# Statistical mechanics of ribbons and thin spherical shells

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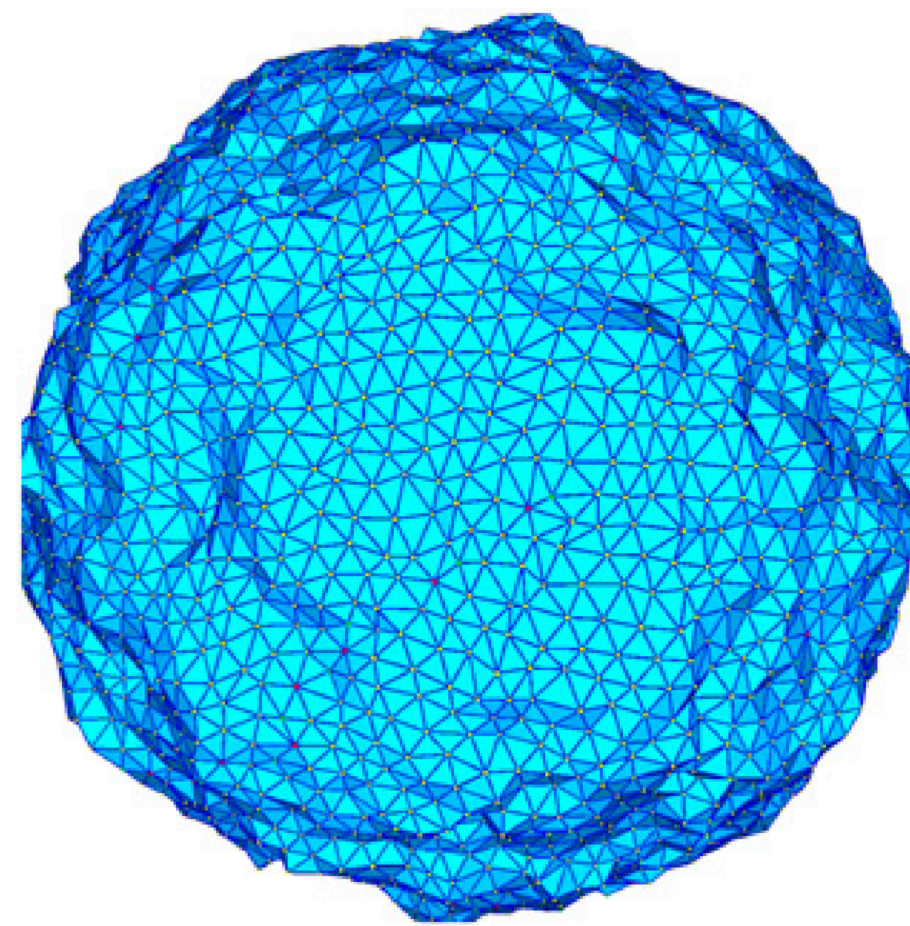


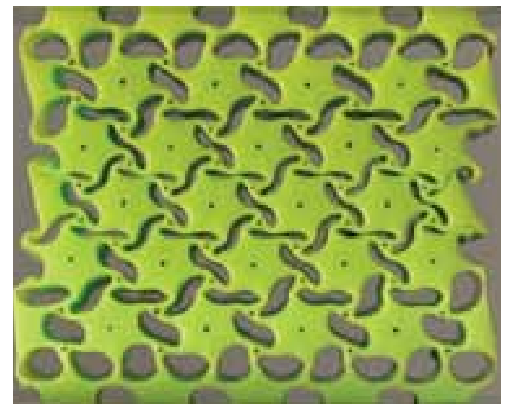
Geometry, elasticity, fluctuations, and order in 2D soft matter,
KITP, February 29, 2016

# Research Interests

## Statistical mechanics of membranes

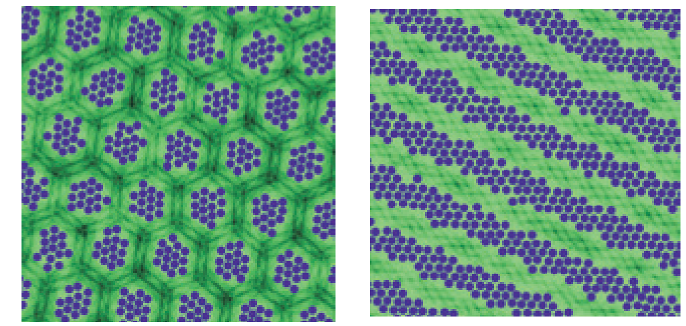
PRE (2013, 2014)
arXiv (2015)

## Mechanics of metamaterials



Soft. Matter (2013), PRL (2014)

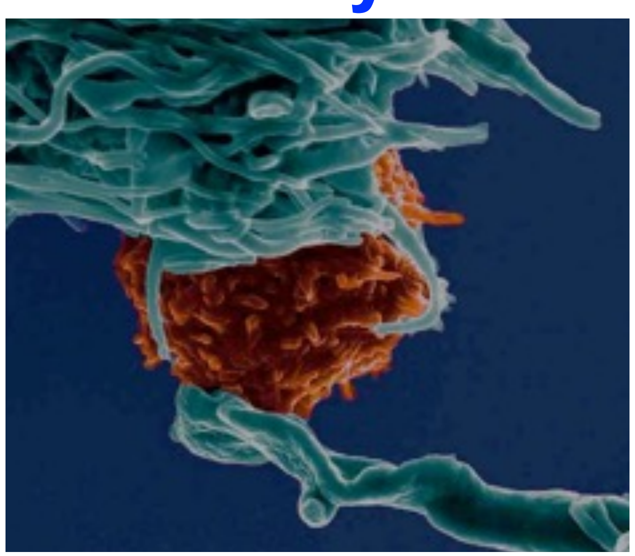
## Assembly of colloids



EPL (2007), J. Phys. Chem. B (2011)

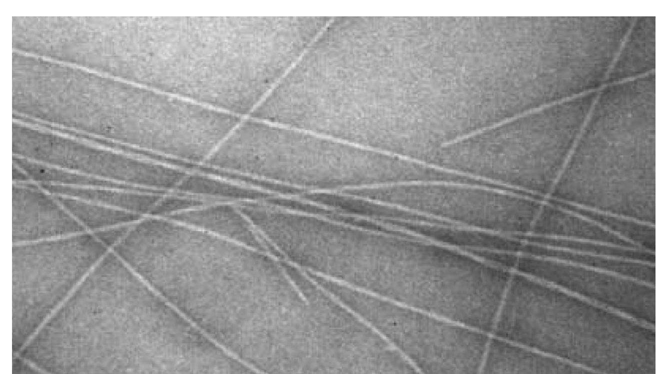
# Statistical mechanics

## Immune system



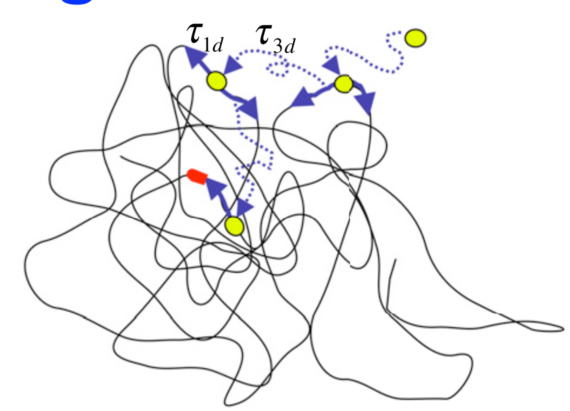
PNAS (2008), PRL (2009), Nature (2010), ARPC (2010), JSP (2011,2012), ARCM (2013)

## Growth of glucagon fibrils



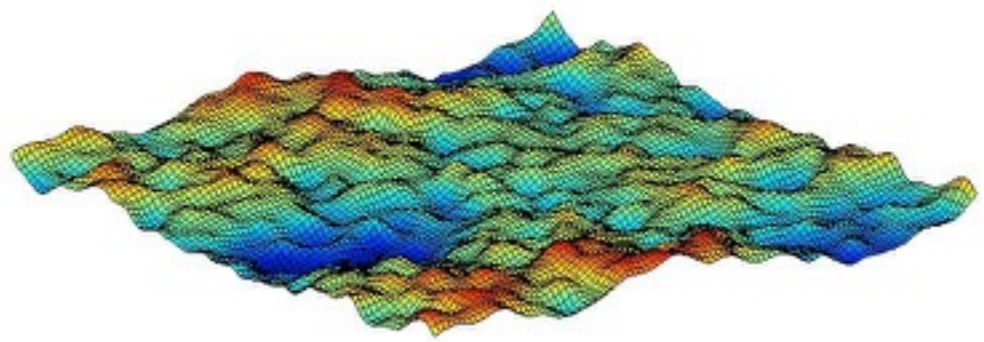
Sci. Rep. (2015)

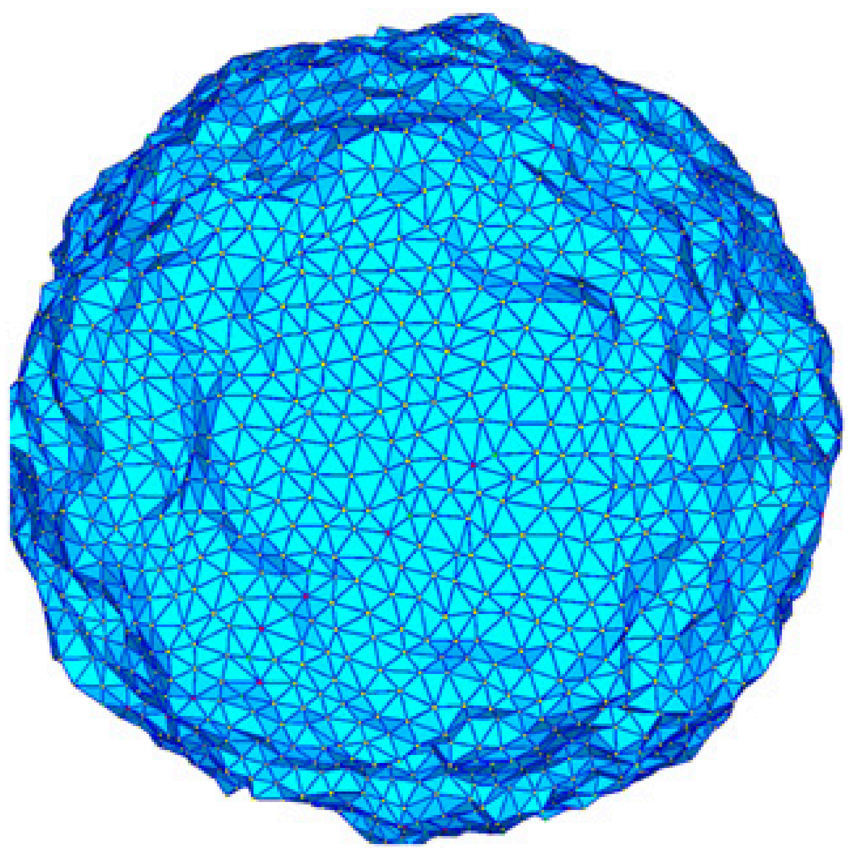
## Protein search for target site on DNA




J. Phys. A (2009)

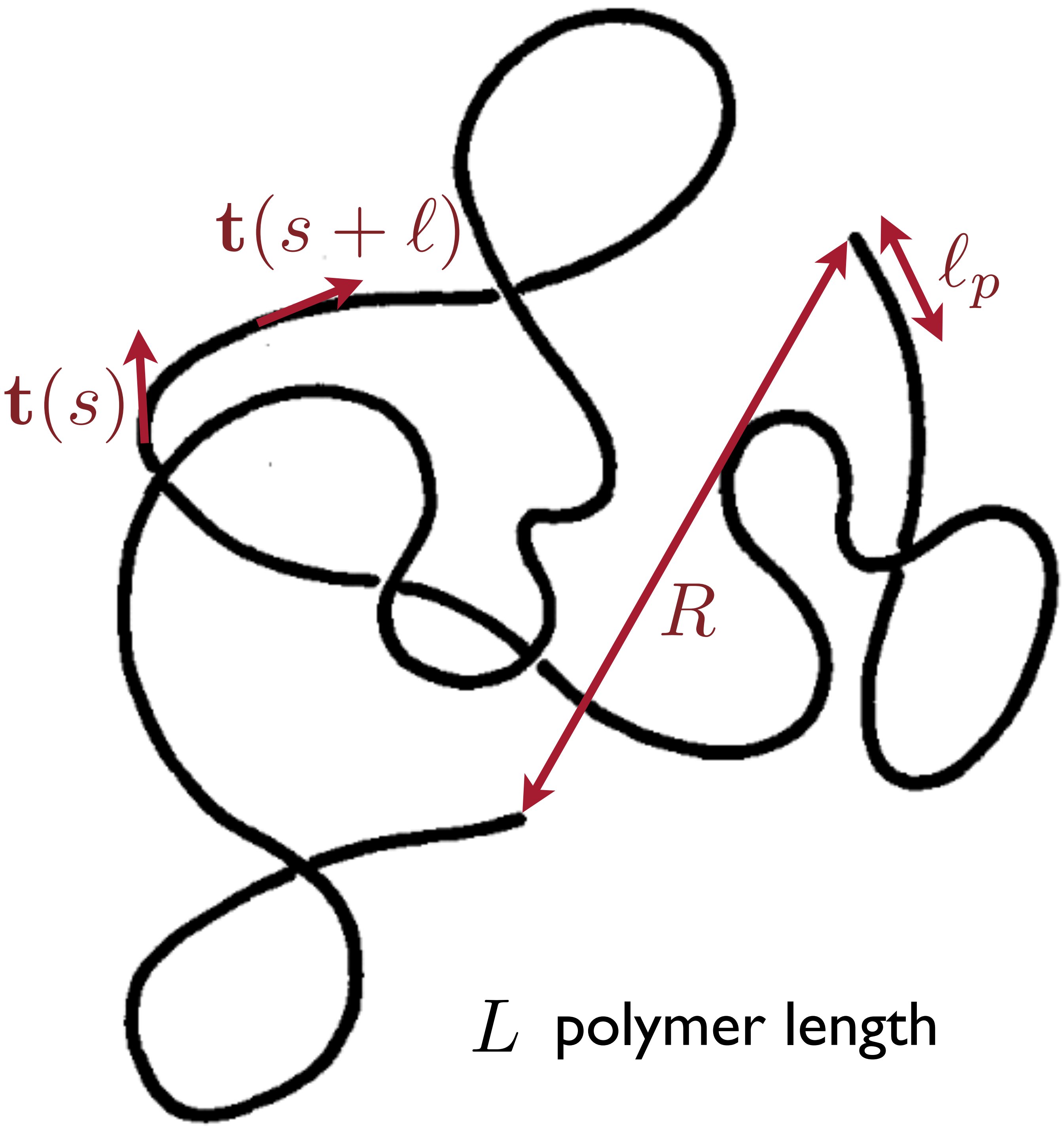
# How thermal fluctuations affect the mechanics of thin solid sheets, ribbons and spherical shells?





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

# Statistical mechanics of polymers




$L$ polymer length

P.-G. de Gennes, *Scaling concepts in polymer physics*

**Short polymers are straight**

$R \approx L \qquad L \ll \ell_p$

**Long polymers perform self-avoiding random walk**

$R \sim \ell_p (L/\ell_p)^\nu \qquad L \gg \ell_p$

Flory exponent $\nu \approx 0.59$

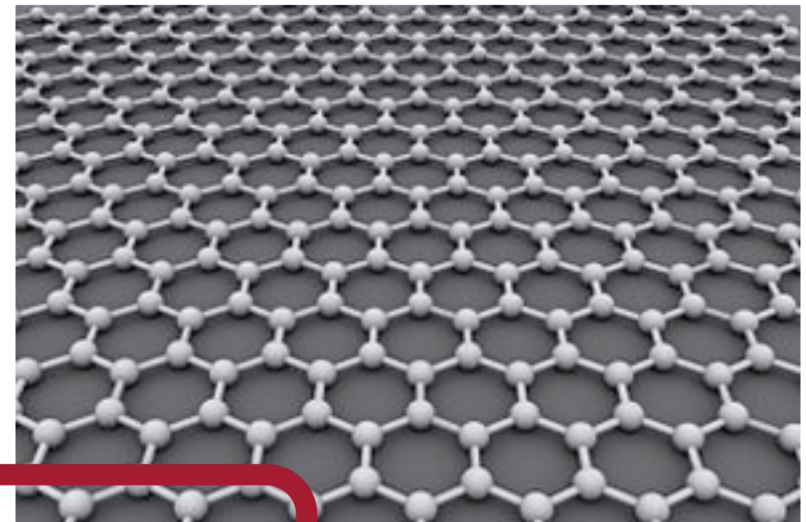
**Persistence length**

$$\langle \mathbf{t}(s+\ell) \cdot \mathbf{t}(s) \rangle = e^{-\ell/\ell_p}$$

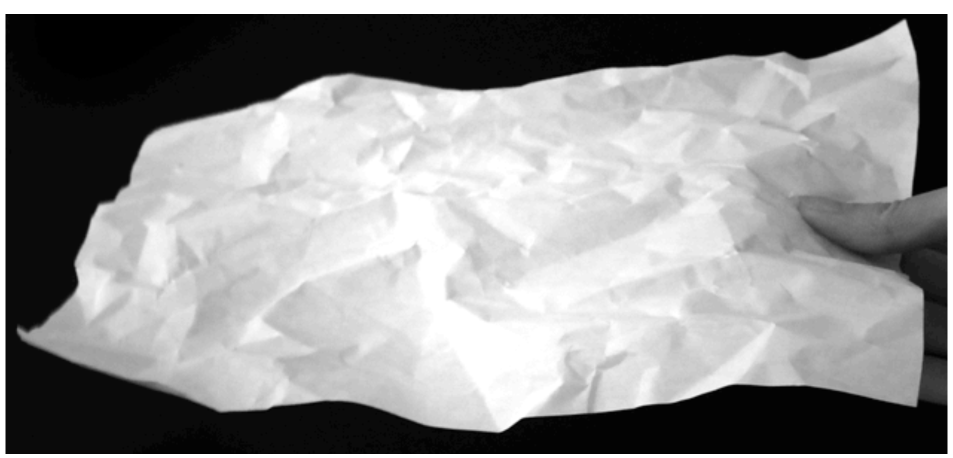
$$\ell_p = A/(k_B T)$$

$A$ polymer bending stiffness

# What happens in 2D solid membranes in the presence of thermal fluctuations?



flat phase



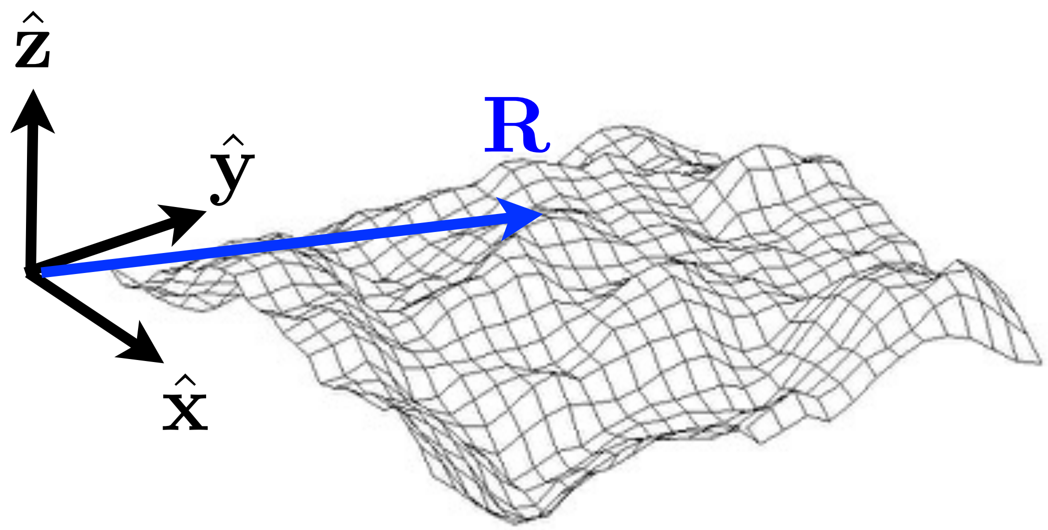
low T phase

isotropic phase

high T phase

# Free energy cost of solid membrane deformations

## Monge representation




$$\mathbf{R}(x,y) = \begin{pmatrix} x \\ y \\ 0 \end{pmatrix} + \begin{pmatrix} u_x(x,y) \\ u_y(x,y) \\ f(x,y) \end{pmatrix}$$

**reference flat state** **small deformations**

$$F = \int dA \, \frac{1}{2} \left[ \lambda u_{ii}^2 + 2\mu u_{ij}^2 + \kappa (\nabla^2 f)^2 \right]$$

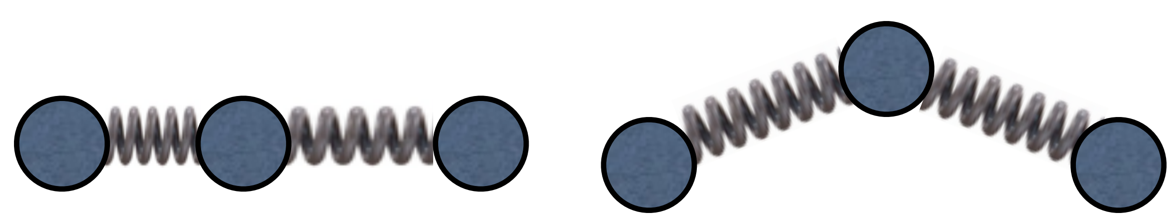
**stretching, shearing** **bending**

scaling with membrane thickness

$\lambda, \mu \sim Et$

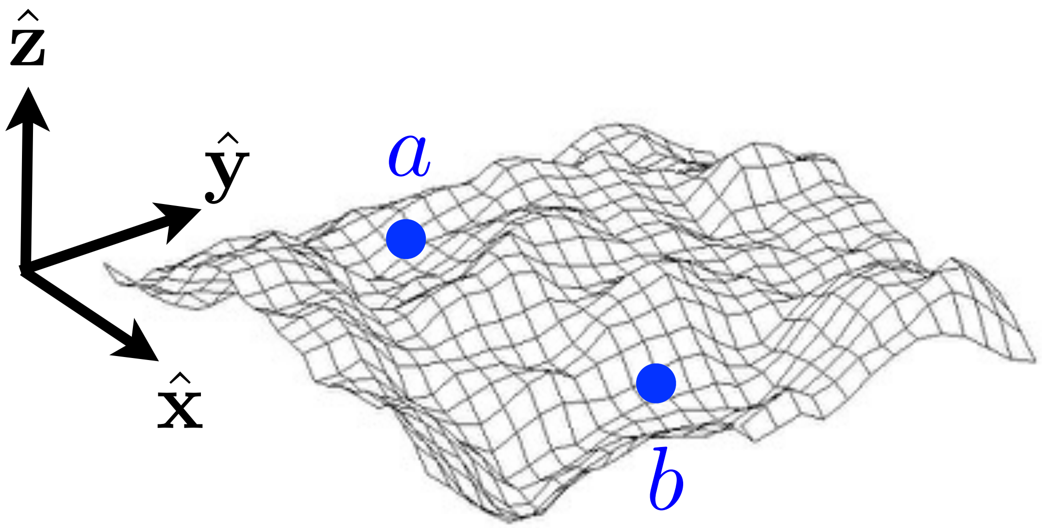
$\kappa \sim Et^3$

**strain tensor** $u_{ij} = \frac{1}{2}(\partial_i u_j + \partial_j u_i) + \frac{1}{2}(\partial_i f)(\partial_j f)$



L.D. Landau and E.M. Lifshitz, *Theory of Elasticity*

# Correlation functions




$$F = \int dA \, \frac{1}{2} \left[ \lambda u_{ii}^2 + 2\mu u_{ij}^2 + \kappa \left( \nabla^2 f \right)^2 \right]$$

$$u_{ij} = \frac{1}{2} \left( \partial_i u_j + \partial_j u_i \right) + \frac{1}{2} (\partial_i f)(\partial_j f)$$

**thermal average**

$$\langle \mathcal{O} \rangle \equiv \int \mathcal{D} \left[ u_x, u_y, f \right] \mathcal{O} e^{-F/k_B T} / Z$$

$$Z \equiv \int \mathcal{D} \left[ u_x, u_y, f \right] e^{-F/k_B T}$$

**out-of-plane fluctuations**

$$G_{ff} \left( \mathbf{r}_a - \mathbf{r}_b \right) \equiv \langle f(\mathbf{r}_a) f(\mathbf{r}_b) \rangle$$

**in-plane fluctuations**

$$G_{u_i u_j} \left( \mathbf{r}_a - \mathbf{r}_b \right) \equiv \langle u_i(\mathbf{r}_a) u_j(\mathbf{r}_b) \rangle$$

**Fourier transform**

$$G(\mathbf{q}) = \int (d^2 \mathbf{r}/A) e^{-i \mathbf{q} \cdot \mathbf{r}} G(\mathbf{r})$$

