The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
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**2254-1**

**Workshop on Sphere Packing and Amorphous Materials**

***25 - 29 July 2011***

**Ancient History: from Linear polymers to tethered surfaces**

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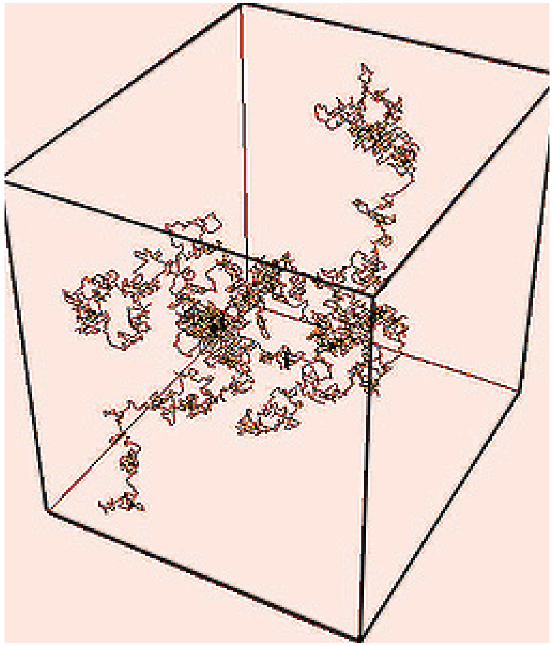
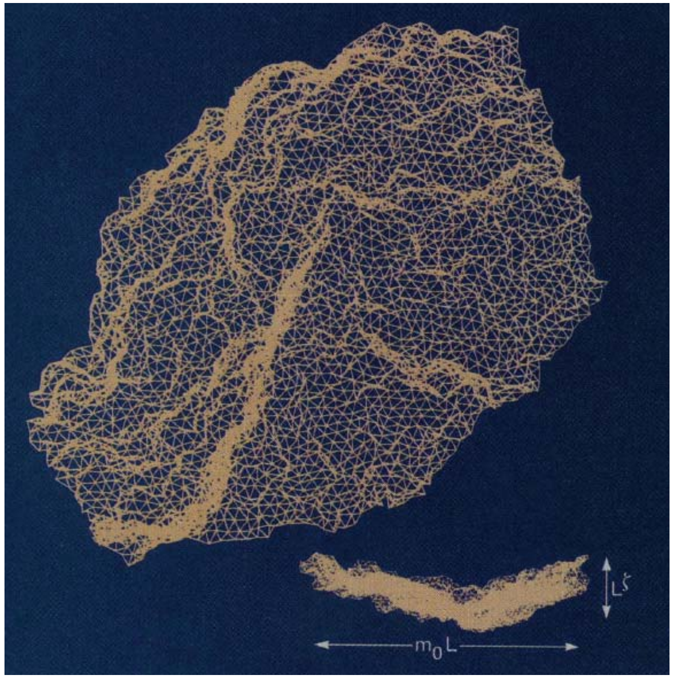
## *Ancient History: from linear polymers to tethered surfaces*

- By the 1990's, theories of linear polymer chains in a good solvent had been generalized to include the statistical mechanics of flexible sheet polymers





F. Abraham and drn, Science 249, 393 (1990)

- Remarkably, "tethered surfaces" with a shear modulus are able to resist thermal crumpling and exhibit a low temperature flat phase!!

# *Pressurized Amorphous Shells, Pollen Grains and Thermal Fluctuations* *(D. Nelson, Harvard)*

**Shell theory: Foppl-von Karman equations and nonlinear elasticity theory**

-- *applicaton to crumpling and folding of pollen grains*

E. Katifori
J. Dumais
E. Cerda
S. Alben

**Flat membranes: elasticity and statistical mechanics**

--*thermal fluctuations lead to scale-dependent elastic constants*

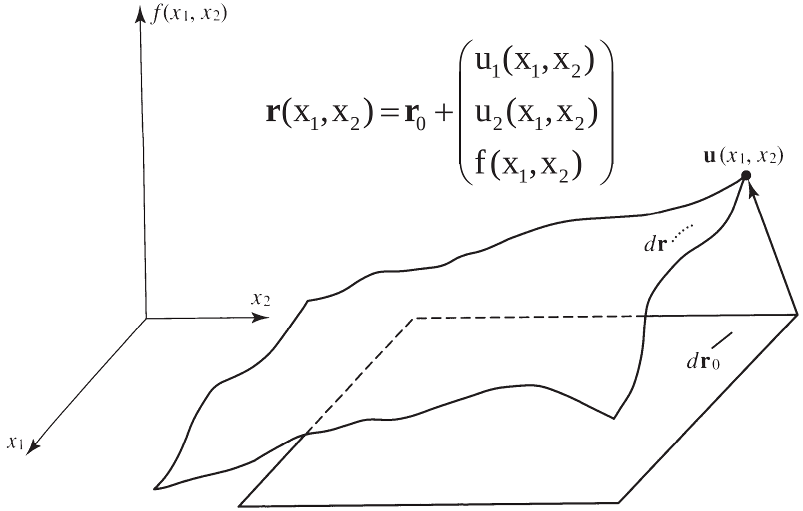
**Shells with thermal fluctuations: deformations of pressurized spherical shells**

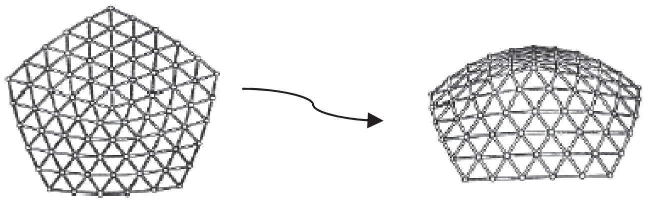
-- *Renormalized bending rigidity, Young's modulus and pressure all diverge as sphere radius* $R \to \infty$*!*

-- *Anomalous height fluctuation and indentation experiments*

J. Paulose
G. Gompper
G. Vliegenhart

## *Physics at T=0 is described by the Foppl-von Karman equations (~1904)*



$$E = \frac{1}{2}\int d^2x[\kappa(\nabla^2 f(\vec{x}))^2 + 2\mu u_{ij}^2(\vec{x}) + \lambda u_{kk}^2(\vec{x})]$$

$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j}\right]$$

*Take functional derrivatives and minimize to get …*

***Foppl-von Karman equations***

$$\begin{cases} \kappa\nabla^4 f = \dfrac{\partial^2\chi}{\partial y^2}\dfrac{\partial^2 f}{\partial x^2} + \dfrac{\partial^2\chi}{\partial x^2}\dfrac{\partial^2 f}{\partial y^2} - 2\dfrac{\partial^2\chi}{\partial x\partial y}\dfrac{\partial^2 f}{\partial x\partial y} \\ \dfrac{1}{Y}\nabla^4\chi = -\dfrac{\partial^2 f}{\partial x^2}\dfrac{\partial^2 f}{\partial y^2} + \left(\dfrac{\partial^2 f}{\partial x\partial y}\right)^2 \end{cases}$$

$$\sigma_{ij}(\vec{r}) = \varepsilon_{im}\varepsilon_{jn}\partial_m\partial_n\chi(\vec{r}) = 2\mu u_{ij}(\vec{r}) + \lambda\delta_{ij}u_{kk}(\vec{r})$$

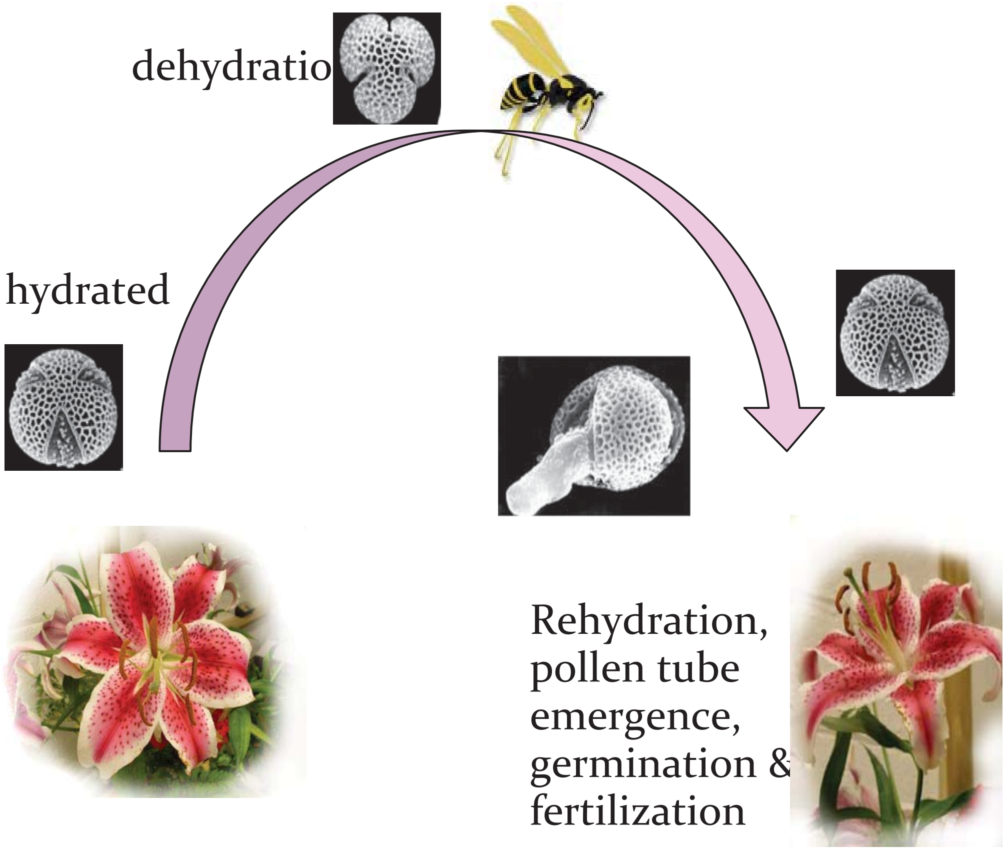
$$Y = \frac{4\mu(\mu+\lambda)}{2\mu+\lambda} = \text{Young's modulus}$$

The limit of high FvK number, $\gamma = YR^2/\kappa >> 1$, is singular, like high Reynold's number turbulence...

