five-fold disclinaiton defects.



increase of radius

sphere to icosahedron



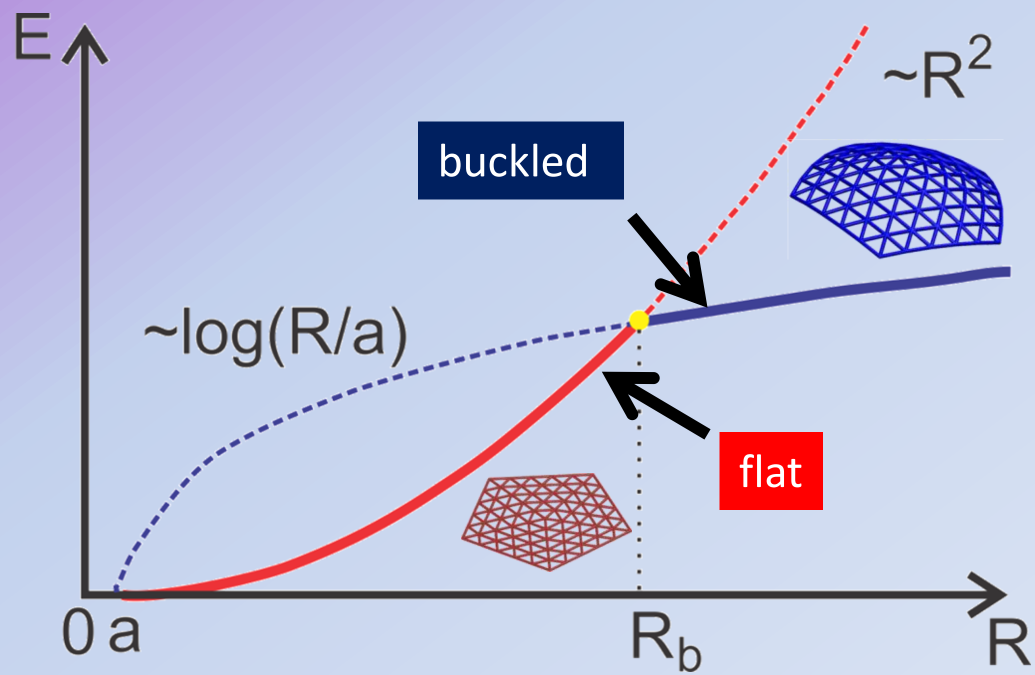
Lidmar, et al., PRE (2003)

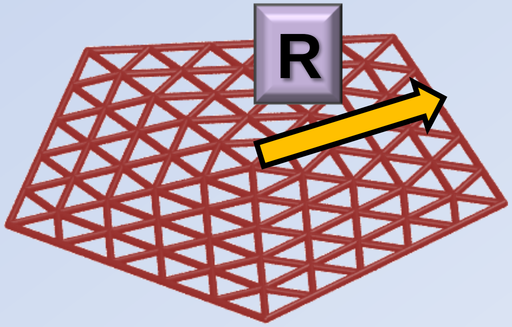
Buckling occurs if $\gamma = \frac{YR^2}{\kappa} \propto \left(\frac{R}{h}\right)^2 \approx 10^2$ Seung & Nelson (1988)

For $h \to 0$ sphere always buckles into an isocahedron.

Mechanics of buckling of a single disclination

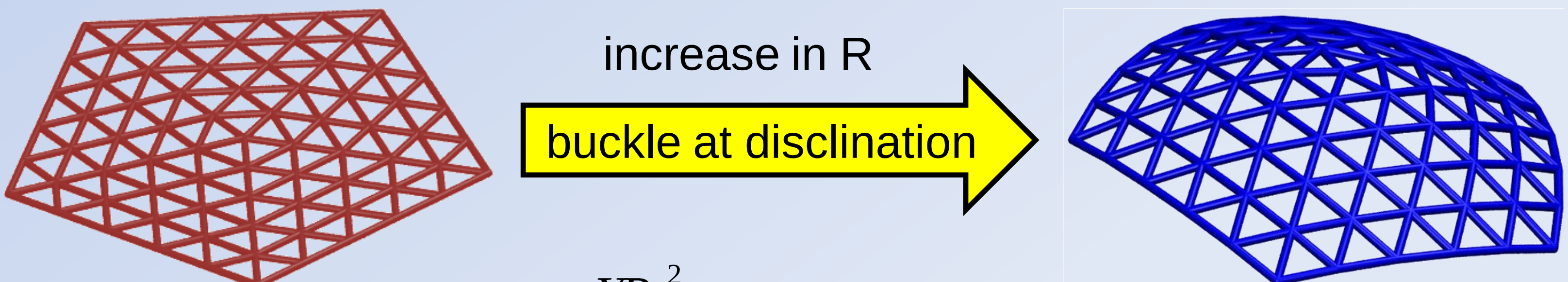
Disclination defects are loaded with strain.





