



Nanomechanics of graphene

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Petersburg Nuclear
Physics Institute



Radboud Universiteit Nijmegen

Gornyi, Kachorovskii, Mirlin,

[Conductivity of suspended graphene at the Dirac point](#), PRB (2012)

[Rippling and crumpling in disordered free-standing graphene](#), PRB (2015)

[Anomalous Hooke's law in disordered graphene](#), 2D Mater. (2017)

Burmistrov, Gornyi, Kachorovskii, Katsnelson, Mirlin, [Quantum elasticity of graphene: Thermal expansion coefficient and specific heat](#), PRB (2016)

Burmistrov, Gornyi, Kachorovskii, Los, Katsnelson, Mirlin,

[Stress-controlled Poisson ratio of a crystalline membrane:](#)

[Application to graphene](#), PRB (2018)

Burmistrov, Kachorovskii, Gornyi, Mirlin, [Differential Poisson's ratio of a crystalline 2D membrane](#), Annals of Physics (2018)

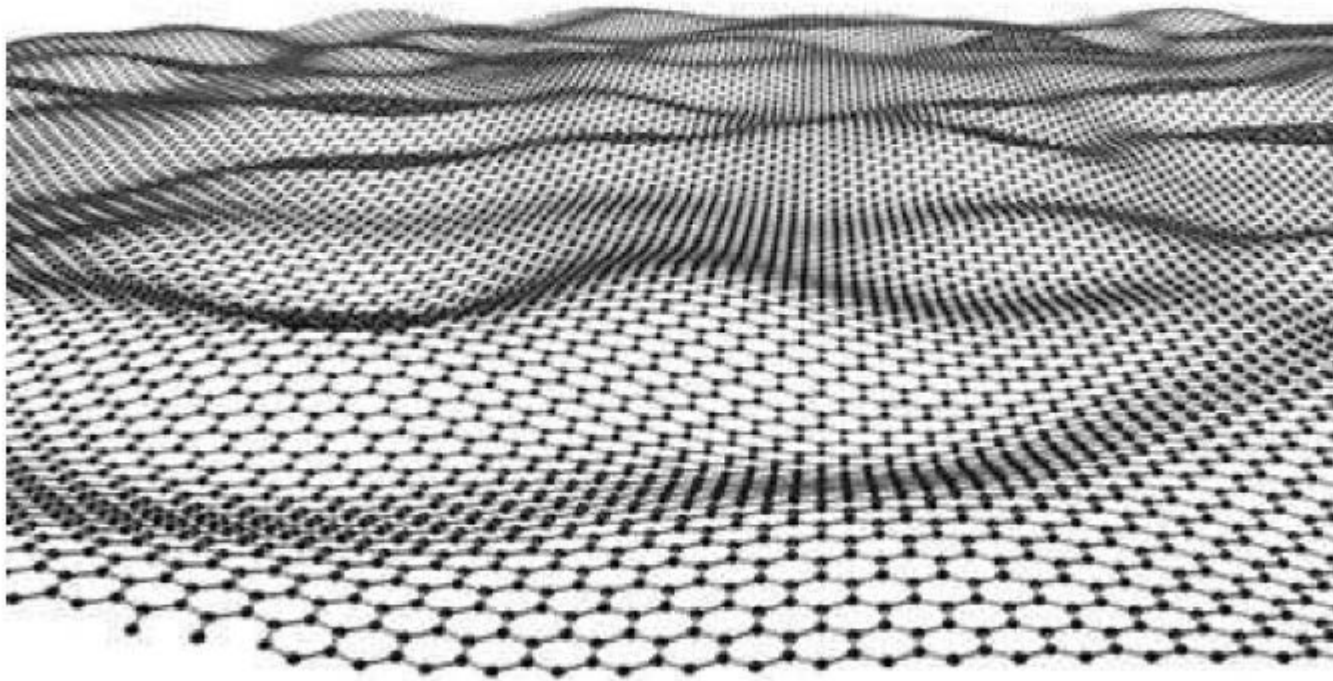
*"Low Dimensional Materials:
Theory, Modeling, Experiment"
Dubna, Russia., July 2018*

Outline

- **Introduction.** Isolated crystalline membrane. Flexural phonons and ripples
- **Phase diagram of clean crystalline membrane.** Crumpling and buckling transitions
- **Anomalous Hooke's law.** Nonlinear scaling of deformation with applied stress
- **Disordered membrane.** Crumpling transition in the membrane with random curvature
- **Thermal expansion.** Negative temperature-independent thermal expansion coefficient
- **Poisson's ratio.** Is graphene an auxetic material?
- **Experiment and numerical simulations.**

Isolated crystalline membrane

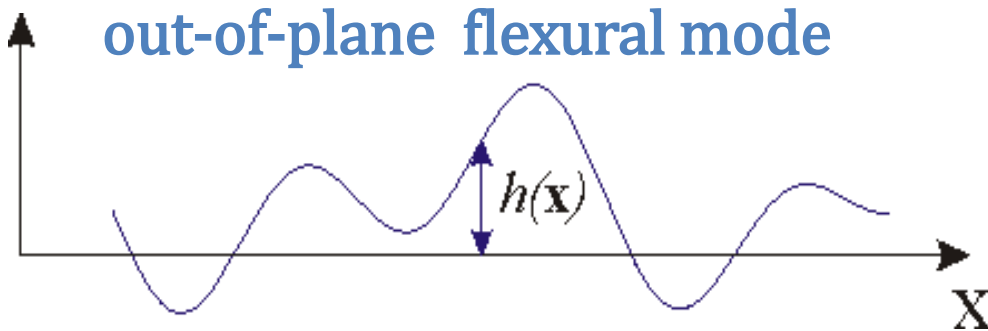
dynamic out-of-plane deformations (**flexural phonons**)
+ static frozen-out deformations (**ripples**)



Meyer, Geim, Katsnelson, Novoselov, Booth, Roth, Nature'07
numerical simulations for suspended graphene

Flexural phonons (FP)

out-of-plane flexural mode



$$E = \frac{1}{2} \int dx \left[\rho \dot{h}^2 + \kappa_0 (\Delta h)^2 \right]$$

$$\kappa_0 \simeq 1 \text{ eV}$$

bending rigidity

$$\omega_q = D q^2$$

soft dispersion
of FP

$$D = \sqrt{\kappa_0 / \rho}$$

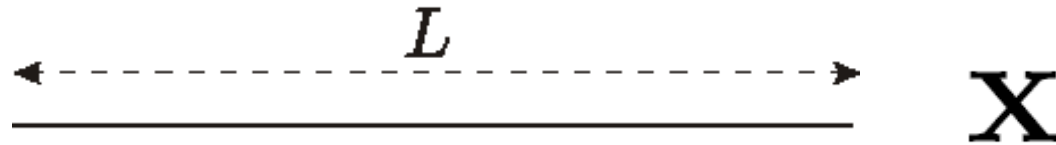
In-plane phonons

$$\omega_q^\perp = \sqrt{\frac{\mu}{\rho}} q, \quad \omega_q^\parallel = \sqrt{\frac{2\mu + \lambda}{\rho}} q$$

μ, λ in-plane
elastic coefficients

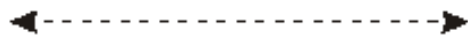
Global shrinking of membrane induced by FP or ripples

membrane without fluctuations



membrane with fluctuations

$$R = \xi L < L$$



hidden area



“Membrane effect”: thermal fluctuations in y -direction lead to shrinking in x direction

I.M. Lifshitz, JETP (1952)

$$\mathbf{R} = \xi \mathbf{x} + \mathbf{u} + \mathbf{h}$$

$\xi < 1$ stretching parameter

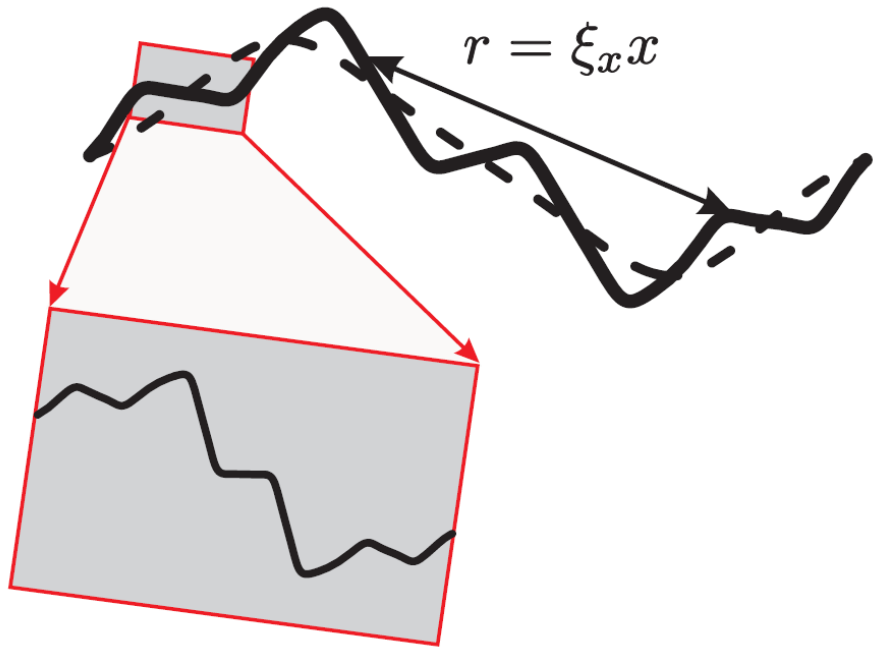
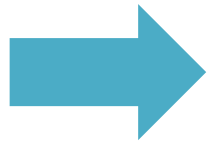
global deformation