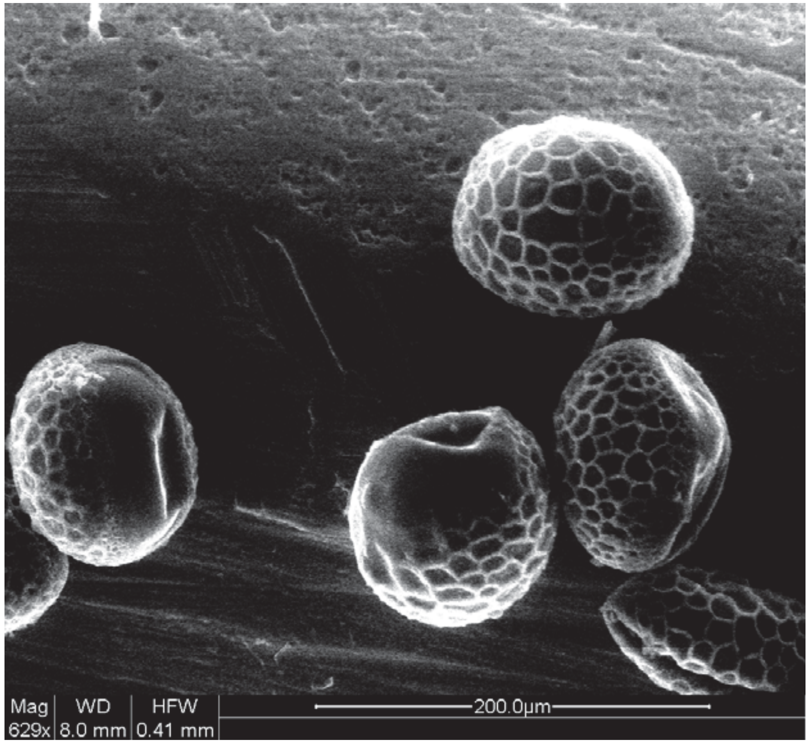
# T = 0 F-vK equations: Cumpling of lily pollen grains

*(Eleni Katifori, J. Dumais lab)*

## Life cycle of pollen

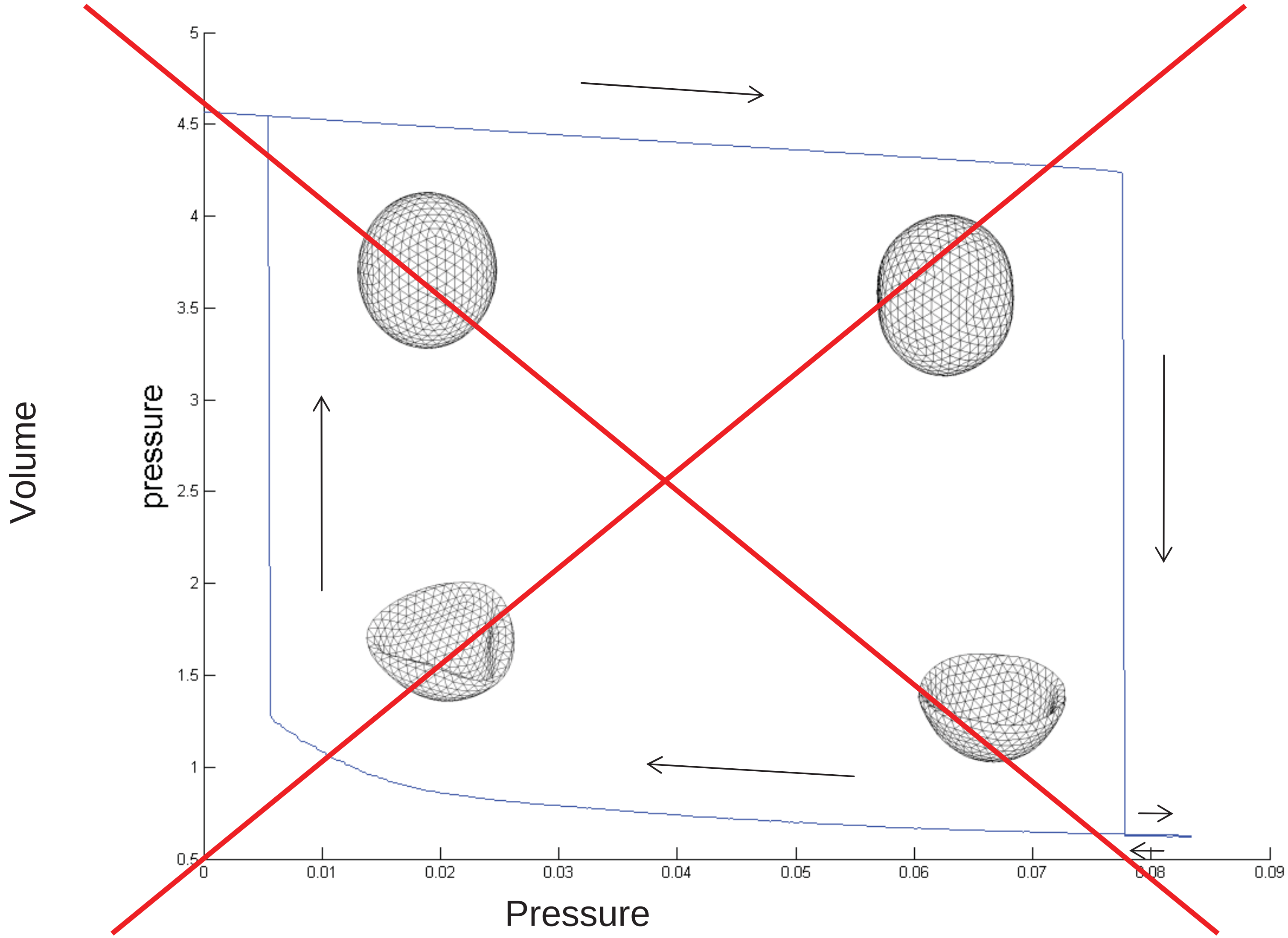



*(Witch hazel)*




*It's reversible!!!*

# Helpful to avoid hysteresis associated with the “snap-through” or buckling transition



# Modeling pollen crumpling with a weak sector

?

✱model an amorphous shell with a weak sector using a triangular mesh

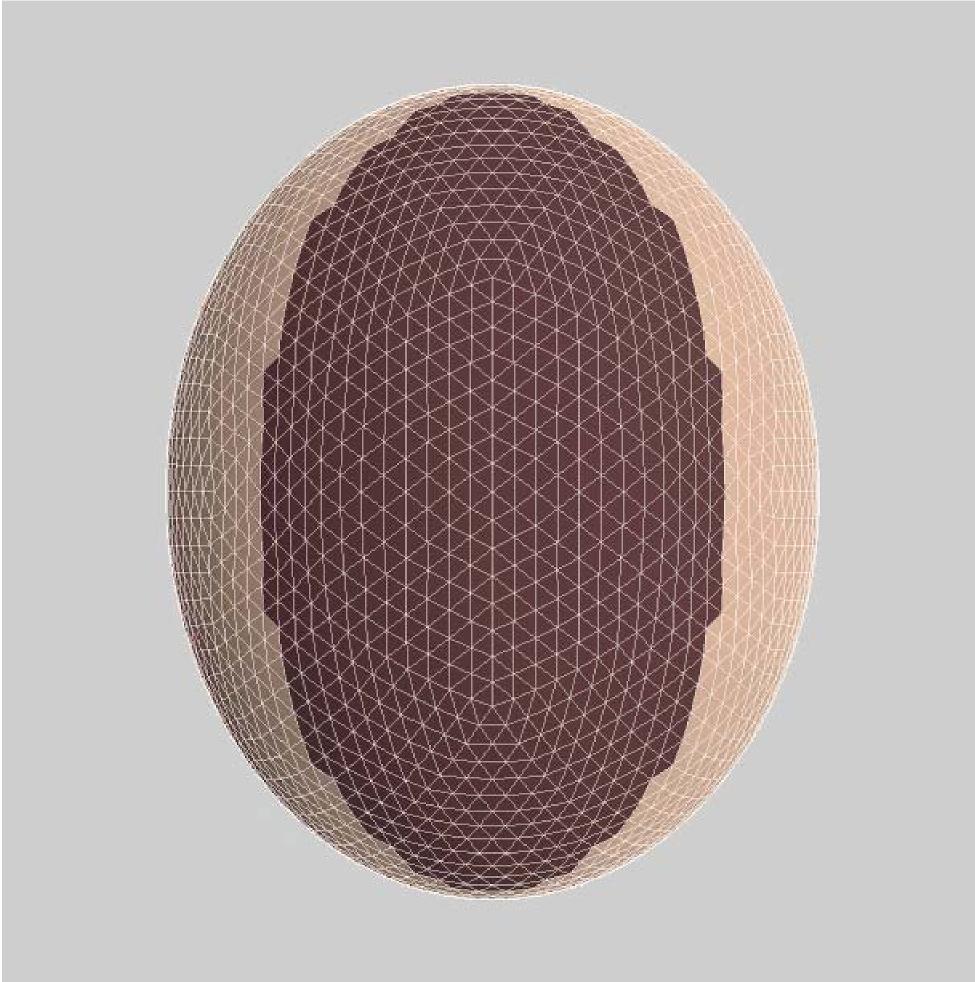
✱minimize artificial effects of the 12 disclinations by *compensating* for different bond lengths:

$$\frac{\varepsilon}{2}\sum_{<ij>}(|\vec{r}_i-\vec{r}_j|-a)^2 \rightarrow \frac{\varepsilon}{2}\sum_{<ij>}(|\vec{r}_i-\vec{r}_j|-a_{ij})^2$$