**Longitudinal and transverse projection operators**

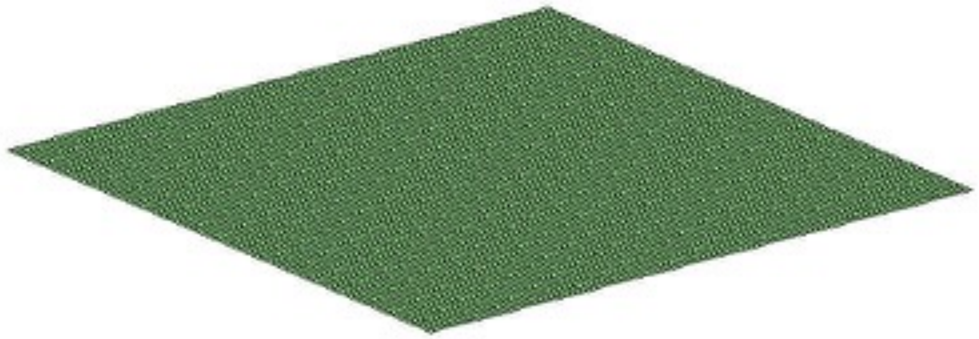
$$P_{ij}^L(\mathbf{q}) = q_i q_j / q^2$$

$$P_{ij}^T(\mathbf{q}) = \delta_{ij} - q_i q_j / q^2$$

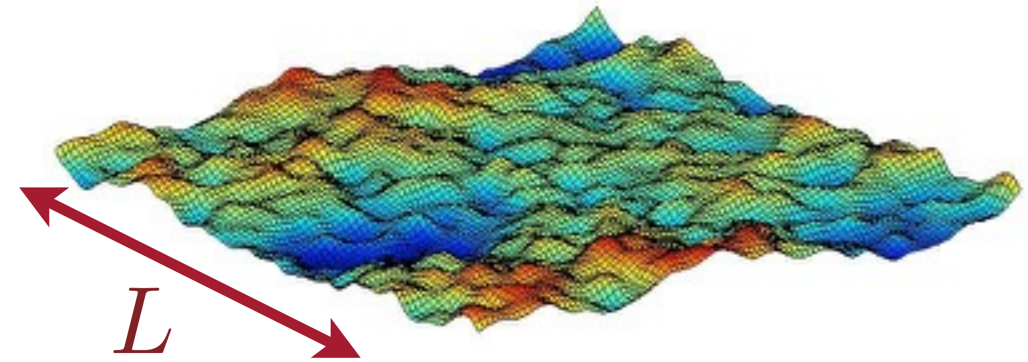
$$G_{ff} \left( \mathbf{q} \right) \equiv \frac{k_B T}{A \kappa_R(q) q^4} \qquad G_{u_i u_j} \left( \mathbf{q} \right) \equiv \frac{k_B T P_{ij}^L(\mathbf{q})}{A (2\mu_R(q) + \lambda_R(q)) q^2} + \frac{k_B T P_{ij}^T(\mathbf{q})}{A \mu_R(q) q^2}$$

# Renormalized elastic constants

$\mathbf{T = 0}$



$\mathbf{T > 0}$




**material elastic constants**

**renormalized scale dependent elastic constants**

**bending rigidity** $\kappa$

**Young's modulus** $Y$

**shear modulus** $\mu$

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

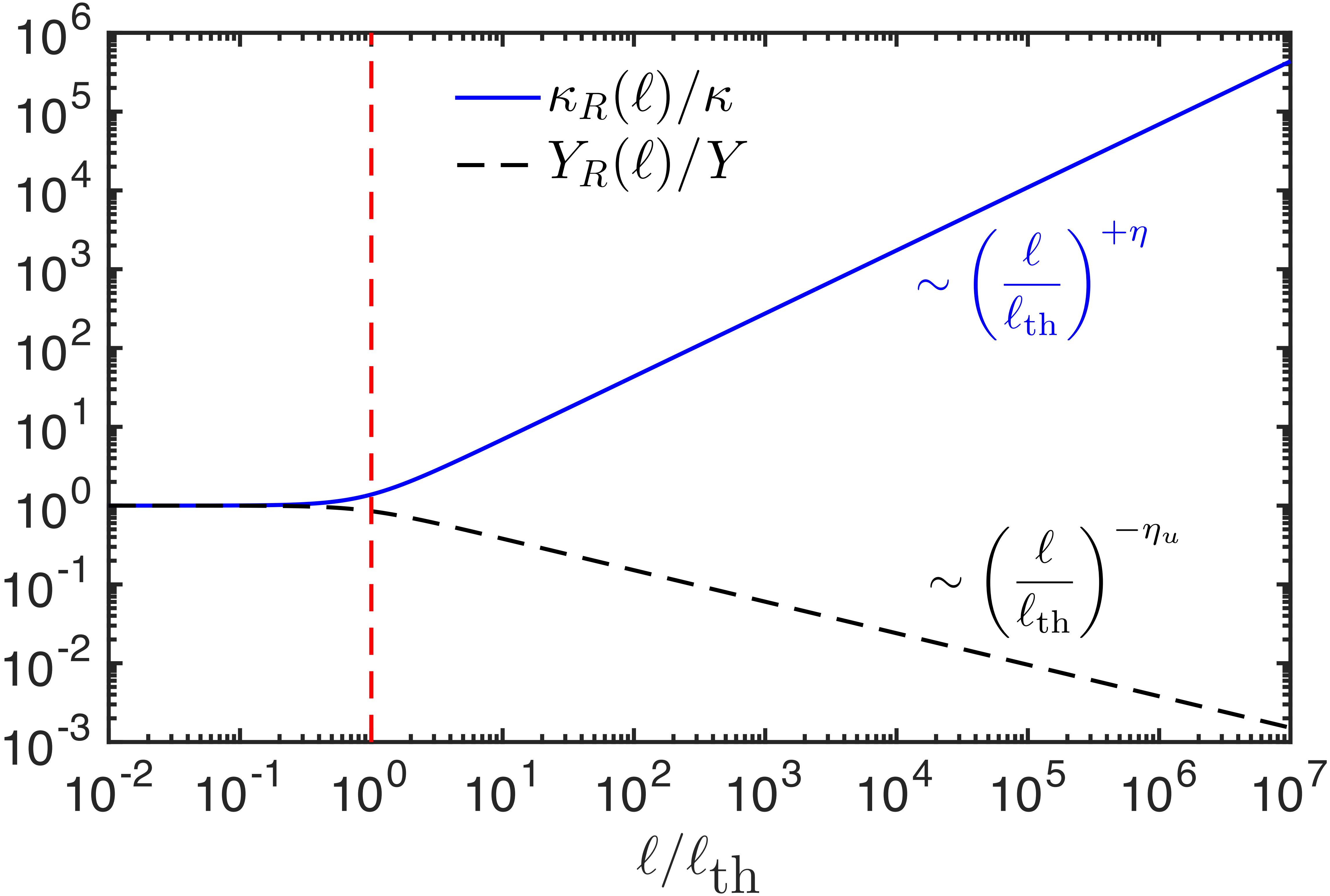
$$\kappa_R \sim (L/\ell_{\text{th}})^{+\eta} \qquad \eta \approx 0.82$$

$$Y_R, \mu_R \sim (L/\ell_{\text{th}})^{-\eta_u} \qquad \eta_u = 2 - 2\eta \approx 0.36$$

**critical size** $\ell_{\text{th}} \sim \frac{\kappa}{\sqrt{k_B T Y}} \sim \sqrt{\frac{E t^5}{k_B T}}$ **amplitude of fluctuations** $\sim$ **membrane thickness**

D. Nelson and L. Peliti, J. de Physique **48**, 1085 (1987)
J. A. Aronovitz and T. C. Lubensky, PRL **60**, 2634 (1988)
E. Guitter, F. David, S. Leibler and L. Peliti, J. de Physique **50**, 1787 (1989)
P. Le Doussal and L. Radzihovsky, PRL **69**, 1209 (1992)

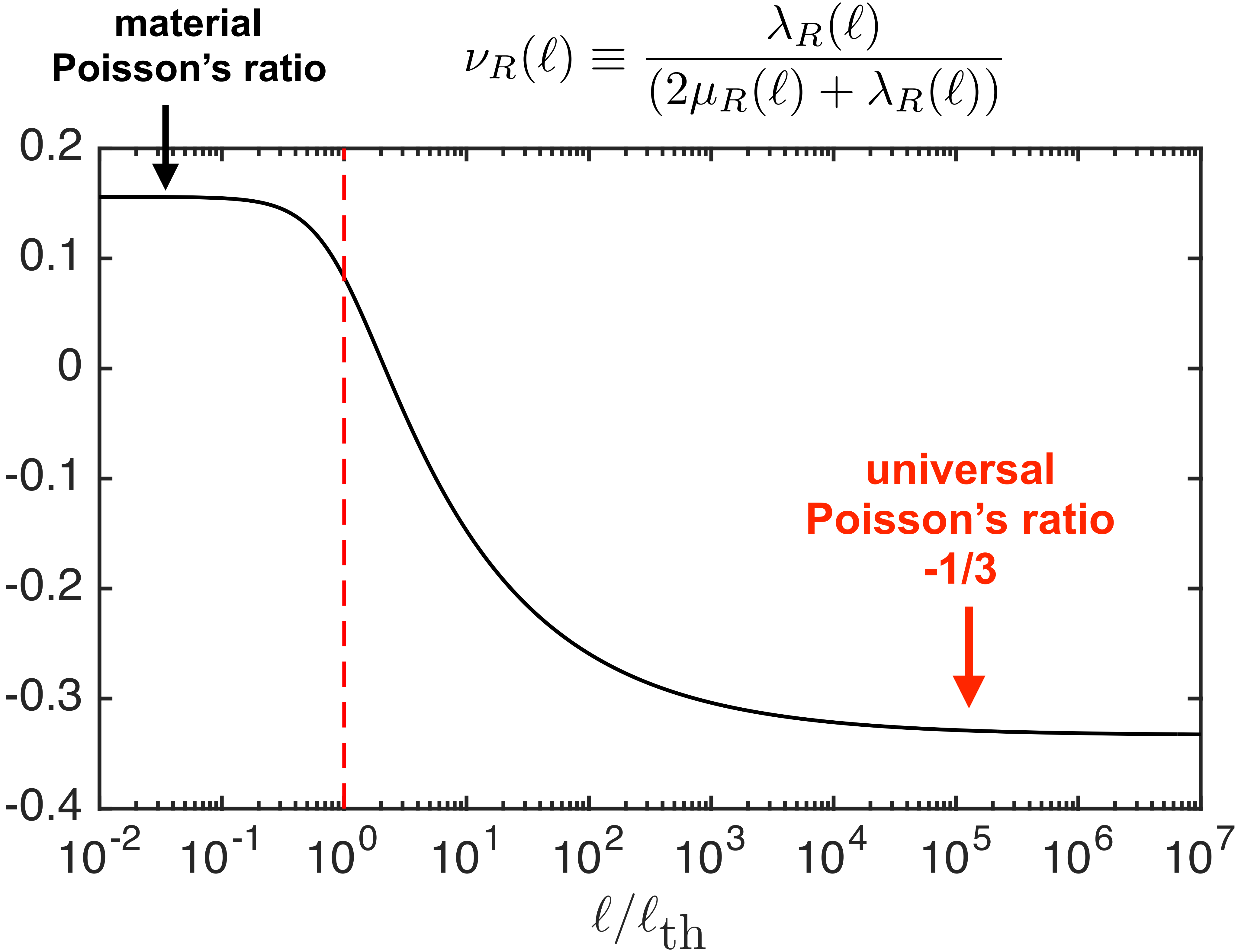
# Renormalized elastic constants




$$\ell \equiv \frac{\pi}{q} \qquad \ell_{\rm th} = \sqrt{\frac{16\pi^3\kappa^2}{3k_BTY}} \qquad \eta \approx 0.82 \qquad \eta_u \approx 0.36$$

# Universal renormalized Poisson's ratio

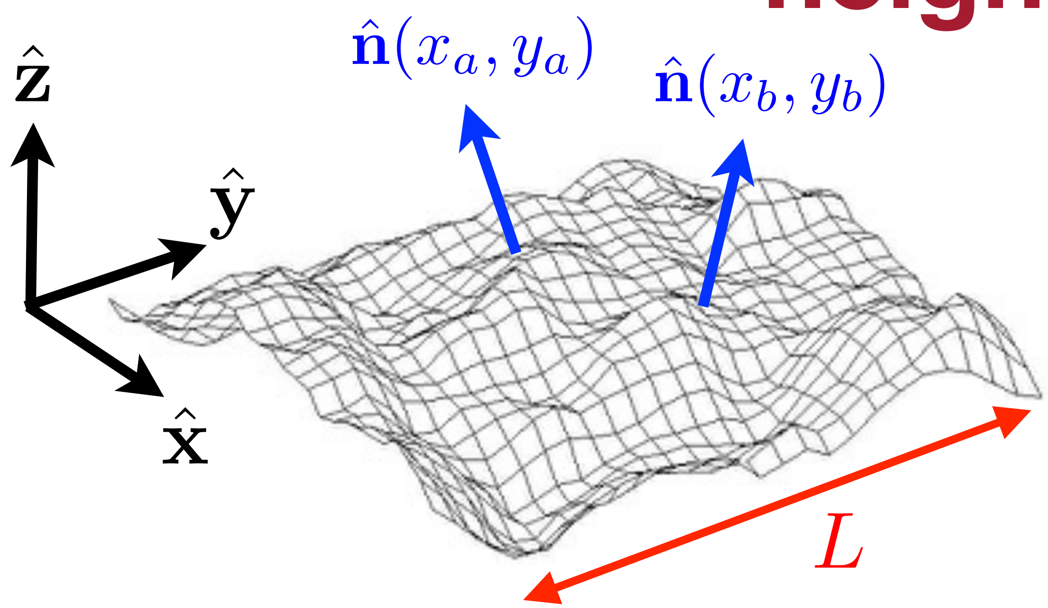
$$\nu_R(\ell) \equiv \frac{\lambda_R(\ell)}{(2\mu_R(\ell) + \lambda_R(\ell))}$$




**theory** P. Le Doussal and L. Radzihovsky, PRL **69**, 1209 (1992)

**Monte Carlo simulations** M. Falcioni *et al.*, Europhys. Lett. **38**, 67 (1997)

# Normal-normal correlations and height fluctuations




$$\hat{\mathbf{n}}(x,y) = \frac{1}{\sqrt{1+(\nabla f)^2}} \begin{pmatrix} -\partial_x f \\ -\partial_y f \\ 1 \end{pmatrix}$$

**thermal length scale** $\ell_{\text{th}} \sim \kappa / \sqrt{k_B T Y}$

**microscopic cutoff** $a_0$

$$\langle \hat{\mathbf{n}}(\mathbf{r}_a) \cdot \hat{\mathbf{n}}(\mathbf{r}_b) \rangle \approx 1 + \langle \nabla f(\mathbf{r}_a) \cdot \nabla f(\mathbf{r}_b) \rangle - \frac{1}{2} \langle |\nabla f(\mathbf{r}_a)|^2 \rangle - \frac{1}{2} \langle |\nabla f(\mathbf{r}_b)|^2 \rangle$$

$$\langle \hat{\mathbf{n}}(\mathbf{r}_a) \cdot \hat{\mathbf{n}}(\mathbf{r}_b) \rangle \approx 1 - \frac{k_B T}{2\pi\kappa} \left[ \eta^{-1} + \ln\left(\frac{\ell_{\text{th}}}{a_0}\right) \right] + C \frac{k_B T}{\kappa} \left( \frac{\ell_{\text{th}}}{|\mathbf{r}_b - \mathbf{r}_a|} \right)^{\eta}$$

**Normal-normal correlations approach constant value at large separation.**

**Signature of long range ordered flat phase!**

**Height fluctuations are small compared to the membrane size**

$$\left\langle \frac{f(\mathbf{r})^2}{L^2} \right\rangle \sim \frac{k_B T}{\kappa} \left( \frac{\ell_{\text{th}}}{L} \right)^{\eta}$$

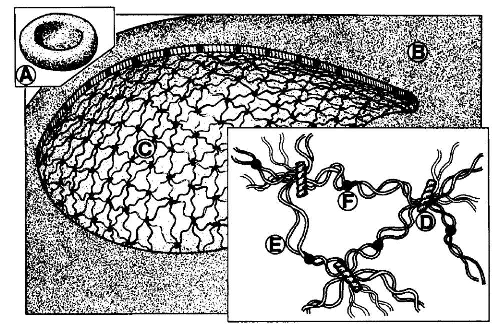
A. Košmrlj and D. Nelson, arXiv:1508.01528 (2015)

# Thermal length scale for various membranes

**sheet of paper**

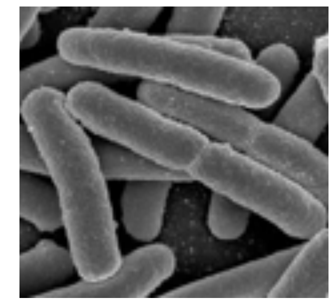
$\ell_{\mathrm{th}} \sim 50\mathrm{km} \sim 30\mathrm{miles}$

**red blood cell membrane**



$\ell_{\mathrm{th}} \sim 1\mu\mathrm{m}$

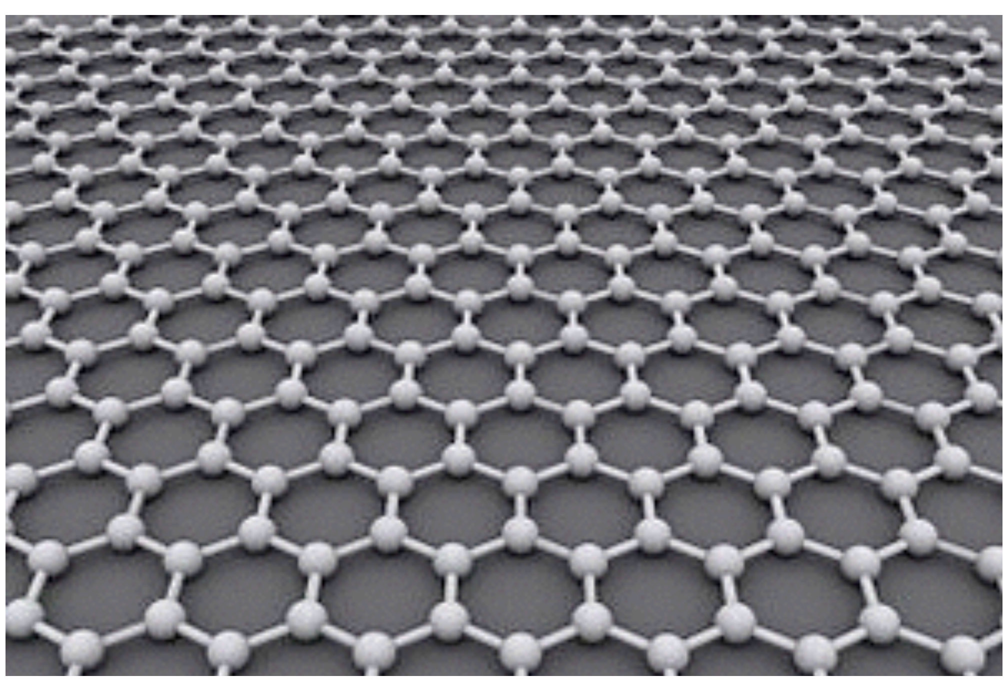
**bacterial cell wall**



← **internal pressure suppresses thermal fluctuations**

$\ell_{\mathrm{th}} \sim 10\mathrm{nm}$

**Graphene is one atom thick 2D crystalline membrane**



**Extremely flexible**

$$\kappa \approx 1.2\mathrm{eV} \approx 2 \times 10^{-19} J$$

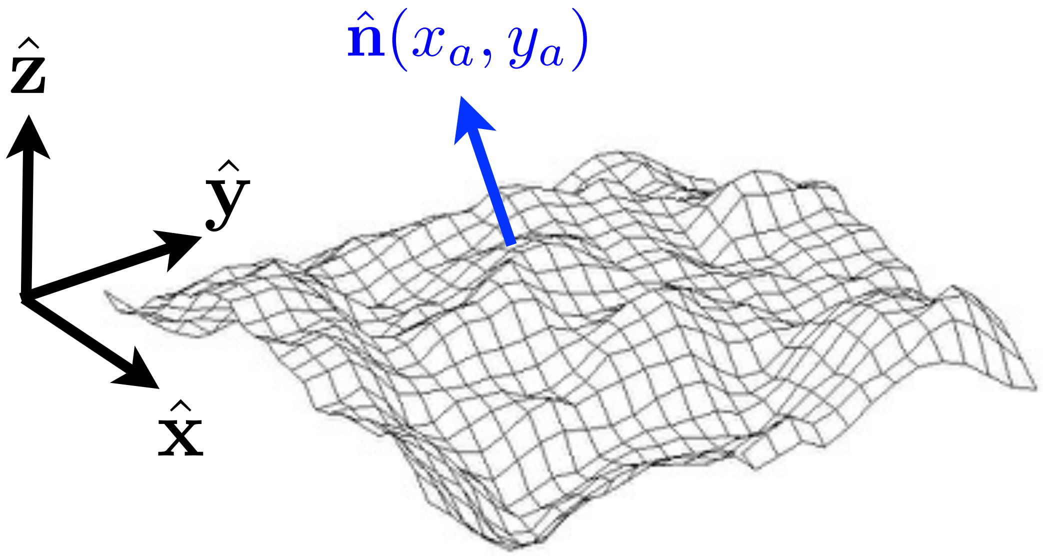
**Very stiff in-plane**

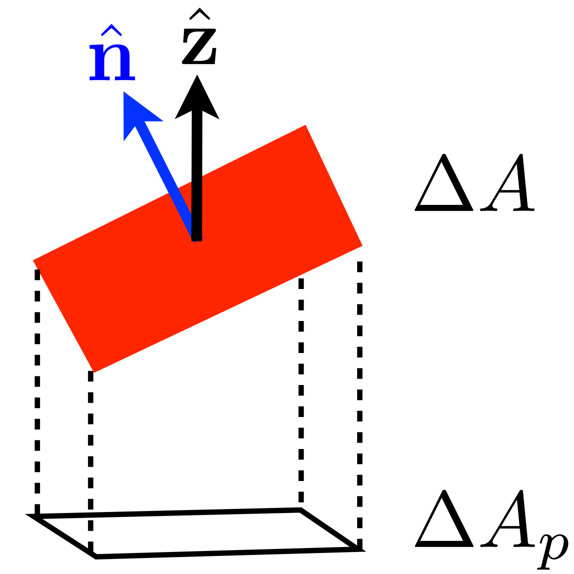
$$Y \approx 350 N/m$$

**At room temperature thermal fluctuations are important at all length scales!**

$$\ell_{\mathrm{th}} \sim \kappa/\sqrt{k_B T Y} \sim 2\mathrm{\AA}$$

# Shrinking of projected area




**projected area on XY plane**

$$\hat{\mathbf{n}}(x,y) = \frac{1}{\sqrt{1+(\nabla f)^2}} \begin{pmatrix} -\partial_x f \\ -\partial_y f \\ 1 \end{pmatrix}$$

$$\Delta A_p = n_z \Delta A$$

**Projected area shrinks due to thermal fluctuations!**

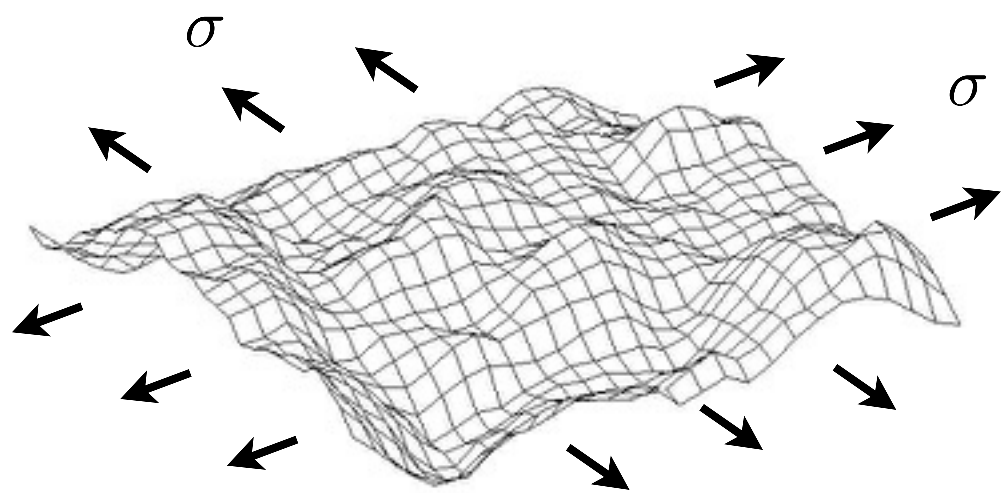
$$\left\langle \frac{\delta A}{A} \right\rangle_0 \approx -\frac{1}{2}\langle |\nabla f|^2 \rangle \approx -\frac{k_B T}{4\pi\kappa}\left[\frac{1}{\eta} + \ln\left(\frac{\ell_{\rm th}}{a_0}\right)\right]$$

**Fluctuating membranes have negative thermal expansion coefficient!**

$$\alpha = \frac{1}{A}\frac{dA}{dT} \approx -\frac{k_B}{4\pi\kappa}\left[\frac{1}{\eta} - \frac{1}{2} + \ln\left(\frac{\ell_{\rm th}}{a_0}\right)\right]$$

$\ell_{\rm th} \sim \kappa/\sqrt{k_B T Y}$

# Membranes under uniform tension




**tension suppresses height fluctuations**

$$G_{ff}(\mathbf{q}) = \frac{k_B T}{A\left(\kappa_R(q) q^4 + \sigma q^2\right)}$$