in-plane and out-of-plane fluctuations

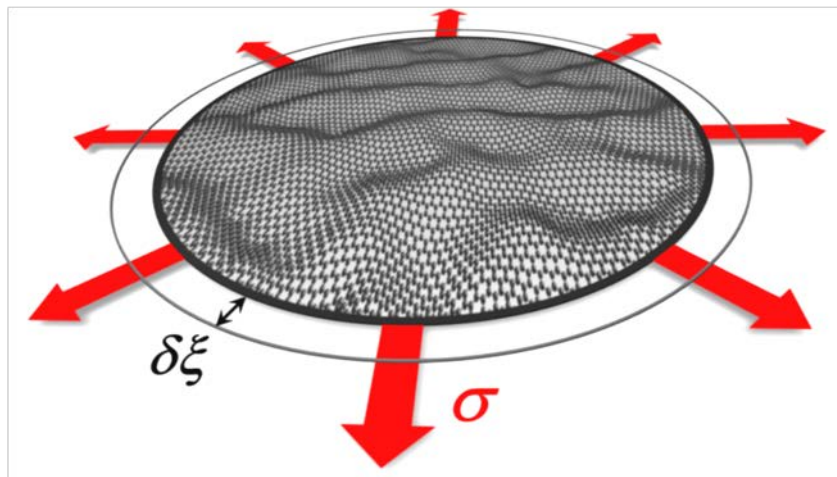
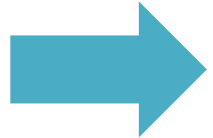
Geometry of the membrane, effect of the external tension

fractal geometry

$$\xi = \xi_L$$



External tension
 σ "irons" thermal
or static fluctuations

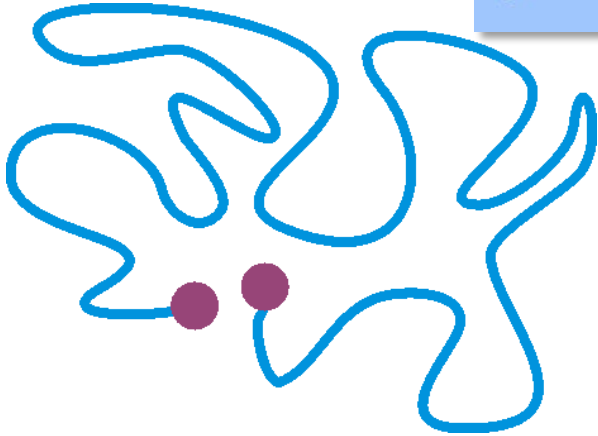


Crumpling transition

Paczuski, Kardar, Nelson, PRL (1988);
David and Gitter, Europhys. Lett. (1988);
Nelson, Piran, Weinberg, "Statistical Mechanics of Membranes and Surfaces" (1989);

Crumpled phase

$$\xi^2 \equiv 0$$

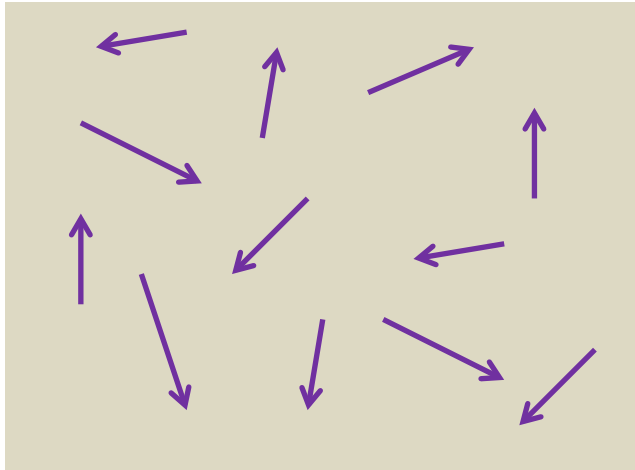


Flat phase

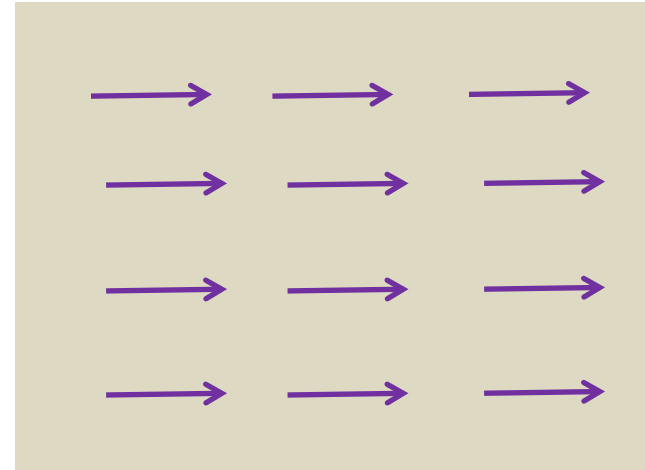
$$\xi^2 = \xi_T^2 > 0$$



Analogy with ferromagnetic transition



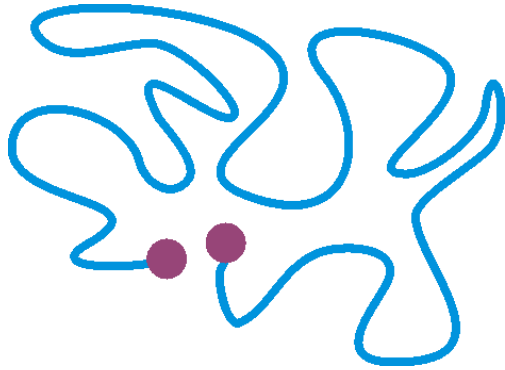
$$T < T_c$$



spontaneous symmetry breaking !!!

Physics behind crumpling transition

Crumpled



CT



Flat



Competition between two effects:

1) “membrane effect”
→ shrinking of
membrane due to FP



**tendency to
crumpling**

2) anharmonic coupling between
FP and in-plane modes → infrared
divergence of bending rigidity



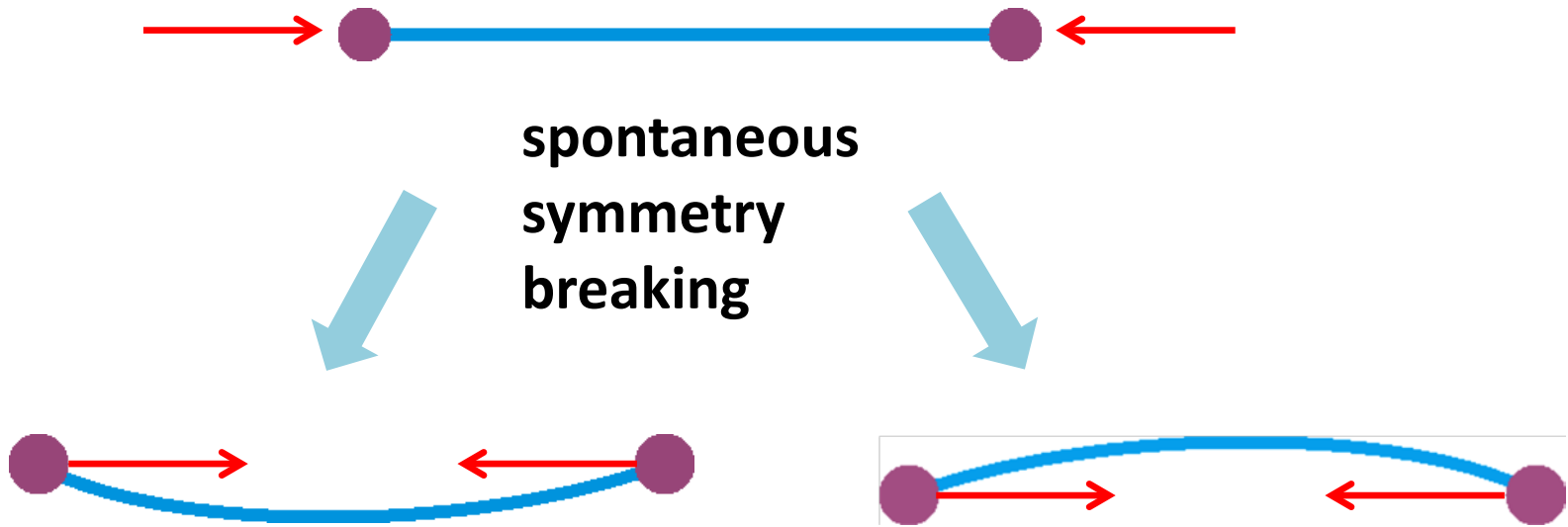
**stabilization of
the flat phase**

$$\kappa \propto L^\eta \propto \frac{1}{q^\eta}$$

$\eta \approx 0.7$ – critical
exponent

Buckling transition (BT)

$T = 0$



Membrane with
fluctuations, $T \neq 0$



???