✱model dehydration by a soft constraint of ever decreasing volumes

✱introduce spontaneous curvature

# Simulation of crumpling/folding upon dehydration of the lily pollen grain



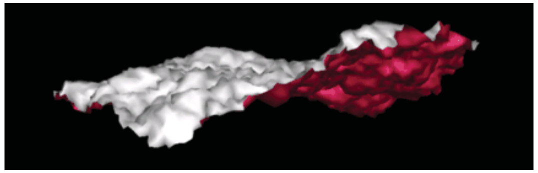
# *Renormalization of Elastic Parameters in Thermally Excited Sheet Polymers I*

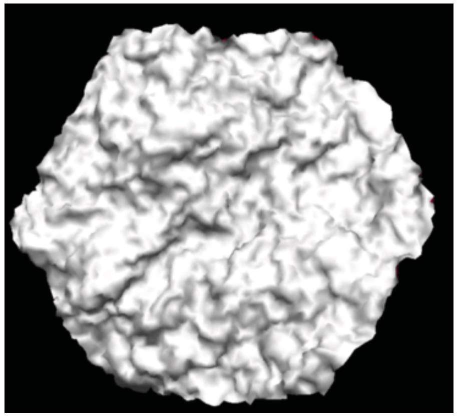
*L. Peliti & drn (~1987)*
*J. Aronovitz and T. Lubenksy*
*P. Le Doussal and L. Radzihovsky*

$$E = \frac{1}{2}\int d^2x[\kappa(\nabla^2 f(\vec{x}))^2 + 2\mu u_{ij}^2(\vec{x}) + \lambda u_{kk}^2(\vec{x})]$$

$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j}\right]$$

$$Z = \int \mathcal{D}\vec{u}(x_1,x_2)\int \mathcal{D} f(x_1,x_2)\exp(-F/k_BT)$$





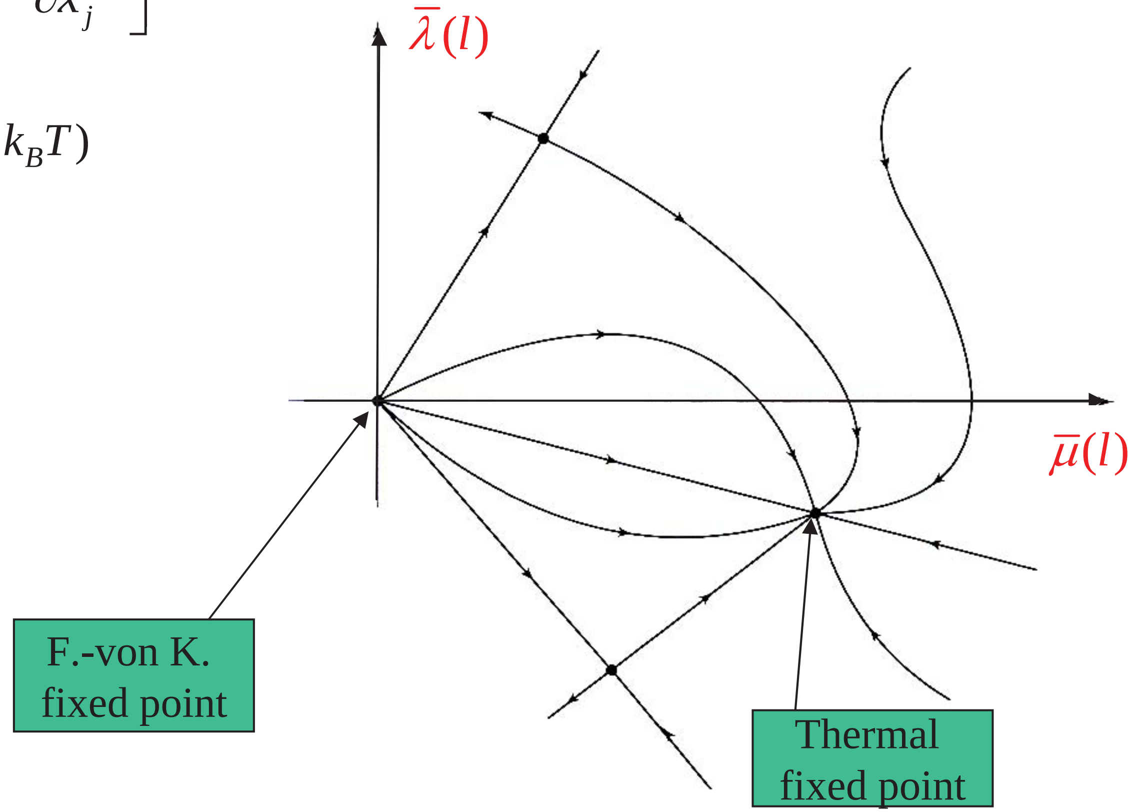
Farid Abraham

define running coupling constants....

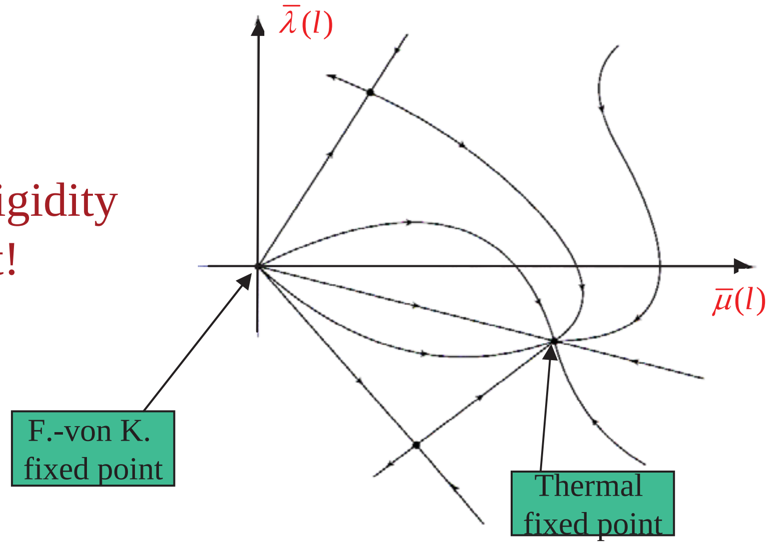
$$\bar{\mu}(l) = k_B T\mu a_0^2/\kappa^2; \qquad \bar{\lambda}(l) = k_B T\lambda a_0^2/\kappa^2$$

Young's modulus is

$$Y(l) = \frac{4\mu(l)[\mu(l)+\lambda(l)]}{2\mu(l)+\lambda(l)}$$



# *Renormalization of Elastic Parameters in Thermally Excited Sheet Polymers II*



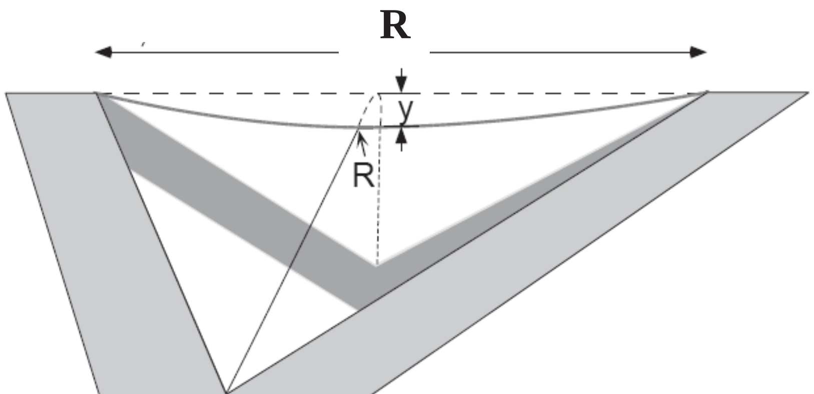

In the presence of thermal fluctuations, the bending rigidity and Young's modulus become strongly scale-dependent!

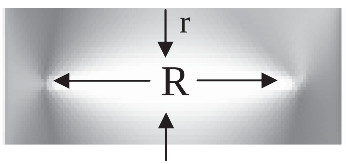
$$\kappa_R(l) \approx \kappa(l/l_{th})^{\eta}, \qquad Y_R(l) \approx Y(l/l_{th})^{-\eta_u}$$

$$\eta \approx 0.75 \qquad \eta_u \approx 0.36$$

$$l_{th} = \sqrt{4\pi^3\kappa^2/(k_B T Y)} \qquad l_{th} \approx 40nm$$

*Consider, e.g., the size r(R) and crease energy E(R) of a bent surface….*




without thermal fluctuations (F-vK limit)

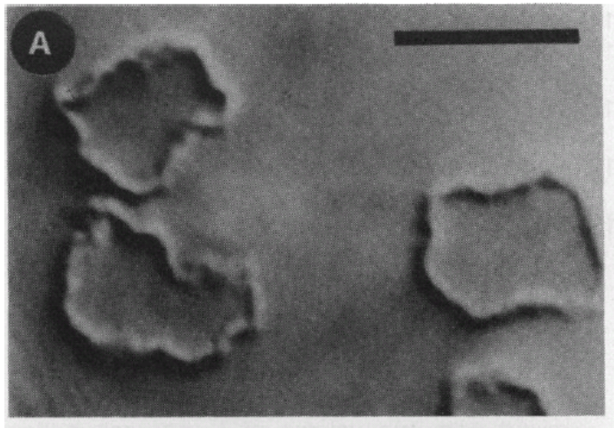
$r \propto R^{2/3}, E \propto R^{1/3}$, (T. Witten et al.)