bending energy

stretching energy



$$\gamma = \frac{YR^2}{\kappa} \geq 154$$

Seung & Nelson, PRA (1988)

Y – Young's modulus, κ – bending rigidity

VESICLE IS MADE OF FLAT FACETS THAT ARE SEPARATED BY SOFTER GRAIN BOUNDARIES ALONG WHICH LOCAL CRYSTALLINE LATTICES ARE MISMATCHED.

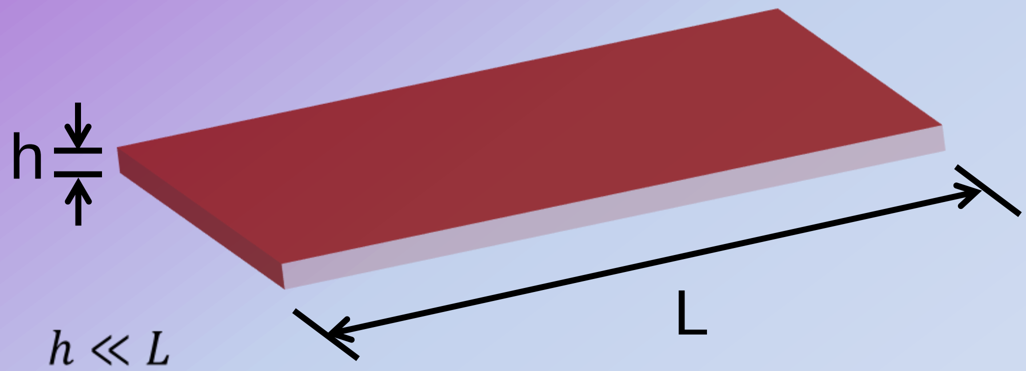
Model the vesicle within the continuum theory of elasticity of thin plates and shells.

Represent vesicle as a two-component system:

- hard facets
- soft boundaries

Eliminate possibility of buckling into an icosahedron by choosing appropriate reference metric.

Use the elastic model for two-component 2D thin sheets



Kirchoff-Love assumptions:

1. Body is in a state of plane stress.
2. Points remain on the same normal after deformation.

Elastic energy:

$$\alpha, \beta = 1,2$$

$$E_{el}^{2D} = E_{bend} + E_{stretch} = \int_S dx_1 dx_2 \sqrt{|G|} A^{\alpha\beta\gamma\delta} \left(\frac{h}{2} u_{\alpha\beta} u_{\gamma\delta} + \frac{h^3}{24} b_{\alpha\beta} b_{\gamma\delta} \right)$$

Isotropic material:

(Koiter, 1966)

$$E_{stretch} = \int_S \frac{Yh}{2(1+\nu)} \left(\frac{\nu}{1-\nu} u_\alpha^\alpha u_\beta^\beta + u_\alpha^\beta u_\beta^\alpha \right)$$

Y – Young's modulus
ν – Poisson's ratio

$$E_{bend} = \int_S \frac{Yh}{12(1+\nu)} \left(\frac{2}{1-\nu} H^2 - K \right)$$

H – mean curvature
K – Gaussian curvature

Thickness h is position dependent.

