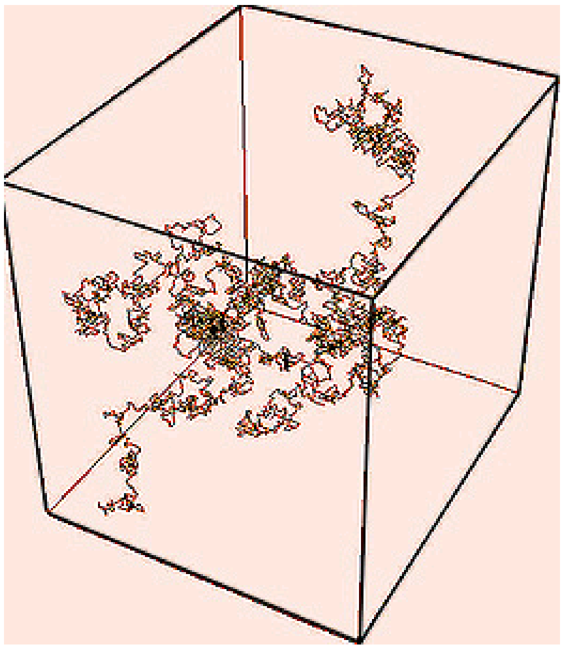
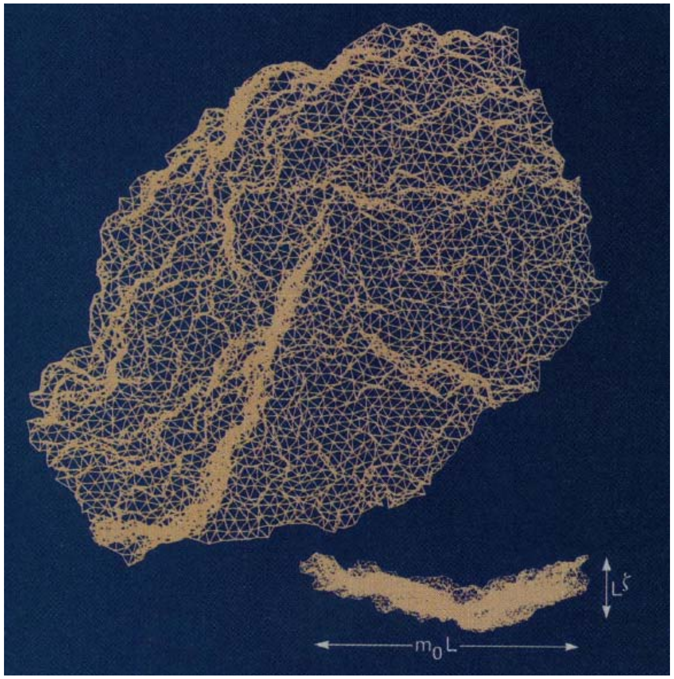
Ancient History: from linear polymers to tethered surfaces

❁By the early 1990's, theories of linear polymer chains in a good solvent were generalized to treat the statistical mechanics of flexible sheet polymers



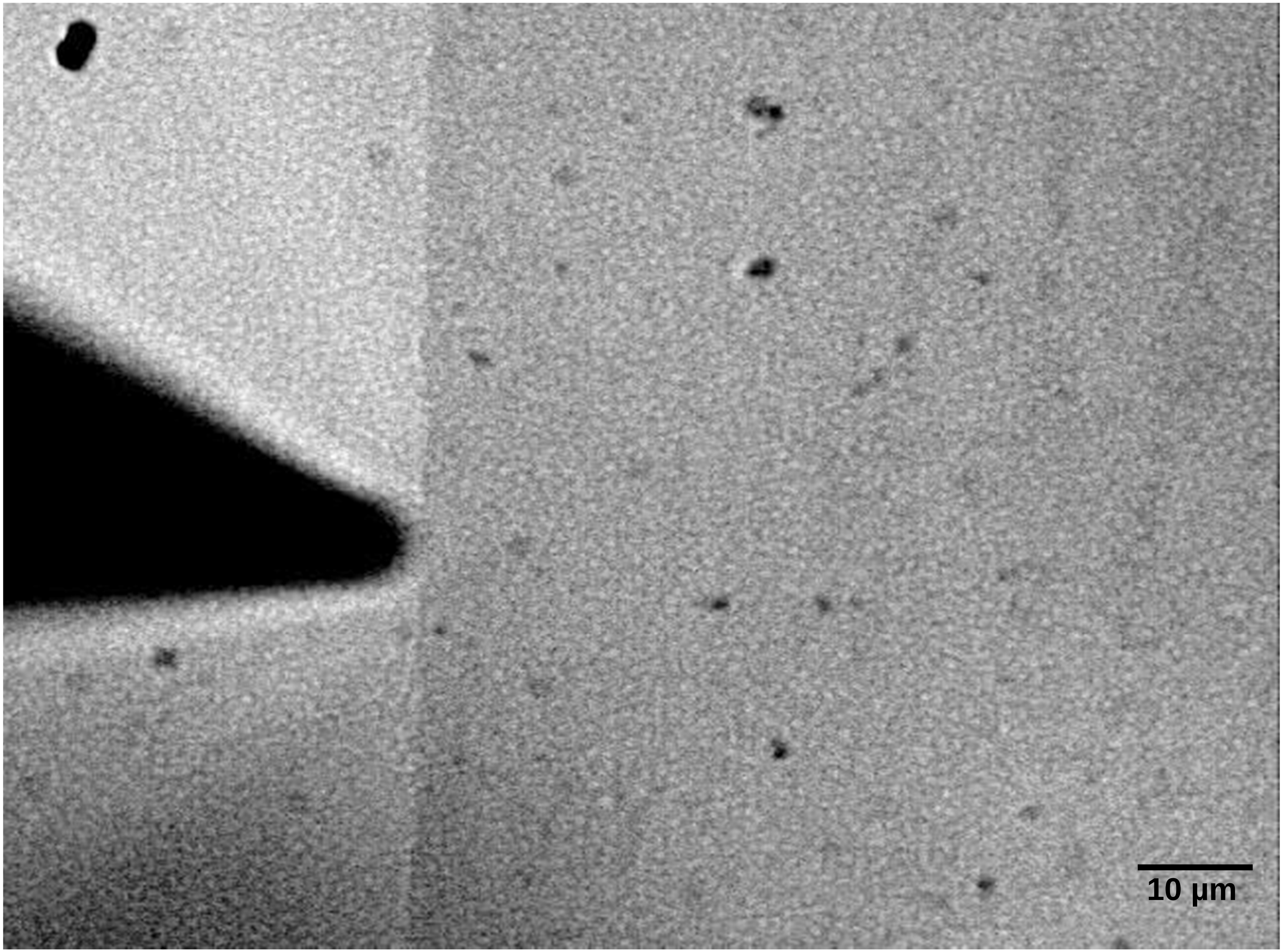
linear polymer



sheet polymer

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

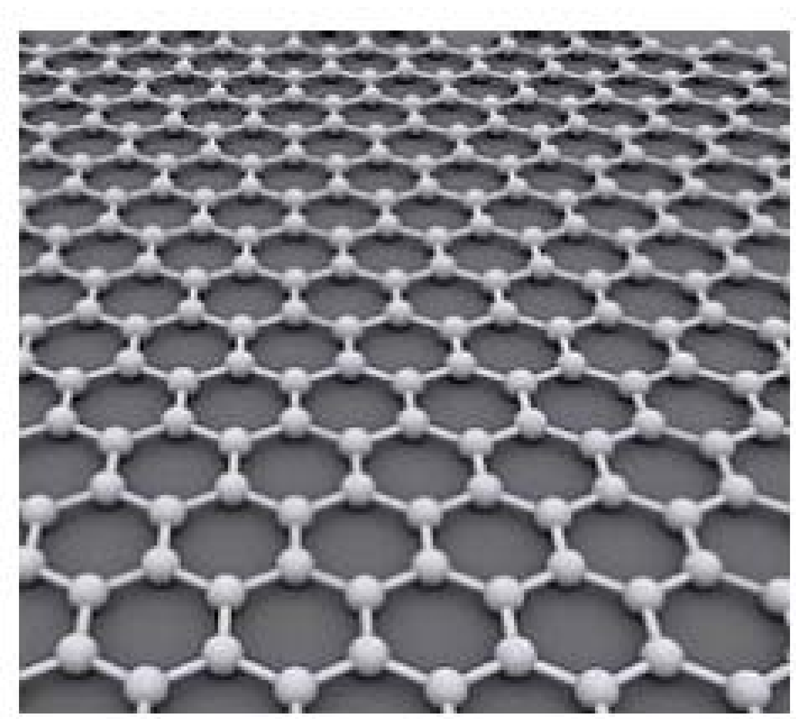
- Remarkably, "tethered surfaces" with a shear modulus are able to resist thermal crumpling and exhibit a low temperature "wrinkled", flat phase…
- A continuous broken symmetry -- long range order in the surface normals -- arises in two dimensions (the Mermin-Wagner-Hohenberg theorem is evaded!)
- Experiments on the spectrin skeleton of red blood cells by Schmidt, Safinya…