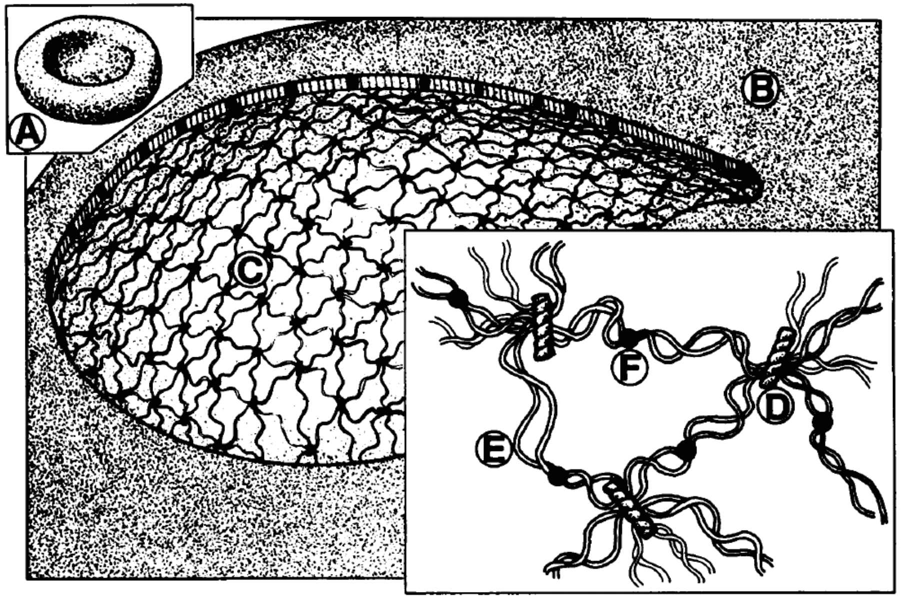
with thermal fluctuations....

$r \sim R^{0.76}$, $E \sim R^{0.74}$

# *Anomalous Fluctuations in the Spectrin Skeleton of Red Blood Cells*

C. Schmidt et al., Science **259**, 952 (1993)



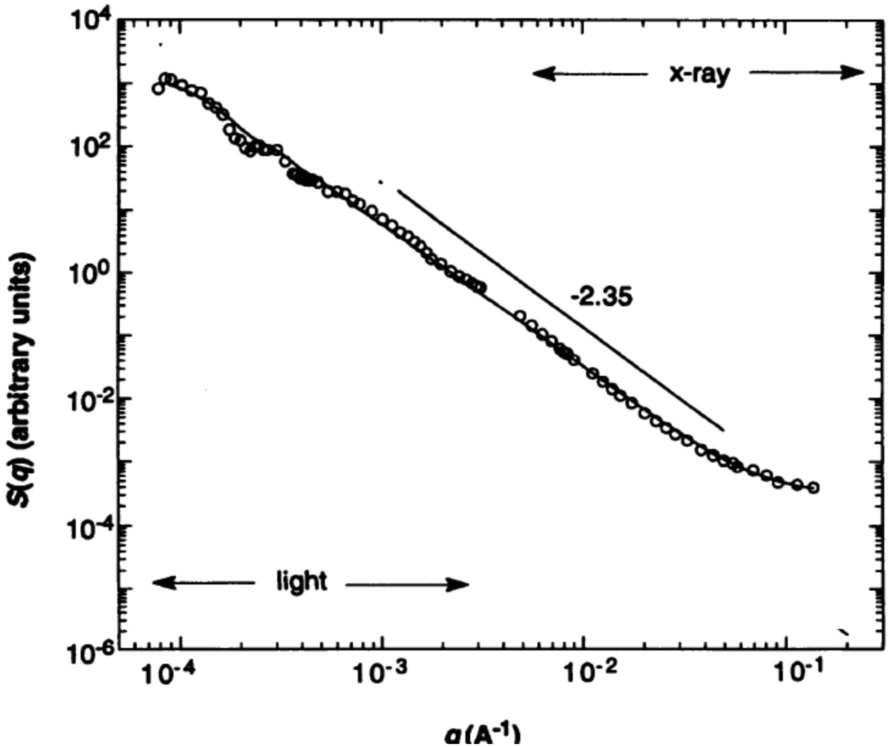




Power law scaling expected for the radially averaged structure of a dilute concentration of spectrin membranes

$$S(q) \sim 1/q^{2+\eta/2}$$

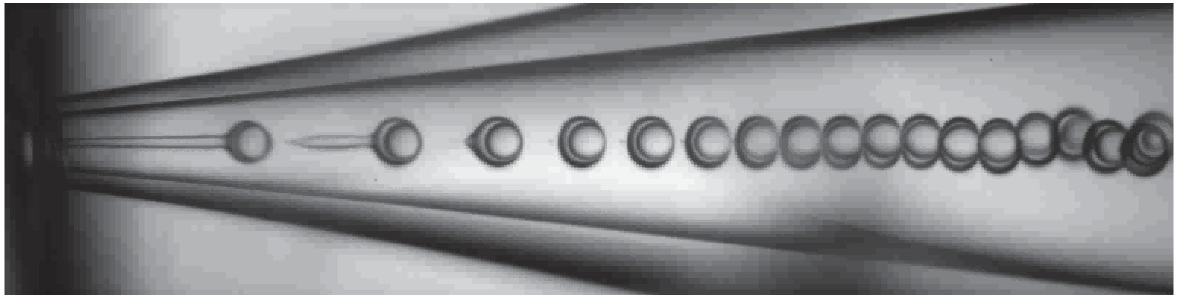
$$\sim 1/q^{2.35}$$

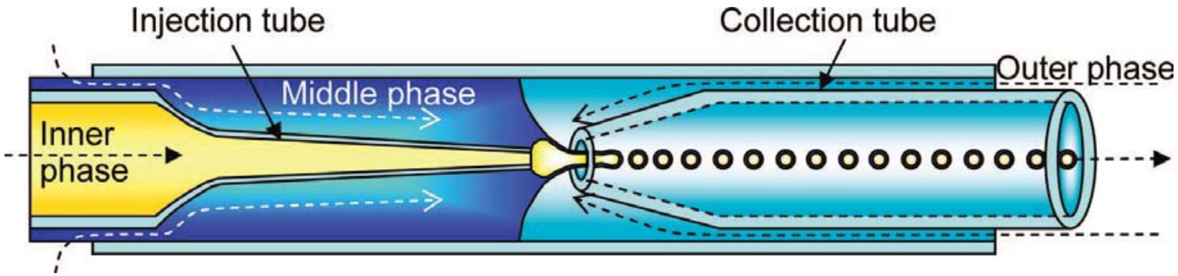
$$\rightarrow \quad \eta = 0.70 \quad (\eta_{theory} = 0.75)$$



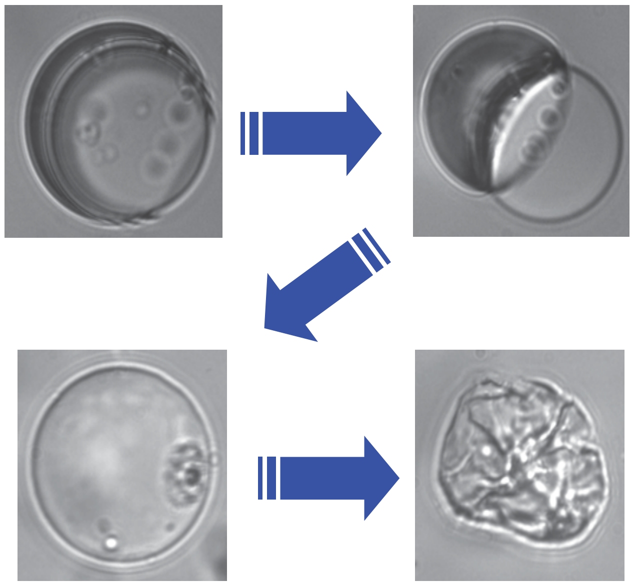
# *Microfluidic fabrication of polymersomes*

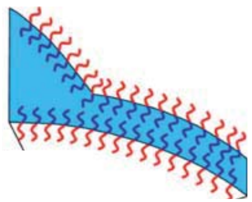
Shum et al., **JACS 2008**, *130*, 9543






- ➢Start with “double emulsion” of ampiphillic diblock copolymers (PEG-b-PLA).
- ➢Tune wetting properties to eject thin *crystalline* bilayer shells.
- ➢Result is a delivery vehicle for dugs, flavors, colorings and fragrances that can be osmotically crushed.