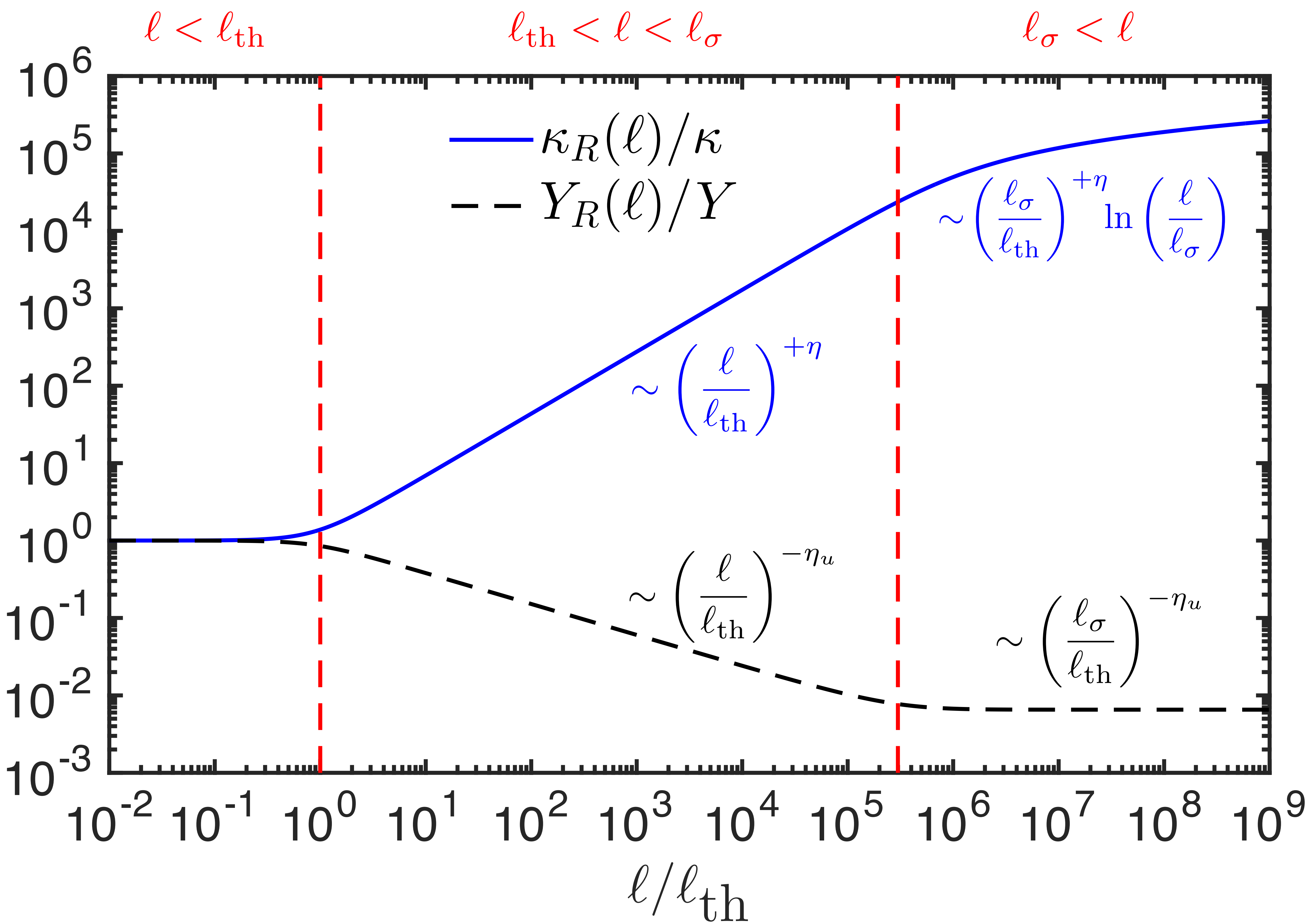
**tension dominates on scales larger than**

$$\ell_\sigma \sim \left(\frac{\kappa}{\sigma \ell_{\mathrm{th}}^\eta}\right)^{1/(2-\eta)} \sim \ell_{\mathrm{th}} \left(\frac{k_B T Y}{\sigma \kappa}\right)^{1/(2-\eta)}$$

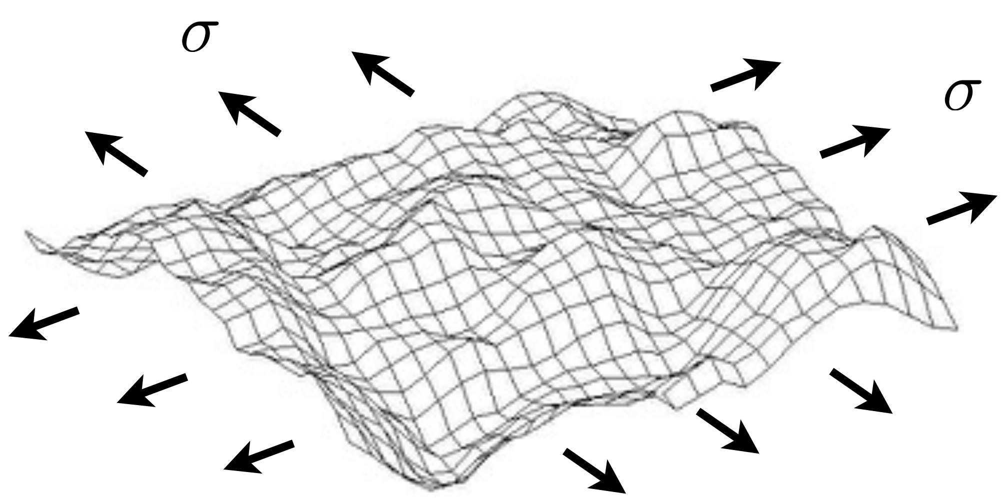
**For large tension, $\sigma \gtrsim k_B T Y/\kappa$ ,**
**thermal fluctuations become irrelevant!**

# External tension provides a cutoff for the renormalization of elastic constants

$\ell_{\rm th} \sim \kappa/\sqrt{k_B T Y}$ $\qquad$ $\ell_\sigma/\ell_{\rm th} \sim [k_B T Y/\sigma\kappa]^{1/(2-\eta)}$



# Area extension under uniform tension




E. Guitter *et al.*, J. de Physique **50**, 1787 (1989)

A. Košmrlj and D. Nelson, arXiv:1508.01528 (2015)

$$\left\langle \frac{\delta A}{A} \right\rangle \approx \frac{\sigma}{(\mu+\lambda)} - \frac{1}{2}\langle |\nabla f|^2 \rangle$$

$$\left\langle \frac{\delta A}{A} \right\rangle \approx \left\langle \frac{\delta A}{A} \right\rangle_0 + \begin{cases} \mathcal{C}_1 \frac{\sigma}{Y} \left(\frac{L}{\ell_{\rm th}}\right)^{\eta_u}; & L < \ell_\sigma \\ \mathcal{C}_2 \frac{k_B T}{\kappa} \left(\frac{\sigma\kappa}{k_B T Y}\right)^{\eta/(2-\eta)} + \frac{\sigma}{(\mu+\lambda)}; & L > \ell_\sigma \end{cases}$$

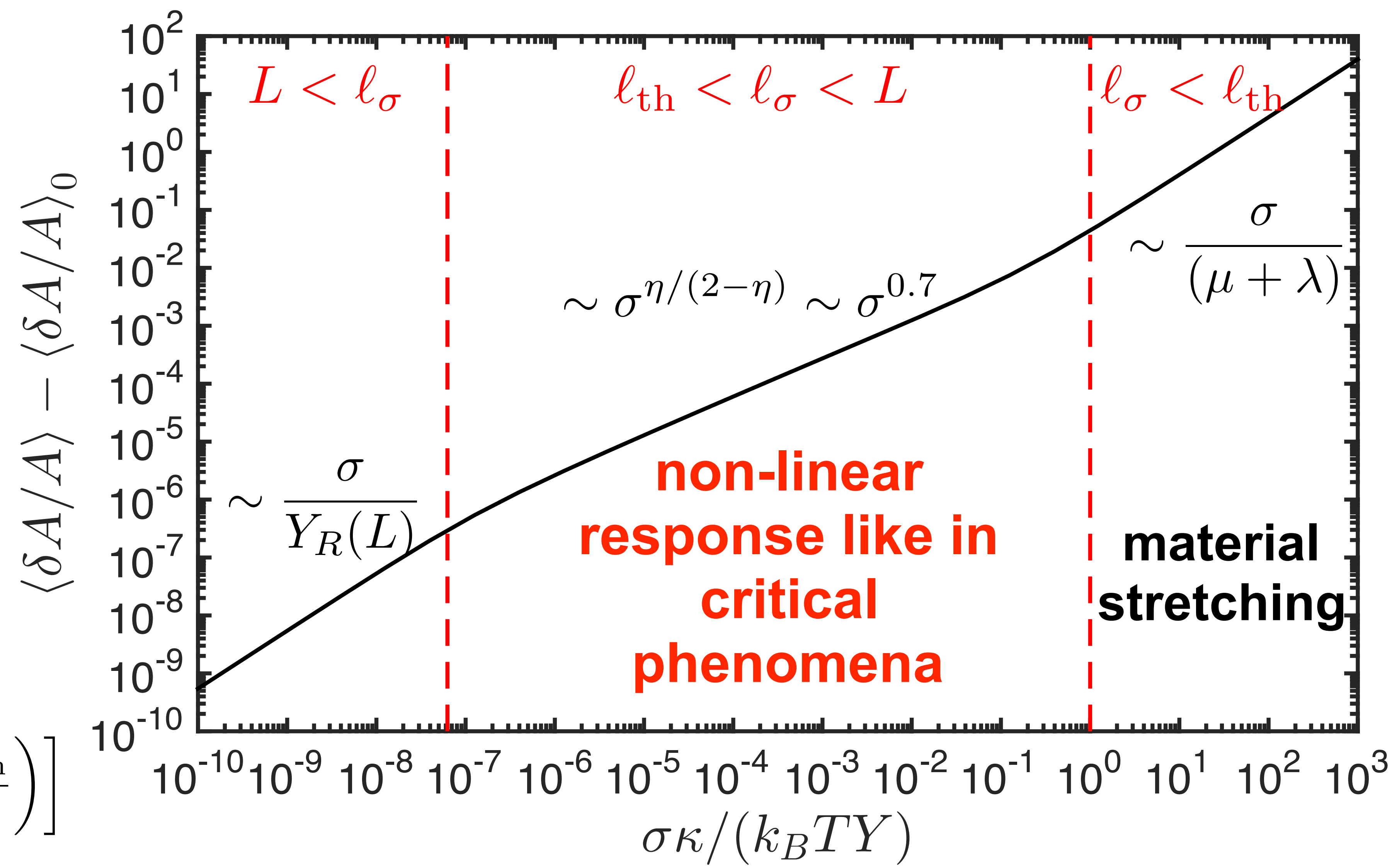
$$\eta \approx 0.82$$

$$\eta_u \approx 0.36$$

$$\ell_{\rm th} \sim \frac{\kappa}{\sqrt{k_B T Y}}$$

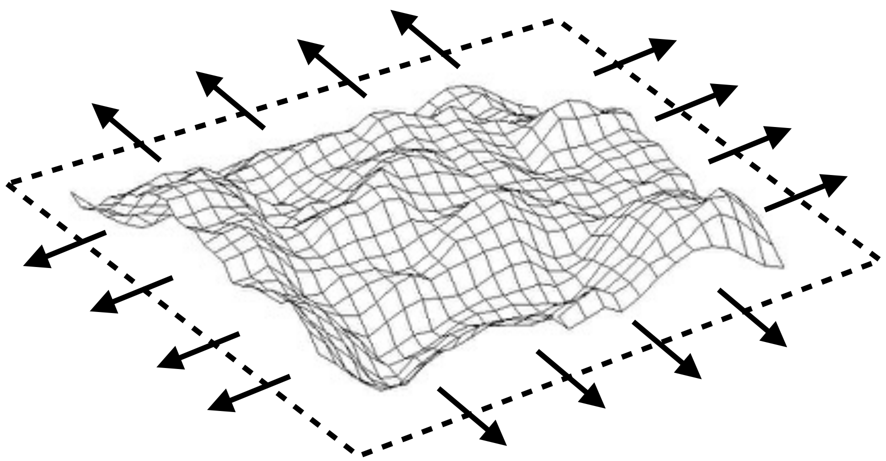
$$\frac{\ell_\sigma}{\ell_{\rm th}} \sim \left(\frac{k_B T Y}{\sigma\kappa}\right)^{1/(2-\eta)}$$

$$\left\langle \frac{\delta A}{A} \right\rangle_0 \approx -\frac{k_B T}{4\pi\kappa}\left[\frac{1}{\eta} + \ln\left(\frac{\ell_{\rm th}}{a_0}\right)\right]$$



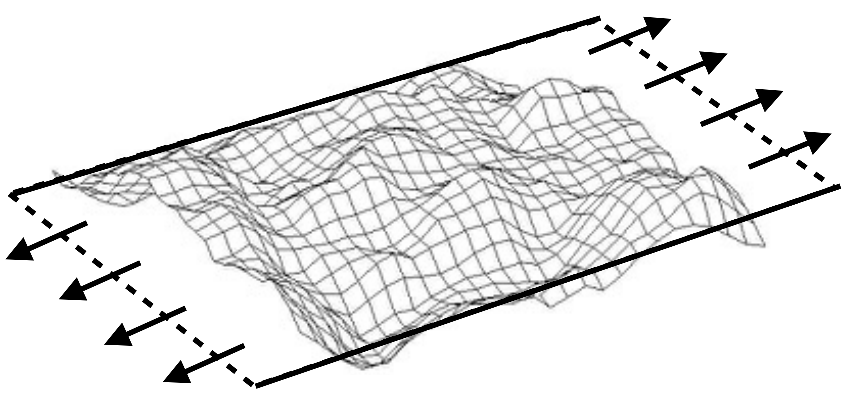
# Scaling of in-plane elastic properties with the system size of graphene membranes

**bulk modulus** $B_{\rm eq}$



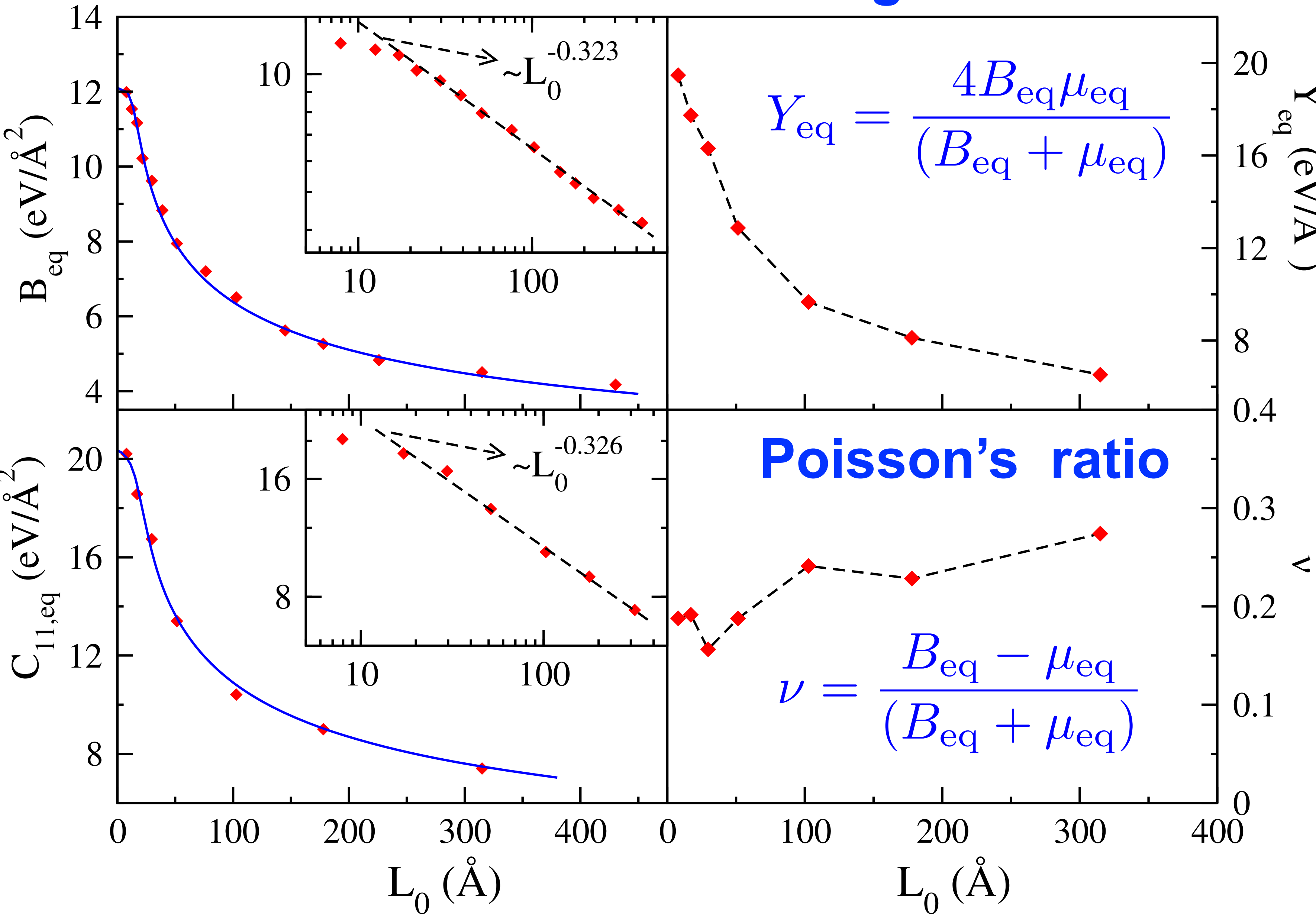
$$B_{\rm eq} = \mu_{\rm eq} + \lambda_{\rm eq}$$

**uniaxial modulus** $C_{11,\rm eq}$



$$C_{11,\rm eq} = B_{\rm eq} + \mu_{\rm eq}$$

**Young's modulus**



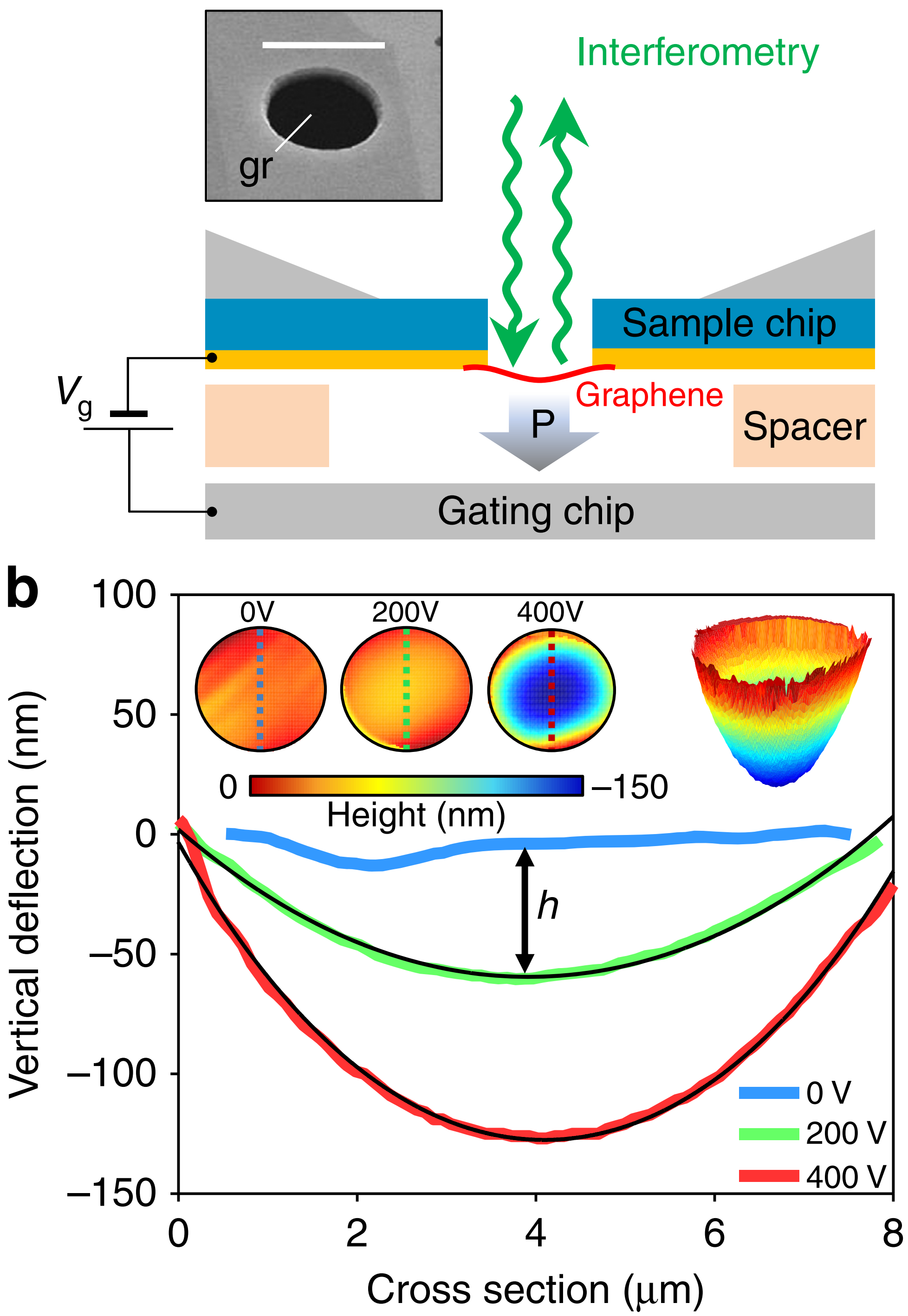

$$B_{\rm eq}, C_{11,\rm eq}, \mu_{\rm eq}, Y_{\rm eq} \sim Y\left(\frac{\ell_{\rm th}}{L}\right)^{\eta_u}$$

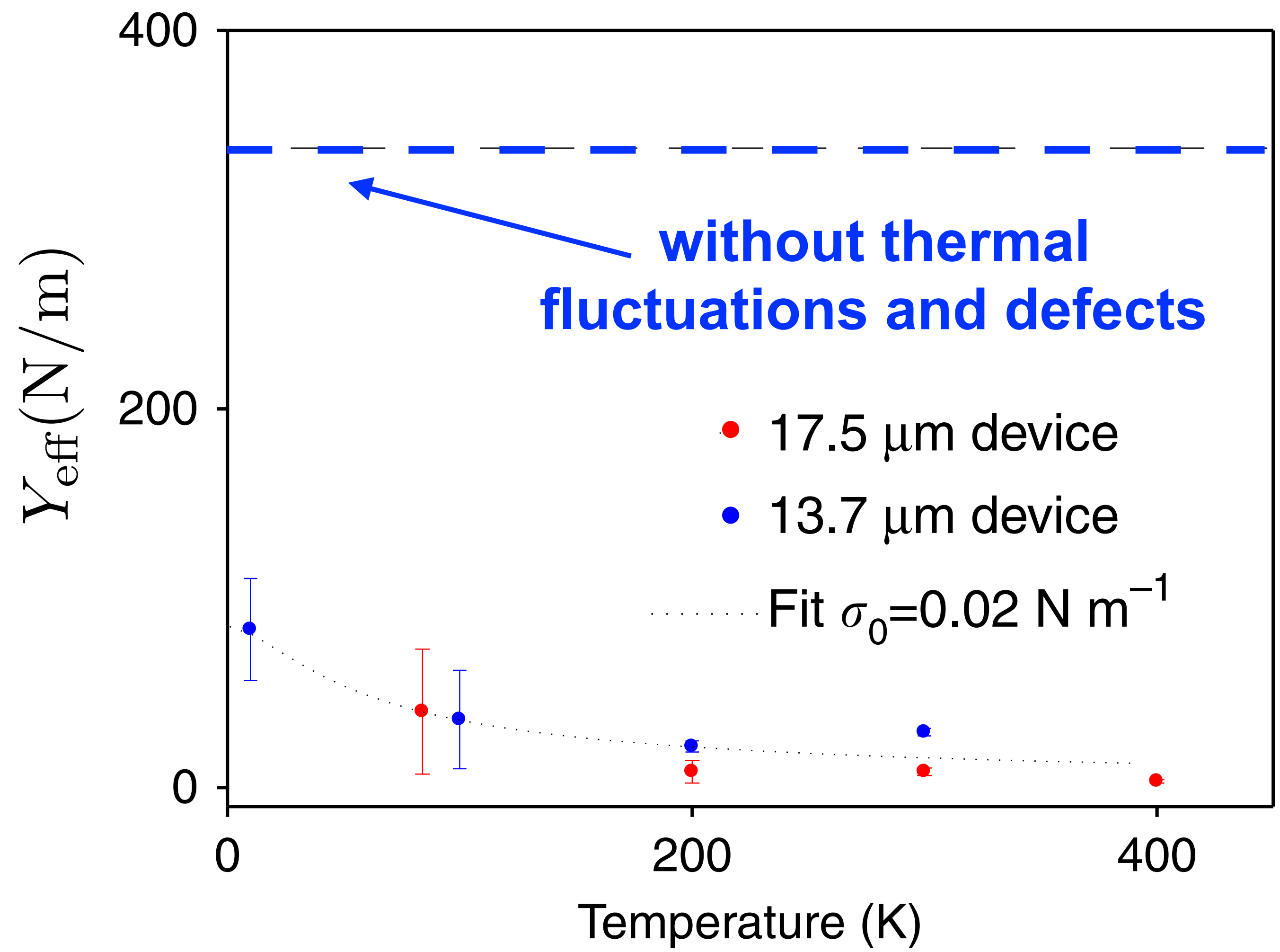
J.H. Los et al., PRL **116**, 015901 (2016)