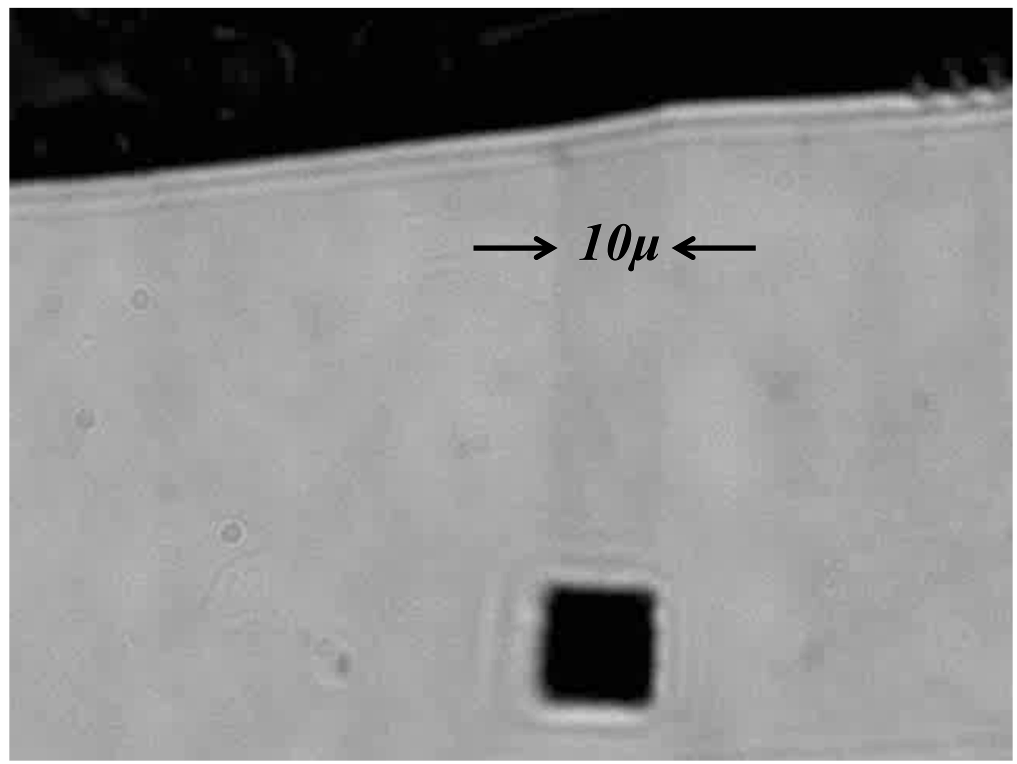

10 µm

Experiments of the McEuen group at Cornell: **"Single molecule polymer physics" for graphene**

M. Blees et al., Nature 524, 204 (2015)

graphene





Thermalized sheets and shells: curvature matters

Equations of thin plate theory

--nonlinear bending and stretching energies

--vK = Föppl-von Karman number = $YR^2/\kappa >> 1$

Physics of thermalized sheets

-- "self-organized criticality" of the flat phase

-- strongly scale-dependent elastic parameters

-- hard condensed matter applications : graphene, MoS_2, BN, WS_2, ….

Physics of thermalized shells

-- shells with zero pressure difference can be crushed by thermal fluctuations for $R > R_c(T)$*!*

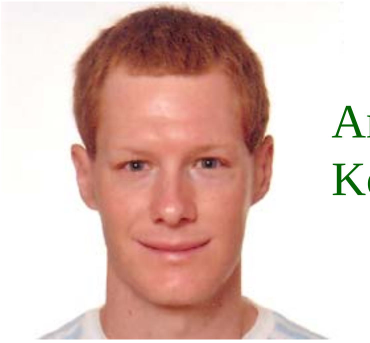
Physics of perforated graphene sheets

Recent experiments:
Paul McEuen group (Cornell)

G. Gompper
G. Vliegenthart

Jayson Paulose

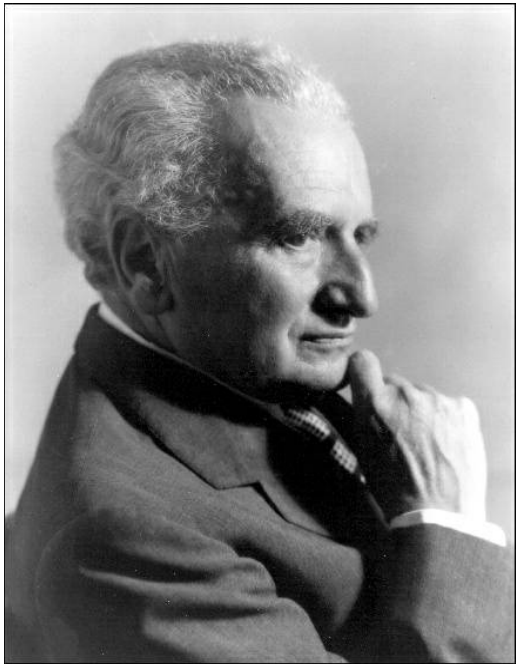
Michael Moshe
Mark Bowick



Andrej Kosmrlj

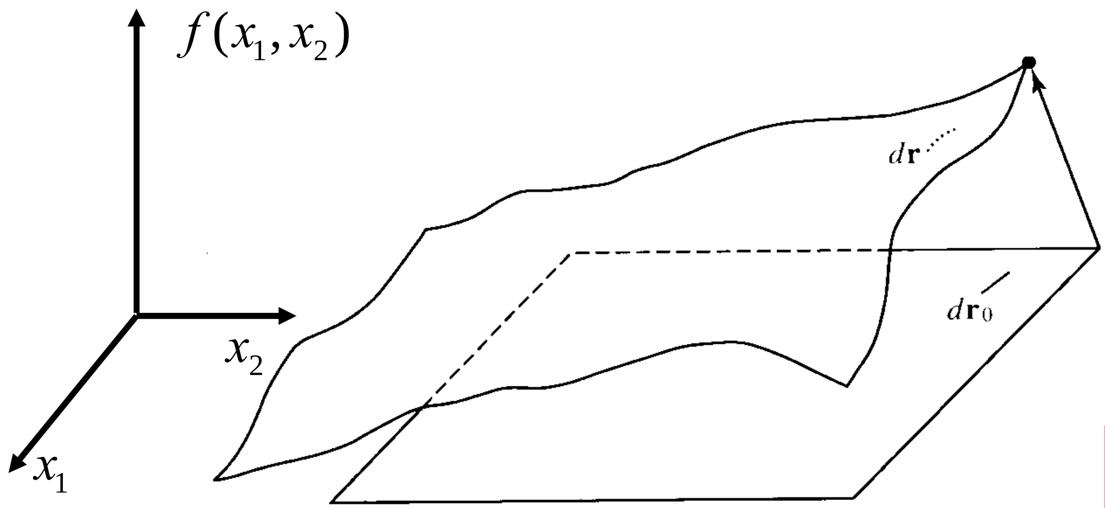
Elastic membranes: in 1904, Föppl & von Kármán studied large deflections of elastic plates

August Föppl (1854-1924) Pioneer of elasticity theory



Theodore von Kármán (1881-1963) Hungarian-American physicist & aeronautical engineer

To study deformed surfaces, expand about a flat reference state…



$$\vec{r}(x_1, x_2) = \vec{r}_0 + \begin{pmatrix} f(x_1, x_2) \\ u_1(x_1, x_2) \\ u_2(x_1, x_2) \end{pmatrix}$$

$$dr^2 = dr_0^2 + 2u_{ij}dx_i dx_j$$

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

$$E = \frac{1}{2}\int d^2x \; [\underbrace{\kappa(\nabla^2 f(\vec{x}))^2}_{\text{bending energy}} + \underbrace{2\mu u_{ij}^2(\vec{x}) + \lambda u_{kk}^2(\vec{x})}_{\text{stretching energy}}]$$

bending energy ***stretching energy***

$\kappa =$ bending rigidity

$\mu =$ shear modulus

$\mu + \lambda =$ bulk modulus

Flexural phonons can escape softly into the 3rd dimension…

Nonlinear Föppl -von Karman Equations (1905)

$$\partial_i \sigma_{ij} = 0 \;\Rightarrow\; \sigma_{ij}(\vec{x}) = 2\mu u_{ij}(\vec{x}) + \lambda \delta_{ij} u_{kk}(\vec{x}) \equiv \varepsilon_{im} \varepsilon_{jn} \partial_m \partial_n \chi(\vec{x})$$

$\chi(\vec{x}) =$ Airy stress function

Bending modes $f(\vec{x})$ coupled to stretching modes $\vec{u}(\vec{x})$;

Minimize energy over $f(\vec{x})$ and $\chi(\vec{x})$...

$$\kappa \nabla^4 f = \frac{\partial^2 \chi}{\partial y^2}\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 \chi}{\partial x^2}\frac{\partial^2 f}{\partial y^2} - 2\frac{\partial^2 \chi}{\partial x \partial y}\frac{\partial^2 f}{\partial x \partial y}$$

$$\frac{1}{Y}\nabla^4 \chi = -\frac{\partial^2 f}{\partial x^2}\frac{\partial^2 f}{\partial y^2} + \left(\frac{\partial^2 f}{\partial x \partial y}\right)^2 = \text{ Gaussian curvature}$$

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

κ = bending rigidity

$\Rightarrow$ resembles a simplified form of general relativity (developed 10 years later....)