Manifestation of BT: anomalous Hooke's law



$$\delta \xi \propto \sigma^\alpha$$

α - critical index of BT

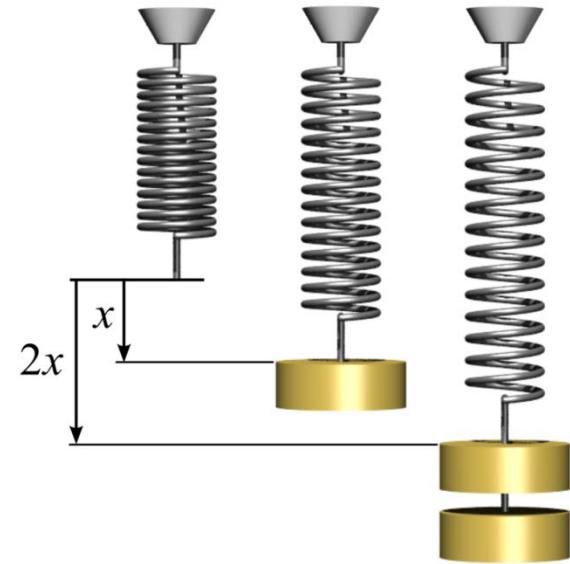
Graphene: $\sigma < \sigma_* \sim \mu \frac{T}{\kappa_0}$

$$1) \alpha_{\text{clean}} = \frac{\eta}{2 - \eta} < 1$$

$$2) \alpha_{\text{clean}} \neq \alpha_{\text{disordered}}$$

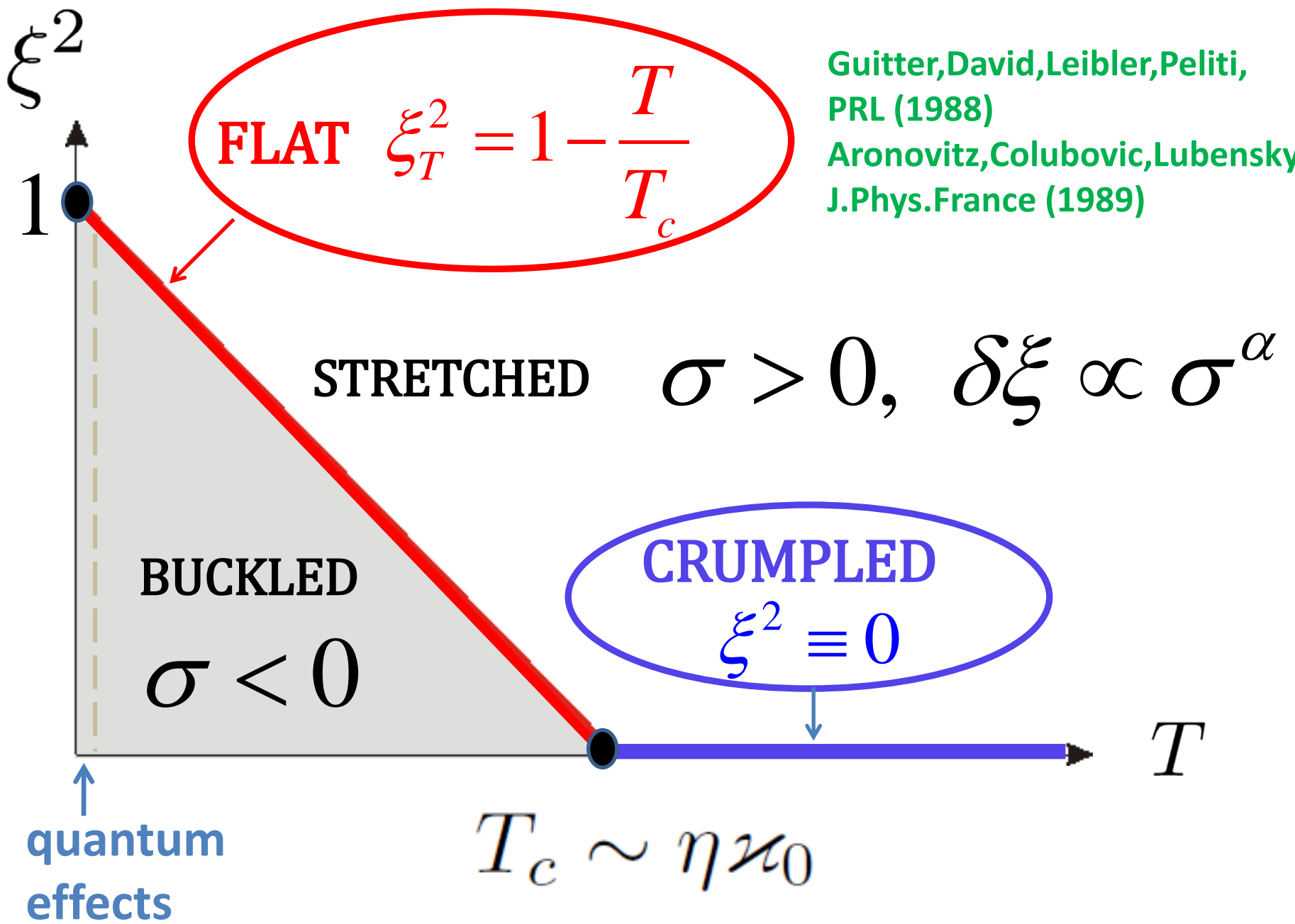
anomalous Hooke's law at SMALL (!) tension

Hooke's law (1678): $\alpha=1$



- 1) Gitter, David, Leibler, Peliti, PRL (1988); Aronovitz, Colubovic, Lubensky J.Phys. France (1989)
- 2) Gornyi, Mirlin, Kachorovskii., 2D Mater. (2017)

Phase diagram of clean crystalline membrane



Gitter, David, Leibler, Peliti, PRL (1988)
 Aronovitz, Colubovic, Lubensky, J.Phys.France (1989)

FLAT $\xi_T^2 = 1 - \frac{T}{T_c}$

CRUMPLED
 $\xi^2 \equiv 0$

$T_c \sim \eta \nu_0$

Experimental evidence of anharmonicity

- huge (unrealistic) theoretical prediction for out-of- plane fluctuations calculated in harmonic approximation
- several order of magnitude discrepancy between theoretical and experimental values of mobility limited by FP
- experimental measurements of anomalous Hooke's law in suspended graphene

▪ Huge out-of-plane fluctuations

$$h(\mathbf{r}) = \sum_{\mathbf{q}} \sqrt{\frac{\hbar}{2\rho\omega_{\mathbf{q}}S}} (b_{\mathbf{q}} + b_{-\mathbf{q}}^{\dagger}) e^{i\mathbf{q}\mathbf{r}}$$

$$b_{\mathbf{q}} = \sqrt{N_{\mathbf{q}}} e^{-i\varphi_{\mathbf{q}}}$$

$$N_{\mathbf{q}} \approx \sqrt{T/\hbar\omega_{\mathbf{q}}} \gg 1$$

Random classical field:

$$h(\mathbf{r}) = \sum_{\mathbf{q}} \sqrt{\frac{2T}{\kappa_0 q^4}} \cos(\mathbf{q}\mathbf{r} + \varphi_{\mathbf{q}})$$



$$\langle h_{\mathbf{q}} h_{-\mathbf{q}} \rangle = \frac{T}{\kappa_0 q^4}$$

correlation function of FP

$$\sqrt{\langle h^2(\mathbf{r}) \rangle} \propto \sqrt{\frac{T}{\kappa_0} \int \frac{d^2\mathbf{q}}{q^4}} \propto \sqrt{\frac{T}{\kappa_0}} L$$

graphene at T=300 K:

$$\sqrt{T/\kappa_0} \approx 0.2$$



**unrealistic (proportional to the system size !!!)
thermal out-of-plane fluctuations**

▪ Scattering off FP in graphene

$$V = g_1 (\nabla h)^2 / 2$$

FP contribution to the deformation potential

$g_1 \simeq 30$ eV deformation coupling constant,

Theory: Golden-rule calculation

$$\sigma_{\text{ph}} = \frac{e^2}{\hbar} \frac{\pi^2 N}{24g^2 \ln(q_T L)} \approx 10^{-3} \frac{e^2}{h}$$

simple theory yields unrealistic (too small) values of conductivity at the Dirac point