**Poisson's ratio deviates from -1/3! Break down of linear response theory? Samples too small?**

# Temperature dependence of Young's modulus for graphene membranes

a



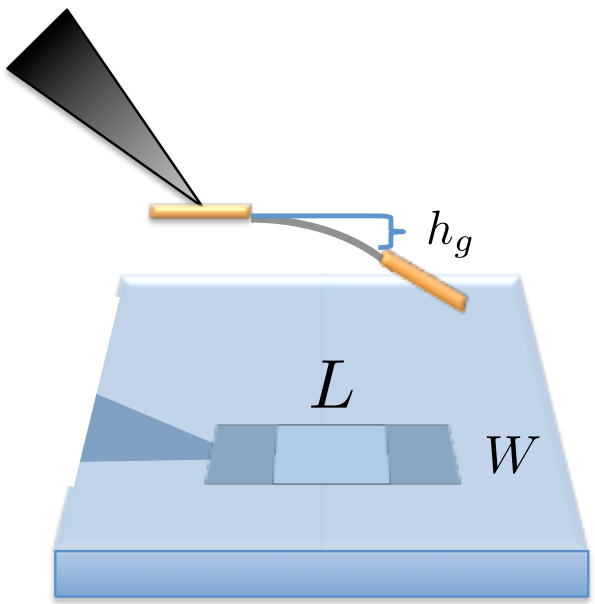




$$P = \frac{4\sigma_0 h}{R^2} + \frac{8Y_{\text{eff}}h^3}{3(1-\nu)R^4}$$

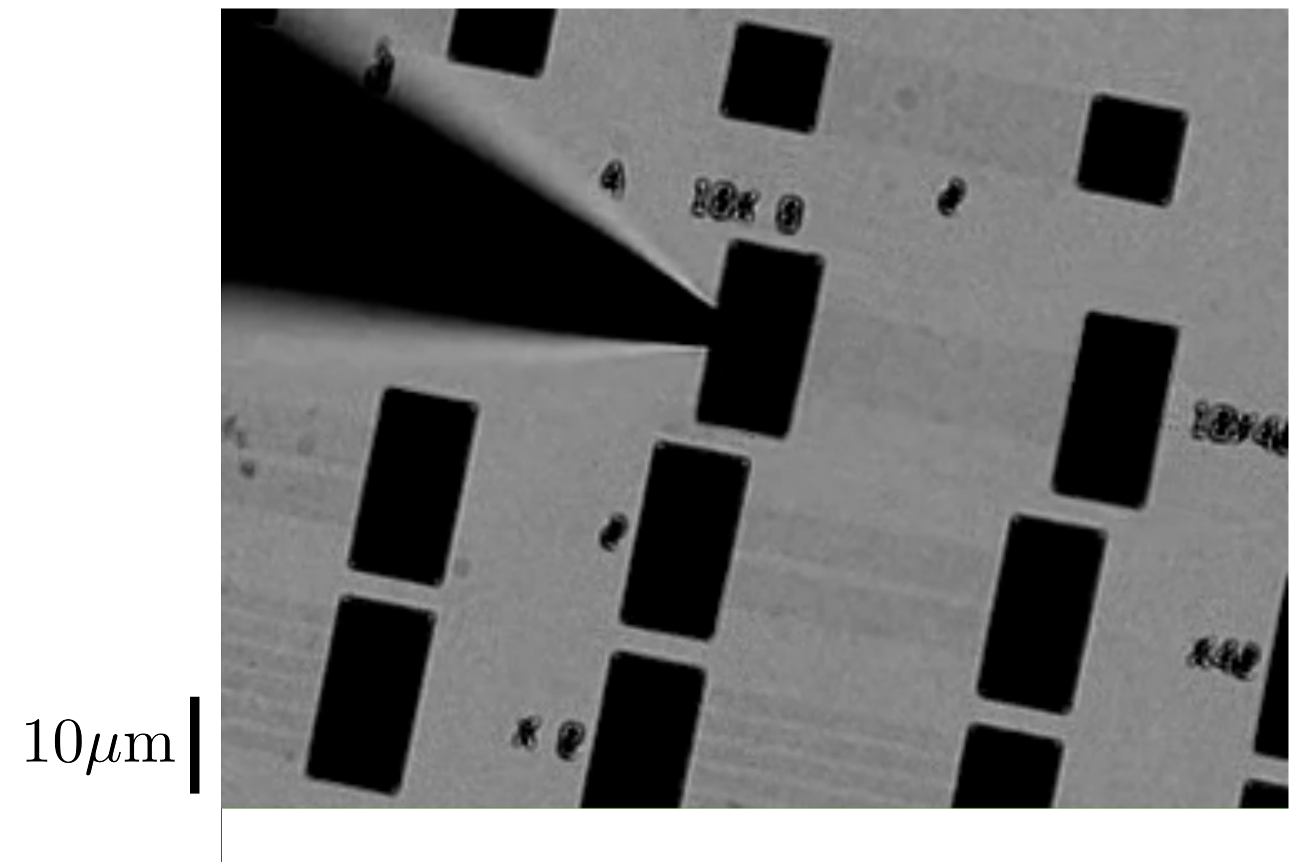
$$Y_{\text{eff}} \sim Y\left(\frac{\ell_{\text{th}}}{R}\right)^{\eta_u} \propto T^{-\eta_u/2}$$

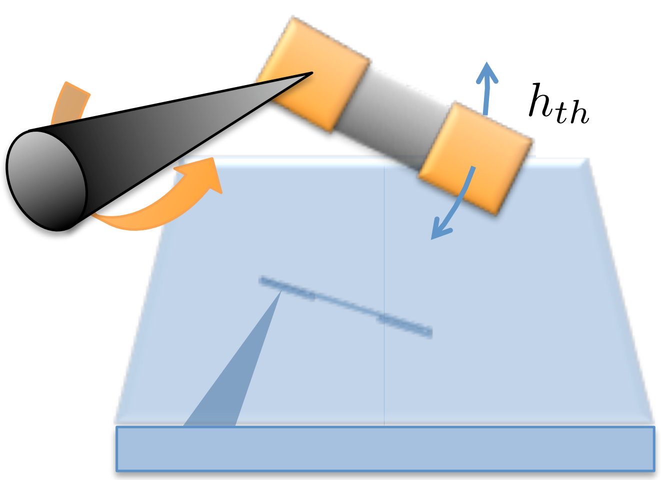
R.J.T. Nicholl et al., Nat. Comm. **6**, 8789 (2015)

# Bending experiments with graphene membranes at room temperature

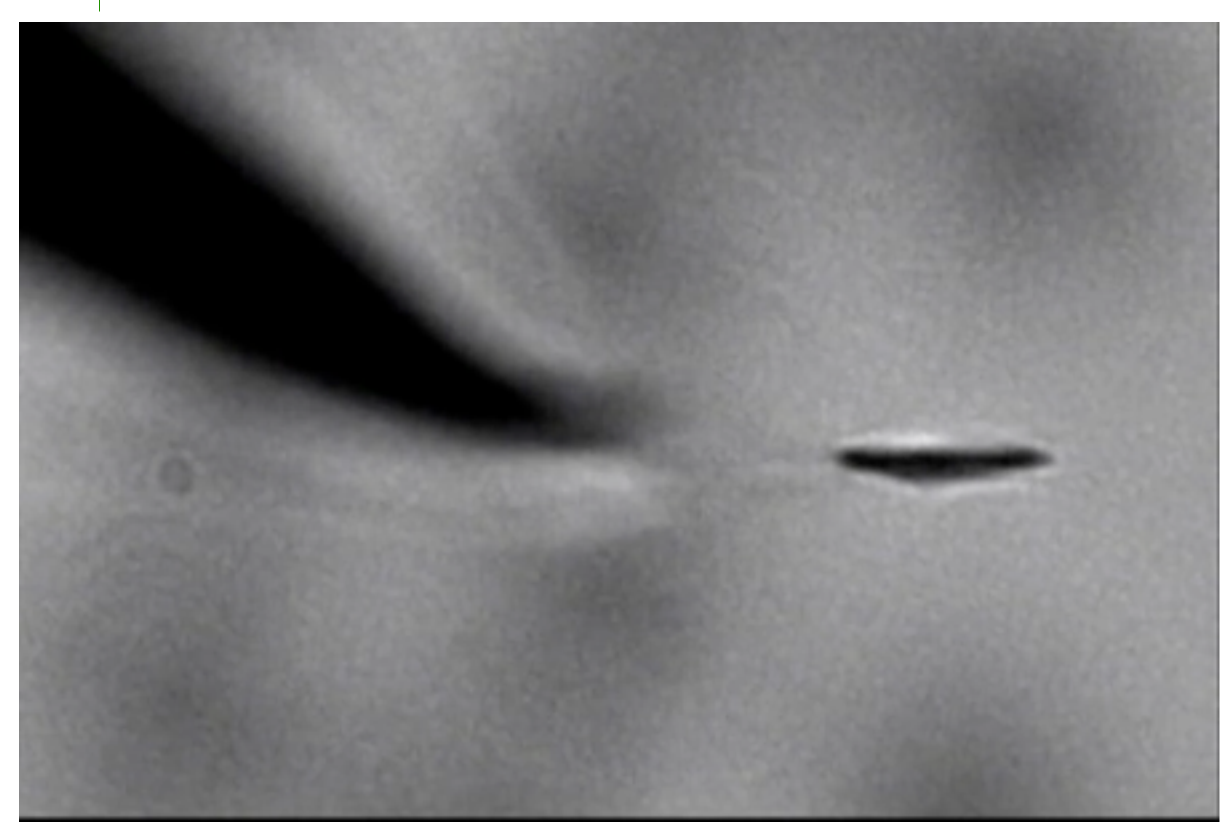



$$mg = kh_g$$




$$k_B T = k\langle h_{th}^2 \rangle$$

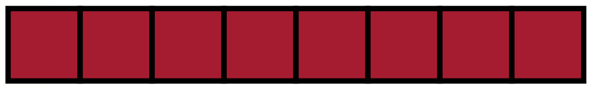


$$k = \frac{3\kappa_R W}{L^3}$$

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

# Bending rigidity of graphene membranes at room temperature

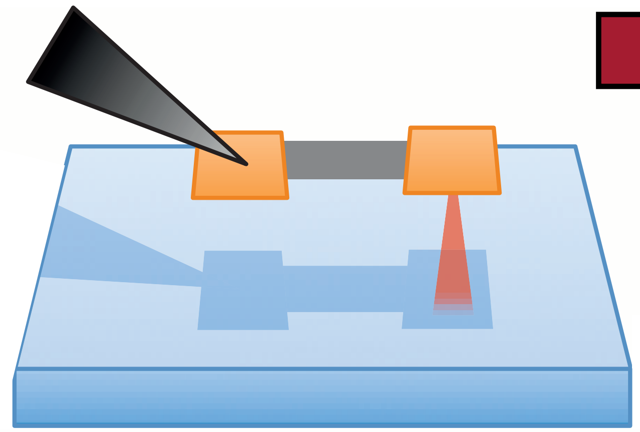
coarse-grained membrane
with WxW blocks



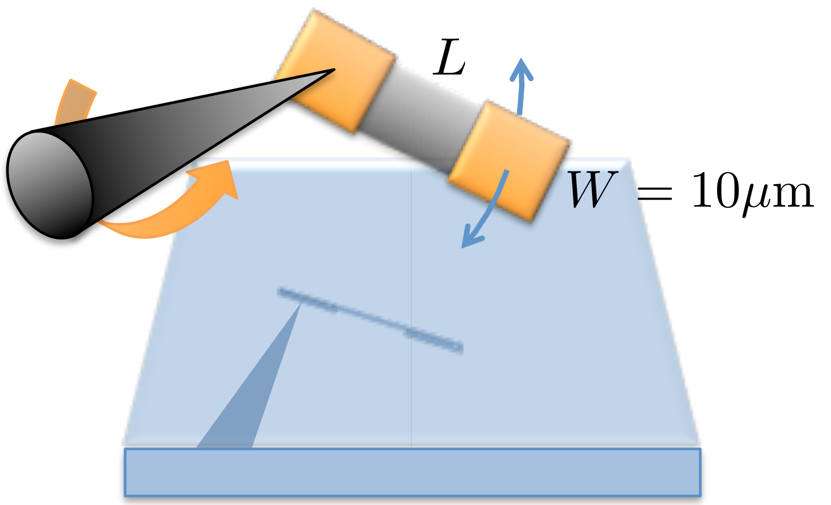
**theory**

$$\kappa_R \sim \kappa \left(\frac{W}{\ell_{\rm th}}\right)^{\eta} \sim 1\mathrm{keV}$$

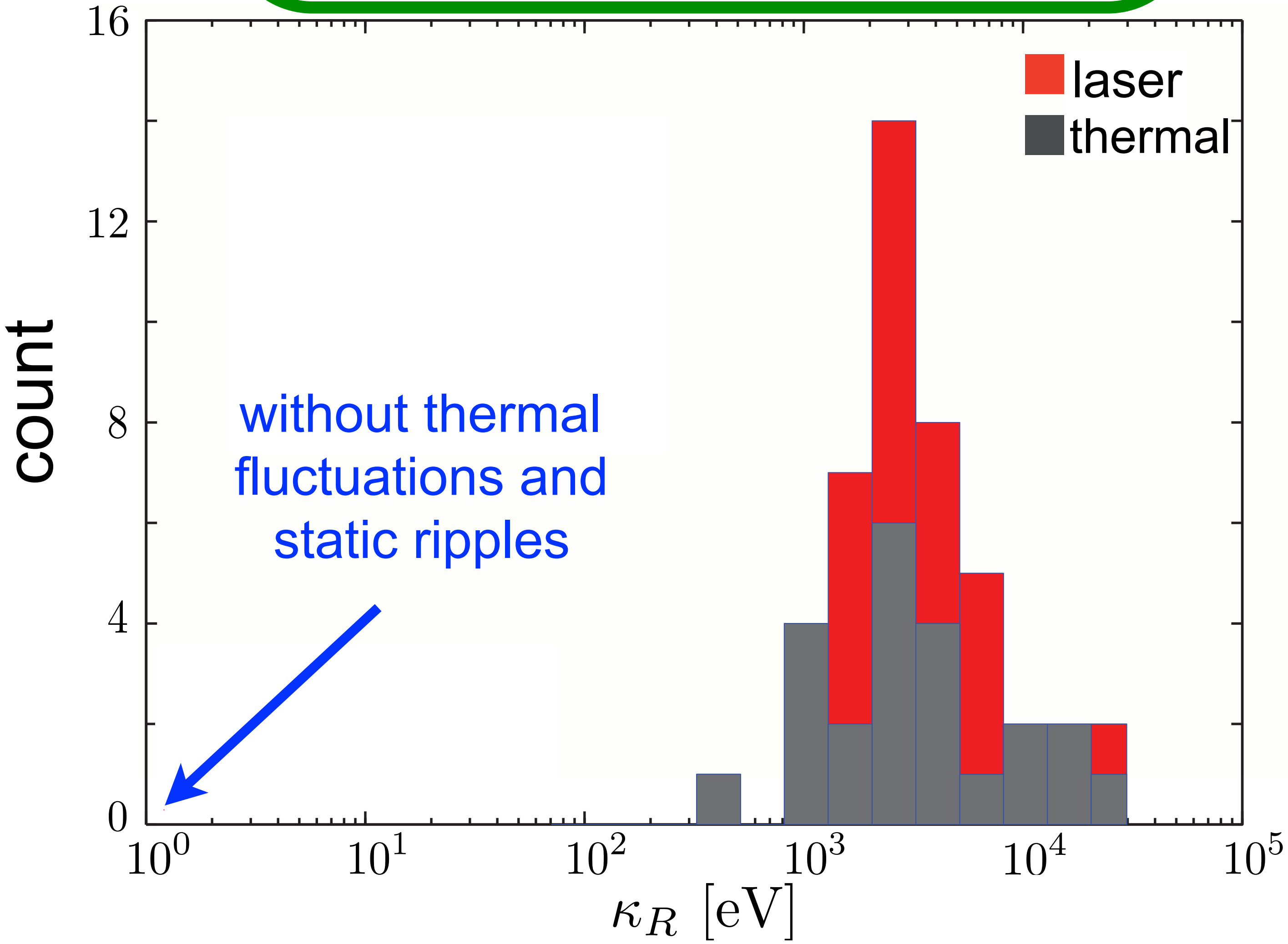
$$\ell_{\rm th} \approx \sqrt{\frac{16\pi^3\kappa^2}{3k_BTY}} \approx 2\mathrm{nm} \quad W \approx 10\mu\mathrm{m}$$



Bending by
laser pressure



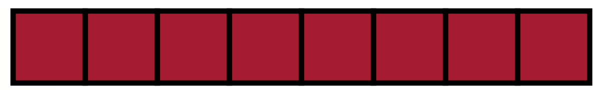

Thermal fluctuations
of free end




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

# Bending rigidity of graphene membranes at room temperature

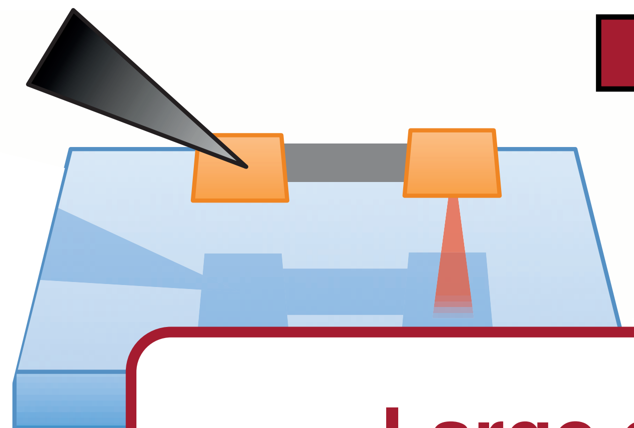
coarse-grained membrane
with WxW blocks

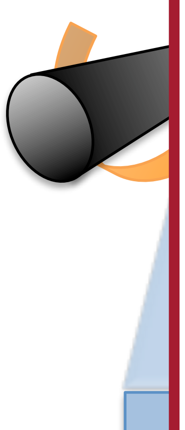


**theory**

$$\kappa_R \sim \kappa \left(\frac{W}{\ell_{\rm th}}\right)^{\eta} \sim 1 \mathrm{keV}$$

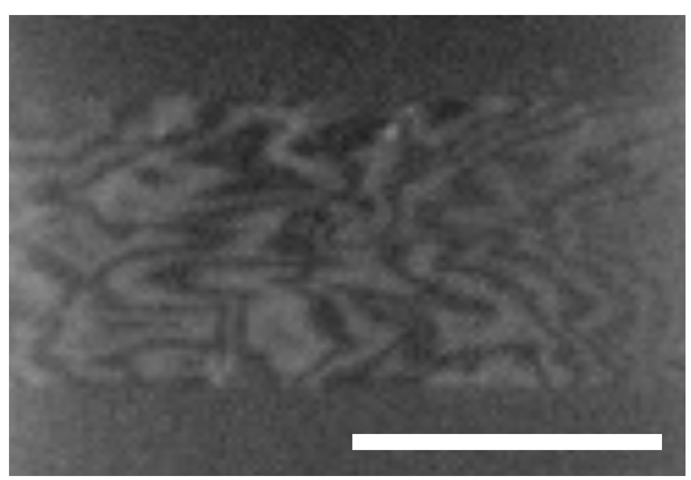
$$\ell_{\rm th} \approx \sqrt{\frac{16\pi^3\kappa^2}{3k_BTY}} \approx 2 \mathrm{nm} \quad W \approx 10 \mu\mathrm{m}$$



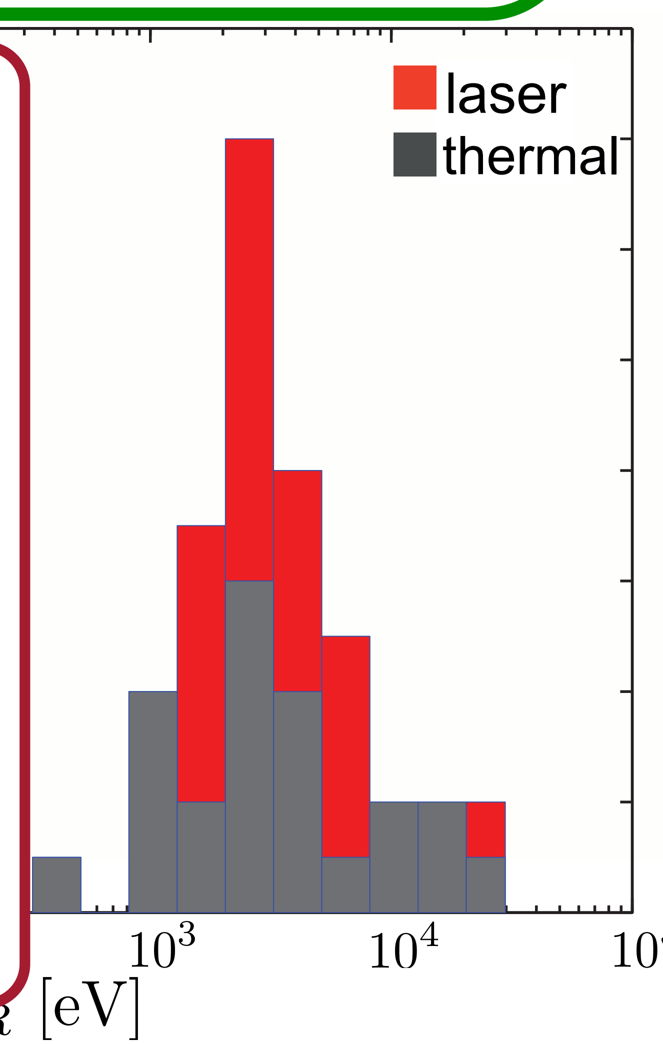


la

**Large data scatter possibly due to defects, which produce static ripples in graphene**



$10\mu$m



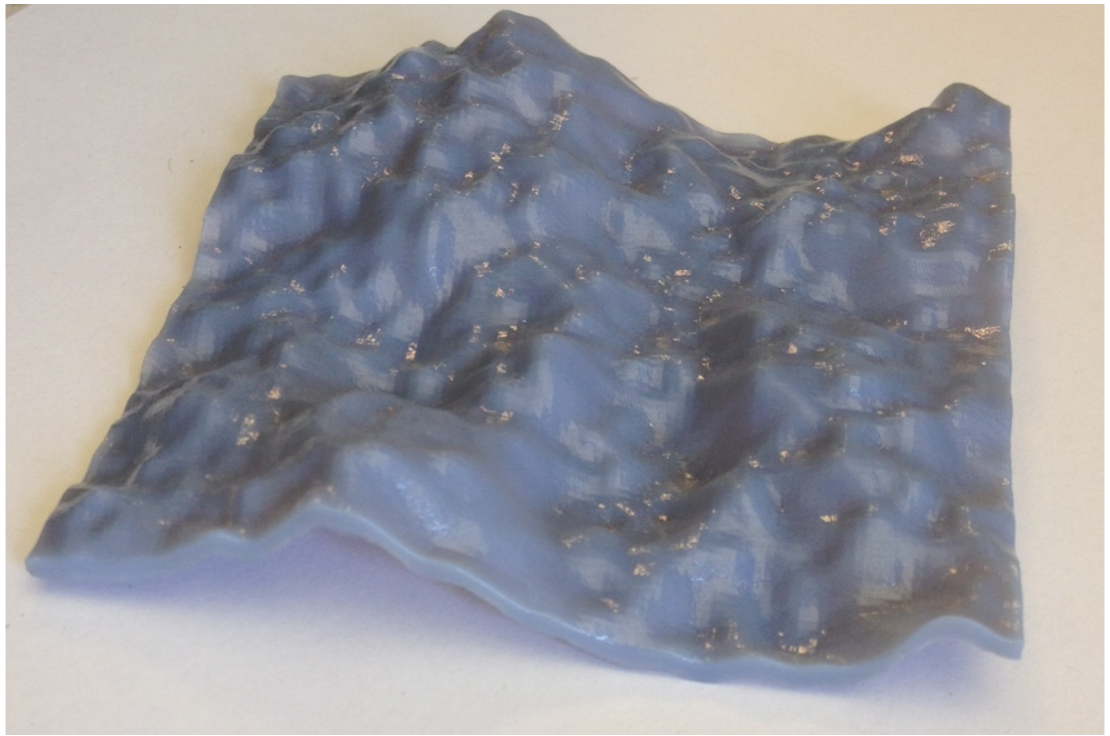

The

of free end

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

# Frozen fluctuations in nearly flat membranes

A. Košmrlj and D. Nelson, PRE **88**, 012136 (2013)
A. Košmrlj and D. Nelson, PRE **89**, 022126 (2014)



**frozen height fluctuations** $h_{\text{eff}}^2 = \frac{1}{A} \int dA\, \overline{h^2}$

**thickness** $t$

## Linear response properties averaged over frozen disorder

$$\overline{\kappa_{\text{eff}}}/\kappa \sim \sqrt{\left(Y h_{\text{eff}}^2\right)/\kappa} \sim h_{\text{eff}}/t$$

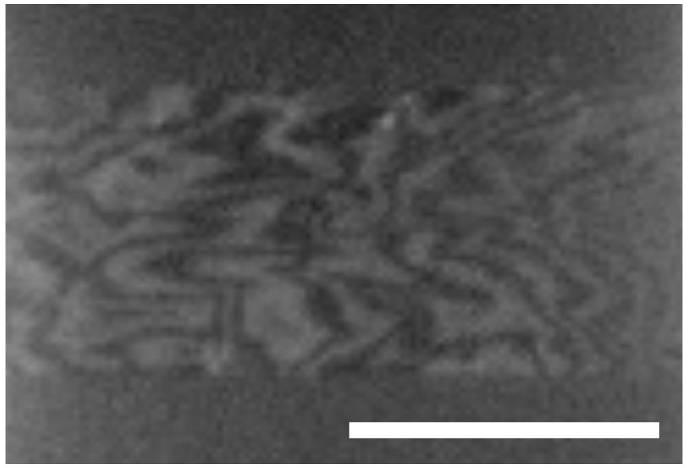
$$\overline{Y_{\text{eff}}}/Y, \overline{\mu_{\text{eff}}}/\mu \sim \sqrt{\kappa/\left(Y h_{\text{eff}}^2\right)} \sim t/h_{\text{eff}}$$

# Thermal and frozen fluctuations of graphene membranes

## frozen fluctuations

$$\kappa_{\text{eff}} \sim \kappa\sqrt{Y h_{\text{eff}}^2/\kappa} \sim 4\text{keV}$$

$$h_{\text{eff}} \sim 80\text{nm}$$

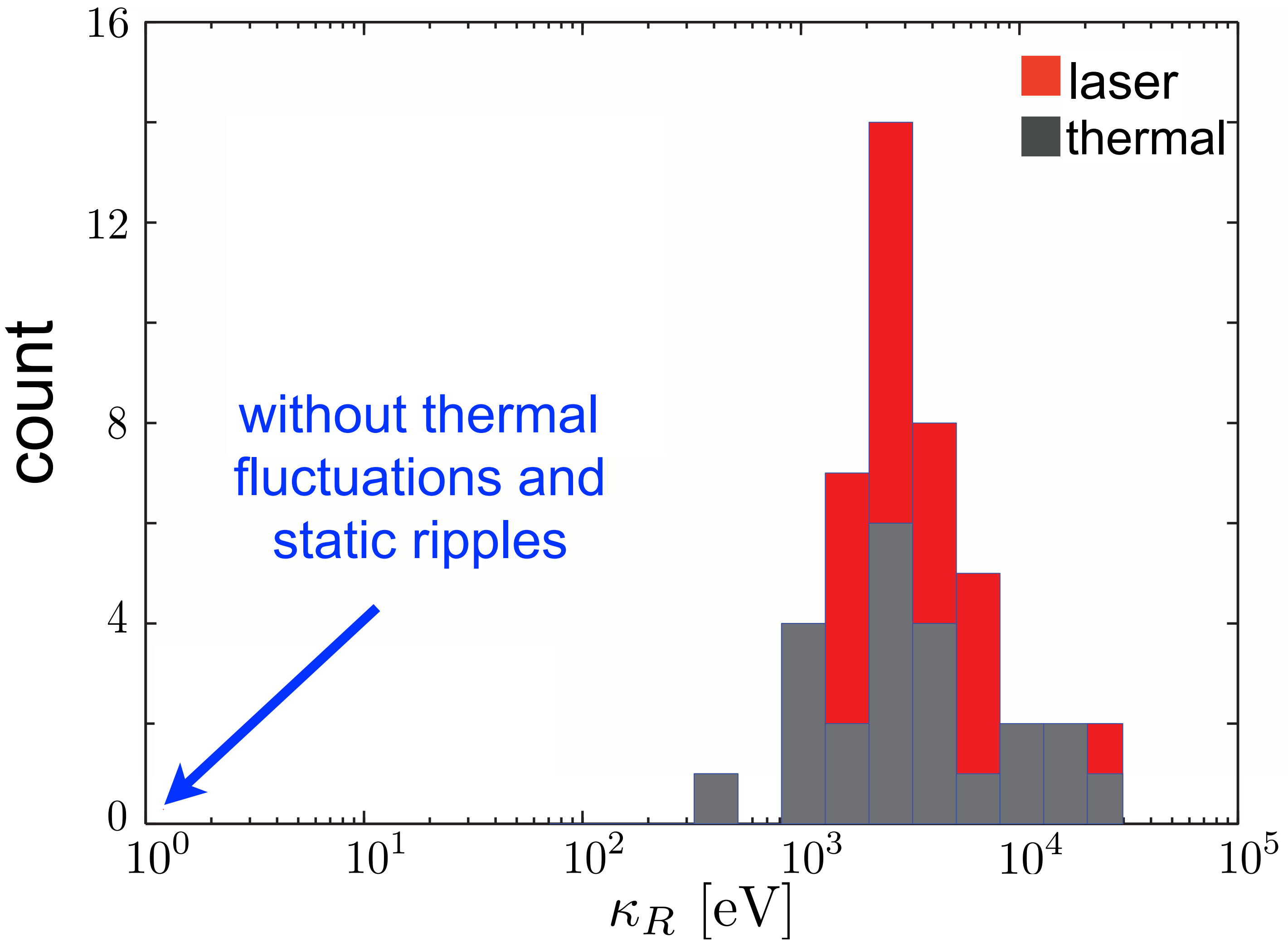


$10\mu$m

## thermal fluctuations

$$\kappa_R \sim \kappa\left(\frac{W}{\ell_{\text{th}}}\right)^{\eta} \sim 1\text{keV}$$