Discrete model – triangulation of the surface

Stretching

$$\hat{g} = \begin{pmatrix} \boldsymbol{a}\cdot\boldsymbol{a} & \boldsymbol{a}\cdot\boldsymbol{b} \\ \boldsymbol{a}\cdot\boldsymbol{b} & \boldsymbol{b}\cdot\boldsymbol{b} \end{pmatrix} \qquad \hat{G} = \begin{pmatrix} \boldsymbol{a}'\cdot\boldsymbol{a}' & \boldsymbol{a}'\cdot\boldsymbol{b}' \\ \boldsymbol{a}'\cdot\boldsymbol{b}' & \boldsymbol{b}'\cdot\boldsymbol{b}' \end{pmatrix}$$

Introduce tensor: $\hat{F} = \hat{g}^{-1}\hat{G} - \hat{I}$

$$E_{stretch} = \sum_{T} \frac{Yh}{8(1+\nu)} \left(\frac{\nu}{1-\nu} \left(Tr\hat{F}_T \right)^2 + Tr\left(\hat{F}_T^{\,2} \right) \right)$$

(Parrinello&Rahman, 1981)

Set g to be that of the initial spherical configuration.

Removes stress due to topological defects.

Bending

$$E_{bend} = \int_S \left\{ \kappa \left(2H^2 - K \right) + \kappa \nu K \right\}$$

$$\kappa = \frac{1}{12} \frac{Yh^3}{1-\nu^2}$$

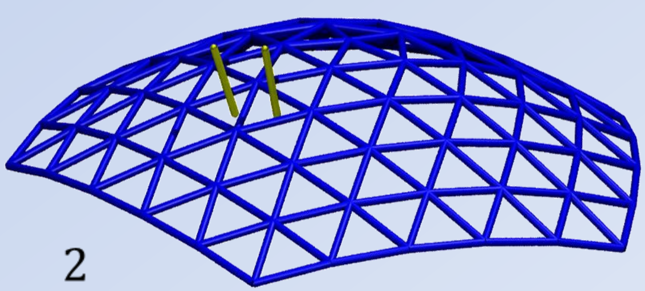
$$\int_S \kappa \left(2H^2 - K \right)$$

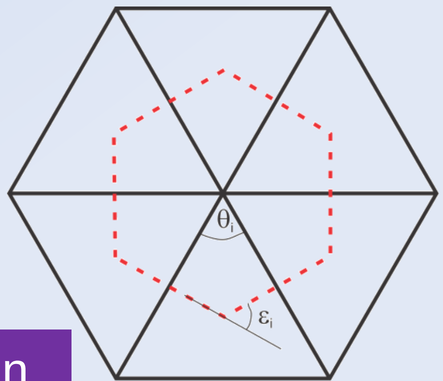
$$\int_S \kappa \nu K$$

(Seung&Nelson, 1988)

$$\tilde{\kappa} = \sum_{T_j n.n. T_i} \left(1 - \vec{n}_{T_i} \cdot \vec{n}_{T_j} \right)$$

$$\sum_i \kappa \nu \left(2\pi - \sum_j \theta_j \right)$$





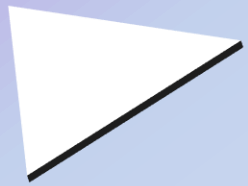
$$\tilde{\kappa} = \frac{2}{\sqrt{3}} \kappa$$

Simulated annealing Monte Carlo optimization

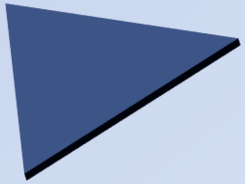
Simulated annealing Monte Carlo optimization