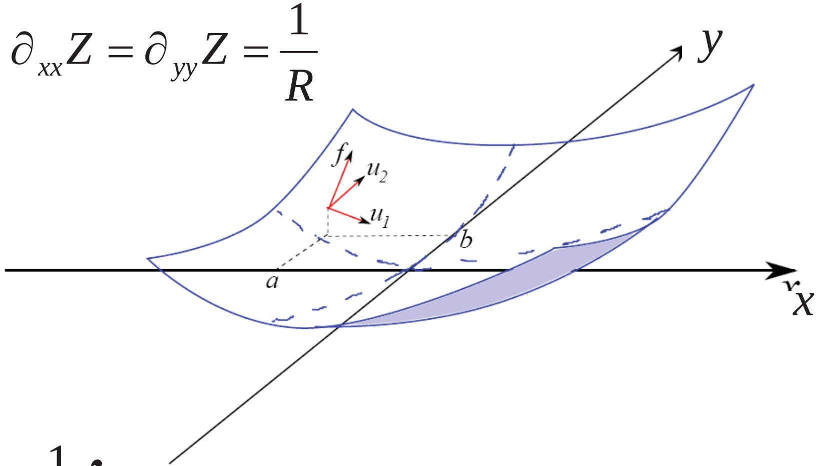
*Polymersome Radius,*
*R = 30 μm*
*Thickness, h = 10 nm*

$$\gamma = \text{Foppl-von Karman number}$$
$$\approx 9(R/h)^2 = 10^7\,!$$

Initial shape: $z = Z(x, y)$

## To address similar questions for spherical shells, we use shallow shell theory….

$$\partial_{xx} Z = \partial_{yy} Z = \frac{1}{R}$$




$$\begin{pmatrix} x \\ y \\ Z(x,y) \end{pmatrix} \rightarrow \begin{pmatrix} x + u_x(x,y) - \partial_x Z(x,y) f(x,y) \\ y + u_y(x,y) - \partial_y Z(x,y) f(x,y) \\ Z(x,y) + f(x,y) \end{pmatrix}$$

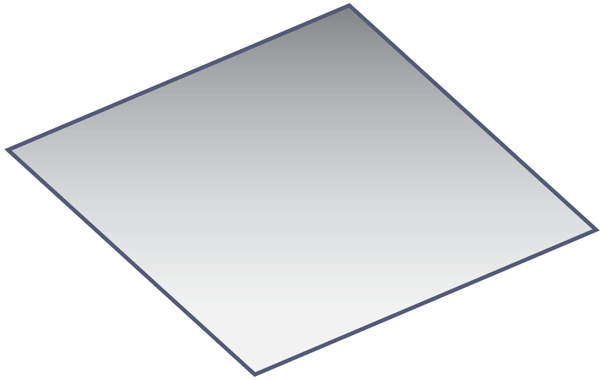
$$E = \frac{1}{2} \int d^2 x [\kappa (\nabla^2 f(\vec{x}))^2 + 2\mu u_{ij}^2(\vec{x}) + \lambda u_{kk}^2(\vec{x})]$$

$$ds'^2 = ds^2 + 2u_{ij} dx_i dx_j$$

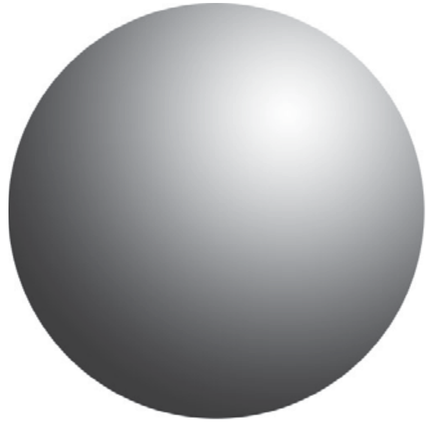
$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j}\right]$$

$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j} - \delta_{ij}\frac{f}{R}\right]$$

# Membranes vs. shells: Curved is different



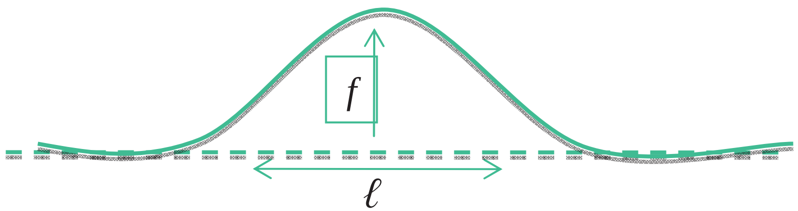
*Bending rigidity*
*Young's modulus*



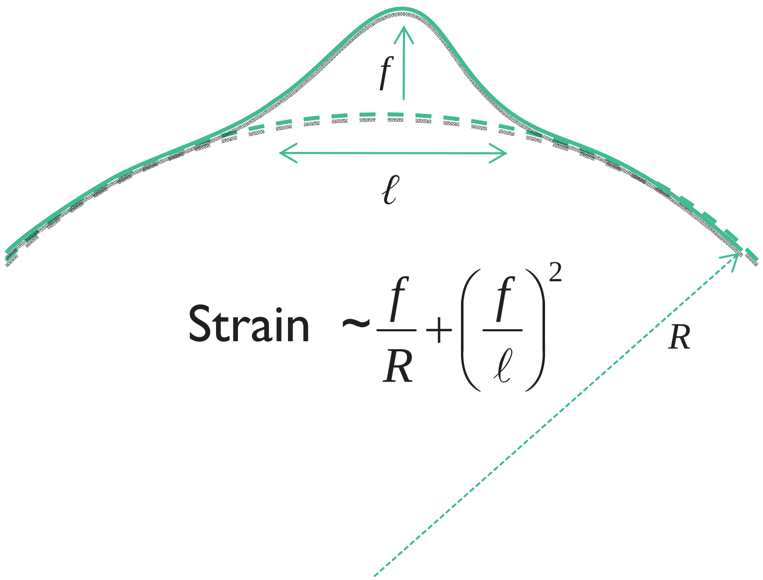
$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j}\right]$$

**vs.**

$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j} - \delta_{ij}\frac{f}{R}\right]$$




Strain $\sim \left(\frac{f}{\ell}\right)^2$

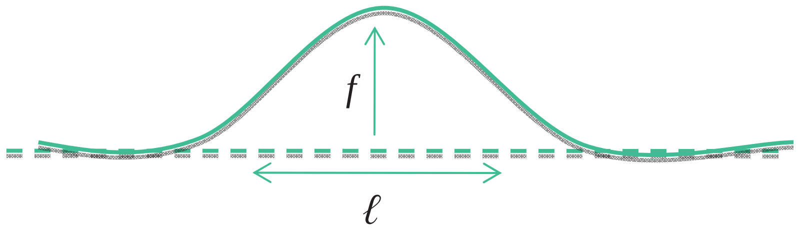



Strain $\sim \frac{f}{R} + \left(\frac{f}{\ell}\right)^2$

# Elastic length scale

$$E = \frac{1}{2}\int d^2x[\kappa(\nabla^2 f(\vec{x}))^2 + 2\mu u_{ij}^2(\vec{x}) + \lambda u_{kk}^2(\vec{x})]$$

$$u_{ij}(\vec{x}) \approx \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \cancel{\frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j}} - \delta_{ij}\frac{f}{R}\right]$$




Bending energy ~ $\kappa \dfrac{f^2}{\ell^4}$

Stretching energy ~ $\dfrac{Y}{R^2} f^2,$

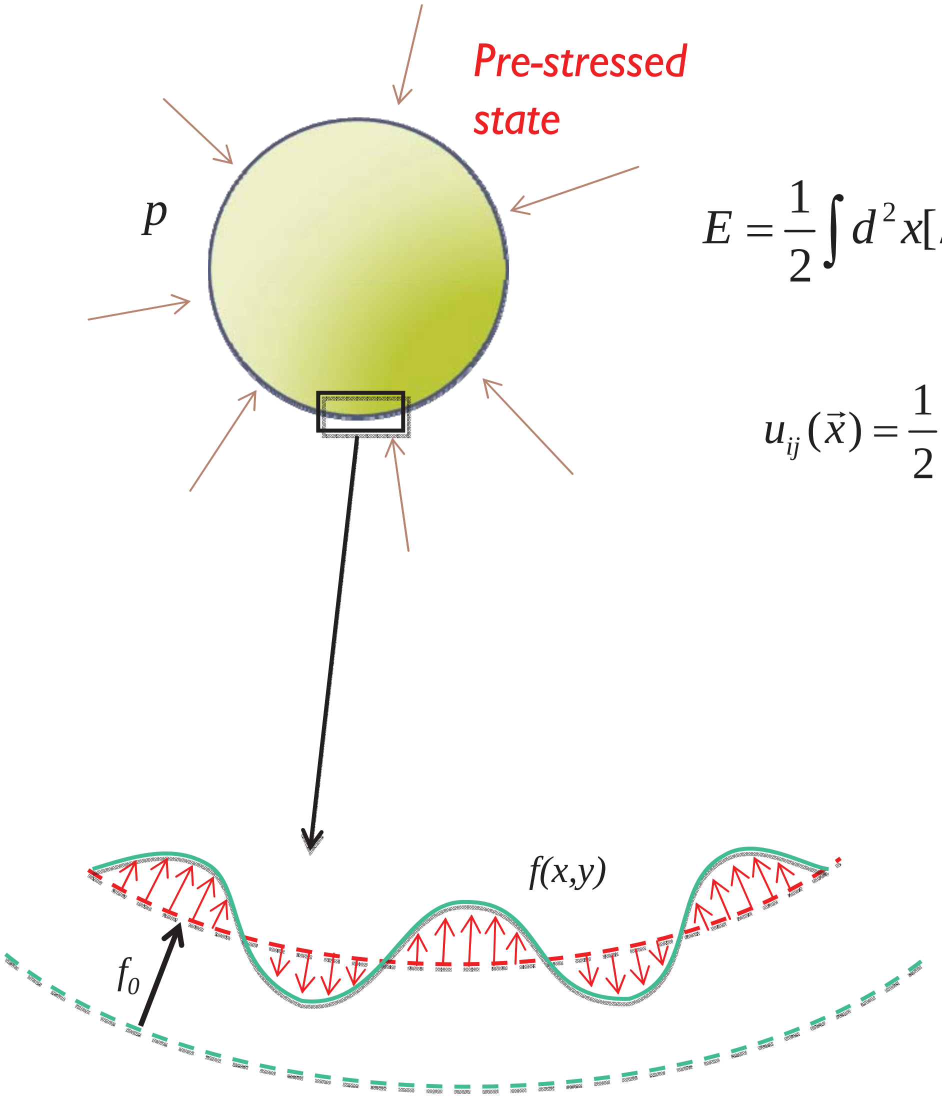
$$\left( Y = \frac{4\mu(\mu+\lambda)}{2\mu+\lambda} = \text{Young's modulus} \right)$$

$$\frac{\kappa}{\ell^4} = \frac{Y}{R^2} \Rightarrow \ell^* = \left(\frac{\kappa R^2}{Y}\right)^{1/4} = R / \gamma^{1/4}$$

$$\left( \gamma = YR^2 / \kappa = \text{Foppl-von Karman number} \right)$$

➢ ***The Föppl-von Kármán length scale $l^*$ provides an infrared cutoff for thermal fluctuations…***

# Shells under external pressure




$$E = \frac{1}{2}\int d^2x\left[\kappa(\nabla^2 f(\vec{x}))^2 + 2\mu u_{ij}^2(\vec{x}) + \lambda u_{kk}^2(\vec{x})\right] - p\int d^2x f(\vec{x})$$

$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j} - \delta_{ij}\frac{f}{R}\right]$$

- Average radius of the shell *shrinks*, both due to the pressure and to thermal fluctuations.

$$\langle f_0 \rangle = \frac{pR^2}{4(\lambda+\mu)} + \frac{R}{4}\left\langle |\nabla f|^2 \right\rangle$$

- Integrate out in-plane phonon displacements to get a (nonlinear) field theory that depends only on $f(x_1,x_2)$ …..