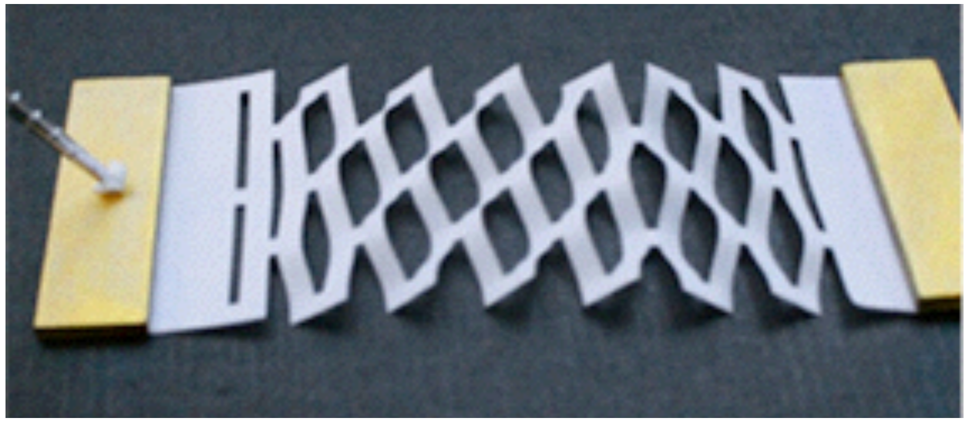
$$\ell_{\text{th}} \approx \sqrt{\frac{16\pi^3\kappa^2}{3k_BTY}} \approx 2\text{nm} \quad W \approx 10\mu\text{m}$$




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

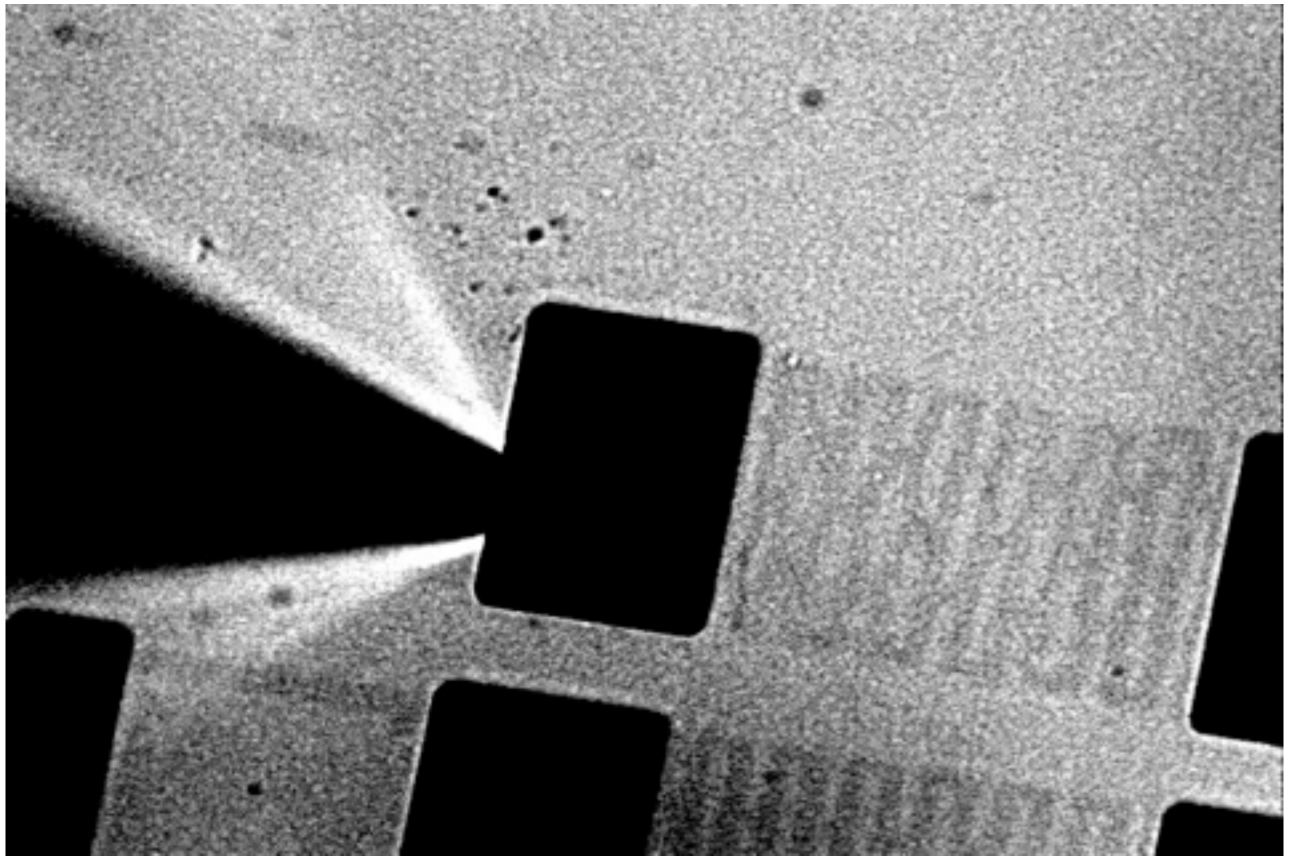
# Graphene kirigami

**paper model of soft spring**



**stretching of soft springs comes from bending of graphene and does not affect the electronic properties**

**graphene model of soft spring**



$10\mu m$

**APPLICATIONS:**

**microscale flexible electronics**

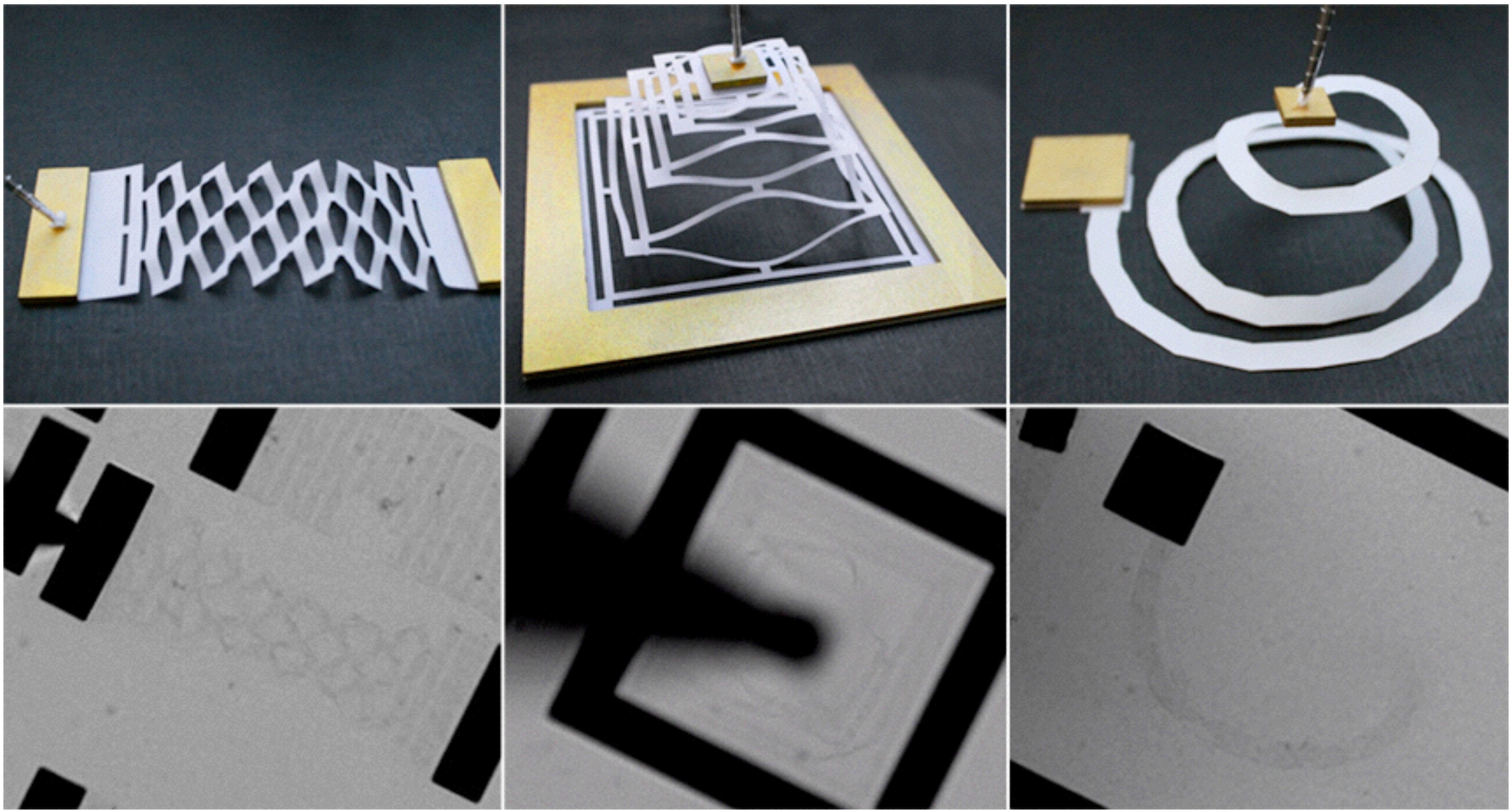
**sensitive force sensors ($10^{-15}$ N)**

**micro-actuators**

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

# Graphene kirigami

## Future directions: Study how thermal fluctuations and disorder affect the mechanics of such structures



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

# How thermal fluctuations affect the mechanics of long ribbons?

# Mechanics of ribbons at T=0

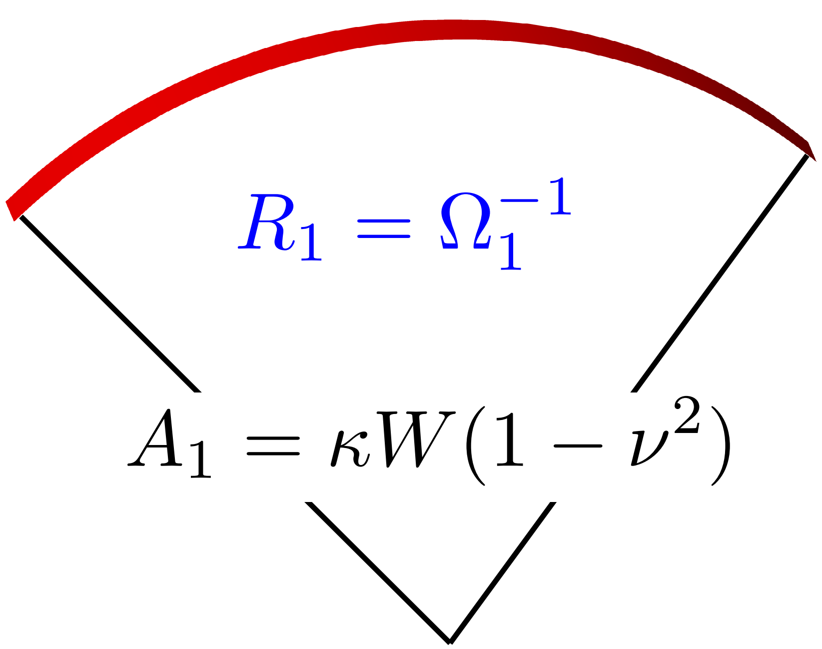

**rotation rate of material frame**

$$\frac{d\mathbf{e}_i}{ds} = \boldsymbol{\Omega} \times \mathbf{e}_i$$

**Energy cost of deformations**

$$E = \int \frac{ds}{2} \left[ A_1 \Omega_1^2 + A_2 \Omega_2^2 + C \Omega_3^2 \right]$$

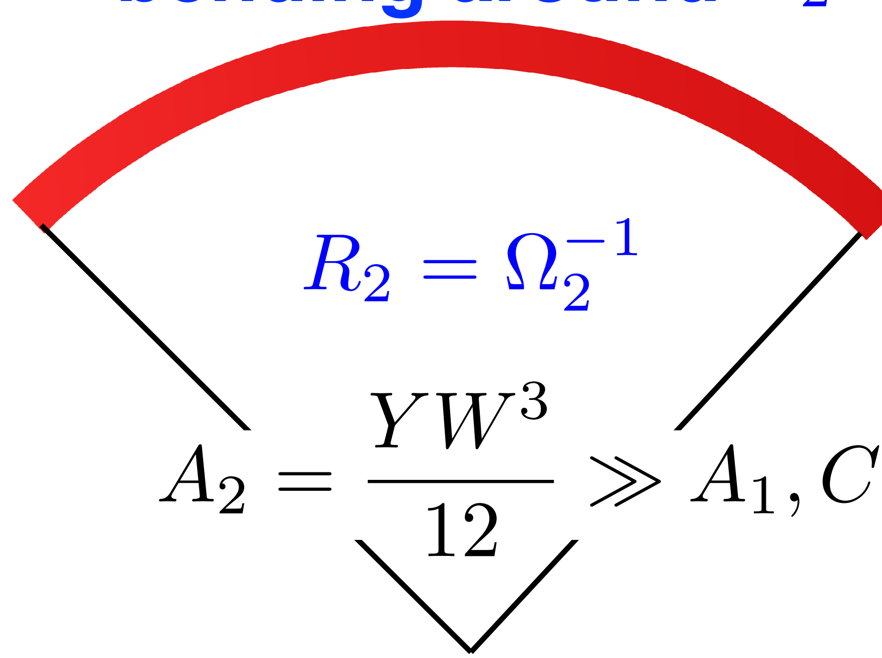
**bending around** $\mathbf{e}_1$



$$R_1 = \Omega_1^{-1}$$

$$A_1 = \kappa W (1 - \nu^2)$$

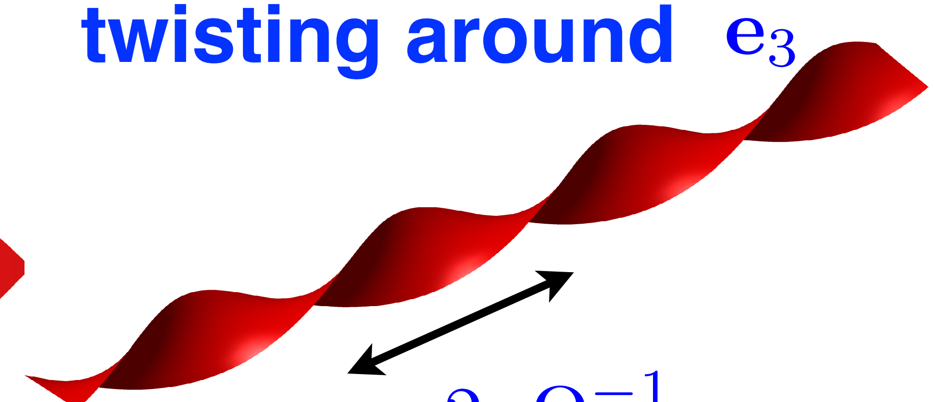
**bending around** $\mathbf{e}_2$



$$R_2 = \Omega_2^{-1}$$

$$A_2 = \frac{Y W^3}{12} \gg A_1, C$$

**twisting around** $\mathbf{e}_3$



$$p = 2\pi \Omega_3^{-1}$$

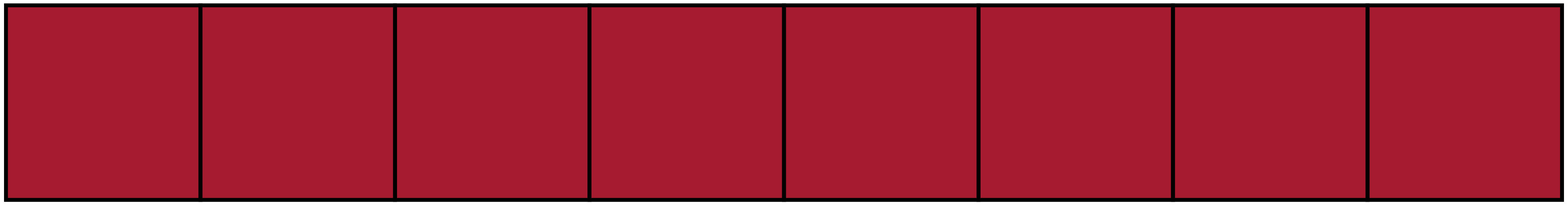
$$C = 2\kappa W (1 - \nu)$$

$Y, \kappa, \nu -$ 2D elastic constants

L.D. Landau and E.M. Lifshitz, *Theory of Elasticity*

# Mechanics of ribbons at T>0

**Construct a ribbon with $L/W \gg 1$ square blocks of size $W$**

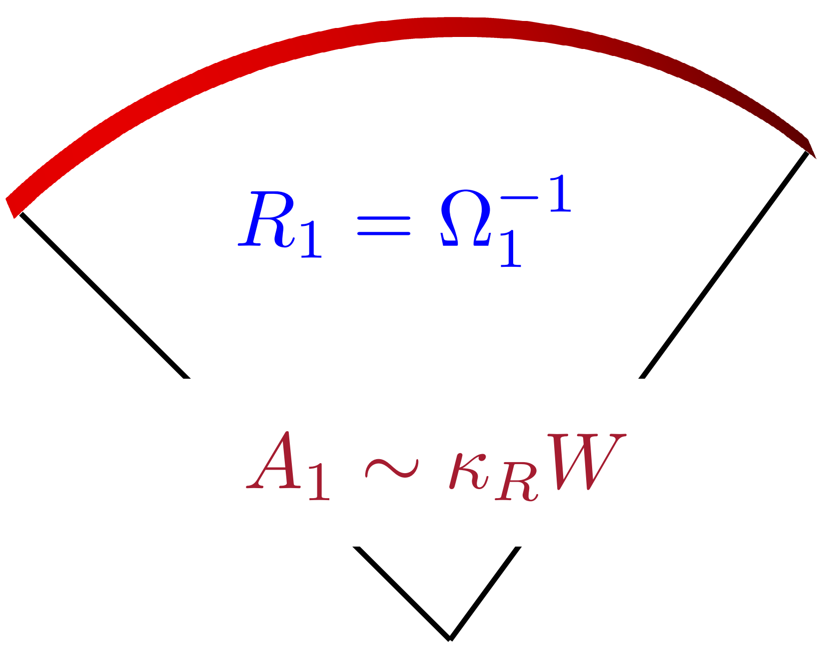


**Thermal fluctuations renormalize elastic constants for each block**

$$\kappa_R \sim \kappa \left(W/\ell_{\mathrm{th}}\right)^{\eta} \quad Y_R \sim Y \left(W/\ell_{\mathrm{th}}\right)^{-\eta_u} \quad \ell_{\mathrm{th}} \sim \kappa/\sqrt{k_B T Y}$$

**Effective elastic constants for a ribbon thus become**

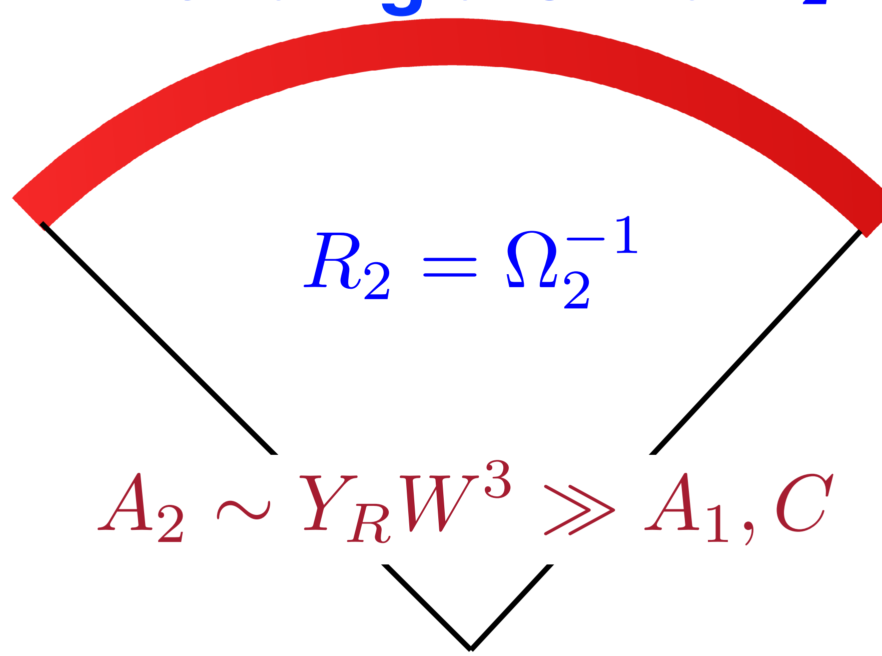
**bending around $\mathrm{e}_1$**



$R_1 = \Omega_1^{-1}$

$A_1 \sim \kappa_R W$

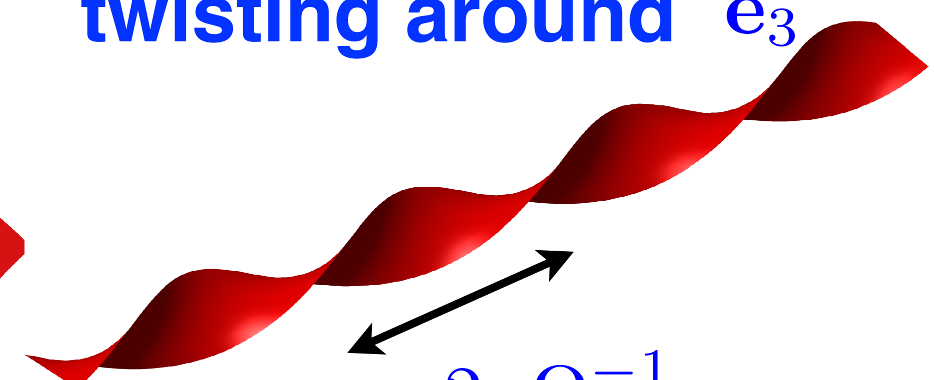
**bending around $\mathrm{e}_2$**



$R_2 = \Omega_2^{-1}$

$A_2 \sim Y_R W^3 \gg A_1, C$

**twisting around $\mathrm{e}_3$**



$p = 2\pi\Omega_3^{-1}$

$C \sim \kappa_R W$

A. Košmrlj and D. Nelson, arXiv:1508.01528 (2015)

# Coupling between bending and twisting


**rotation rate of material frame**

$$\frac{d\mathbf{e}_i}{ds} = \mathbf{\Omega} \times \mathbf{e}_i$$

**Energy cost of deformations**

$$E = \int \frac{ds}{2} \left[ A_1(T)\Omega_1^2 + A_2(T)\Omega_2^2 + C(T)\Omega_3^2 \right]$$