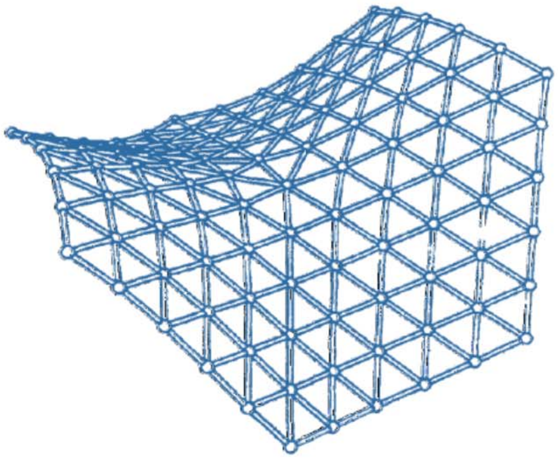
$\Rightarrow$ exact solutions available only in very special cases

$\Rightarrow$ dimensionless "Foeppl-von Karman number" $vK = YL^2/\kappa \gg 1$ (linear size = L)

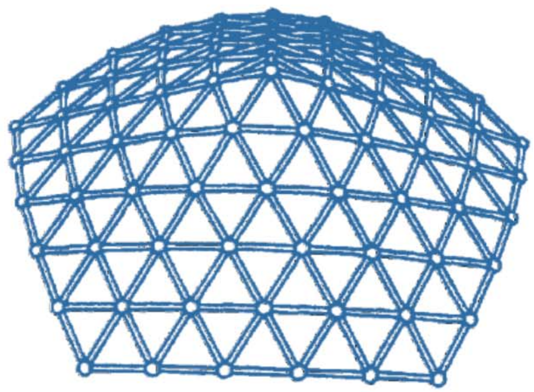
[compare Reynolds number in fluid mechanics, $\mathrm{Re} = uL/\nu$]

Buckling into the 3rd dimension matters, even at T = 0…

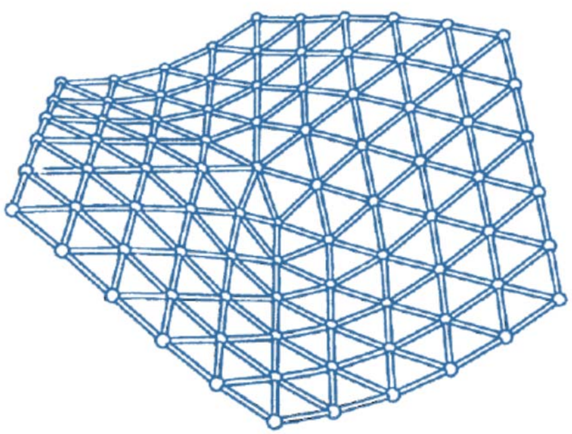
(triangular lattice is dual the honeycomb lattice of graphene)



7-fold disclination

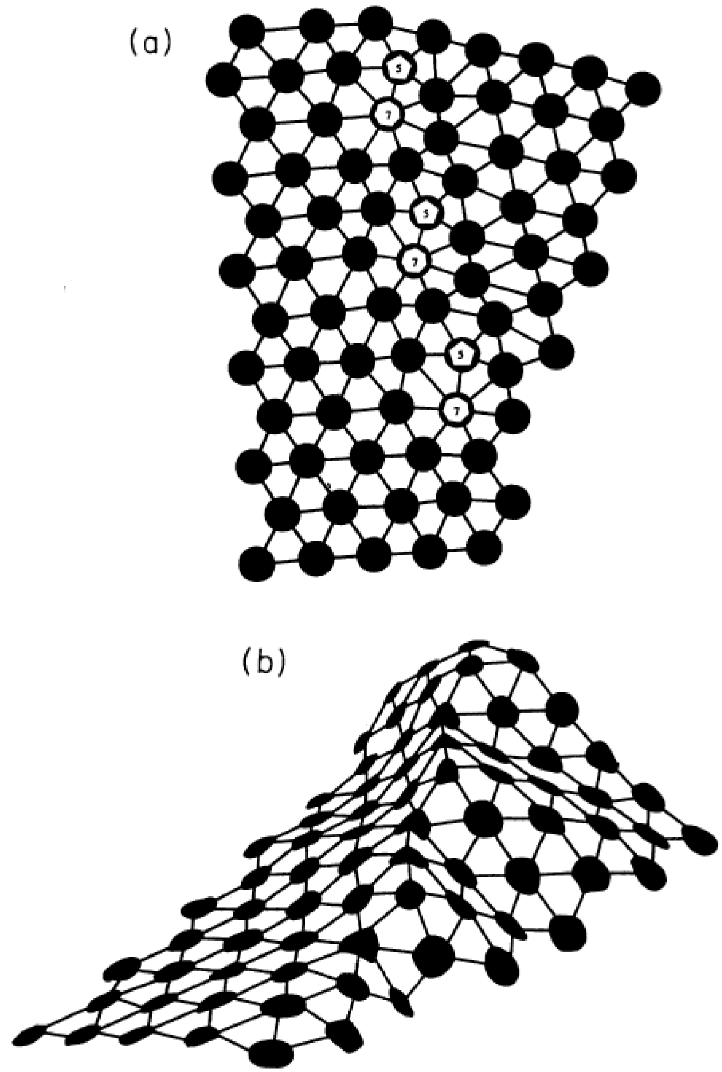


5-fold disclination



dislocation

H. S. Seung
and drn, 1988



grain boundary

L. Radzihovsky and drn, 1992
C. Carraro and drn, 1993

Applications: thin solid shells and structures

macroscopic (1cm - 100m)

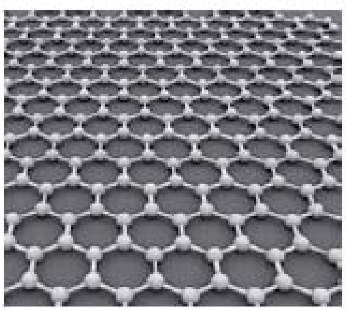
plant
leaves

egg
shell

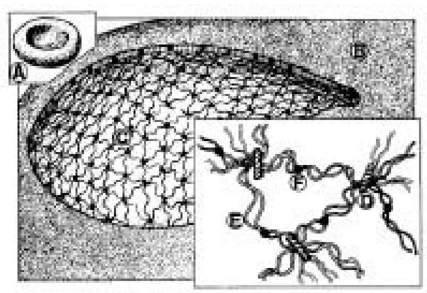
aluminum foil

pipes

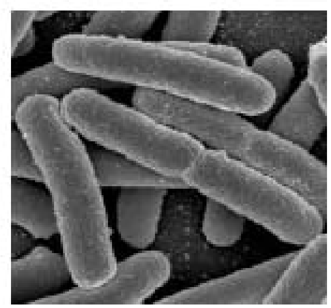
& microscopic (0.1nm - 1μm) -- is Brownian motion important ??



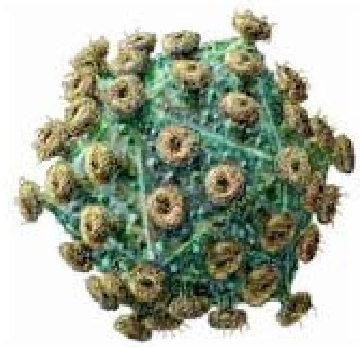
graphene



cell membrane
with cytoskeleton



bacterial
cell wall



viral
capsid

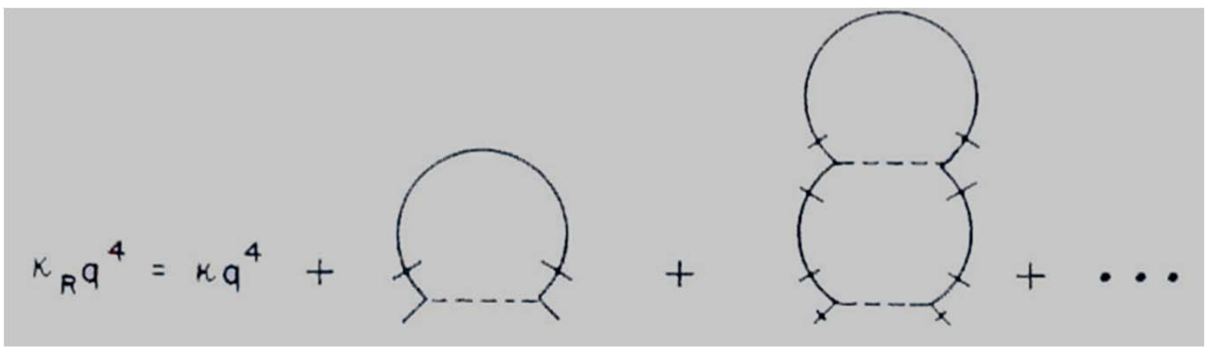
What About Thermally Excited Membranes? *(L. Peliti & drn)*