# Nonlinear Field Theory for Thermally Excited Shells…

- Trace out in-plane phonons and upward radial shrinkage $f_0$ …

$$F_{\text{eff}} = -k_B T \ln\left(\int D\{u_x(x,y)\}\int D\{u_y(x,y)\}\int df_0\, e^{-F/k_BT}\right)$$

New for curved membranes!

$$F_{\text{eff}} = \frac{\kappa}{2}\int d^2x (\nabla^2 f)^2 + \frac{Y}{2}\int d^2x \left(\frac{1}{2}P^{\text{T}}_{ij}\partial_i f \partial_j f - \boxed{\frac{f}{R}}\right)^2 - \boxed{\frac{pR}{4}\int d^2x |\nabla f|^2}$$

$$F_{eff} = F_0 + F_1 \quad \begin{cases} F_0 = \dfrac{1}{2}\displaystyle\int d^2x\left[\kappa(\nabla^2 f)^2 - \dfrac{pR}{2}(\vec{\nabla} f)^2 + \dfrac{Y}{R^2} f^2\right] \\ F_1 = \displaystyle\int d^2x\left[\dfrac{1}{4}P^T_{ij}(\partial_i f \partial_j f)^2 - \dfrac{f}{R}P^T_{ij}\partial_i f \partial_j f\right] \end{cases}$$

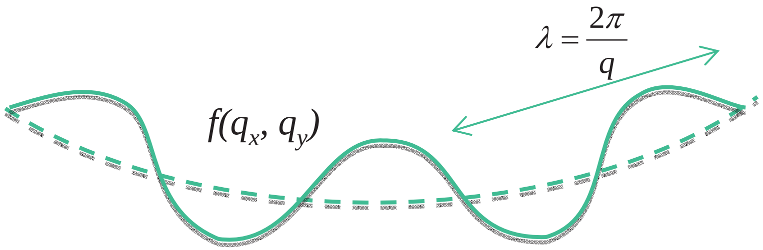
# Gaussian Fluctuation Spectrum in Fourier Space

$$F_0 = \frac{1}{2}\int d^2x\left[\kappa(\nabla^2 f)^2 - \frac{pR}{2}(\vec{\nabla} f)^2 + \frac{Y}{R^2} f^2\right]$$

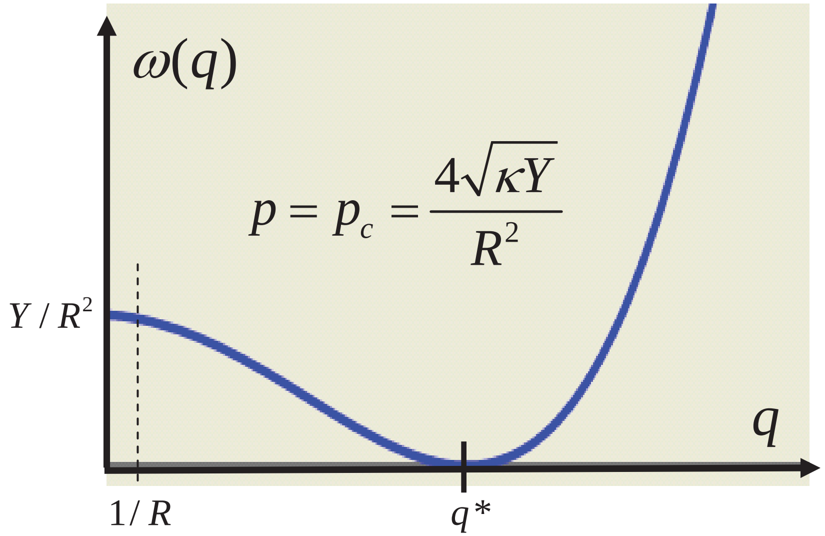
$$= \frac{1}{2}\int \frac{d^2q}{(2\pi)^2}\left(\kappa q^4 - \frac{pR}{2}q^2 + \frac{Y}{R^2}\right)\left|f_{\mathbf{q}}\right|^2$$

$$F_0 \equiv \frac{\kappa}{2}\int \frac{d^2q}{(2\pi)^2}\omega(q)\left|f_{\mathbf{q}}\right|^2, \quad \omega(q) = \frac{Y}{R^2} - \frac{pR}{2}q^2 + \kappa q^4$$

There is a soft phonon mode above a critical pressure!