random triangulation

Assign types to triangles



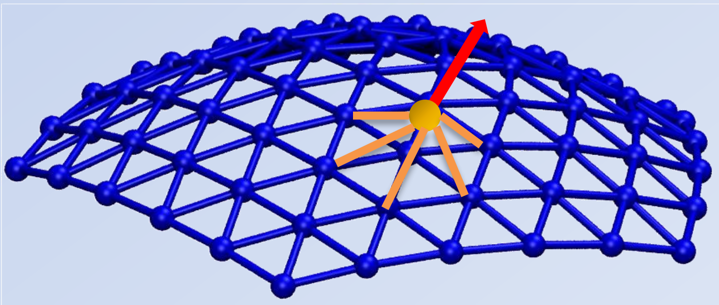
hard



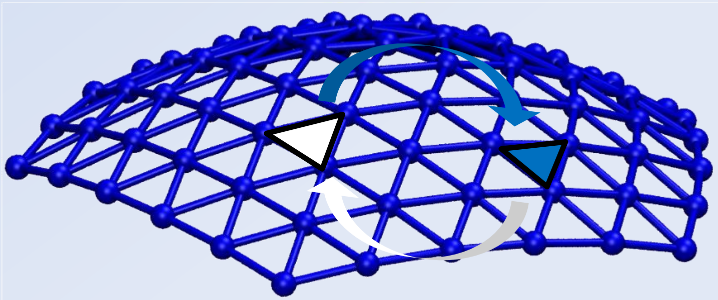
soft

Bending rigidity and stretching modulus are related → Relative thickness and fraction of components

Monte Carlo moves



vertex move

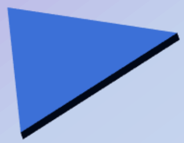


triangle type swap

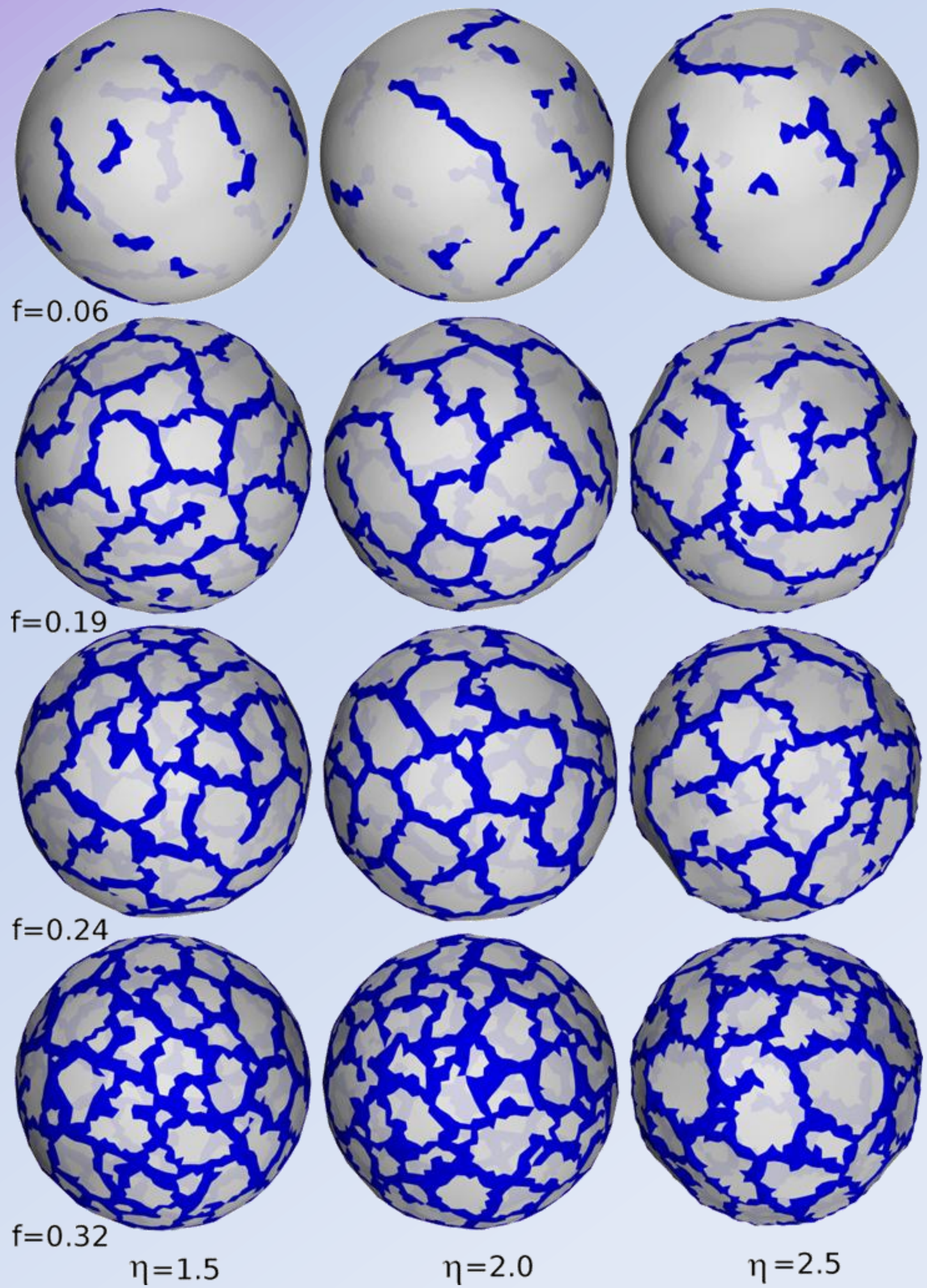
Set reference metric to be that of the initial spherical configuration.