Experiment:

$$\sigma_{\text{ph}} \sim 10 \div 50 \frac{e^2}{h}$$

K. Bolotin *et al.*, PRL (2008)

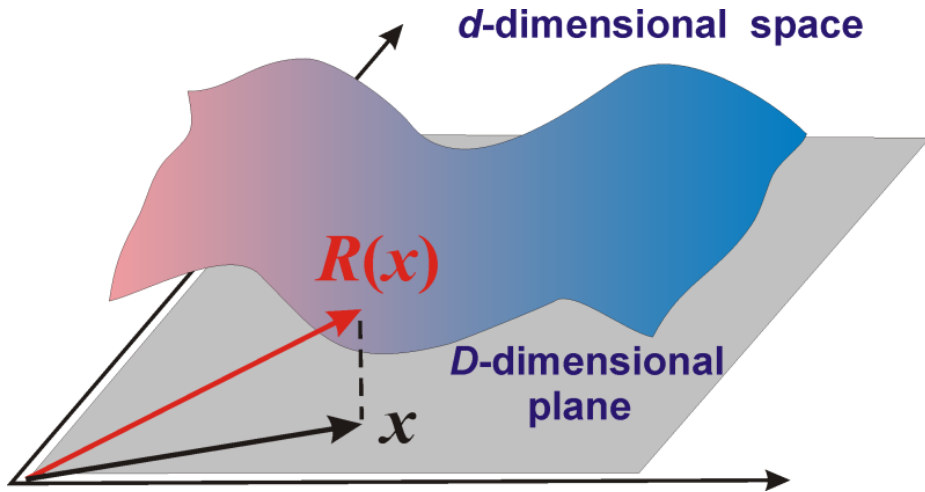
$$g = \frac{g_1}{\sqrt{32}\epsilon_0} \simeq 5.3$$

dimensionless e-ph coupling constant

$N = 4$ spin \times valleys,

$q_T = T/\hbar v$

Theory of crumpling transition



Paczuski, Kardar, Nelson , PRL (1988) ;
 David and Gitter, Europhys. Lett. (1988);
 Nelson, Piran, Weinberg , "Statistical Mechanics
 of Membranes and Surfaces " (1989);

$$E = \int d^D x \left\{ \frac{\kappa_0}{2} (\partial_\alpha \partial_\alpha \mathbf{R})^2 - \frac{t}{2} (\partial_\alpha \mathbf{R} \partial_\alpha \mathbf{R}) + u (\partial_\alpha \mathbf{R} \partial_\beta \mathbf{R})^2 + v (\partial_\alpha \mathbf{R} \partial_\alpha \mathbf{R})^2 \right\}$$

$\alpha, \beta = 1, \dots, D$

$\mathbf{R}(x)$ is d-dimensional vector
 x is D-dimensional vector

For physical membranes $d=3, D=2$

$$\mathbf{R} = \underbrace{\xi \mathbf{x}}_{\text{global deformation}} + \underbrace{\mathbf{u} + \mathbf{h}}_{\text{in-plane and out-of-plane fluctuations}}$$

global
deformation

in-plane and
out-of-plane
fluctuations

Energy of membrane

stretching energy

energy of fluctuations

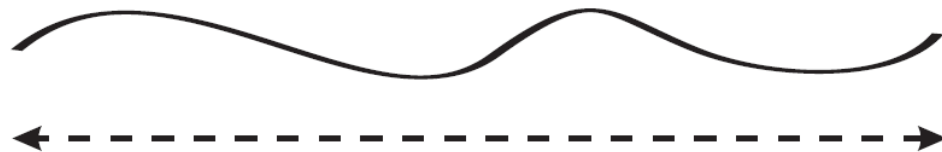
$$E_0 = \frac{L^2(\mu + \lambda)}{2} \left[(\xi^2 - 1)^2 + (\xi^2 - 1) \int \frac{d^2\mathbf{x}}{L^2} \partial_\alpha \mathbf{h} \partial_\alpha \mathbf{h} \right] + E(\tilde{\mathbf{u}}, \mathbf{h})$$

$$\tilde{\mathbf{u}} = \xi \mathbf{u}$$

coupling between stretching and fluctuations

In the absence of fluctuations $\xi=1$

Membrane effect: transverse fluctuations lead to decrease of membrane size in x-direction



$$R = \xi_L L$$

Energy of fluctuations

$$E = \int d^2 \mathbf{x} \left\{ \frac{\kappa_0}{2} (\Delta \mathbf{h})^2 + \mu u_{ij}^2 + \frac{\lambda}{2} u_{ii}^2 \right\}$$

**strong
anharmonicity**

$$u_{\alpha\beta} = \frac{1}{2} (\partial_\alpha u_\beta + \partial_\beta u_\alpha + \partial_\alpha \mathbf{h} \partial_\beta \mathbf{h})$$

strain tensor

Scaling of ξ

minimization
of energy



$$\xi^2 = 1 - \frac{\langle \nabla h \nabla h \rangle}{2}$$

$$E_h = \frac{1}{2} \int \kappa_0 (\Delta h)^2 d^2 \mathbf{x}$$

$$\langle \nabla h \nabla h \rangle = \int (\nabla h \nabla h) e^{-E_h/T} \{dh\}$$

$$\langle h_{\mathbf{q}} h_{-\mathbf{q}} \rangle = \frac{T}{\kappa_0 q^4}$$



$$\langle \nabla h \nabla h \rangle = \frac{T}{\kappa_0} \int \frac{d^2 \mathbf{q}}{(2\pi)^2 q^2} \propto \ln L$$

$$\xi^2 = 1 - \frac{\langle \nabla h \nabla h \rangle}{2}$$

logarithmic divergence \rightarrow scaling with L

$$\frac{d\xi^2}{d\Lambda} = -\frac{T}{4\pi\kappa_0}$$

$\xi \rightarrow 0$, for certain value of L

flat phase is destroyed
by thermal fluctuations

$$\Lambda = \ln L \leftrightarrow \ln(1/q)$$

How to stabilize the flat phase?

$$\mathcal{N}_0 \longrightarrow \mathcal{N}_q$$

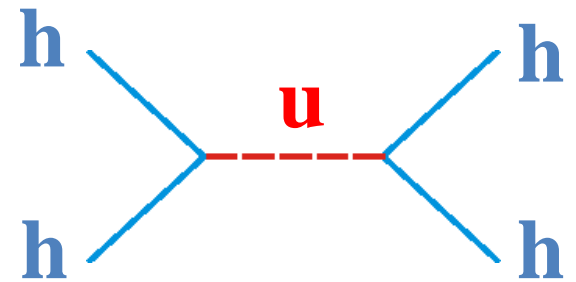
$$\frac{d\xi^2}{d\Lambda} = -\frac{T}{4\pi\mathcal{N}_0}$$

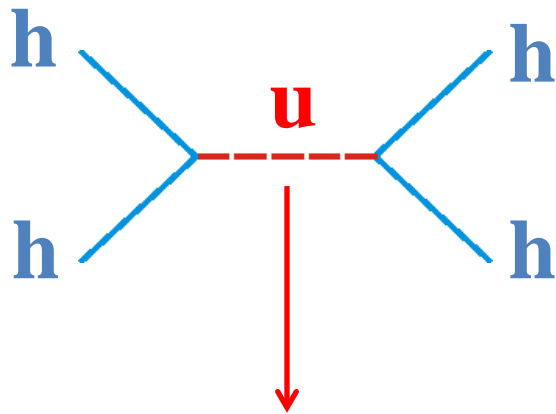


$$\frac{d\xi^2}{d\Lambda} = -\frac{T}{4\pi\mathcal{N}_q}$$

Physical mechanism:

anharmonicity \rightarrow interaction
between h-modes due to the
exchange of u-modes





$$E_h = \frac{1}{2} \sum_{\mathbf{q}} \chi_0 q^4 h_{\mathbf{q}} h_{-\mathbf{q}} + \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}} q^4 R_{\mathbf{k}, \mathbf{k}'}^{\mathbf{q}} h_{-\mathbf{k}} h_{\mathbf{k}+\mathbf{q}} h_{\mathbf{k}'} h_{-\mathbf{q}-\mathbf{k}'}$$

pairing

RPA

$$h_{-\mathbf{k}} h_{-\mathbf{q}-\mathbf{k}'} \rightarrow \langle h_{-\mathbf{k}} h_{-\mathbf{q}-\mathbf{k}'} \rangle$$

$$E_h = \frac{1}{2} \sum_{\mathbf{q}} \chi_{\mathbf{q}} q^4 h_{\mathbf{q}} h_{-\mathbf{q}}$$

Anharmonicity-induced increase of the bending rigidity

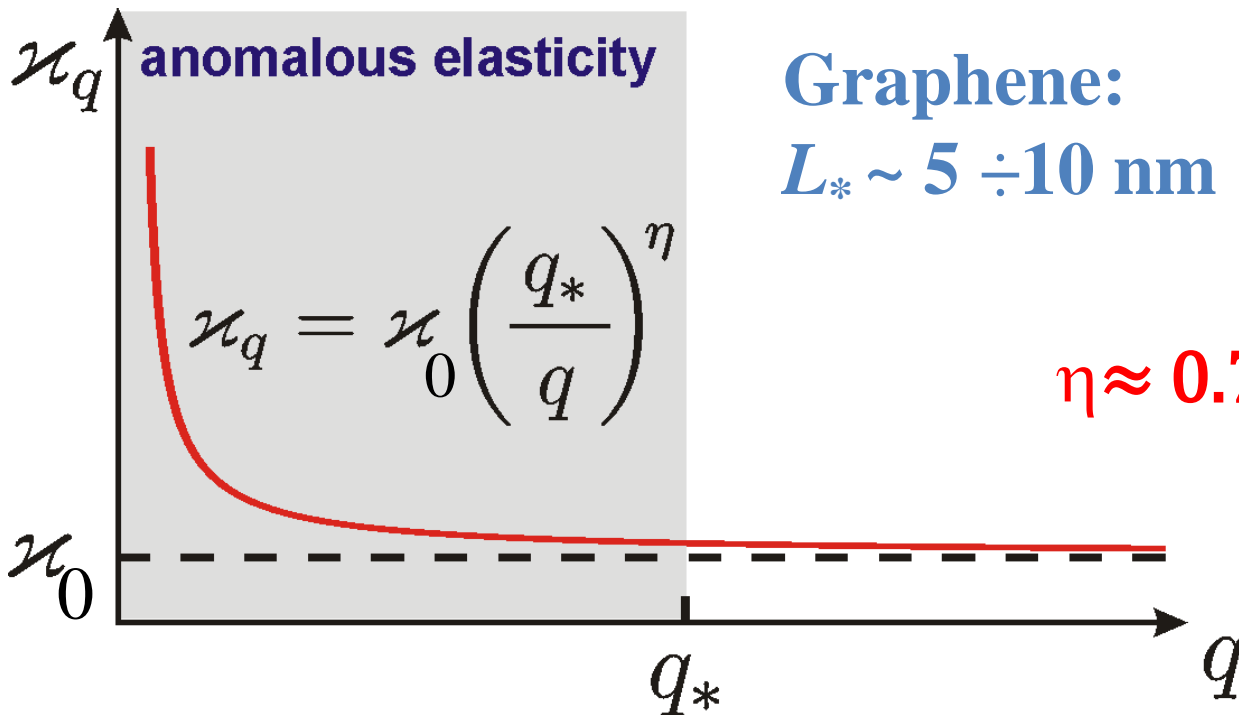
$q \ll q_*$ \rightarrow universal scaling