- Tracing out in-plane phonon degrees of freedom yields a massless nonlinear field theory

$$F_{\text{eff}} = -k_B T \ln\left(\int D\left\{u_x(x,y)\right\}\int D\left\{u_y(x,y)\right\} e^{-E/k_BT}\right) \qquad \text{Y}=\frac{4\mu(\mu+\lambda)}{2\mu+\lambda} = \text{Young's modulus}$$

$$F_{eff} = \frac{1}{2}\kappa\int d^2x\left[(\nabla^2 f)^2\right] + \frac{1}{4}Y\int d^2x\left[P_{ij}^T(\partial_i f\partial_j f)\right]^2 \equiv F_0 + F_1; \quad P_{ij}^T = \delta_{ij} - \frac{\partial_i\partial_j}{\nabla^2}$$

- *Assume $k_BT/\kappa << 1$, and do low temperature perturbation theory*



$$\kappa_R(q) = \kappa + k_B TY\int\frac{d^2k}{(2\pi)^2}\frac{\hat{q}_i P_{ij}^T(\vec{k})\hat{q}_j}{\kappa|\vec{q}+\vec{k}|^4} + \ldots.$$

$$\lim_{q\to 0}\kappa_R(q) \approx \kappa[1 + (vK)k_BT/(4\pi^3\kappa) + \ldots]$$

$vK = YL^2/\kappa \approx (L/h)^2 \gg 1$

L = membrane size

h = membrane thickness

Self-consistent bending rigidity, $\kappa_R(q)$~1/q & diverges as $q \to 0$!

Renormalization Group for Thermally Excited Sheets

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

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

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

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

define running coupling constants....

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

scale dependent Young's modulus

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

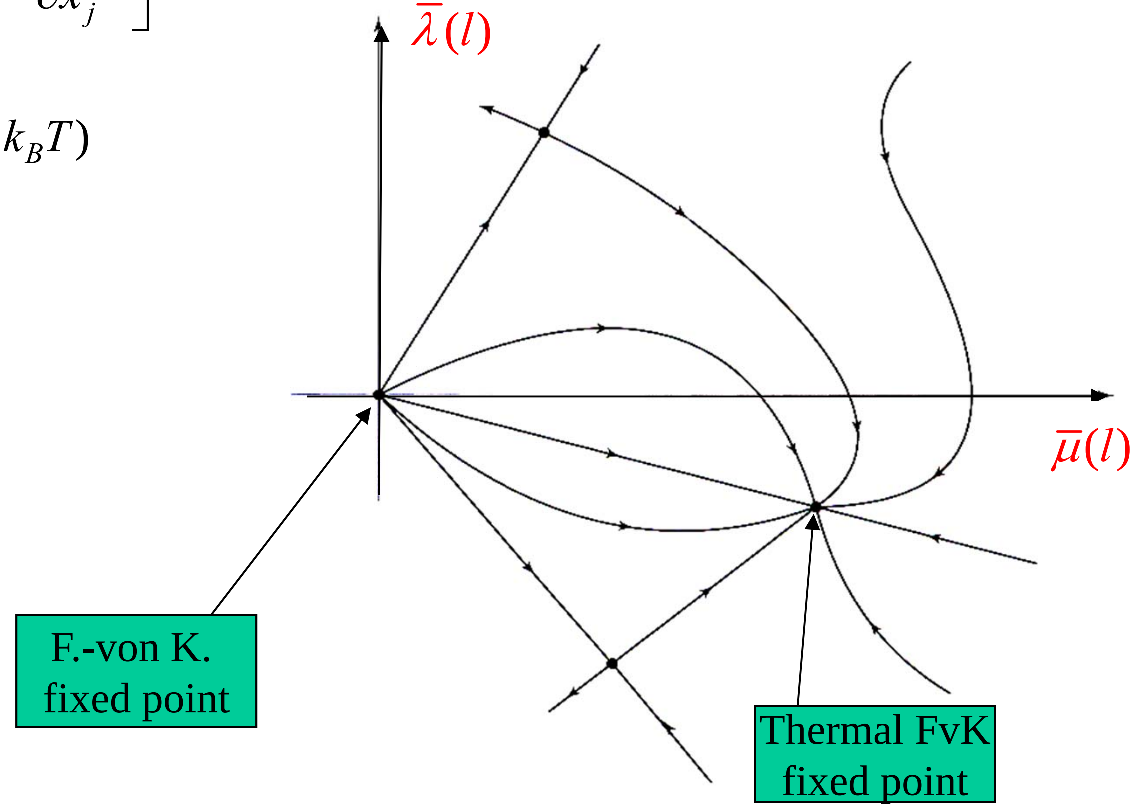
$$\kappa_R(l) \approx \kappa(l/l_{th})^{\eta}$$

$$Y_R(l) \approx Y(l_{th}/l)^{\eta_u}$$

$$\eta \approx 0.82, \quad \eta_u \approx 0.36$$

Thermal fluctuations dominate whenever $L > l_{th}$

$$l_{th} \approx \sqrt{\kappa^2/(k_BTY)}$$



Freely supported ($\sigma_{ij} = 0$) graphene tests the theory

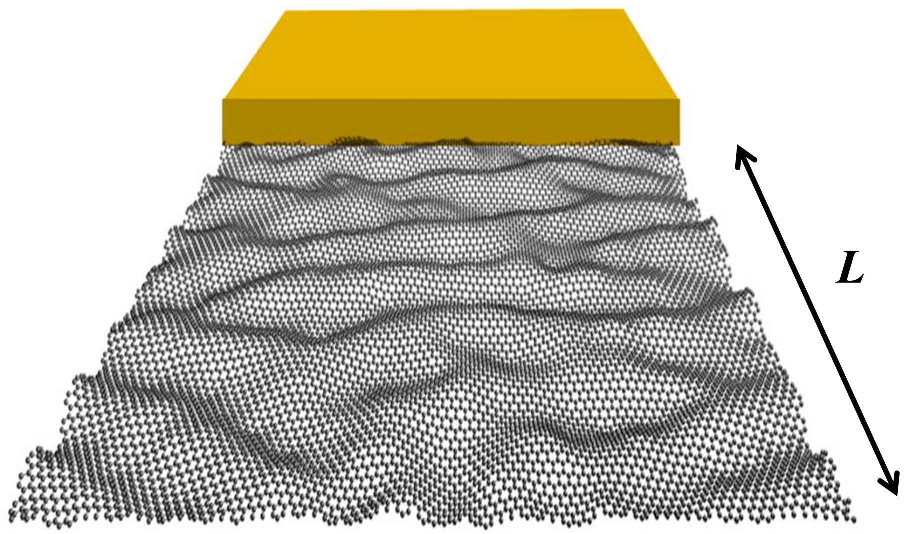
Graphene is the ultimate 2D crystalline membrane:

- One atom thick
- Very stiff in-plane (Young's modulus $Y = 20eV/A^2$)
- $L = 10\mu$
- $\kappa = 1.2eV$

With graphene, we have reached the "Moore's Law" limit of large Foppl-von Karman numbers

$vK = YL^2/\kappa \sim 10^{12}$

graphene



(atomistic calculations)

$$\kappa_0 \approx 1.2\text{eV} \approx 2 \times 10^{-19} J$$

Extremely flexible!

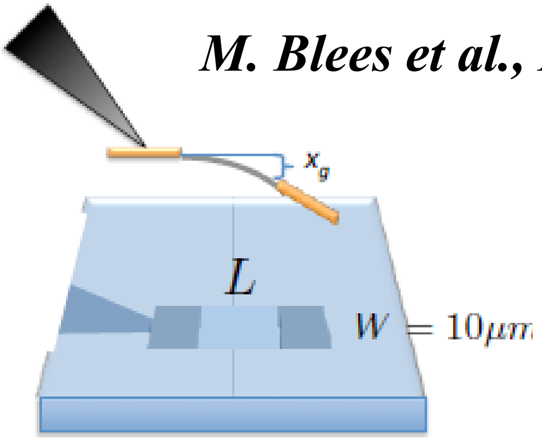
R. Nicklow, N. Wakabayashi and H. G. Smith, PRB 5, 4951 (1972)