Results

hard



soft

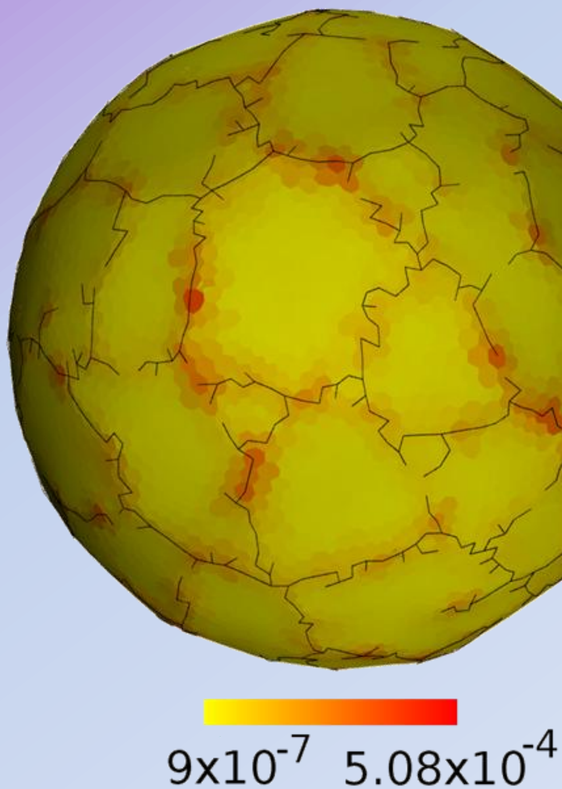


$$\eta = \frac{h_{hard}}{h_{soft}}$$

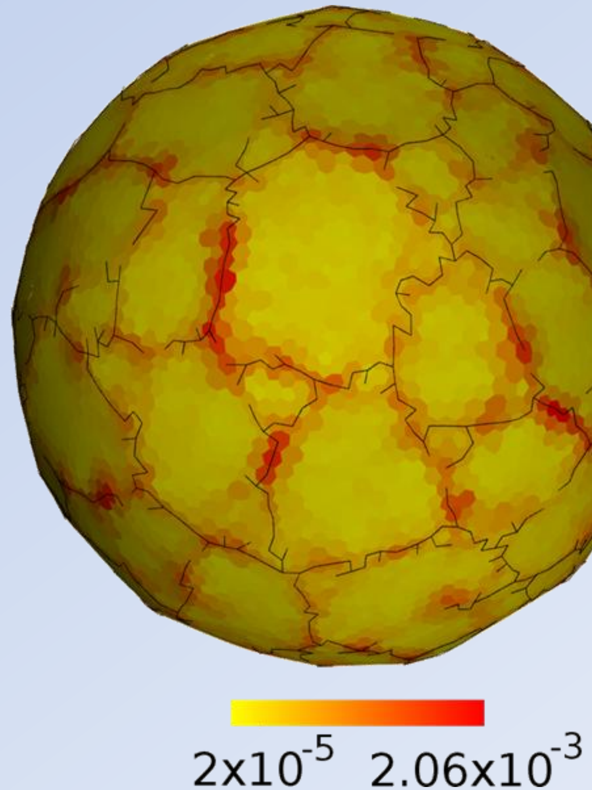
f – fraction soft component

≈10,000 triangles

Elastic energy distribution



$E_{stretch}$

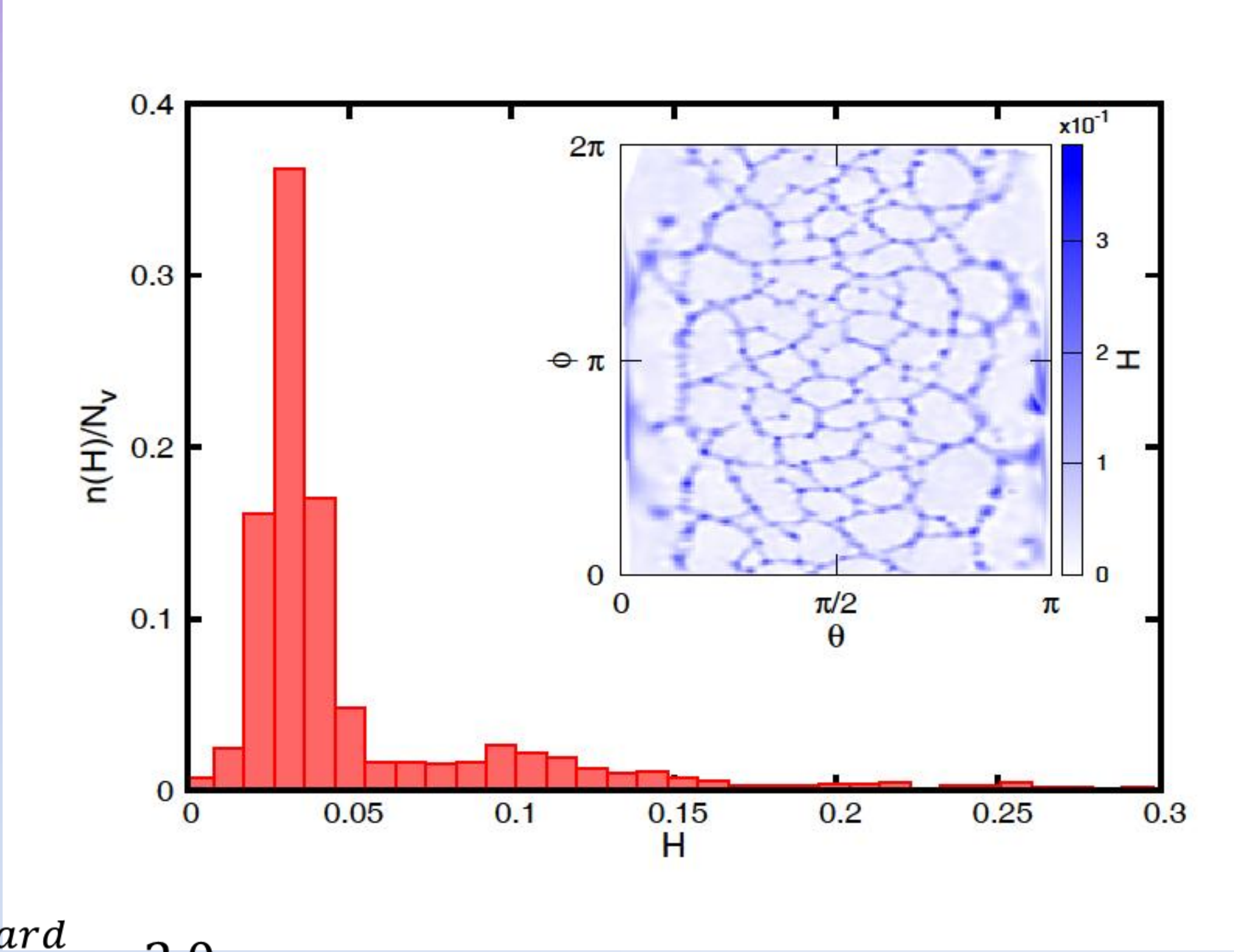


E_{bend}

f = 0.25

$$\eta = \frac{h_{hard}}{h_{soft}} = 2.0$$