$$f_{\mathbf{q}} = \int d^2x\, e^{i\mathbf{q}\cdot\mathbf{x}} f(\mathbf{x})$$

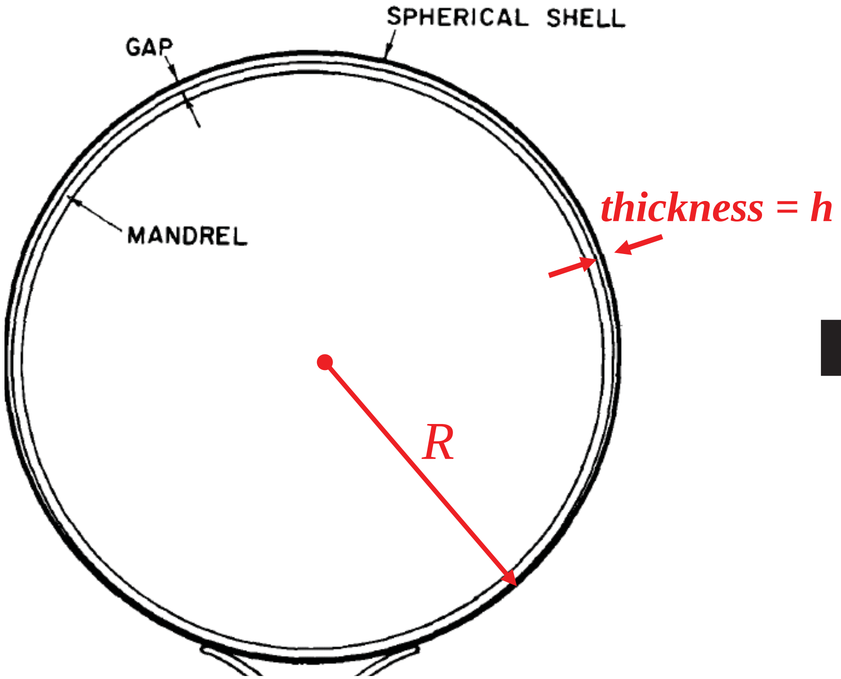


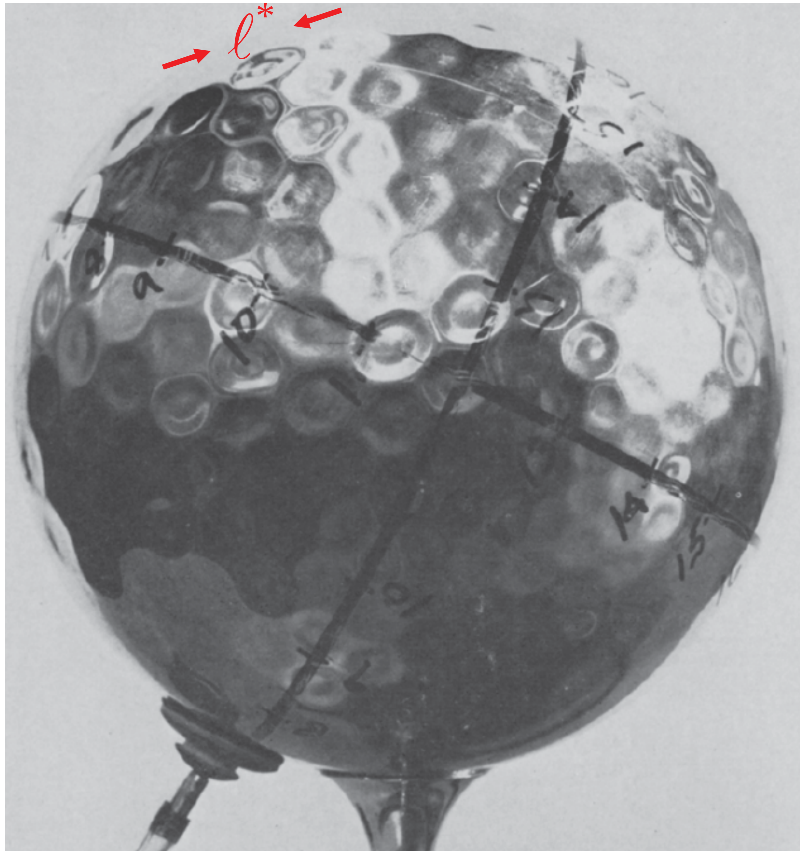

$$q^* = \gamma^{1/4}/R = 1/l^* \qquad (\gamma = YR^2/\kappa)$$

# *Macroscopic Buckling Instability Arrested by a Wax Mandrel…*

*R. L. Carlson et al.,*
*Exp. Mech.* ***7****, 281 (1962)*

$$\ell^* = R / \gamma^{1/4} \propto \sqrt{Rh} << R$$



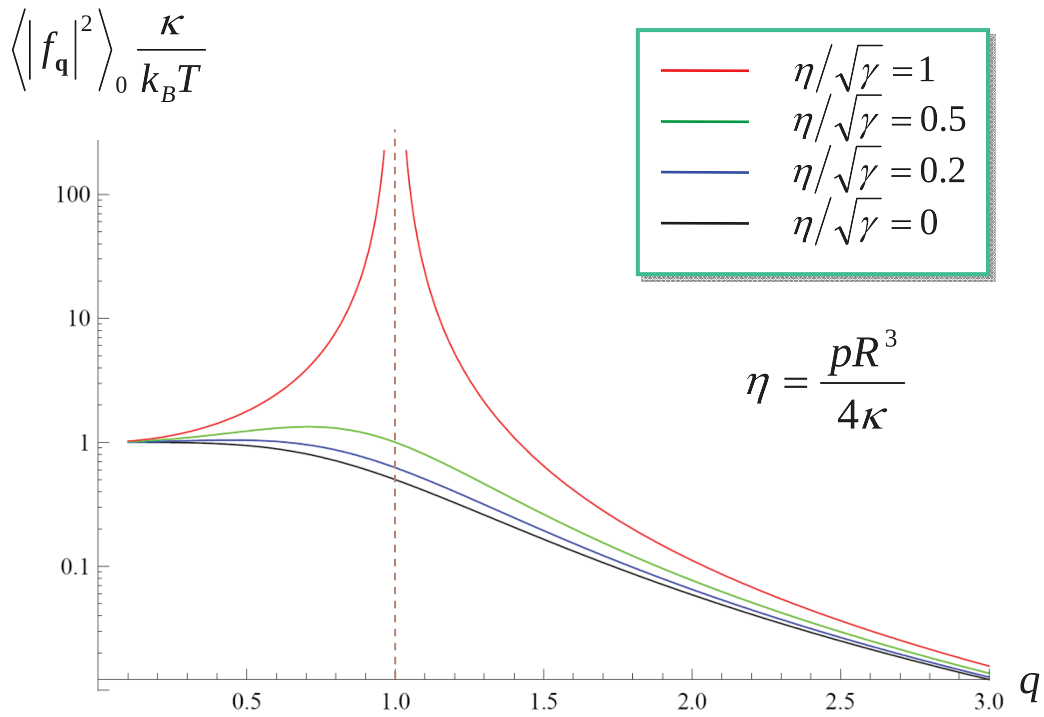

***R = 4.25 in., R/h ~ 2000***

| |
|---|
| **Classical shell theory** |

Koiter, 1963 (1945)
Hutchinson, 1967

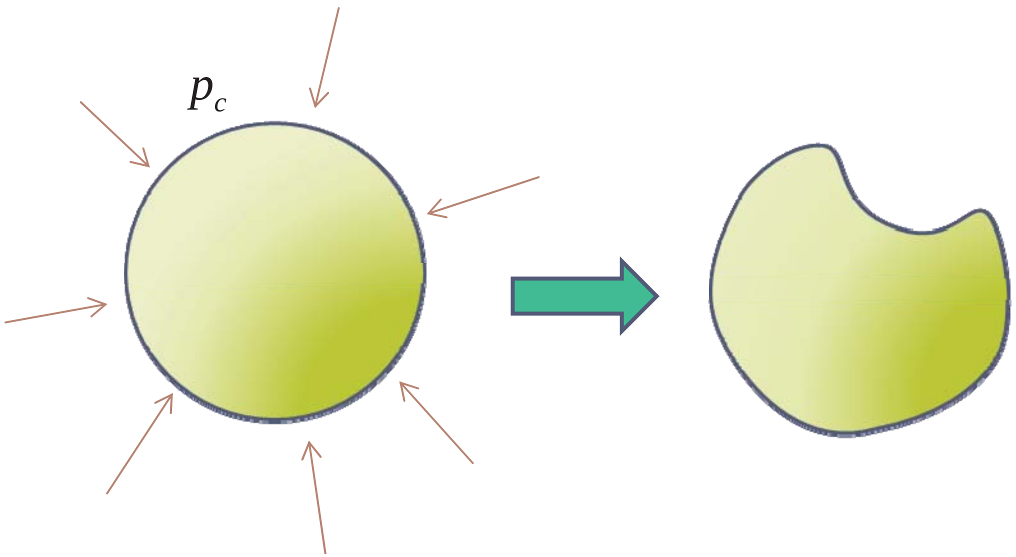
# *Singular Response to Thermal Fluctuations as $p \rightarrow p_c$*

$$\left\langle \left| f_{\mathbf{q}} \right|^2 \right\rangle_0 = \frac{k_B T}{Y/R^2 - pRq^2/2 + \kappa q^4}$$




*Modes with $q = 1/l^*$ unstable when*

$$p \rightarrow p_c \equiv \frac{4\sqrt{\kappa Y}}{R^2}$$



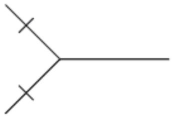
# *Evaluate effect of nonlinearities with perturbation theory…*


$$\frac{k_B T}{Y/R^2 - pRq^2/2 + \kappa q^4}$$

Bare propagator

$$\frac{Y}{2}\int d^2x \left(\frac{1}{2} P_{ij}^{\mathrm{T}} \partial_i f \partial_j f\right)^2$$

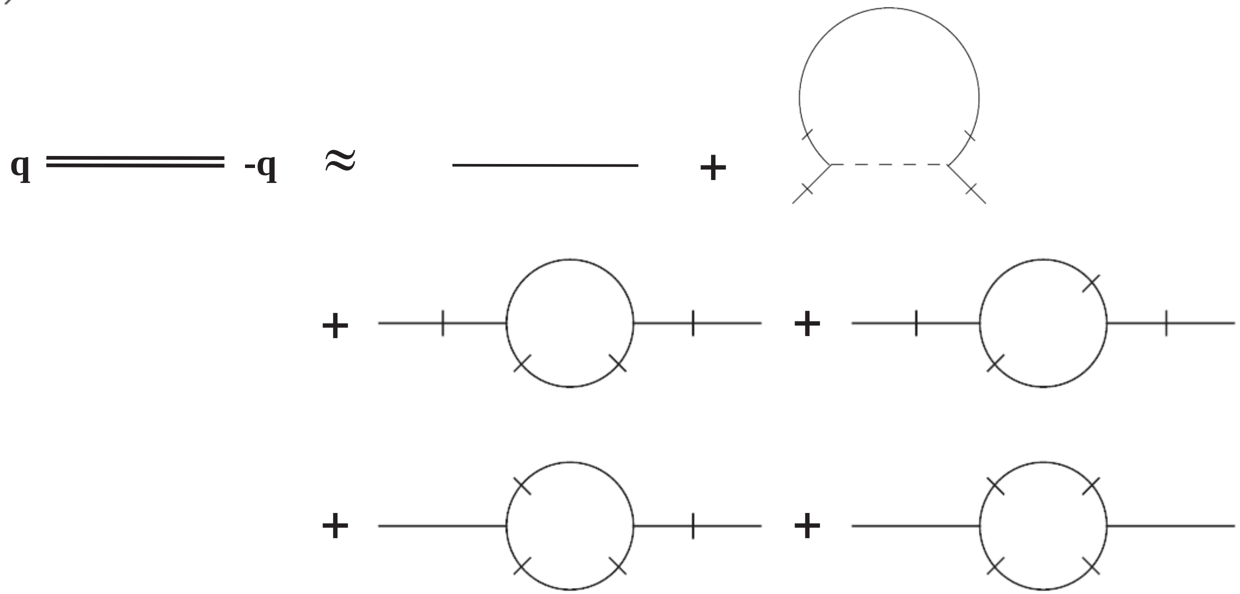
Interaction vertex



$$\frac{Y}{R}\int d^2x \left( f\, P_{ij}^{\mathrm{T}} \partial_i f \partial_j f \right)$$

Interaction vertex

$$\left\langle \left| f_{\mathbf{q}} \right|^2 \right\rangle \equiv$$




One-loop correction

# *Effective theory including thermal corrections*

$$k_B T \left\langle \left| f_{\mathbf{q}} \right|^2 \right\rangle^{-1} = \kappa q^4 + \frac{Y}{R^2} \; + \; \text{corrections}$$

$$\equiv \kappa_R q^4 - \sigma_R q^2 + \frac{Y_R}{R^2}$$

$$Y_R = Y\left(1 - \frac{3}{256}\frac{k_B T}{\kappa}\sqrt{\frac{Y R^2}{\kappa}}\right)$$

*Young's modulus is reduced*

$$\kappa_R = \kappa\left(1 + \frac{61}{4096}\frac{k_B T}{\kappa}\sqrt{\frac{Y R^2}{\kappa}}\right)$$

*Bending rigidity is increased*

$$\sigma_R = \frac{1}{12\pi}\frac{k_B T}{\kappa} Y$$

*A "negative surface tension" is generated from thermal fluctuations!*

# Effective elastic constants

$$Y_R = Y\left[1 - \frac{3}{256}\frac{k_B T}{\kappa}\left(\sqrt{\gamma} + \frac{4}{\pi}\eta\right)\right] + O(\eta^2)$$

*Young's modulus is reduced*

$$\kappa_R = \kappa\left[1 + \frac{k_B T}{\kappa}\left(\frac{61}{4096}\sqrt{\gamma} - \frac{49}{1920\pi}\eta\right)\right] + O(\eta^2)$$

*Bending rigidity is increased*

$$\sigma_R = -\frac{pR}{2} - \frac{k_B T}{R^2}\sqrt{\gamma}\left(\frac{1}{12\pi}\sqrt{\gamma} - \frac{21}{512}\eta\right) + O(\eta^2)$$