fluctuations dominate for $L > l_{th}$

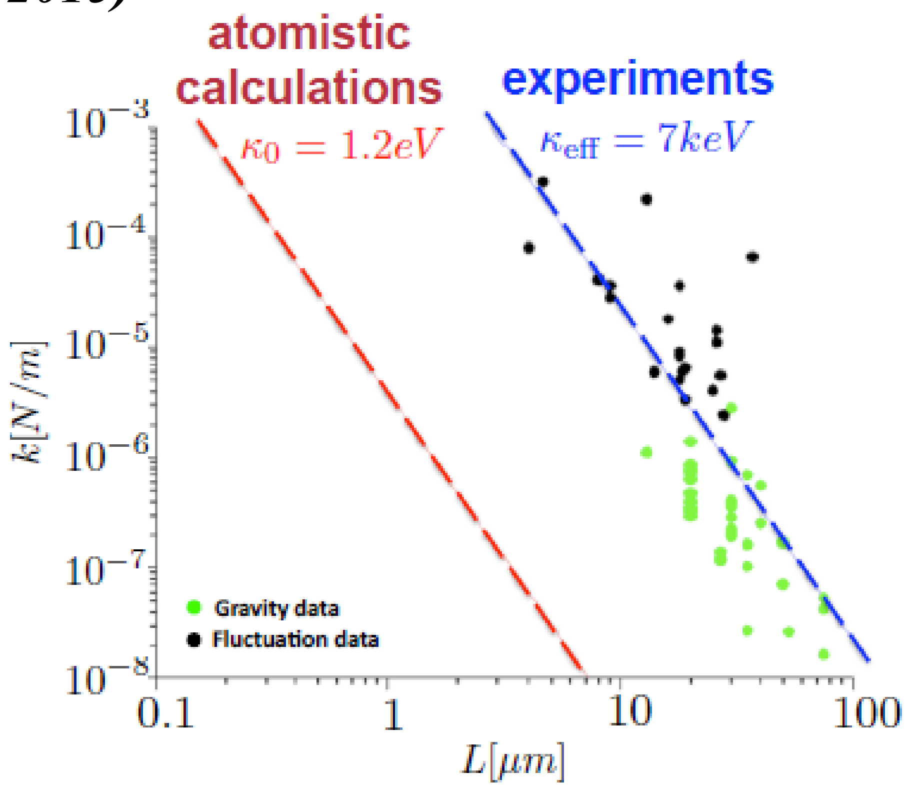
$$l_{th} \approx \sqrt{\kappa^2 / (k_B T Y)} \approx 0.2\text{nm!}$$

Bending rigidity of graphene membranes

M. Blees et al., Nature 524, 204 (2015)



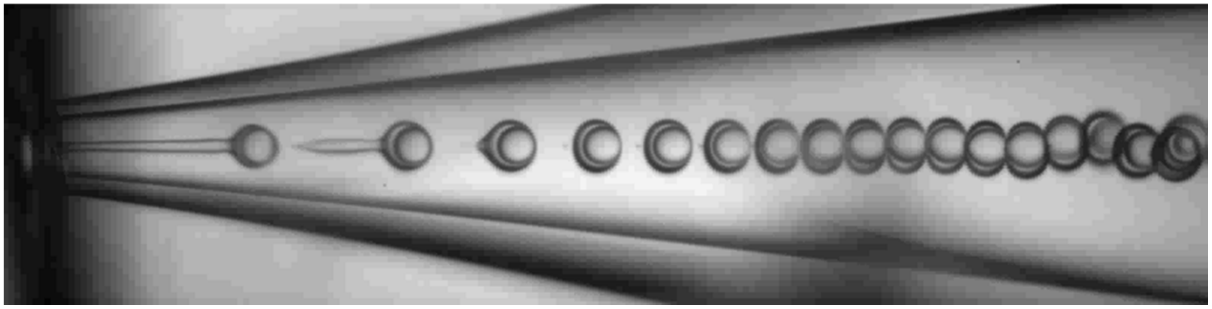
Galileo Galilei (1638)
Cantilever experiment



Bending rigidity enhanced ~4000 fold

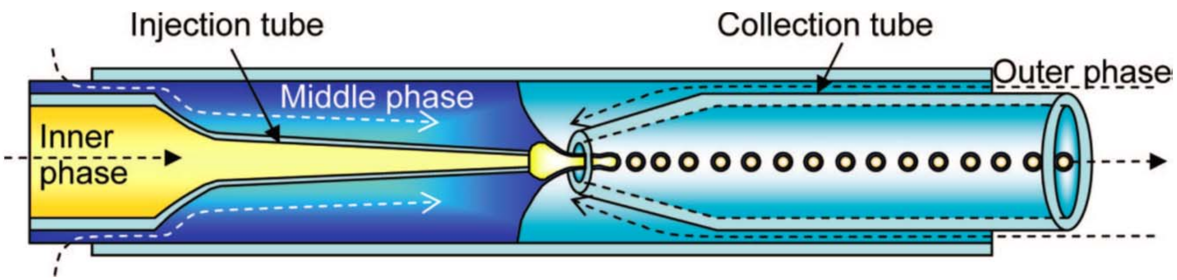
Agrees with $\kappa_R(l) \approx \kappa(W/l_{th})^{0.8}$

(l_{th} ~ 0.2nm for graphene)

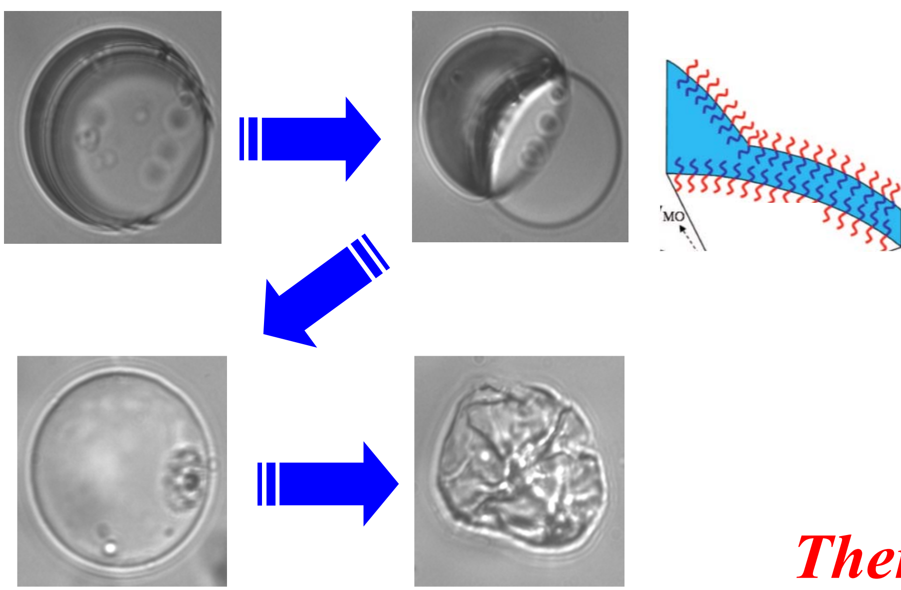


Microfluidic fabrication of polymersomes

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 crushed by osmotic pressure



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

$$\nu K = \text{Foppl-von Karman number}$$

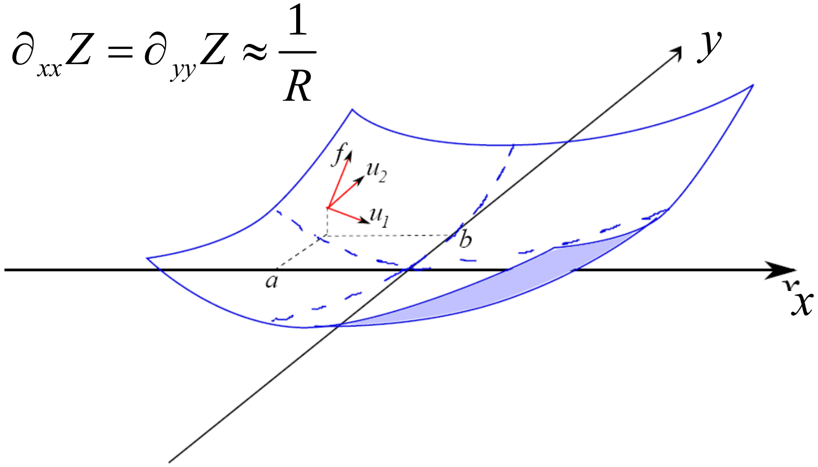
$$\approx 12(R/h)^2(1-\nu^2) \approx 10^9$$

Thermal fluctuations again matter…

Initial shape: $\begin{cases} z = Z(x,y) \\ z = \sqrt{R^2 - x^2 - y^2} \end{cases}$

To study thermal deformations of spherical shells, we use shallow shell theory….