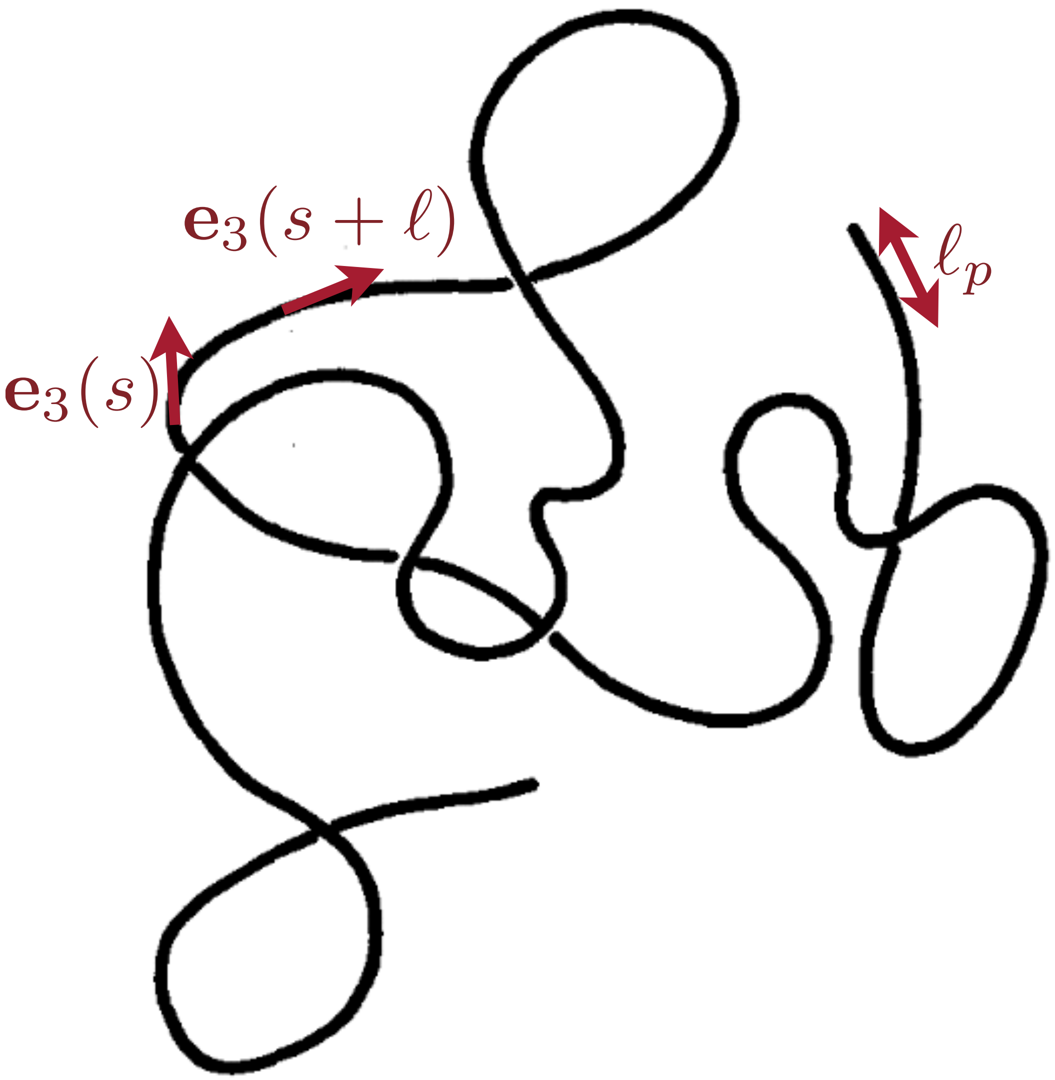
**bending and twisting modes are coupled!**

**Successive rotations do not commute!**

$$R_y\left(\frac{\pi}{2}\right) R_z\left(\frac{\pi}{2}\right) \hat{\mathbf{z}} = R_y\left(\frac{\pi}{2}\right) \hat{\mathbf{z}} = \hat{\mathbf{x}}$$

$$R_z\left(\frac{\pi}{2}\right) R_y\left(\frac{\pi}{2}\right) \hat{\mathbf{z}} = R_z\left(\frac{\pi}{2}\right) \hat{\mathbf{x}} = \hat{\mathbf{y}}$$

# Persistence length for ribbons




$$\langle \mathbf{e}_3(s+\ell)\cdot\mathbf{e}_3(s)\rangle = e^{-\ell/\ell_p}$$

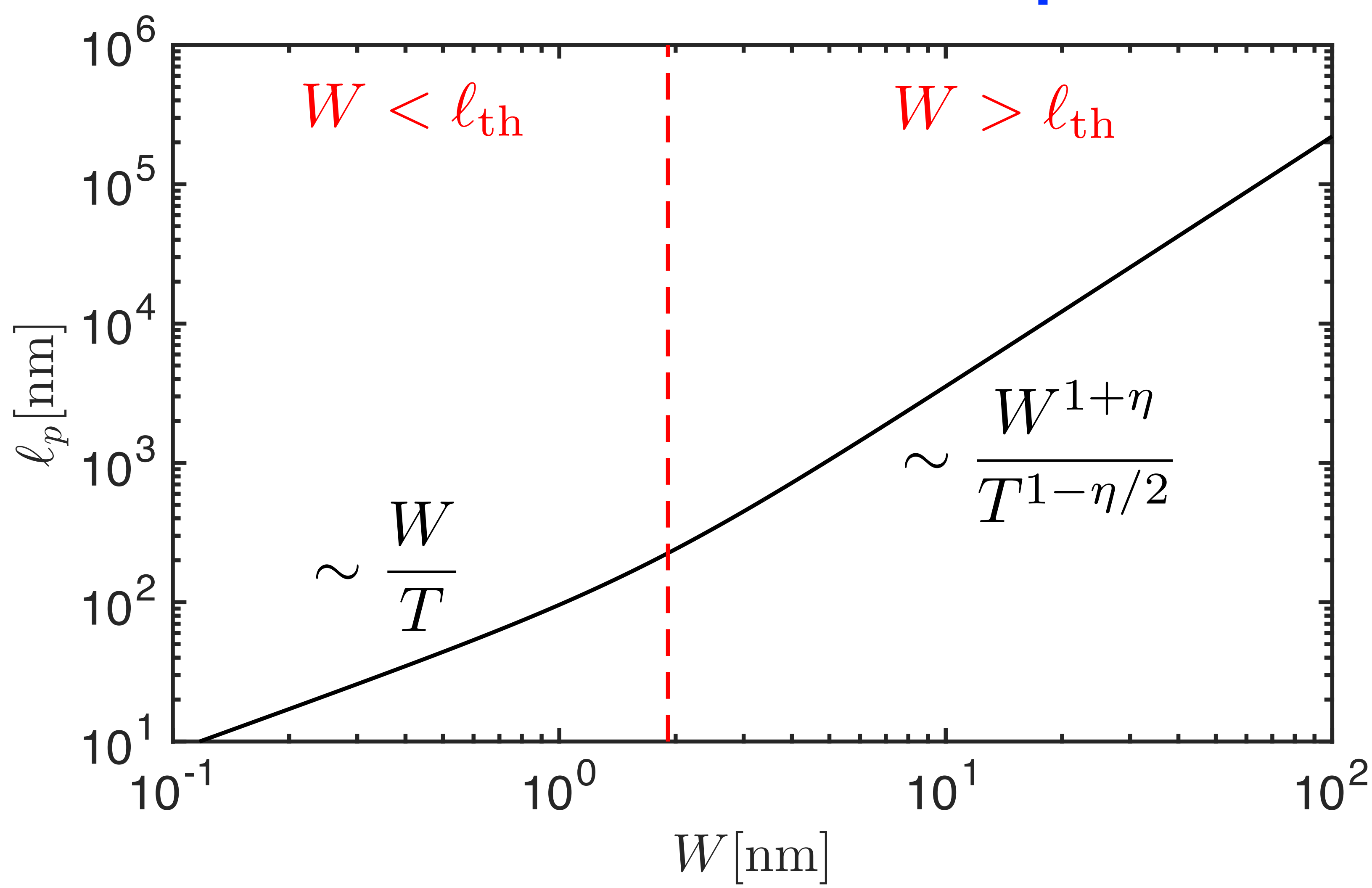
$$\ell_p = \frac{2}{k_B T}\left(A_1^{-1}+A_2^{-1}\right)^{-1}$$

S. Panyukov and Y. Rabin, PRE **62**, 7136 (2000)

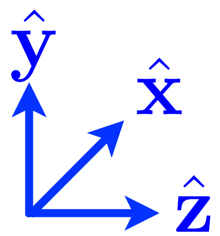
$$\ell_p \approx \frac{2\kappa_R W}{k_B T} \sim \frac{\kappa W^{1+\eta}}{k_B T \ell_{\text{th}}^{\eta}}$$

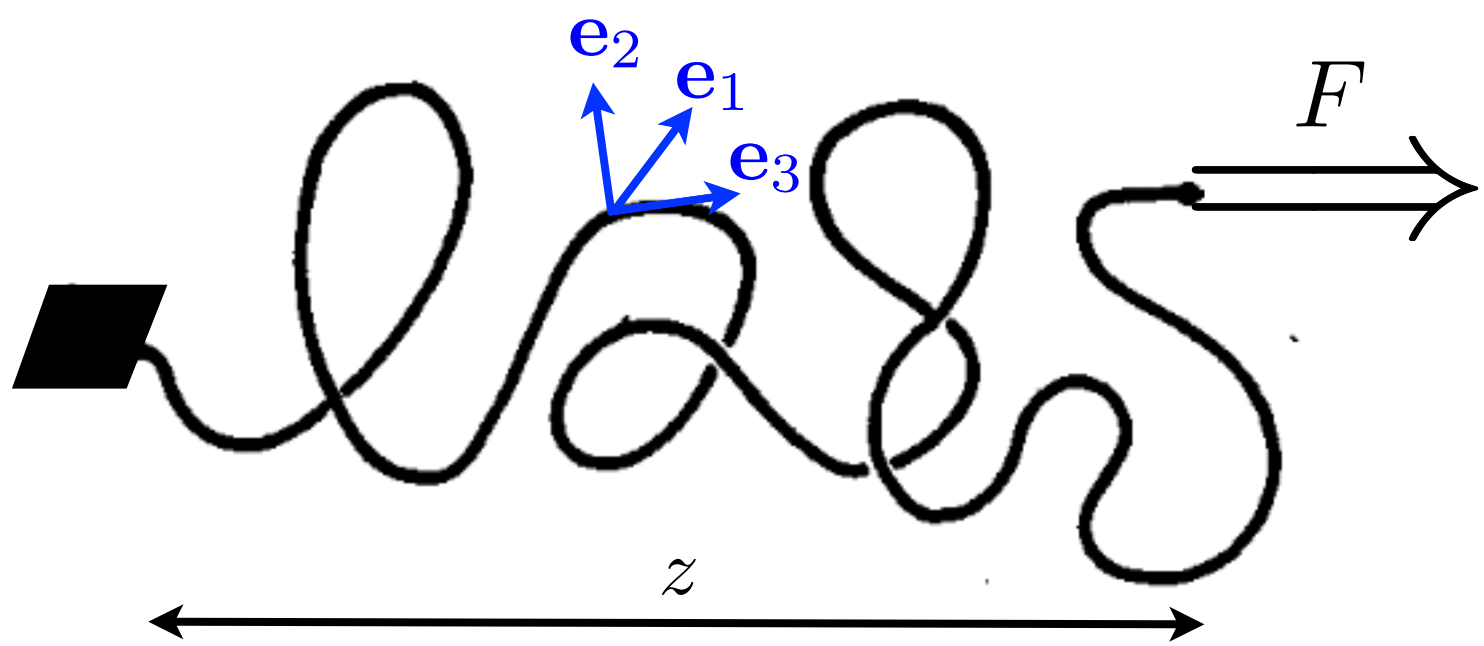
$$\ell_{\text{th}} \sim \kappa/\sqrt{k_B T Y}$$

**Persistence length for graphene nano ribbons at room temperature**



# Pulling of long ribbons




**rotation rate of material frame**

$$\frac{d\mathbf{e}_i}{ds} = \boldsymbol{\Omega} \times \mathbf{e}_i$$

**Energy cost of deformations**

$$E = \int \frac{ds}{2} \left[ A_1 \Omega_1^2 + A_2 \Omega_2^2 + C \Omega_3^2 \right] - F z$$

**Partition function**

$$Z = \sum_{\text{configurations}} e^{-E/k_B T}$$

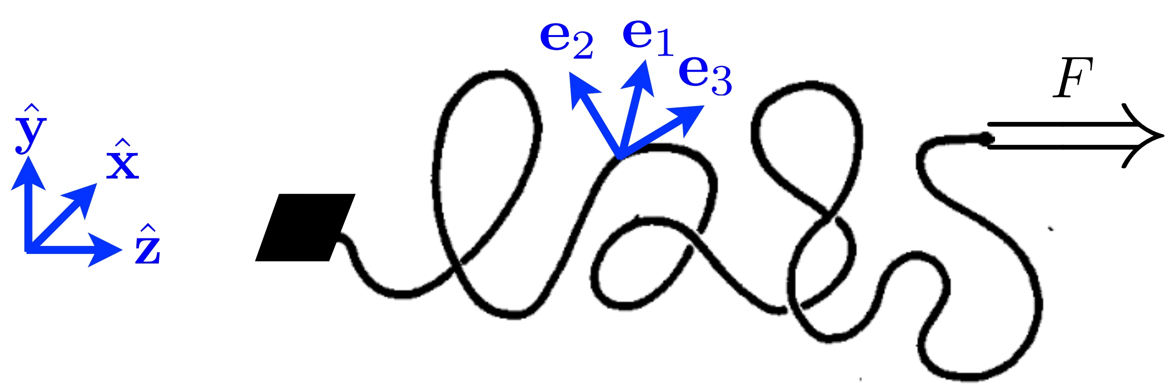
**Ribbon end to end distance**

$$\langle z \rangle = k_B T \frac{\partial \ln Z}{\partial F}$$

**It is very hard to calculate the partition function directly!**

# Analogy with the quantum mechanical rotating top

## Statistical mechanics




ribbon backbone coordinate

$s$

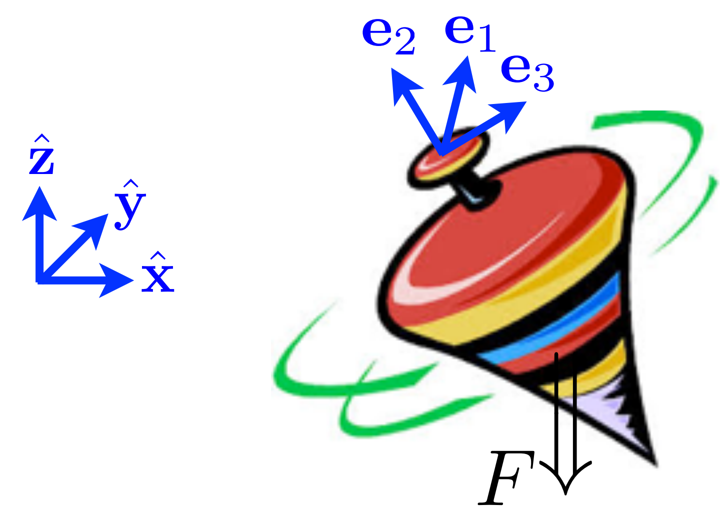
bending and twisting rigidities

$A_1(T), A_2(T), C(T)$

pulling force

$F$

## Quantum mechanics




time

$t$

moments of inertia

$I_1, I_2, I_3$

gravitational force

$F$

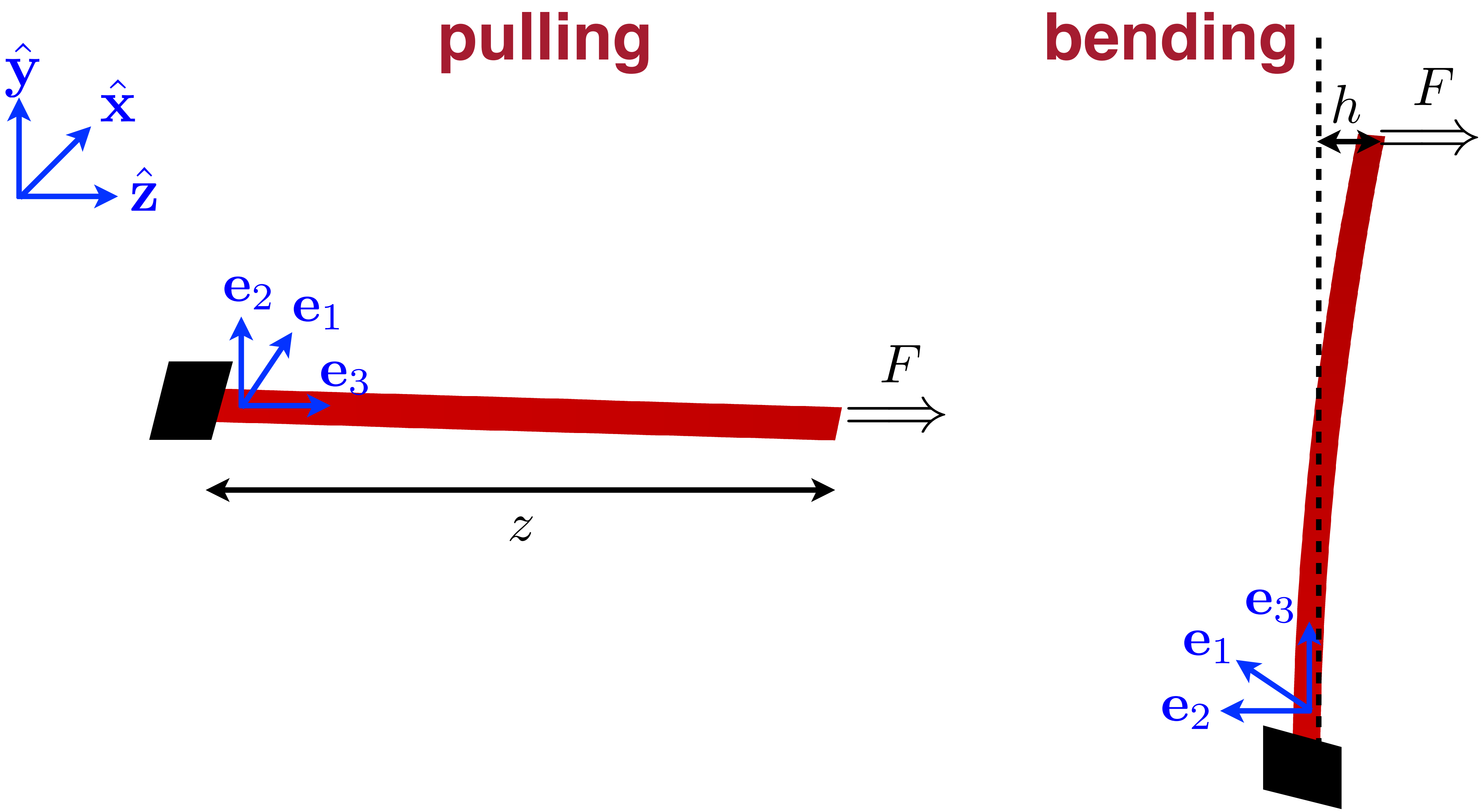
## Use tools from quantum mechanics!

H. Yamakawa, Pure Appl. Chem. **46**, 135 (1976)

**Note: in classical mechanics this corresponds to the Kirchhoff kinetic analogy**

# Pulling and bending of ribbons

**Pulling and bending can be described with the same formalism by properly setting the initial material frame orientation.**



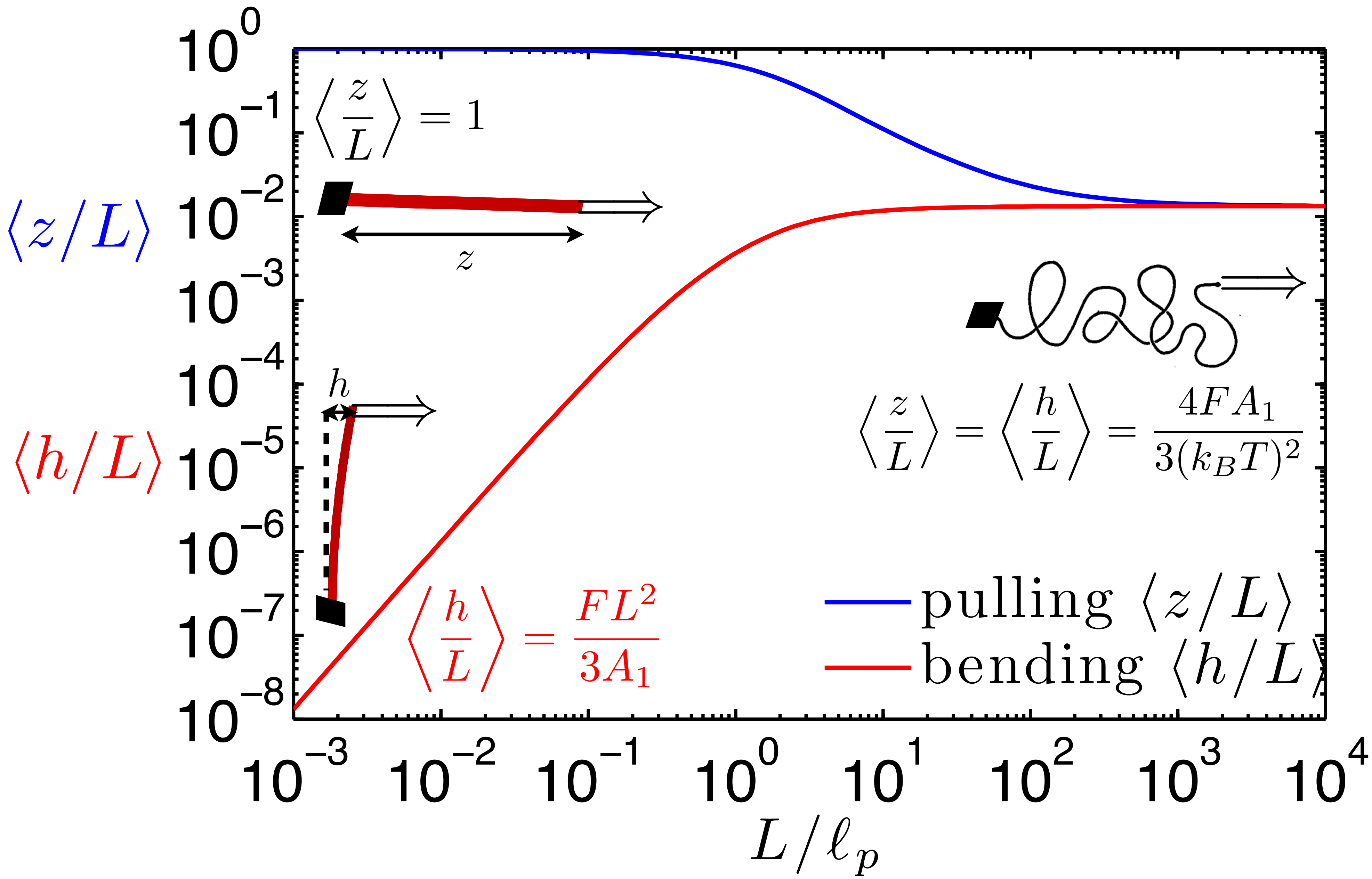
# Pulling and bending of ribbons of varying lengths

**Fixed force, temperature and ribbon width** $\frac{FA_1}{(k_BT)^2} = 0.01$

$C = A_1$

$A_2/A_1 \to \infty$

$\ell_p \approx \frac{2A_1}{k_BT} \sim \frac{\kappa W^{1+\eta}}{k_BT\ell_{th}^{\eta}}$