$$q_* \sim \frac{1}{L_*} \sim \sqrt{\frac{\mu T}{\kappa_0^2}} \quad \text{Ginzburg scale}$$

$$\frac{d\kappa}{d\Lambda} = \eta \kappa$$

\downarrow $\Lambda = \ln(q^*/q)$

$$\kappa \propto L^\eta \propto \frac{1}{q^\eta}$$



$\eta \approx 0.7-0.8$ – critical index

David ,Gutter,
Europhys. Lett. (1988);
Gutter, David, Leibler, Peliti,
J. Phys. France (1989);
Le Doussal , Radzihovsky,
PRL (1992)

Crumpling transition, $\sigma=0$

$$\left\{ \begin{array}{l} \frac{d\kappa}{d\Lambda} = \eta\kappa \quad \longrightarrow \quad \kappa = \kappa_0 e^{\eta\Lambda} \\ \frac{d\xi^2}{d\Lambda} = -\frac{T}{4\pi\kappa} \quad \longrightarrow \quad \xi = \xi_{q \rightarrow 0} \end{array} \right.$$

$$\Lambda = \ln(q^*/q)$$

$$\xi^2 = 1 - \frac{T}{T_c}$$

**second-order
phase transition**

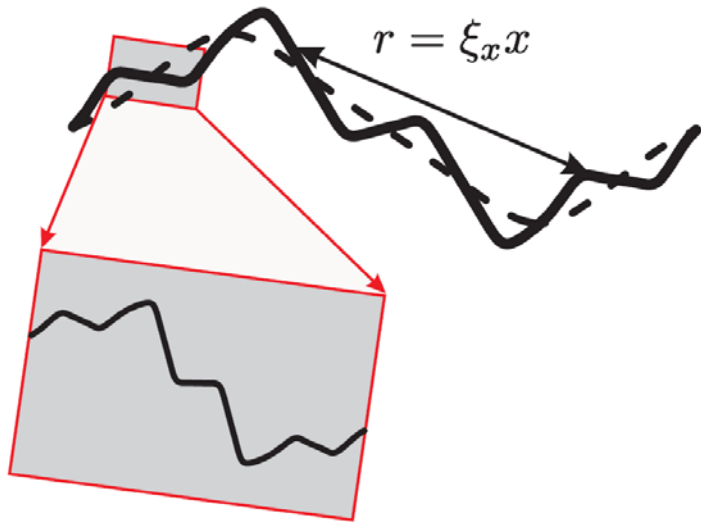
$$T_c = 4\pi\eta\kappa_0$$

**critical temperature of CT
for fixed bending rigidity**

$$\kappa_c = \frac{T}{4\pi\eta}$$

**critical bending rigidity
for fixed temperature**

Fractal geometry of the membrane



Exactly at the transition point

$$\xi \propto \frac{1}{L^{\eta/2}}$$

$$R = \xi_L L$$

$$R^{D_H} \propto L^2$$



$$D_H = \frac{2}{1 - \eta/2} > 2$$

fractal (Hausdorff) dimension

Anomalous Hooke's law

External tension $\rightarrow E_{\mathbf{h}} = \frac{1}{2} \int [\kappa(\Delta \mathbf{h})^2 + \sigma(\nabla \mathbf{h})^2] d^2 \mathbf{x}$

new scale $q = q_{\sigma}$:

$$\begin{cases} \kappa_q q^4 \sim \sigma q^2 \\ \kappa_q = \kappa_0 \left(\frac{q_*}{q} \right)^\eta \end{cases}$$



$$q_{\sigma} = q_* \left(\frac{\sigma}{\sigma_*} \right)^{1/(2-\eta)}$$

scaling stops at $q = q_{\sigma}$

$$\sigma_* \sim (\mu + \lambda) \frac{T}{\kappa_0}$$

Finite tension

1) $T=0, \sigma \neq 0 \rightarrow$ fluctuations are absent

$$\frac{\sigma}{\lambda + \mu} = \xi^2 - 1 \approx 2(\xi - 1)$$

linear Hooke's law

2) $T \neq 0 \rightarrow$ fluctuations

$$\frac{\sigma}{\lambda + \mu} = \xi^2 - 1 + \underbrace{\frac{T}{T_c}}_{\text{contribution of fluctuations at } \sigma = 0}$$

does not take into account suppression of fluctuations by σ

contribution
of fluctuations
at $\sigma = 0$

3) Effect of tension on fluctuations

$$\frac{\sigma}{\mu + \lambda} = \xi^2 - 1 + \frac{\langle \nabla h \nabla h \rangle}{2}$$

$$\langle \nabla h \nabla h \rangle = \int_{q_\sigma} \frac{T}{\kappa_q} \frac{d^2 \mathbf{q}}{q^2}$$

$$q_\sigma = q_* \left(\frac{\sigma}{\sigma_*} \right)^{1/(2-\eta)}$$

$$\sigma_* \sim (\mu + \lambda) \frac{T}{\kappa_0}$$

$$\frac{\sigma}{\mu + \lambda} = \xi^2 - 1 + \frac{T}{T_c} \left[1 - \left(\frac{\sigma}{\sigma_*} \right)^\alpha \right]$$

**stress suppresses
fluctuations !!!**

“hidden area”

Balance equation for membrane under isotropic tension

$$\frac{\sigma_*}{\mu + \lambda} \left[\frac{\sigma}{\sigma_*} + \frac{1}{\alpha} \left(\frac{\sigma}{\sigma_*} \right)^\alpha \right] = \xi^2 - \xi_T^2$$

normal

anomalous

$$\xi_T^2 = 1 - \frac{T}{T_c} \quad \text{global deformation for } \sigma = 0 \quad \sigma_* \sim (\mu + \lambda) \frac{T}{\kappa_0} \quad \text{crossover tension}$$

$$\sigma \ll \sigma_* \rightarrow \delta\xi = \xi - \xi_T \propto \sigma^\alpha$$

$$\alpha = \frac{\eta}{2 - \eta} < 1 \quad \text{critical index of buckling transition}$$

Disordered membrane: Random curvature

$$E = \int d^2 \mathbf{x} \left\{ \frac{\kappa_0}{2} [\Delta \mathbf{h} + \beta(\mathbf{x})]^2 + \mu u_{ij}^2 + \frac{\lambda}{2} u_{ii}^2 \right\}$$

↑
random field

Radzihovsky, Nelson,
PRA (1991);

Other models of disorder, see Le
Doussal, Radzihovsky, PRB (1993)

$$P(\beta) = Z_{\beta}^{-1} \exp \left(-\frac{1}{2b} \int \beta^2(\mathbf{x}) d^2 \mathbf{x} \right)$$

b – strength of
the disorder

Similar to dynamical
fluctuations

$$\frac{T}{\kappa} \rightarrow b$$

Calculations: RPA + replica trick

Scaling in disordered graphene

$$\frac{d\xi^2}{d\Lambda} = -\frac{1}{4\pi} \left(\frac{T}{\varkappa} + b \right)$$