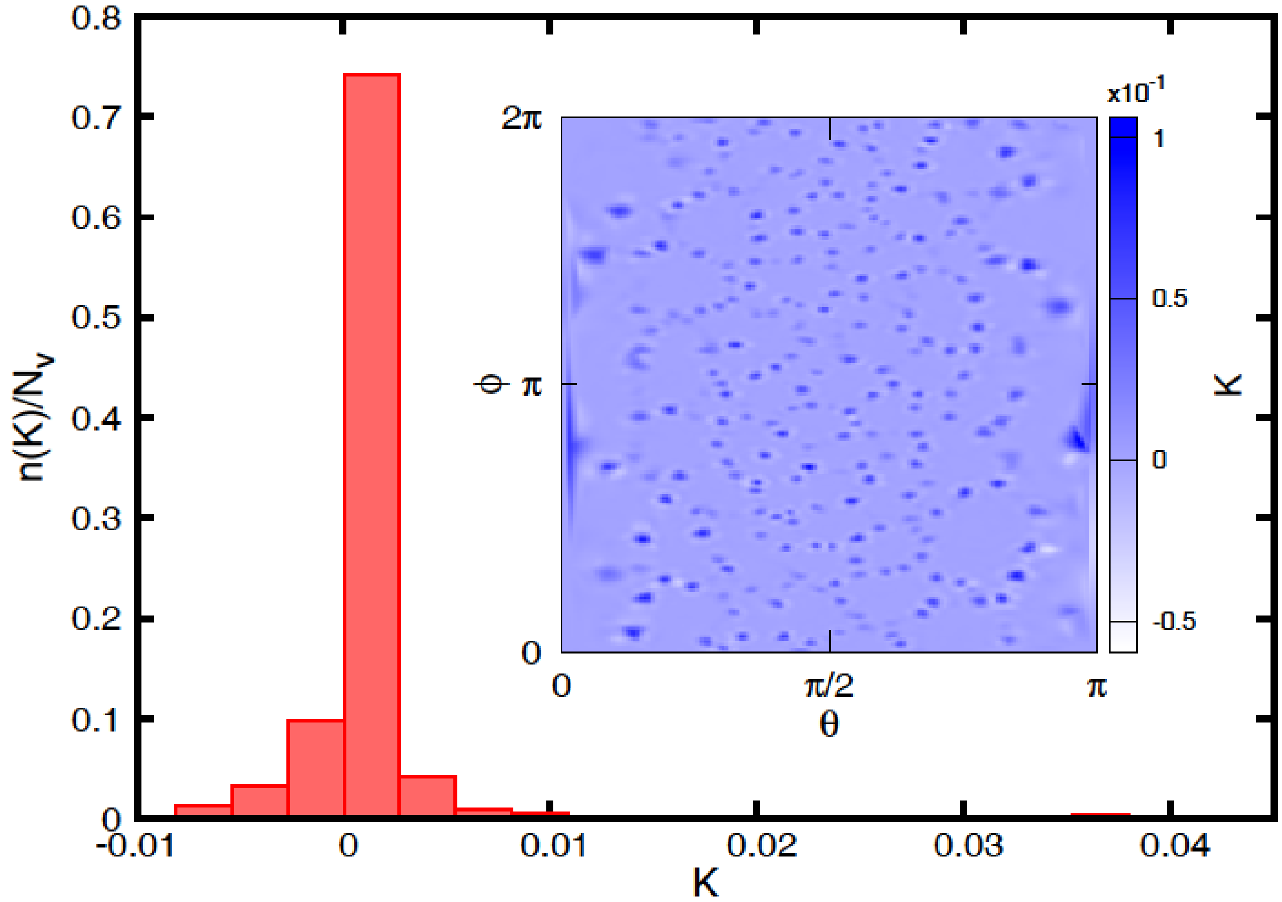
Mean curvature distribution



$$\eta = \frac{h_{hard}}{h_{soft}} = 2.0$$

f = 0.25

Gaussian curvature distribution



$$\eta = \frac{h_{hard}}{h_{soft}} = 2.0$$

f = 0.25

Summary

- Developed a continuum elastic model for a crystalline vesicle with grain boundaries.
- Vesicle is modeled as a two component medium with hard facets and soft boundaries.
- Elastic approach allows for the separation of the effects produced by topological defects.
- Model predicts that the vesicle facets even without explicitly present topological defects.
- A novel, grain boundary driven faceting mechanism.

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