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



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

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

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

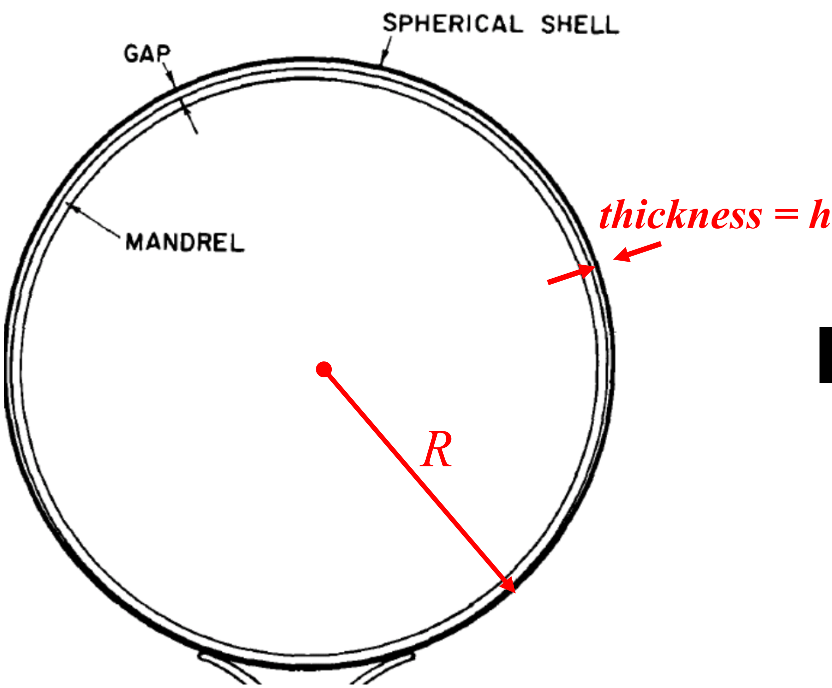
$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j}\right]$$

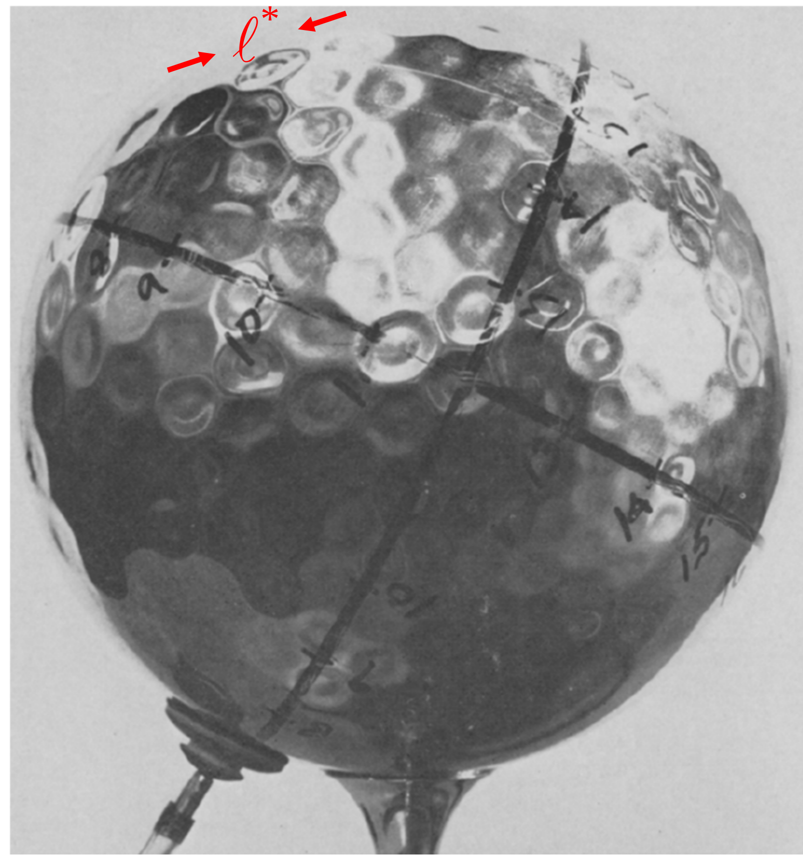
$$u_{ij}(\vec{x}) = \frac{1}{2}\left[\frac{\partial u_i(\vec{x})}{\partial x_j} + \frac{\partial u_j(\vec{x})}{\partial x_i} + \frac{\partial f(\vec{x})}{\partial x_i}\frac{\partial f(\vec{x})}{\partial x_j} - \delta_{ij}\frac{f}{R}\right]$$

Macroscopic Buckling Instability Arrested by a Wax Mandrel…

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

$$\ell^* = R / \nu K^{1/4} \sim \sqrt{Rh} \ll R$$





R = 4.25 in., R/h ~ 2000

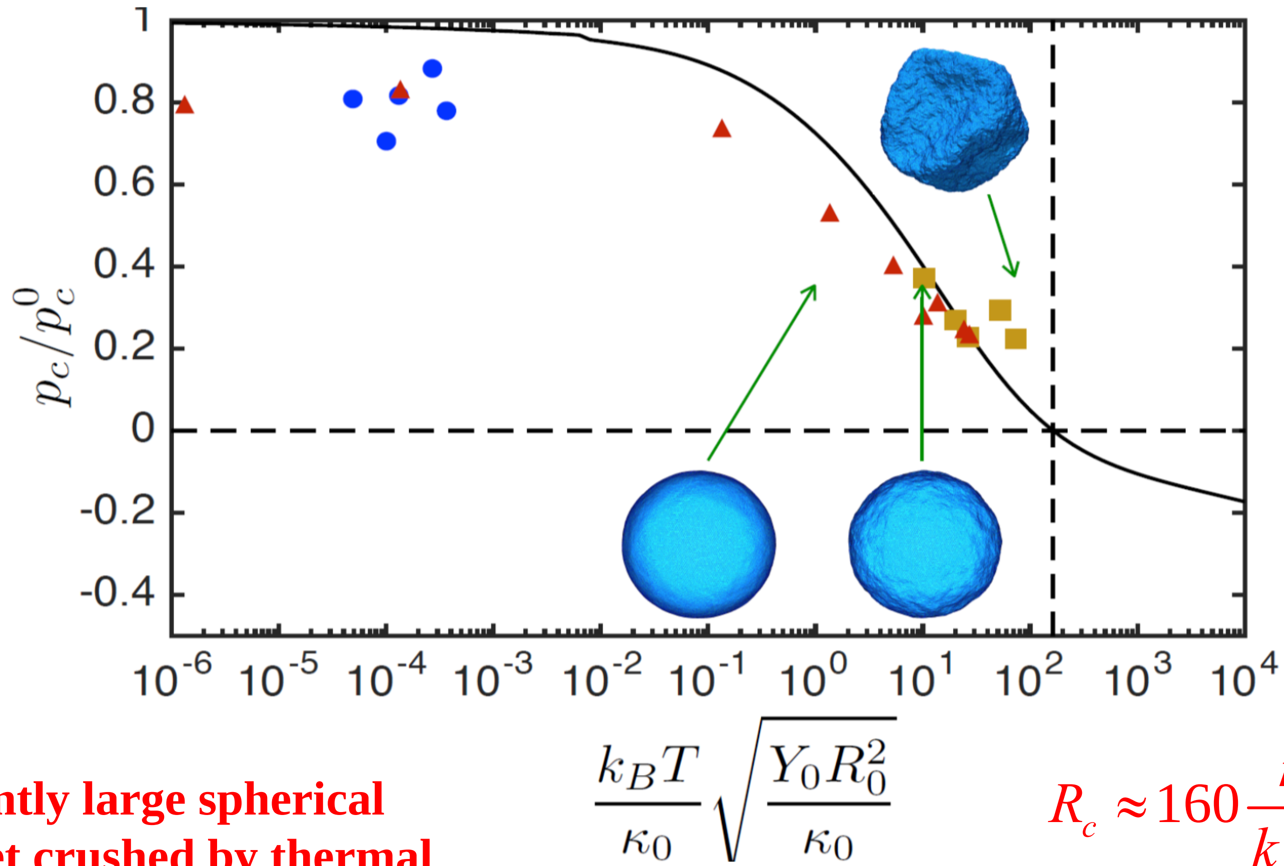
Classical shell theory

{ Koiter, 1963 (1945)
Hutchinson, 1967

Buckling of thermalized shells

Spherical shells, even at zero microscopic pressure, are crushed when the thermally renormalized pressure exceeds the critical buckling threshold

$$p_R \approx p + \frac{k_B T}{6\pi\kappa R} > p_{cR} = \frac{4\sqrt{\kappa_R Y_R}}{R^2}$$



Sufficiently large spherical shells get crushed by thermal fluctuations alone…

$$R_c \approx 160 \frac{\kappa}{k_B T}\sqrt{\frac{\kappa}{Y}} \sim \frac{Eh^4}{k_B T}$$