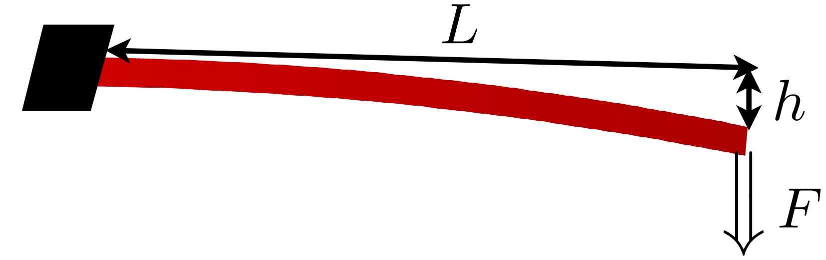


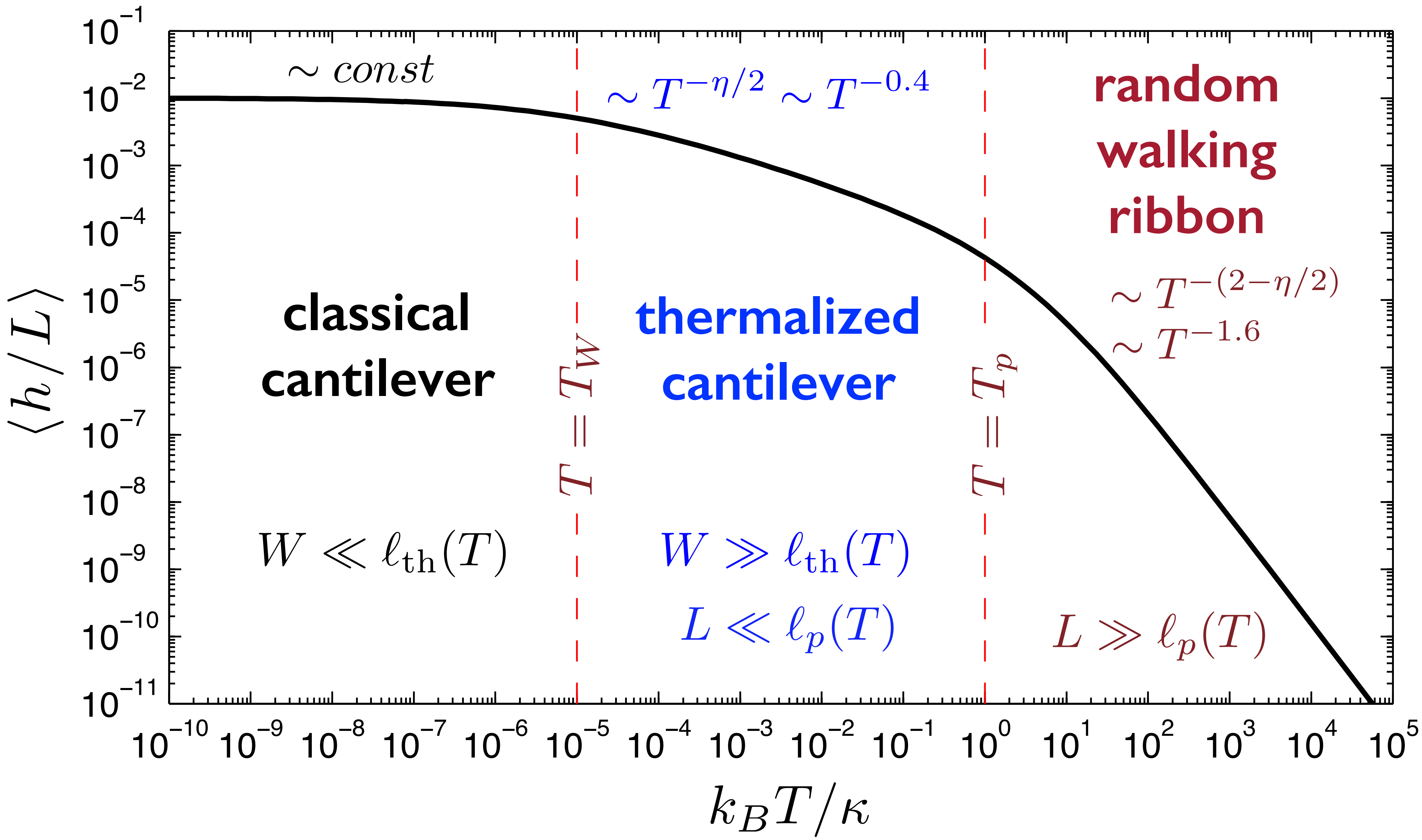

**For long ribbons direction of pulling force is irrelevant!**

A. Košmrlj and D. Nelson, arXiv:1508.01528 (2015)

# Bending of ribbons at varying temperature

**Fixed force and ribbon dimensions**




$$\ell_{\rm th} \sim \frac{\kappa}{\sqrt{k_B T Y}}$$

$$\ell_p \sim \frac{\kappa W^{1+\eta}}{k_B T \ell_{\rm th}^{\eta}}$$

$$\ell_p \propto \frac{1}{(k_B T)^{1-\eta/2}}$$

A. Košmrlj and D. Nelson, arXiv:1508.01528 (2015)

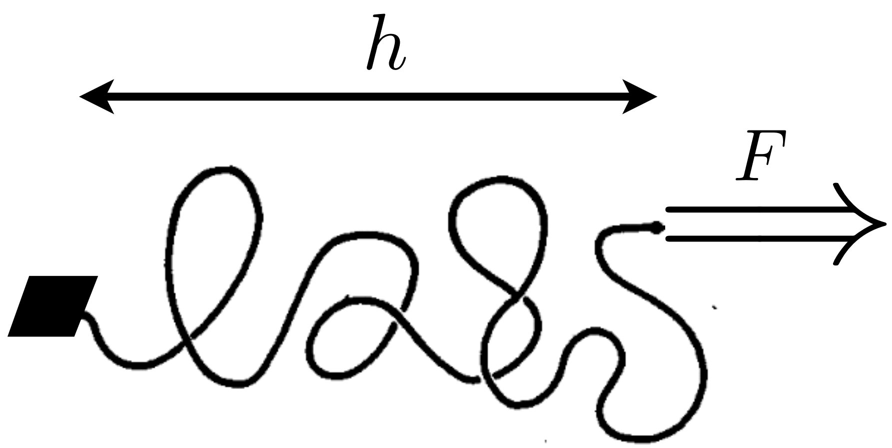
# Pulling of long ribbons

$L \gg \ell_p \sim \kappa W^{1+\eta_f}/(k_B T \ell_c^{\eta_f})$

A. Košmrlj and D. Nelson, arXiv:1508.01528 (2015)

## Small pulling force

$F\ell_p \ll k_B T$




$$\frac{\langle h \rangle}{L} \approx \frac{2F\ell_p}{3k_B T}$$

## Large pulling force

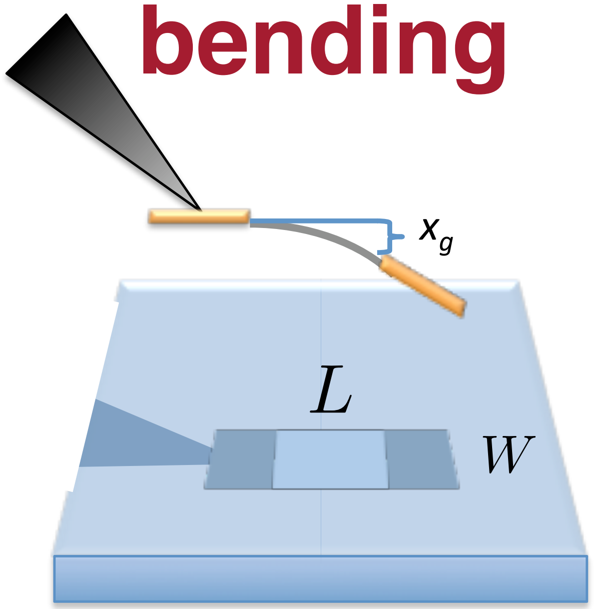
$F\ell_p \gg k_B T$

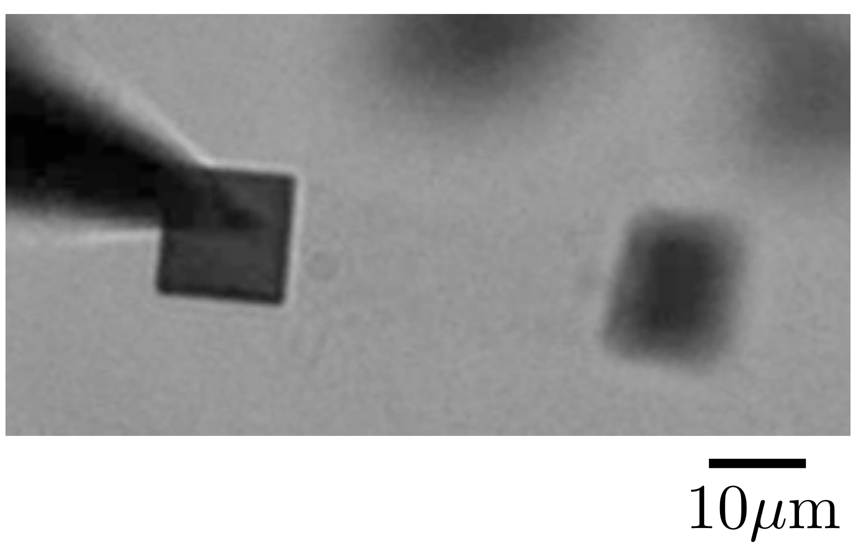

$$\frac{\langle h \rangle}{L} \approx 1 + C\frac{k_B T}{\kappa}\left(\frac{\kappa F}{k_B T Y W}\right)^{1/\delta} + \frac{F}{YW}$$

**Non-linear response is reflecting the 2D nature of ribbons!**

# Potential experimental tests

## bending



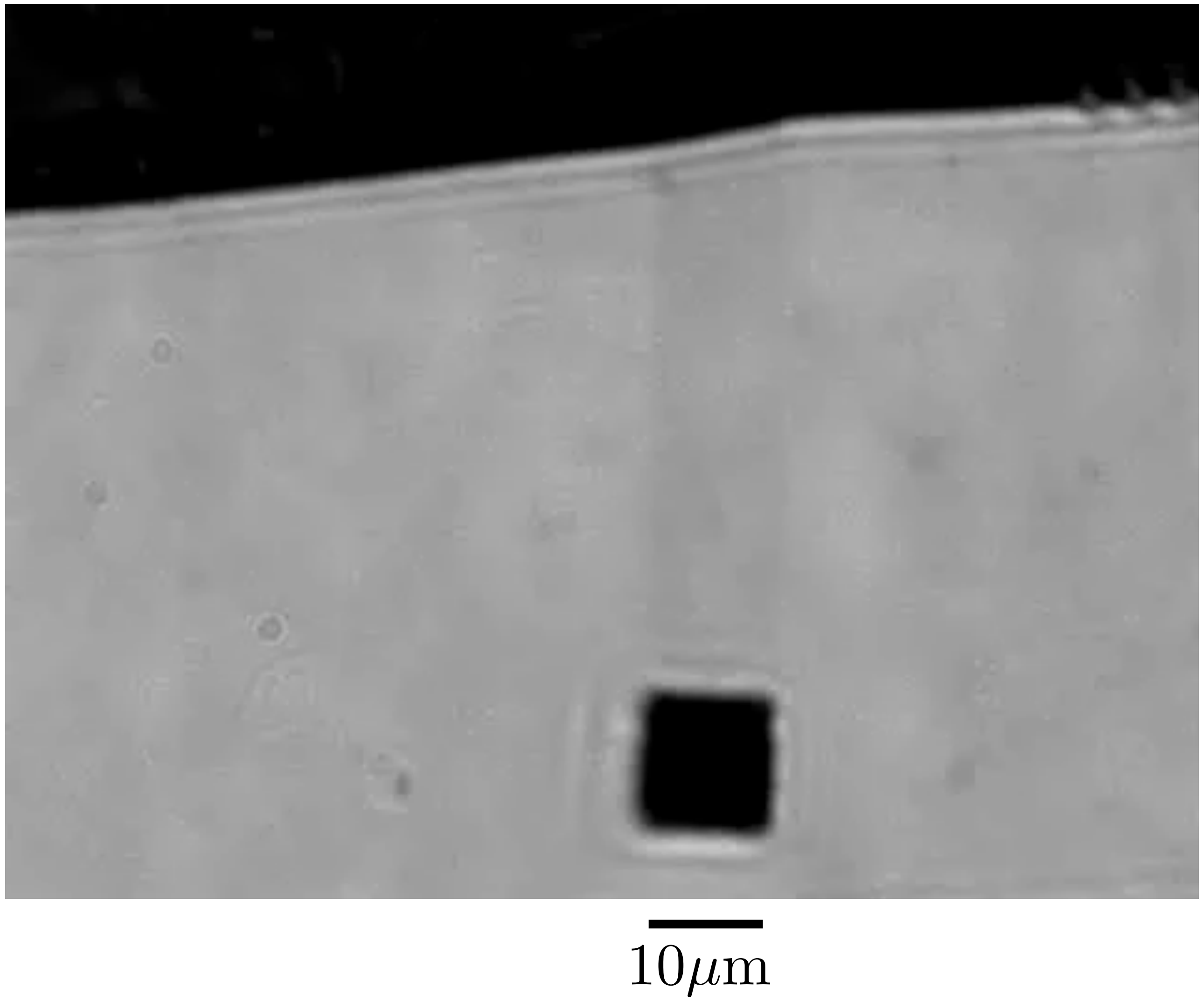




**Prepare nano-ribbons**

$W \sim 10\text{nm}$

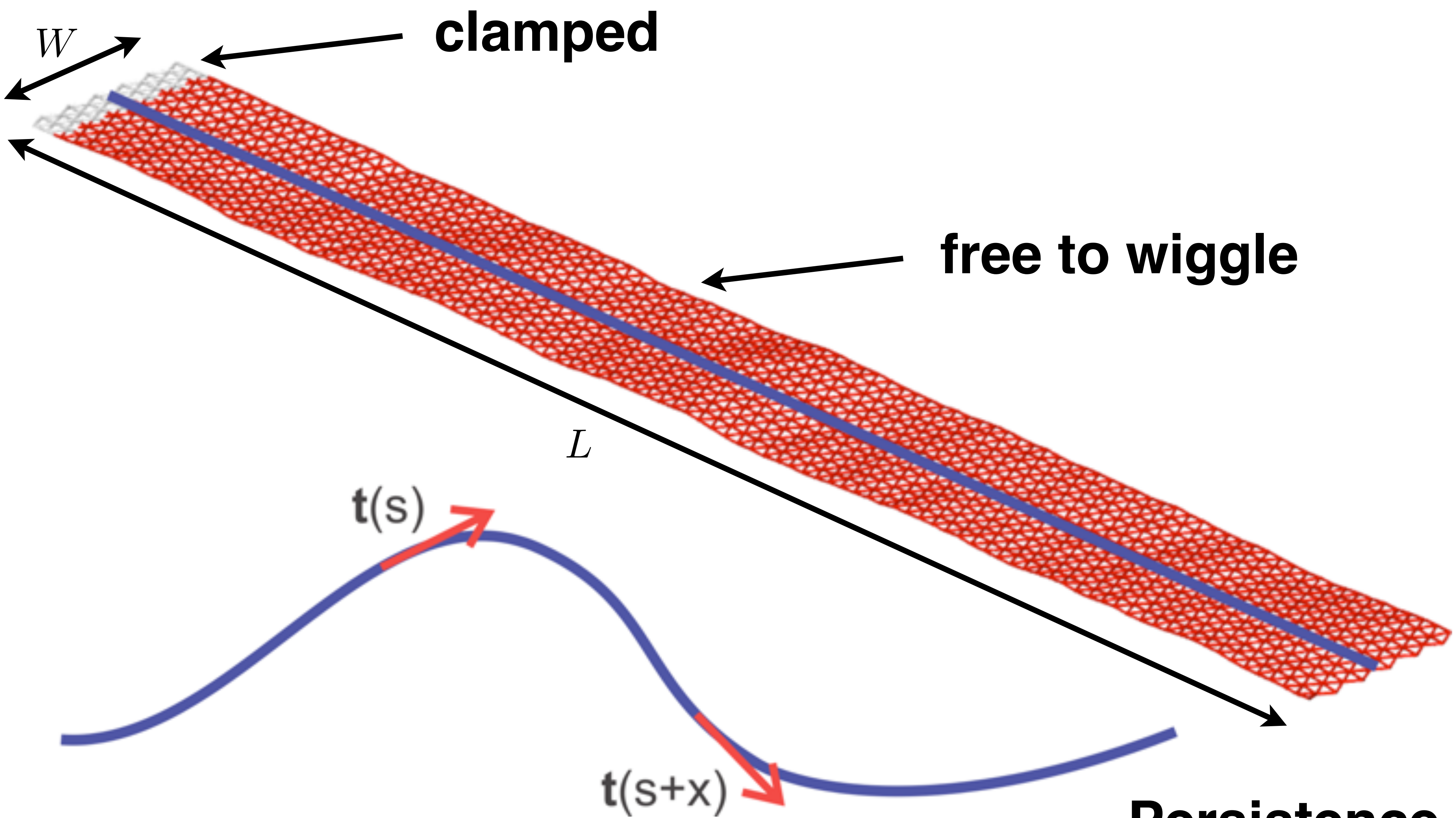
$L \gtrsim \ell_p \sim 10\mu\text{m}$

## pulling (gravity)
## twisting (magnetic field)




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

# Molecular dynamics simulations of ribbons




**Persistence length**

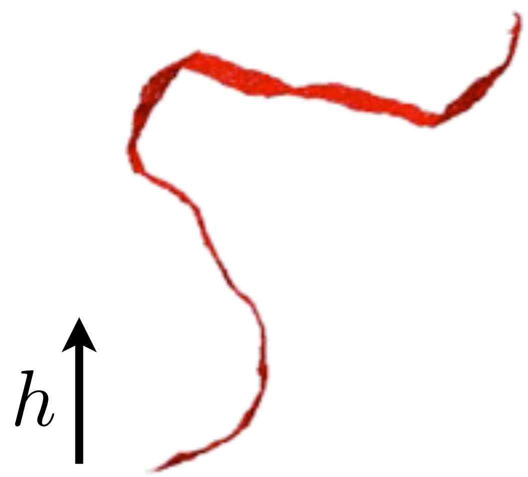
$$\langle \mathbf{t}(s) \cdot \mathbf{t}(s+x) \rangle = e^{-x/\ell_p}$$

$$\ell_p \approx \frac{2W\kappa_R(W)}{k_B T}$$

Rastko Sknepnek (Dundee)
Mark Bowick (Syracuse)

# Molecular dynamics simulations of ribbons

$W = 10, L = 250$




**Measure height fluctuations along the ribbon backbone**

$$\langle h^2(s) \rangle$$

**Persistence length**

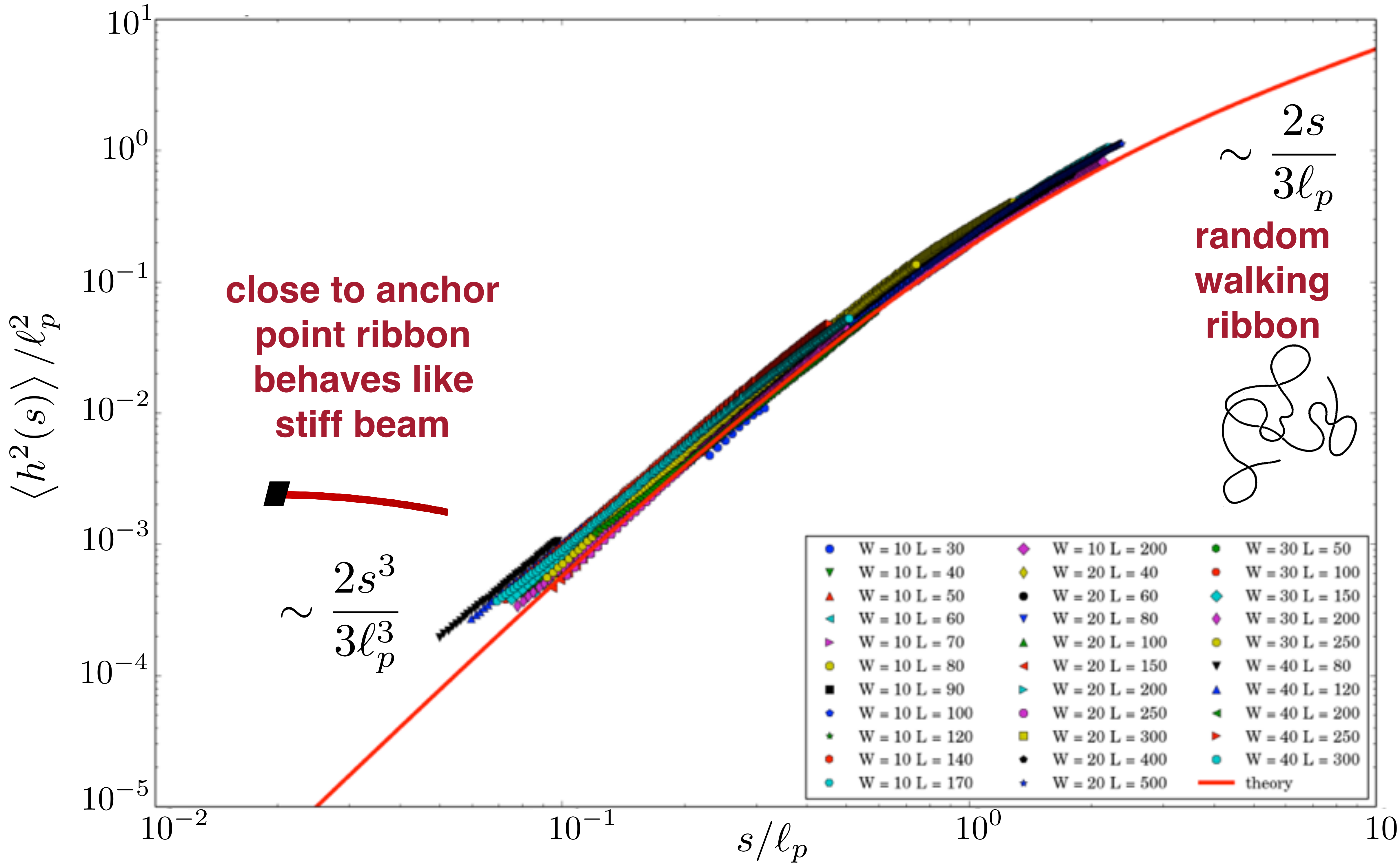
$$\langle \mathbf{t}(s) \cdot \mathbf{t}(s+x) \rangle = e^{-x/\ell_p}$$

$$\ell_p \approx \frac{2W\kappa_R(W)}{k_B T}$$

Rastko Sknepnek (Dundee)
Mark Bowick (Syracuse)

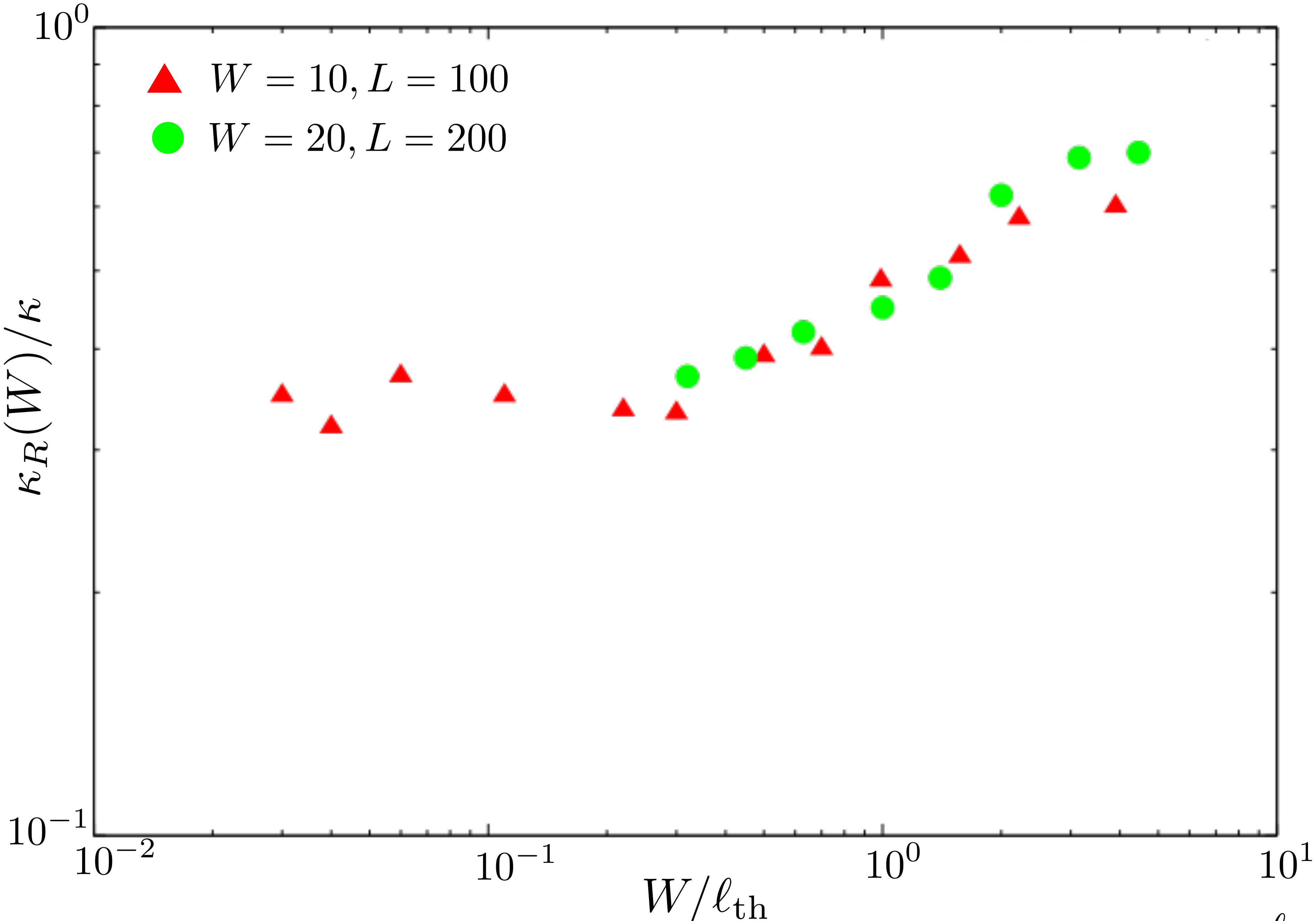
# Ribbon fluctuations from molecular dynamics simulations

## Data collapse without adjustable parameters!



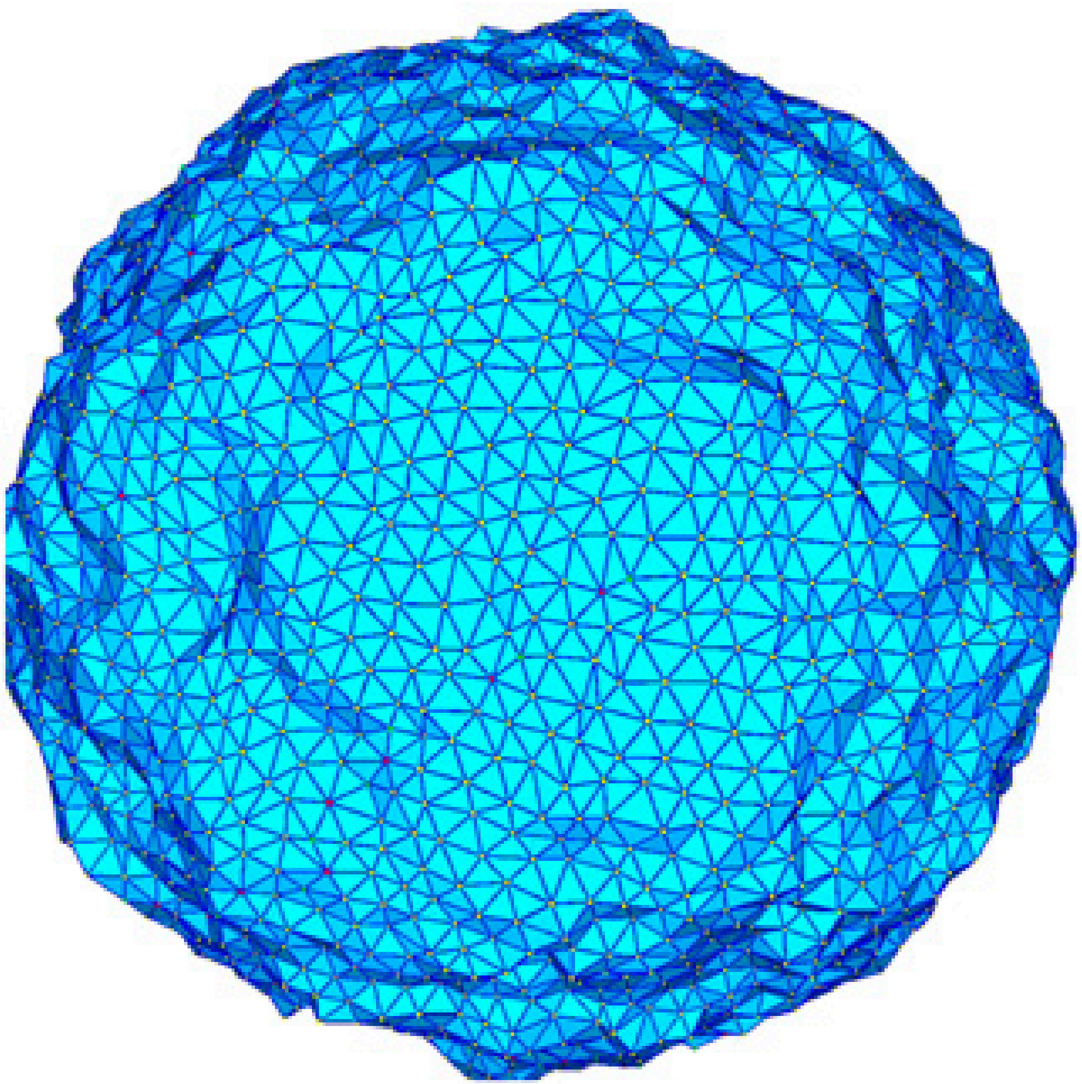
# Measured renormalized bending rigidity

$$\kappa_R(W) \approx \frac{k_B T \ell_p}{2W}$$




$$\ell_{\rm th} \sim \frac{\kappa}{\sqrt{k_B T Y}}$$

# How thermal fluctuations affect the mechanics of spherical shells?



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

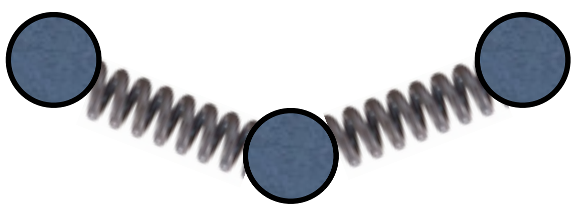
# Mechanics of spherical shells

**free energy cost of deformations**

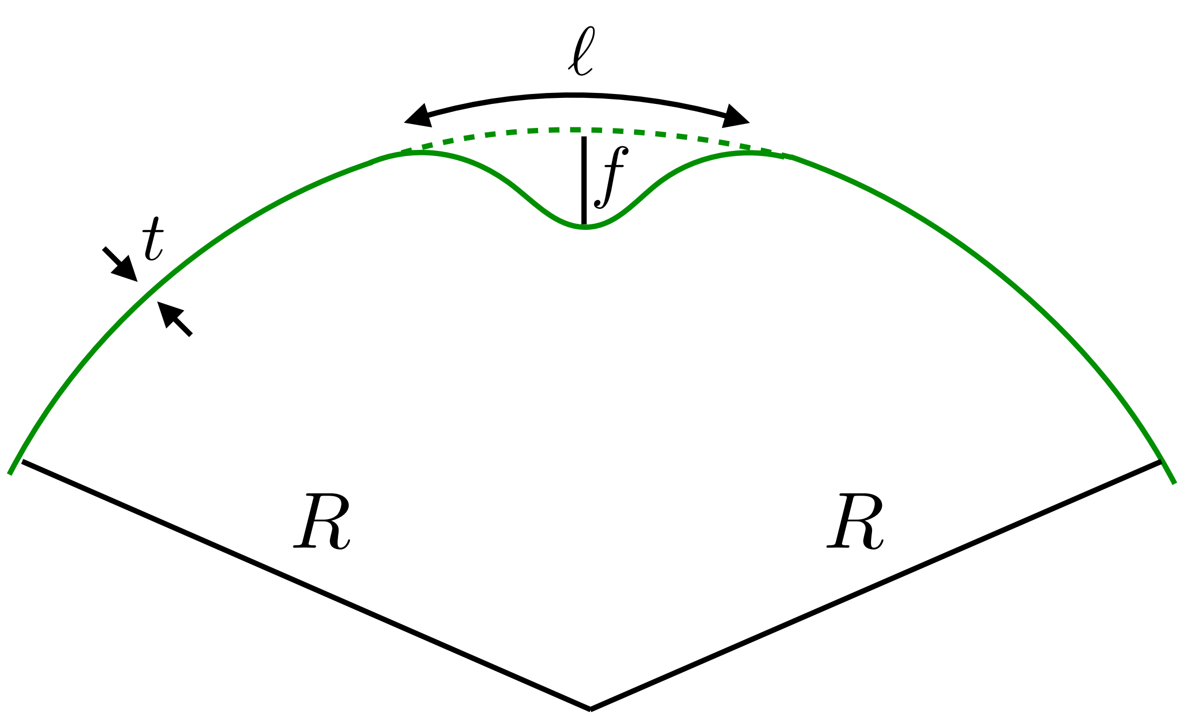
$$F = \int dA\, \frac{1}{2} \left[ \lambda u_{ii}^2 + 2\mu u_{ij}^2 + \kappa (\nabla^2 f)^2 \right]$$