$$\frac{df}{d\Lambda} = -\eta \frac{f(1+3f)}{(1+2f)^2}$$

$$\frac{d\varkappa}{d\Lambda} = \eta \varkappa \frac{1+3f+f^2}{(1+2f)^2}$$



$$f = \frac{b\varkappa}{T}$$

**key
parameter**

$f \gg 1 \rightarrow$ ripples dominate

$f \ll 1 \rightarrow$ thermal fluctuations
(FP) dominate

$f \gg 1$



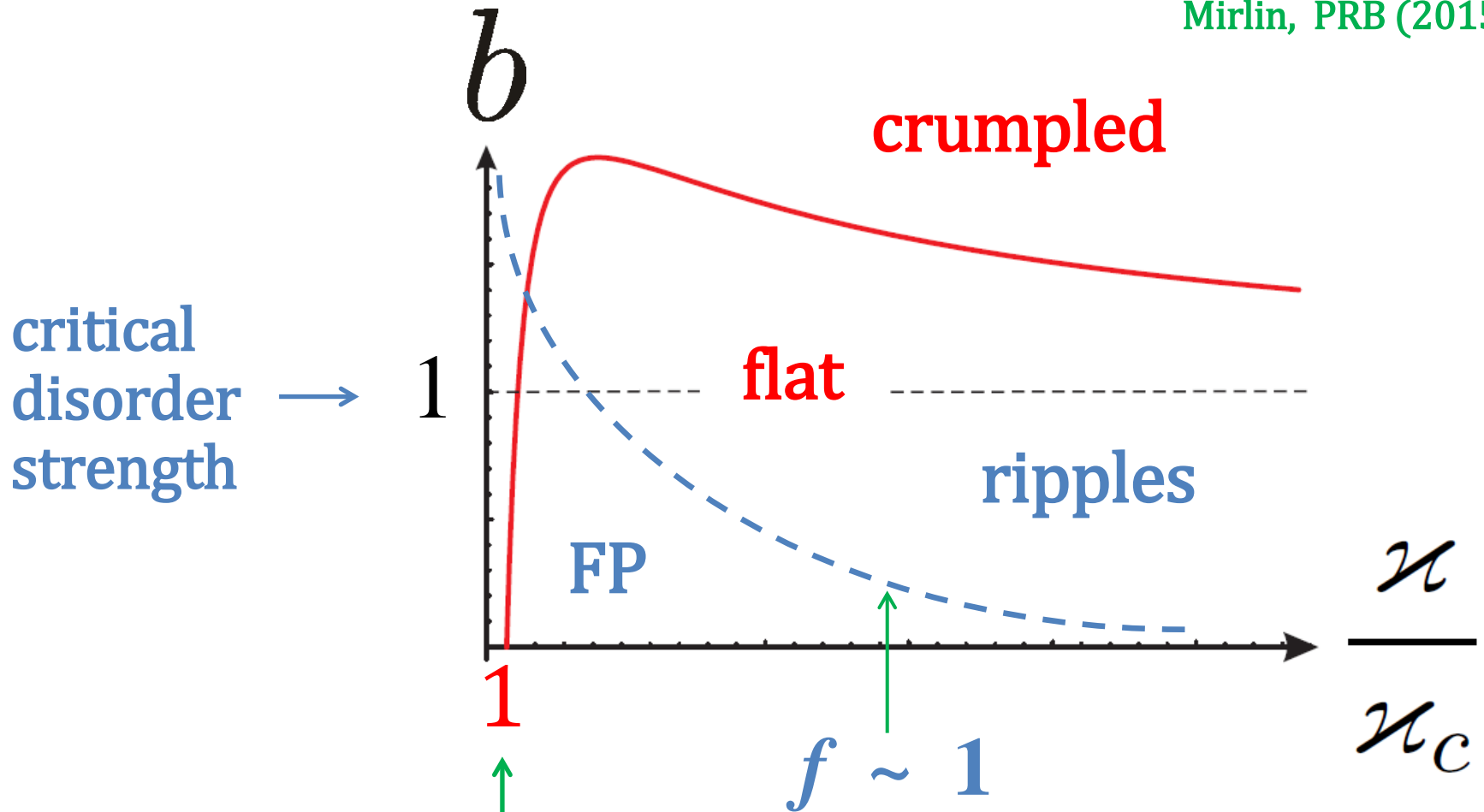
$$\frac{d\varkappa}{d\Lambda} = \frac{\eta}{4} \varkappa$$

strongly disordered case:

$$\eta \rightarrow \frac{\eta}{4}$$

Crumpling transition in disordered membrane, $\sigma = 0$

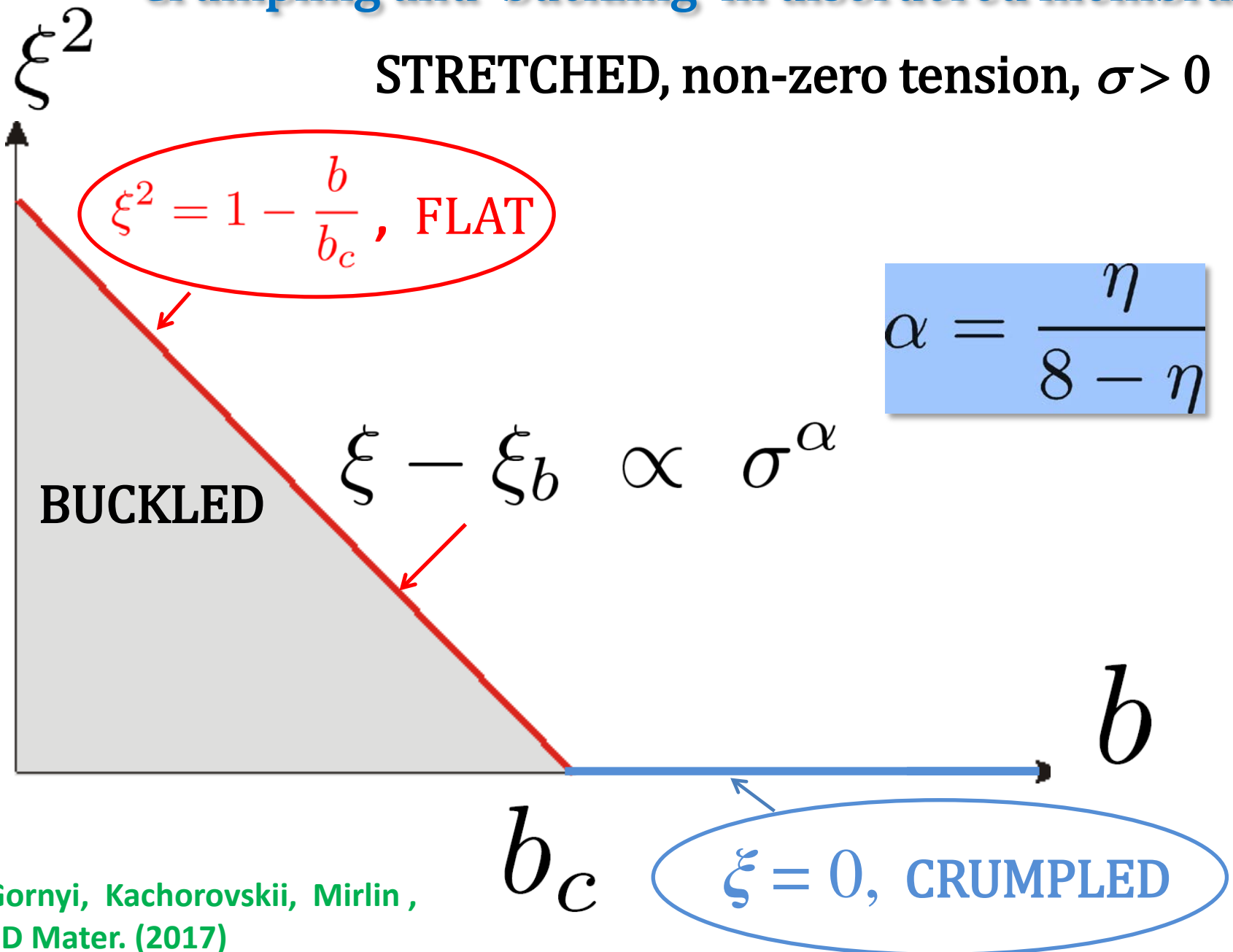
Gornyi, Kachorovskii,
Mirlin, PRB (2015)



$$\kappa_c = \frac{T}{4\pi\eta} - \text{critical bending rigidity for fixed temperature}$$

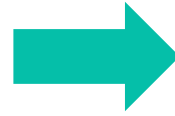
Crumpling and buckling in disordered membrane

STRETCHED, non-zero tension, $\sigma > 0$



Negative thermal expansion coefficient

$$\xi^2 = 1 - \frac{T}{T_c}$$



$$\alpha_T = -\frac{1}{T_c}$$

$$T_c = 4\pi\eta\kappa_0 \sim \kappa_0$$

Agrees with experiment:

Chen et al., 2009; Singh et al., 2010;

Bao et al., 2009; Bolotin et al 2014

Uniaxial stress

$$\nu = -\frac{\epsilon_y}{\epsilon_x}$$

Poisson's
ratio (PR)