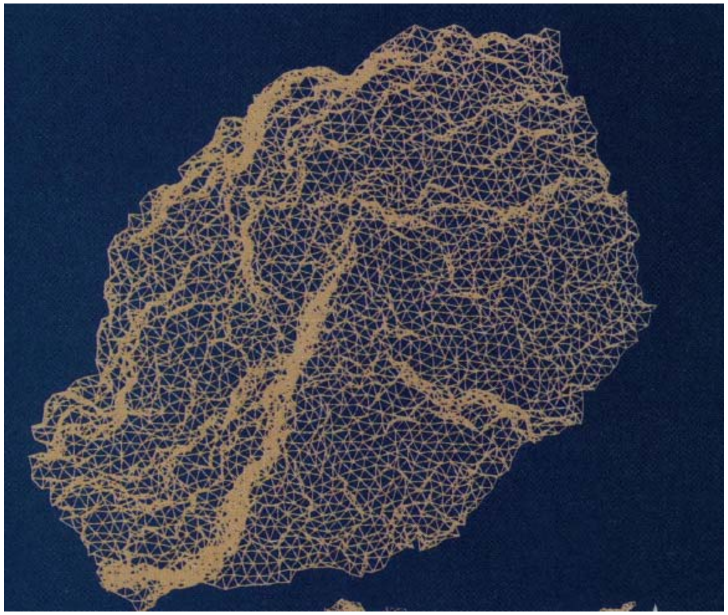
$R_c \approx 160nm$ for graphene

J. Paulose et al., PNAS **109**, 19551 (2012)

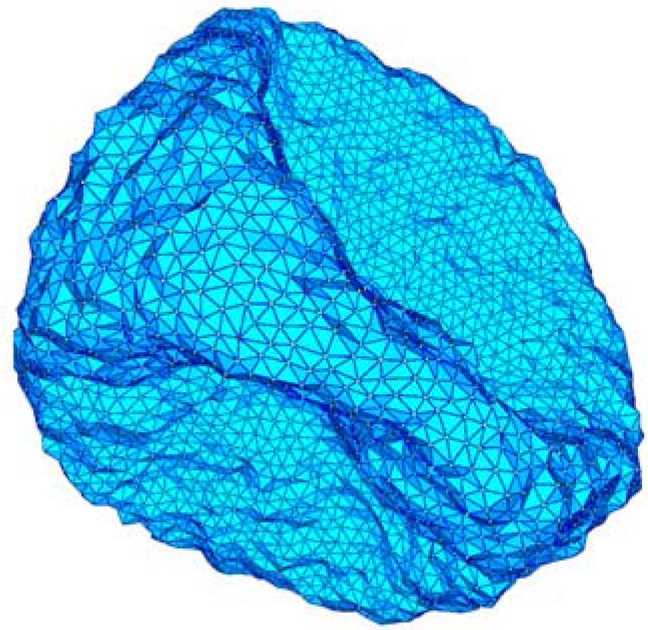
A, Kosmrlj and drn, http://arxiv.org/abs/1606.06750

Thermalized sheets and shells: curvature matters

F. Abraham



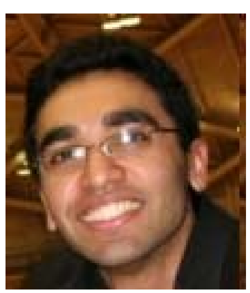
vs.



G. Gompper & G. Vliegenthart

Scale-dependent bending rigidity κ
~5000 fold enhancement for graphene at room temperture

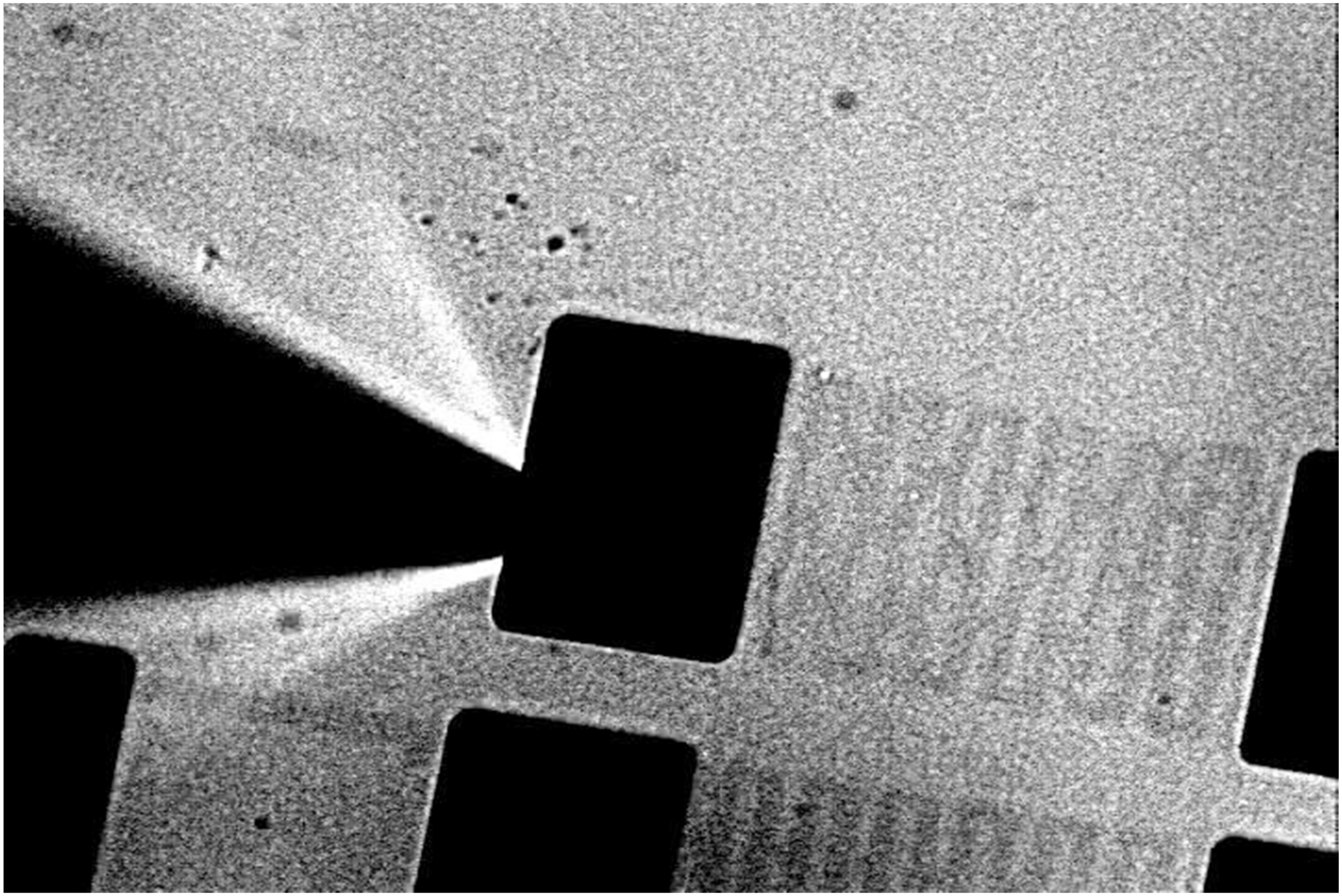
Enhancement of bending rigidity κ only ~70 fold at room temperature; but spheres (and hemispheres) crush themselves for $R > R_c = 160[\kappa^3 / Y(k_B T)^2]^{1/2}$



Jayson Paulose

Andrej Kosmrlj

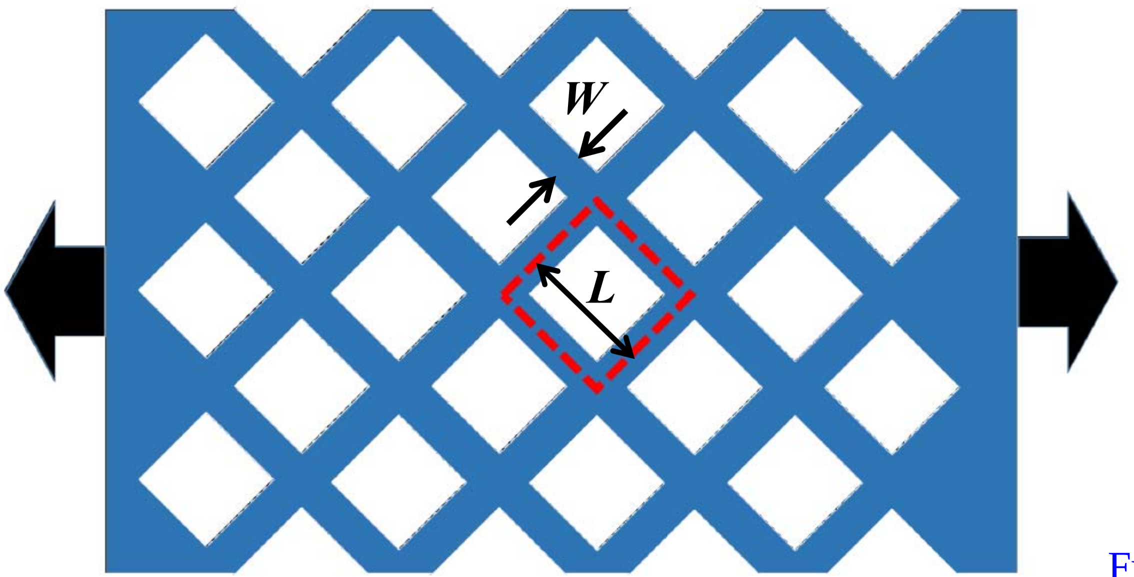
Future directions: new, atomically thin springs