**strain tensor**

$$u_{ij} = \frac{1}{2} (\partial_i u_j + \partial_j u_i) + \frac{1}{2} (\partial_i f)(\partial_j f) - \frac{f \delta_{ij}}{R}$$



## Elastic length scale




**bending energy** $E_b \sim \frac{\kappa f^2}{\ell^4}$

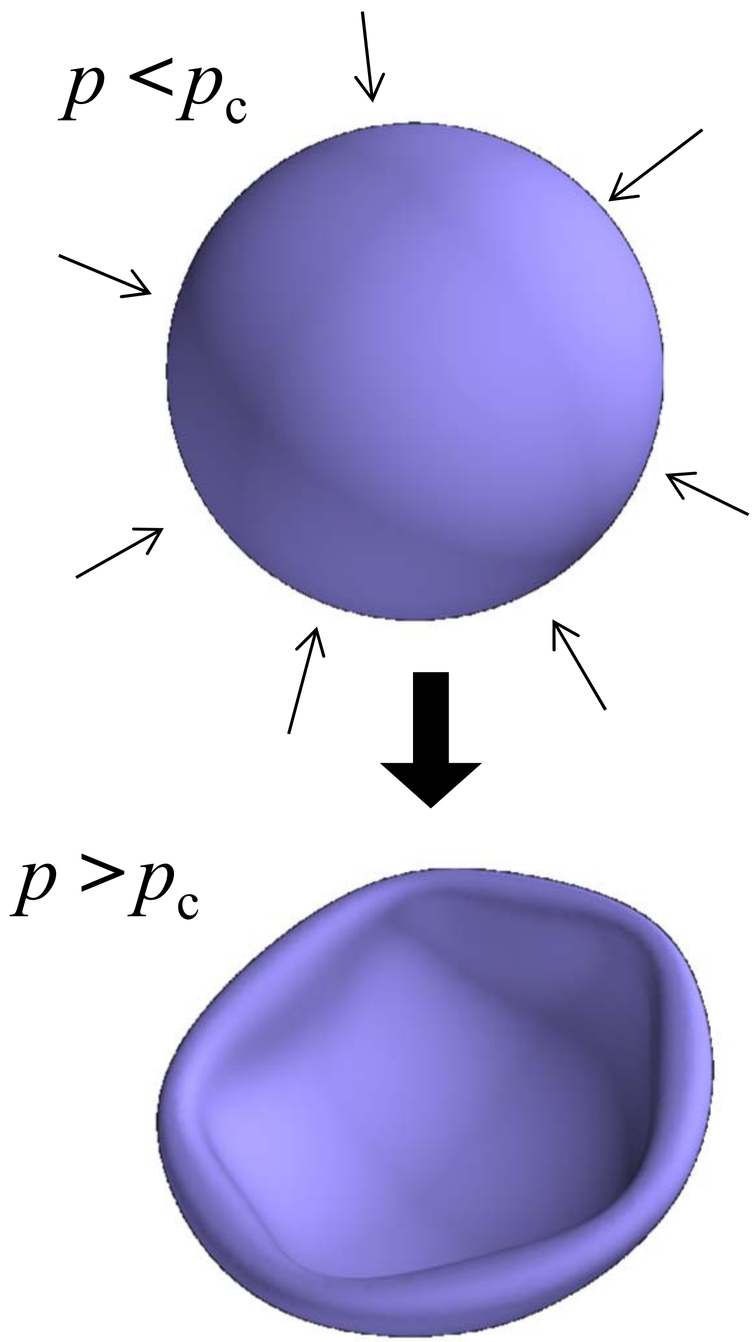
**stretching energy** $E_s \sim \frac{Y f^2}{R^2}$

**stretching energy dominates for**

$$\ell > \ell^* \sim \left( \frac{\kappa R^2}{Y} \right)^{1/4} \sim \sqrt{Rt}$$

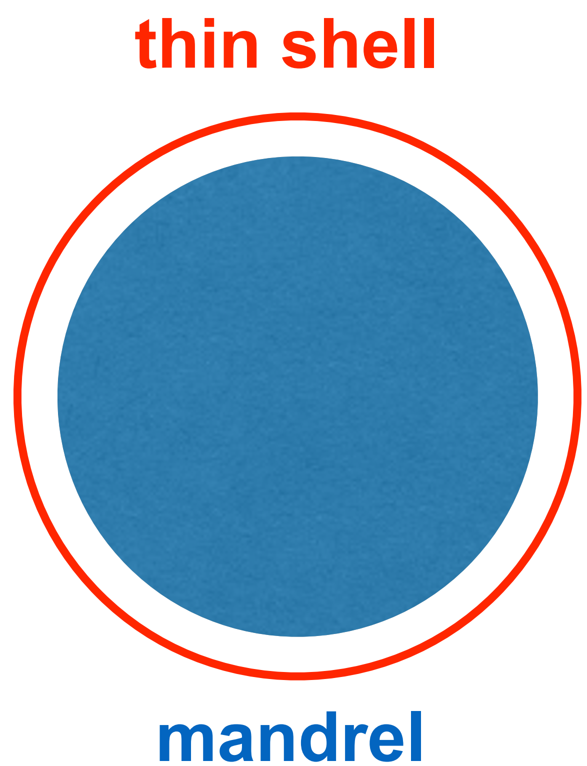
# Buckling of spherical shells by external pressure

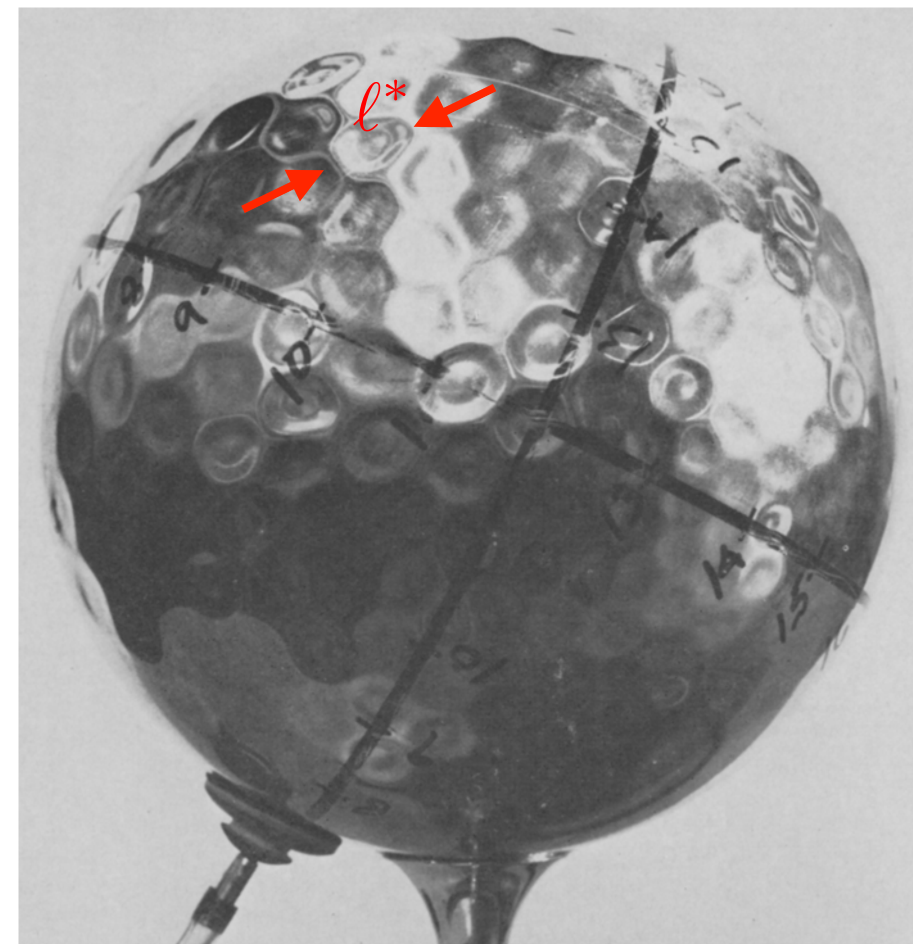
$$p_c = 4\sqrt{\kappa Y}/R^2 \sim Et^2/R^2$$




**Macroscopic buckling instability arrested by a wax mandrel**

$$\ell^* \sim \left(\kappa R^2/Y\right)^{1/4} \sim \sqrt{Rt}$$



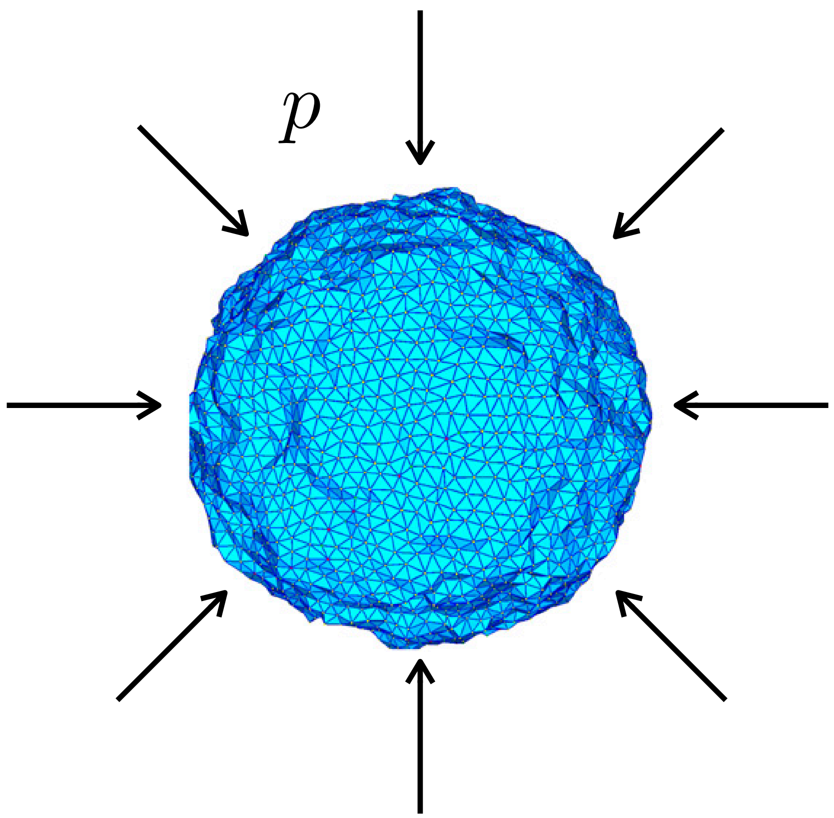




$R = 10.8\text{cm}$

$R/t \approx 2000$

R. L. Carlson *et al.*, Exp. Mech. **7**, 281 (1967)

# Thermal fluctuations of spherical shells




**strain tensor**

$$u_{ij} = \frac{1}{2}\left(\partial_i u_j + \partial_j u_i\right) + \frac{1}{2}(\partial_i f)(\partial_j f) - \frac{f\delta_{ij}}{R}$$

**radial fluctuations**

$$G_{ff}(\mathbf{q}) \equiv \frac{k_B T}{A\left[\kappa_R(q)q^4 - \frac{1}{2}p_R(q)Rq^2 + \frac{Y_R(q)}{R^2}\right]}$$

**Elastic length scale provides a cutoff for the renormalization**

$$\kappa_R \sim \kappa(\ell^*/\ell_{\mathrm{th}})^{\eta} \qquad \eta \approx 0.82$$

$$Y_R \sim Y(\ell^*/\ell_{\mathrm{th}})^{-\eta_u} \qquad \eta_u \approx 0.36$$

**thermal length scale**

$$\ell_{\mathrm{th}} \sim \frac{\kappa}{\sqrt{k_B T Y}} \sim \sqrt{\frac{Et^5}{k_B T}}$$

**elastic length scale**

$$\ell^* \sim \left(\kappa R^2/Y\right)^{1/4} \sim \sqrt{Rt}$$

**Thermal fluctuations generate compressive “pressure”!**

$$p_R \approx p + \frac{k_B T Y}{6\pi\kappa R}$$

**Shells buckle at a lower external pressure due to thermal fluctuations**

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

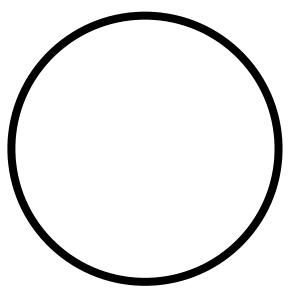
# Thermal fluctuations alone crush large spherical shells

**Spherical shells get crushed when thermally generated "pressure" exceeds the critical buckling threshold**

$$p_R \approx \frac{k_B T Y}{6\pi\kappa R} > p_c = \frac{4\sqrt{\kappa_R Y_R}}{R^2}$$

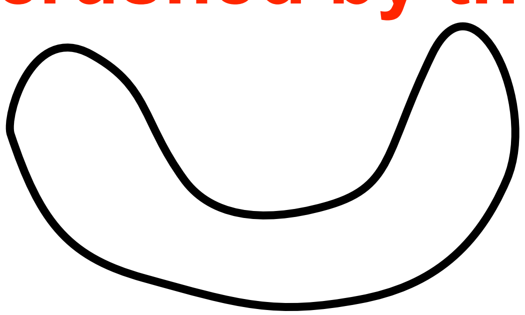
$$R_c \approx 54 \frac{\kappa}{k_B T}\sqrt{\frac{\kappa}{Y}} \sim \frac{Et^4}{k_B T}$$

**Small spherical shells are stable to thermal fluctuations**



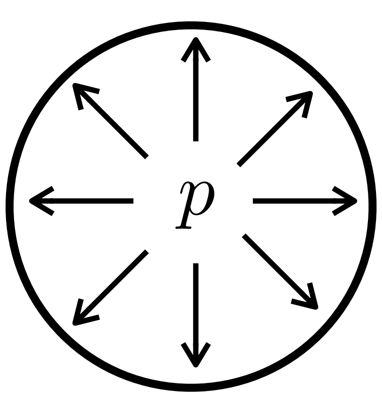
$R < R_c$

**Large spherical shells get crushed by thermal fluctuations**



$R > R_c$

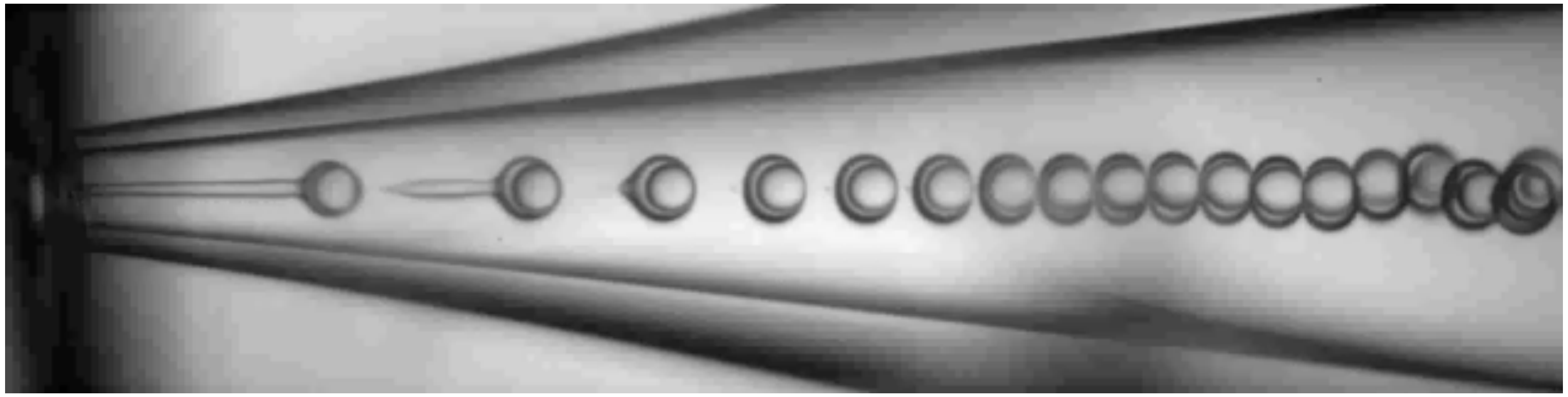
| | |
|---|---|
| **graphene-like shell** | $R_c \sim 60\text{nm}$ |
| **E. Coli-like shell** | $R_c \sim 1\mu\text{m}$ |
| **red blood cell-like shell** | $R_c \sim 400\mu\text{m}$ |

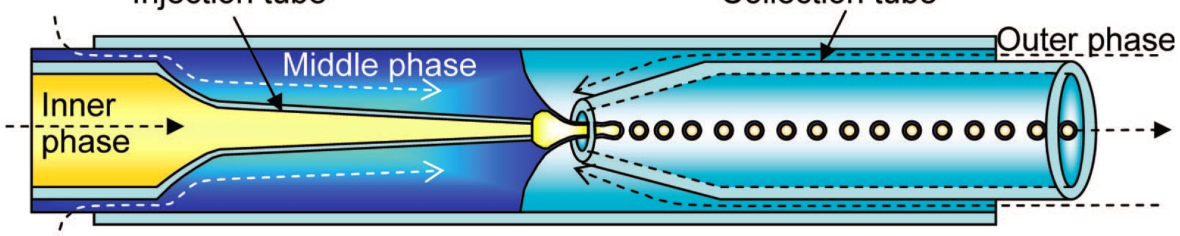



**shells can be inflated with internal pressure**

$$\left\langle \frac{\delta R}{R} \right\rangle = -\frac{k_B T}{8\pi\kappa}\left[\eta^{-1} + \ln(\ell_{\text{th}}/a_0)\right] + C_1 \frac{k_B T}{\kappa}\left(\frac{p\kappa R}{k_B T Y}\right)^{\eta/(2-\eta)} + \frac{pR}{4(\mu+\lambda)}$$

# Potential experimental test with polymersomes






**Can make polymersomes of size $R \sim 100\mu\mathrm{m}$, but they may be under osmotic pressure!**

**thickness**

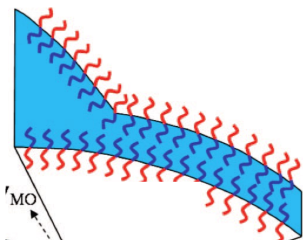
$t \approx 10\mathrm{nm}$

**If osmotic pressure can be matched, then**

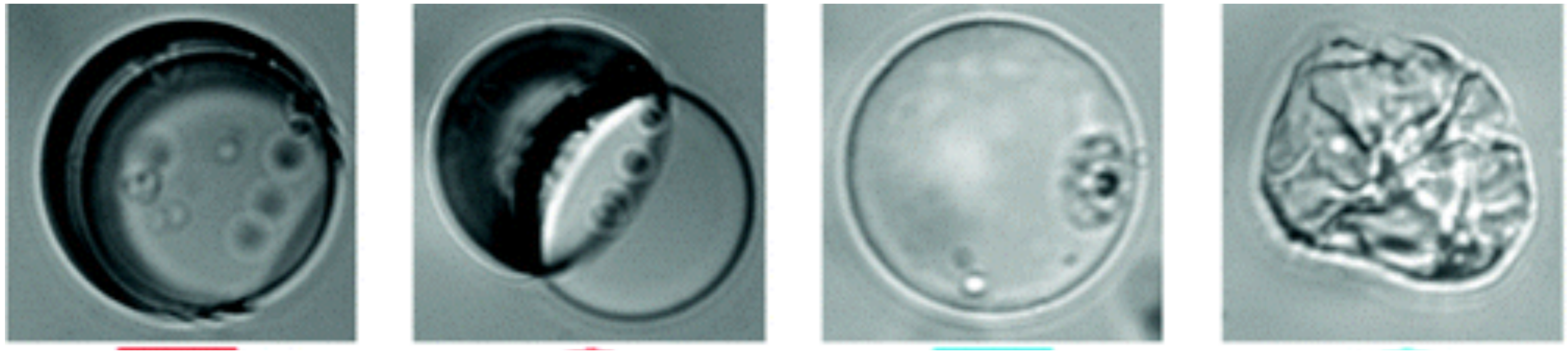
$R_c \sim 100\mu\mathrm{m}$

**"double emulsion" of ampiphillic diblock copolymers (PEG-b-PLA)**

**tune wetting properties to eject thin crystalline bilayer shells**

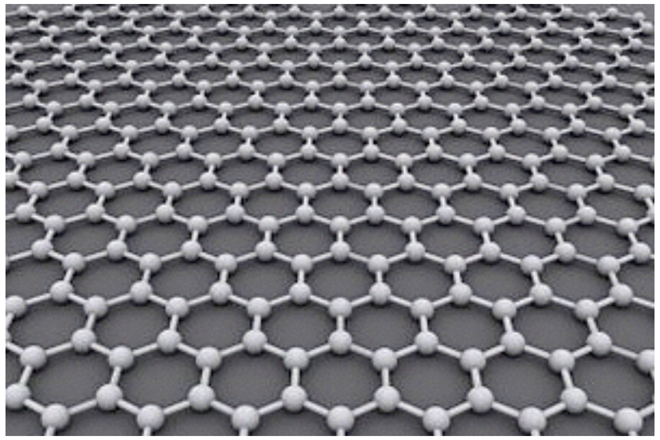


**crush polymersomes with osmotic shock**



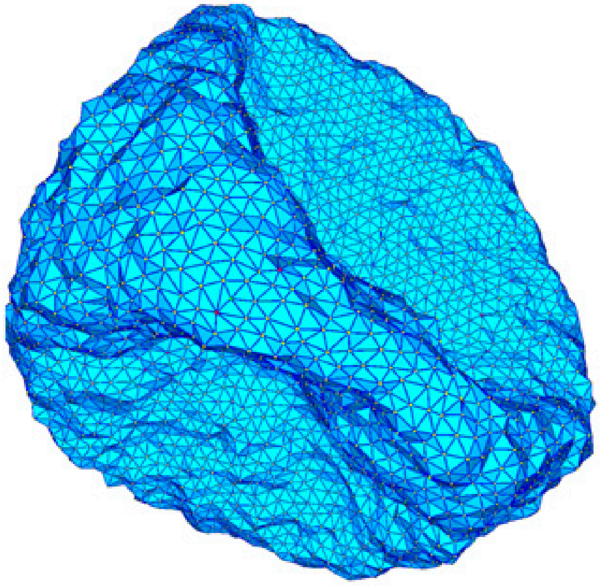
Shum *et al.*, JACS **130**, 9543 (2008)

# Summary



**thermal fluctuations are important for graphene (and BN, $MoS_2$, $WS_2$ , ...)**

**long narrow ribbons behave like flexible 1D polymers, but retain features of 2D membranes**



**thermal fluctuations spontaneously crush large spherical shells**

increased scale dependent bending and twisting rigidities

non-linear response to stretching

# Acknowledgements


## Collaborators

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