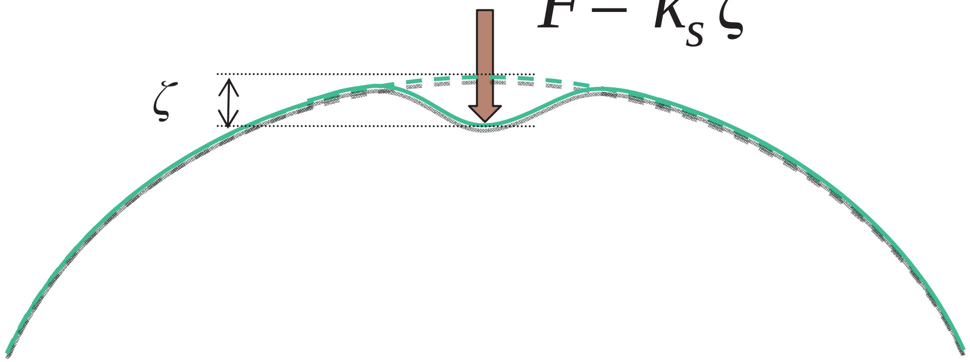
*A "negative surface tension" is thermally generated*

$\gamma = YR^2/\kappa \qquad \eta = pR^3/4\kappa$

- *Long- wavelength elastic constants become temperature, pressure and system-size dependent.*
- *Corrections* *<u>diverge</u>* *as* $\gamma, R \to \infty$*!*
- *Corrections* *<u>diverge</u>* *as* $\eta/\sqrt{\gamma} \to 1$ *,i.e.* $p \to p_c$*!*

# Corrections: Linear response

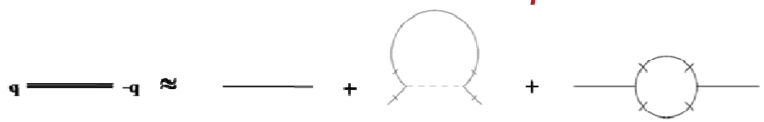
$$F = k_s \zeta$$




Response to force field $h_{\mathbf{q}}$: $\langle f_{\mathbf{q}} \rangle = \chi_{\mathbf{q}} h_{\mathbf{q}}$

Fluctuation-response theorem: $\chi_{\mathbf{q}} = \frac{1}{k_B T} \langle |f_{\mathbf{q}}|^2 \rangle$

*Use corrected spectrum!*




$$k_s = \frac{4\sqrt{\kappa Y}}{R}\left(1 - 0.007\frac{k_B T}{\kappa}\sqrt{\gamma}\right)$$

- *Nonlinearities <u>soften</u> the shell.*
- *Linear shell theory <u>breaks down</u> when correction term* $\to 1$.

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

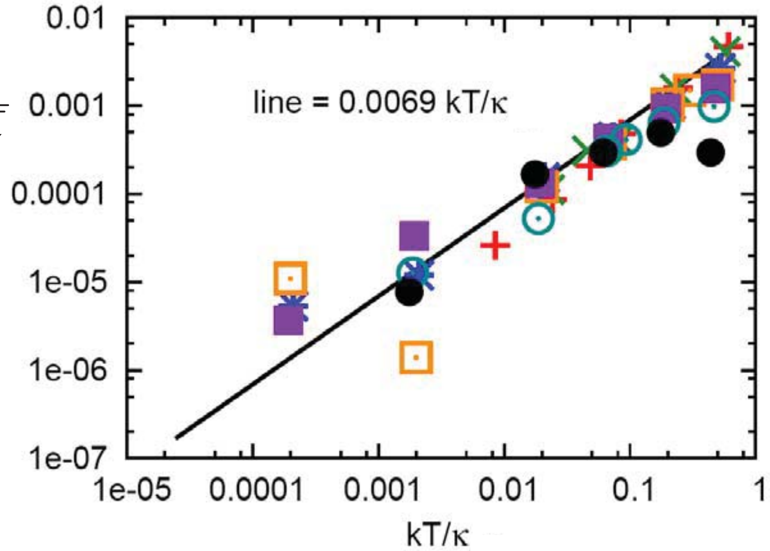
# Preliminary simulation results

*Mean square fluctuations averaged over the sphere:*

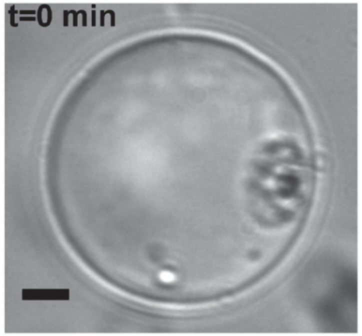
$$\langle \overline{f^2} \rangle = \frac{R k_B T}{8\sqrt{\kappa Y}} \left[ 1 + \left( \frac{1}{12\pi^2} - \frac{13}{8192} \right) \frac{k_B T}{\kappa} \sqrt{\frac{Y R^2}{\kappa}} \right]$$

$$\approx \frac{R k_B T}{8\sqrt{\kappa Y}} \left[ 1 + 0.0069 \frac{k_B T}{\kappa} \sqrt{\frac{Y R^2}{\kappa}} \right]$$

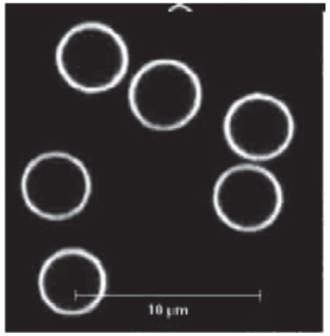
$$8 \frac{\langle \bar{f}^2 \rangle}{R^2} \frac{\kappa}{k_B T} - \frac{1}{\sqrt{\gamma}}$$



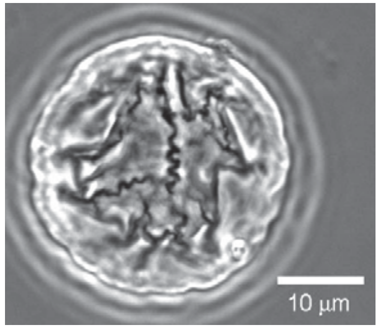
# How thin is thin?




(a) Polymersomes
Radius, R = 10-30 μm
Thickness, h = 10 nm




(b) Polyelectrolyte capsules
R = 2 μm, h = 10 nm




(c) Spider silk protein capsules
R = 15 μm, h = 6 nm

Bending rigidity $\kappa \sim Eh^3$
2D Young's modulus $Y \sim Eh$
Shell radius $R$

E: 3D elastic modulus
h: Shell thickness

**Föppl-von Kármán number**

$$\gamma = \frac{YR^2}{\kappa} \sim \left(\frac{R}{h}\right)^2$$

~$10^7$

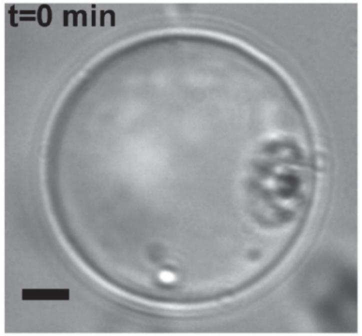
**Amplitude of thermal fluctuations**

$$\frac{k_B T}{\kappa}$$

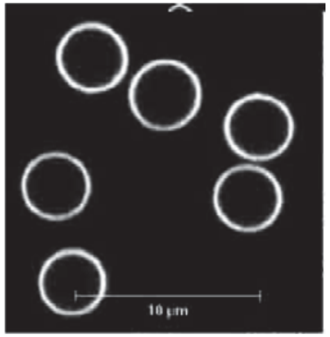
~$10^{-3}$ for 10 nm thickness

- Thermal effects scale as $\frac{k_B T}{\kappa}\sqrt{\gamma} \sim \frac{k_B T R^2}{Eh^4}$.
- Corrections significantly boosted by external pressure.

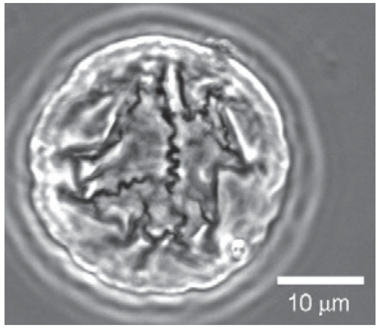
# How thin is thin?




*(a) Polymersomes*
*Radius, R = 10-30 μm*
*Thickness, h = 10 nm*




*(b) Polyelectrolyte capsules*
*R = 2 μm, h = 10 nm*




*(c) Spider silk protein capsules*
*R = 15-30 μm, h = 6 nm*

Spider silk capsules (Bausch et al *Adv Mater* 19:1810) :

<u>Point indentation correction:</u>

*Reported:* R = 30 microns, *h* = 6 nm → corrections < 5%

*Half thickness:* R = 30 microns, *h* = 3 nm → corrections ~ 50%

- *Thermal effects scale as* $\frac{k_B T}{\kappa}\sqrt{\gamma} \sim \frac{k_B T R^2}{E h^4}$.
- *Corrections significantly boosted by external pressure.*

# *Pressurized Amorphous Shells, Pollen Grains and Thermal Fluctuations*

**Shell theory: Foppl-von Karman equations and nonlinear elasticity theory**

-- *applicaton to crumpling and folding of pollen grains*

E. Katifori
J. Dumais
E. Cerda
S. Alben

**Flat membranes: elasticity and statistical mechanics**

--*thermal fluctuations lead to scale-dependent elastic constants*

**Shells with thermal fluctuations: deformations of pressurized spherical shells**

-- *Renormalized bending rigidity, Young's modulus and pressure all diverge as sphere radius* $R \rightarrow \infty$*!*

-- *Anomalous height fluctuation and indentation experiments*

J. Paulose
G. Gompper
G. Vliegenhart