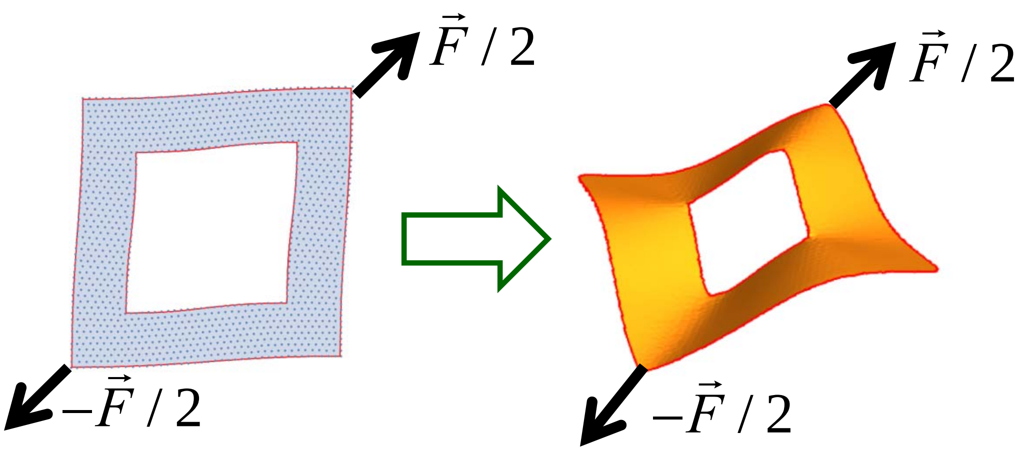
10 μm

Arrays of holes in graphene (or paper) drastically reduce the stretching modulus

M. Moshe,
M. Bowick
and drn



Consider a thin perforated graphene sheet with Young's modulus Y and bending rigidity κ

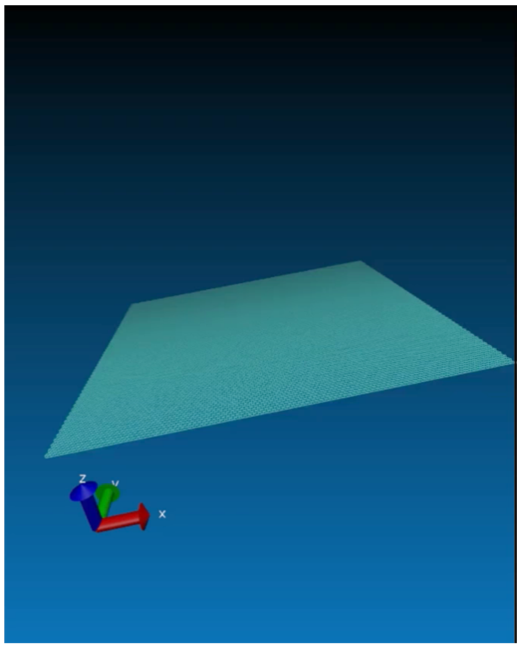


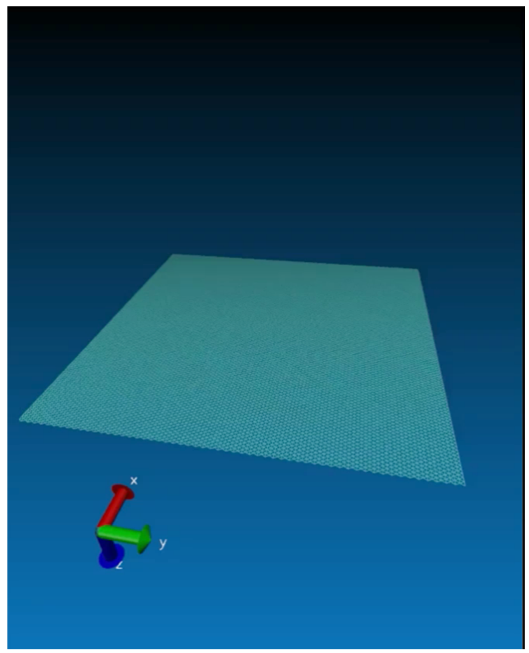
Frames buckle into the third dimension if $F > F_c$ such that $s = s_c = W\kappa / YL^3$. Thin perforated sheets trade stretching energy for bending energy and $Y \to \kappa / L^2 \ll Y$ Young's modulus suffers a large reduction

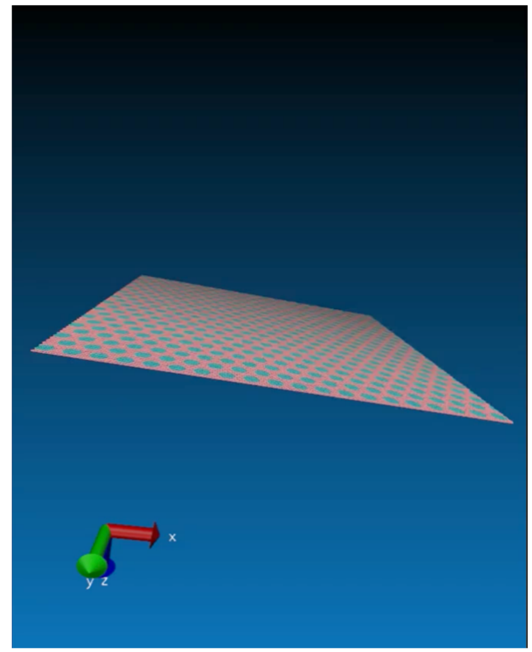
But what about thermal fluctuations?

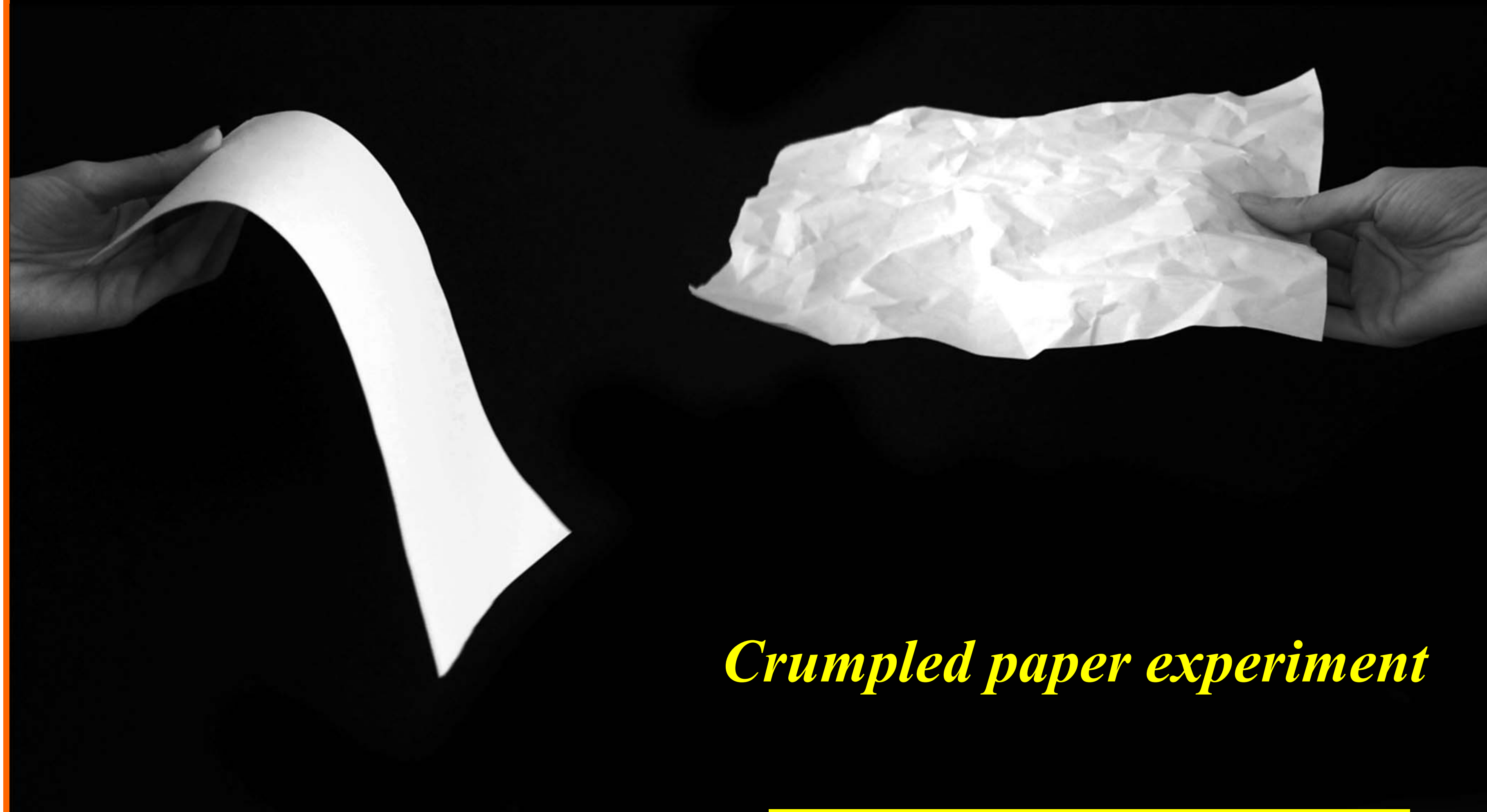
Graphene with holes may undergoe a crumpling transition at sufficiently high temperatures!!

(Molecular dynamics simulations by David Yllanes and Mark Bowick, Syracuse University)









Crumpled paper experiment

Figure: Melina Blees, Cornell

Thank you!!