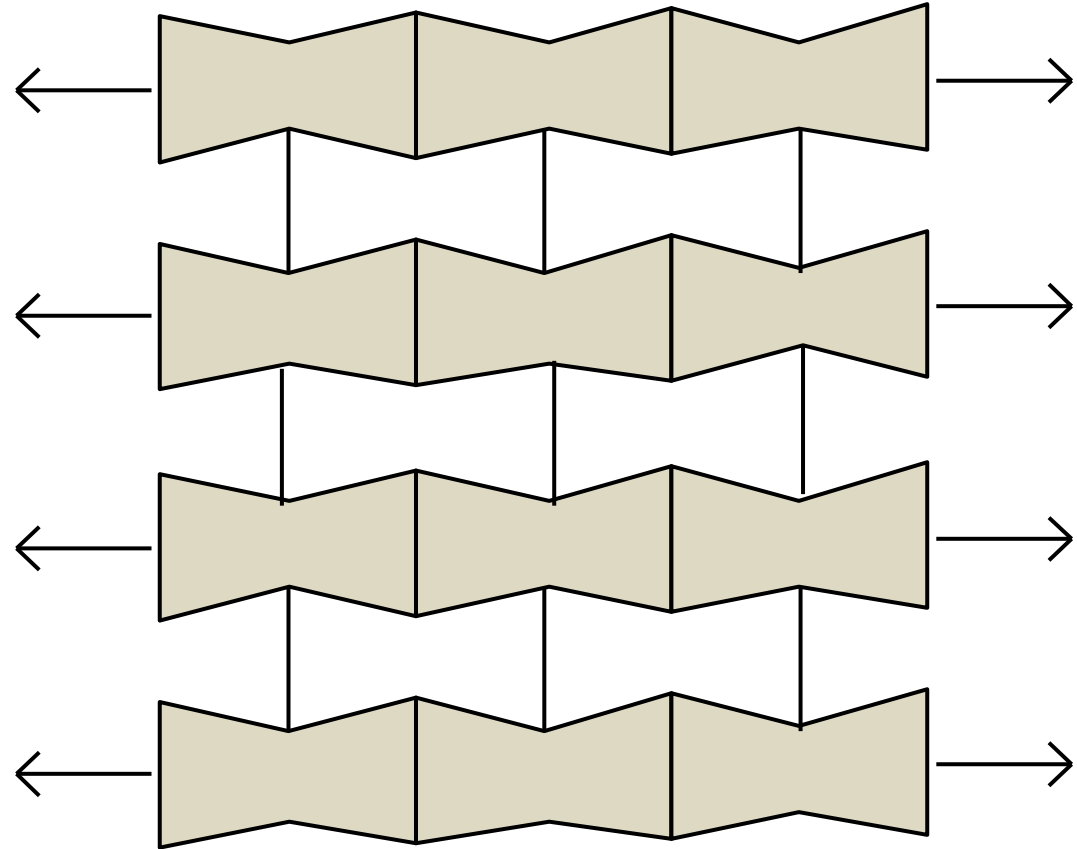
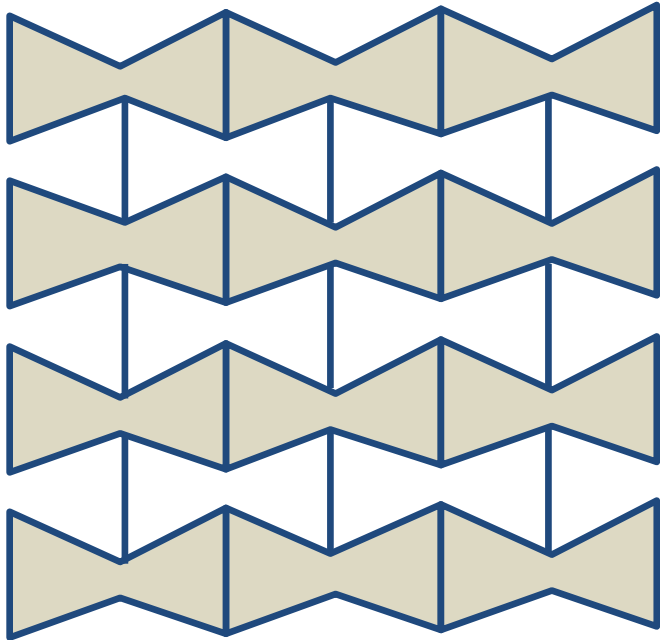
Conventional materials ($\nu > 0$)



Auxetic materials ($\nu < 0$)



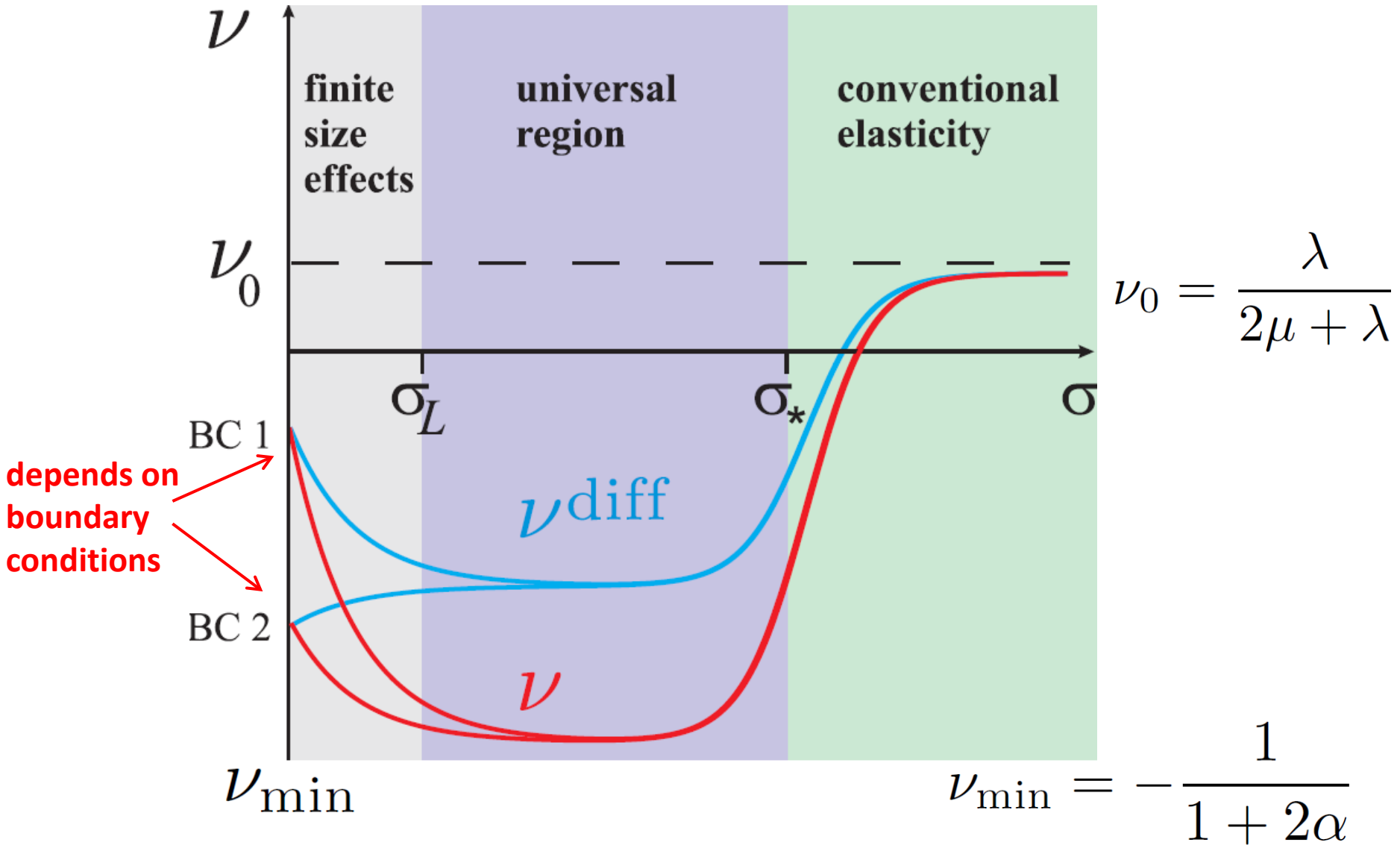
Example: engineered auxetic structure with $PR < 0$



PR of graphene: **negative or positive?**

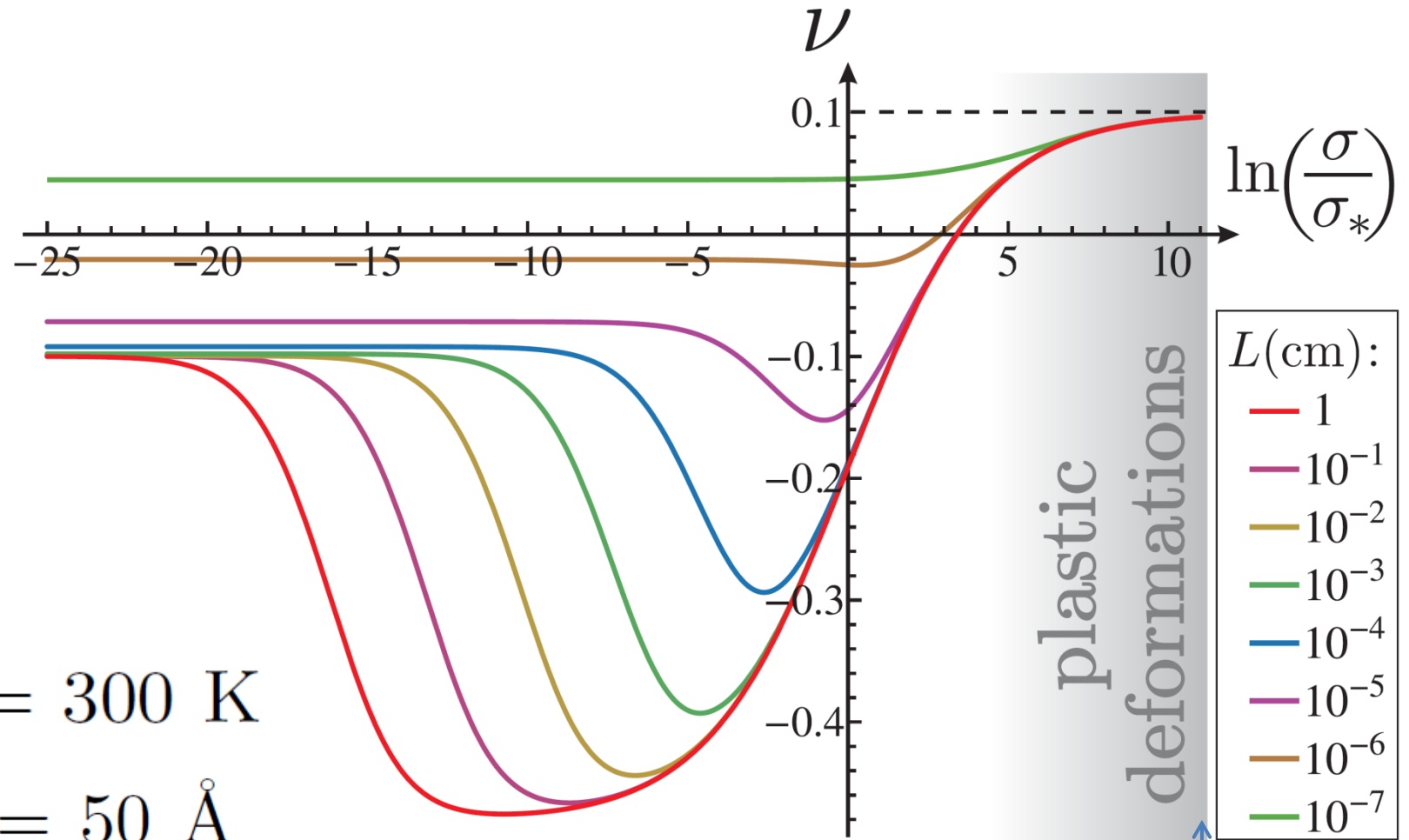
Poisson ratio of a generic membrane

Burmistrov, Gornyi, Kachorovskii,
Los, Katsnelson, Mirlin PRB (2018)



Poisson ratio of graphene

Burmistrov, Gornyi, Kachorovskii,
Los, Katsnelson, Mirlin PRB (2018)



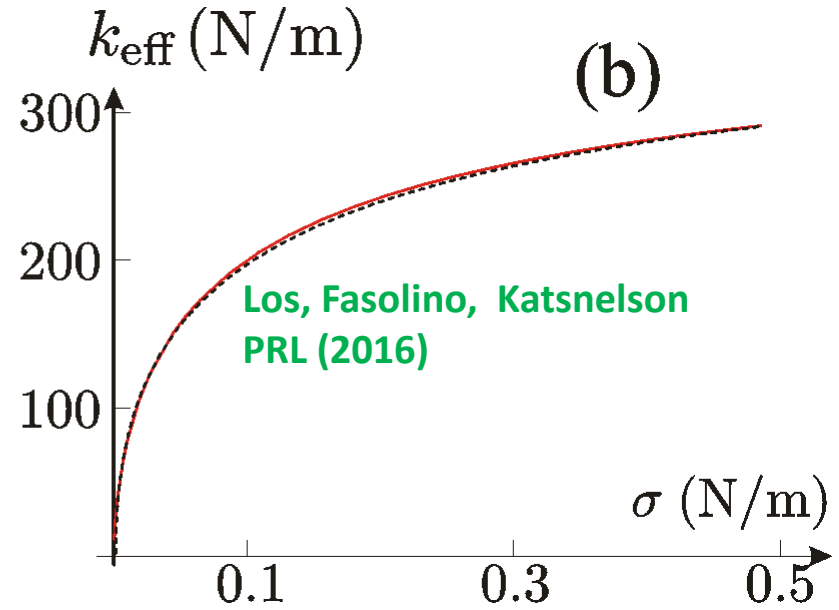
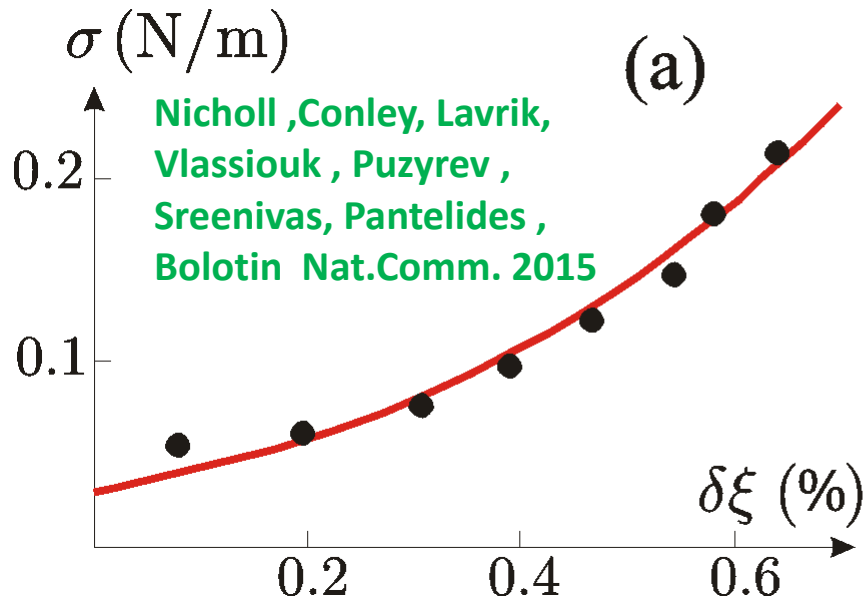
$$T = 300 \text{ K}$$

$$L_* = 50 \text{ \AA}$$

$$\sigma_* = 0.1 \text{ N/m}$$

$$\sigma > 50 \text{ N/m}$$

Anomalous Hooke's law (experiment+simulation)



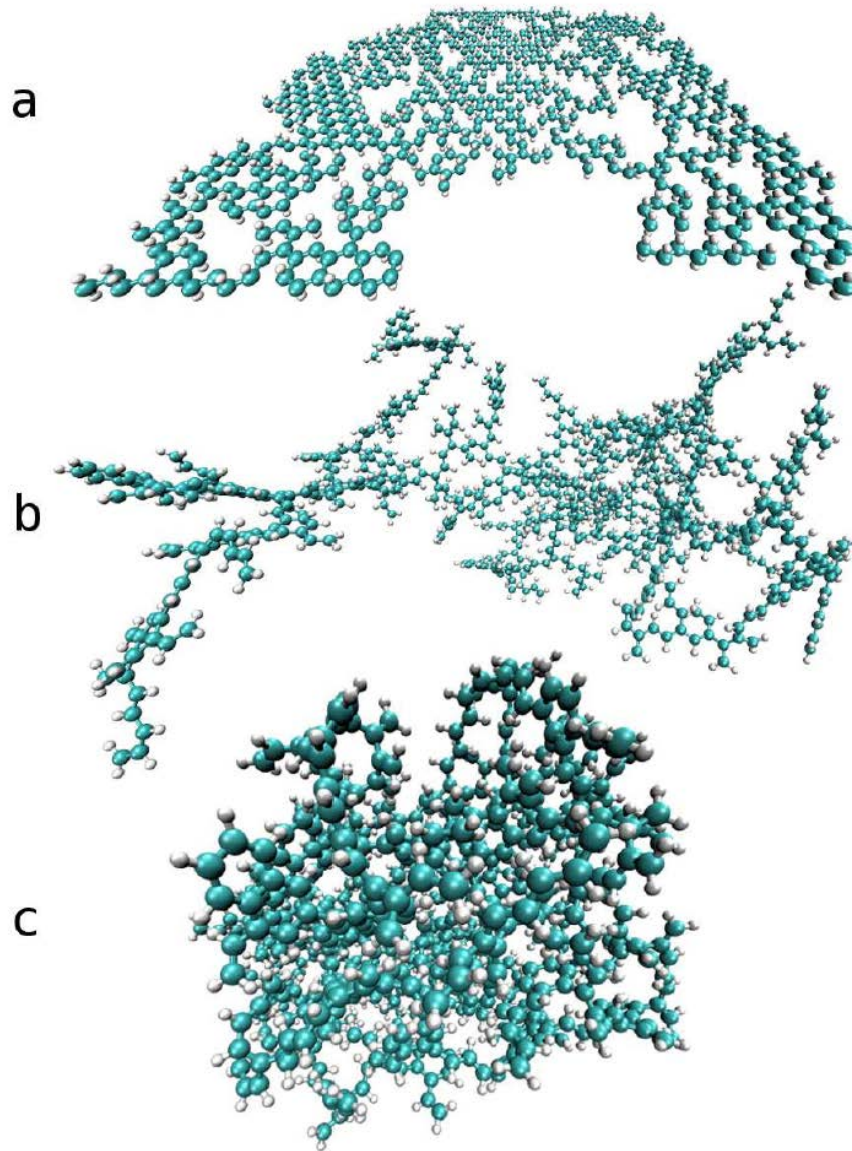
(a) Stress-strain dependence. Dots – experiment (Nicholl et al), red line – theory (Gornyi et al) for strongly disordered case $\alpha = 0.1$ with degree of disorder $B = 0.004$.

(b) Effective stiffness k_{eff} vs. stress σ in clean graphene at $T = 300\text{K}$. Dashed line – numerical simulations (Los et al), red line – theory (Gornyi et al) with $\alpha = 0.62$ (i.e., $\eta = 0.765$) and $\sigma_* \simeq 0.1 \text{ N/m}$.

$$k_{\text{eff}} = \partial\sigma / \partial\xi \simeq k_0 \frac{(\sigma/\sigma_*)^{1-\alpha}}{1 + (\sigma/\sigma_*)^{1-\alpha}}$$

Gornyi, Kachorovskii, Mirlin , 2D Mater. (2017)

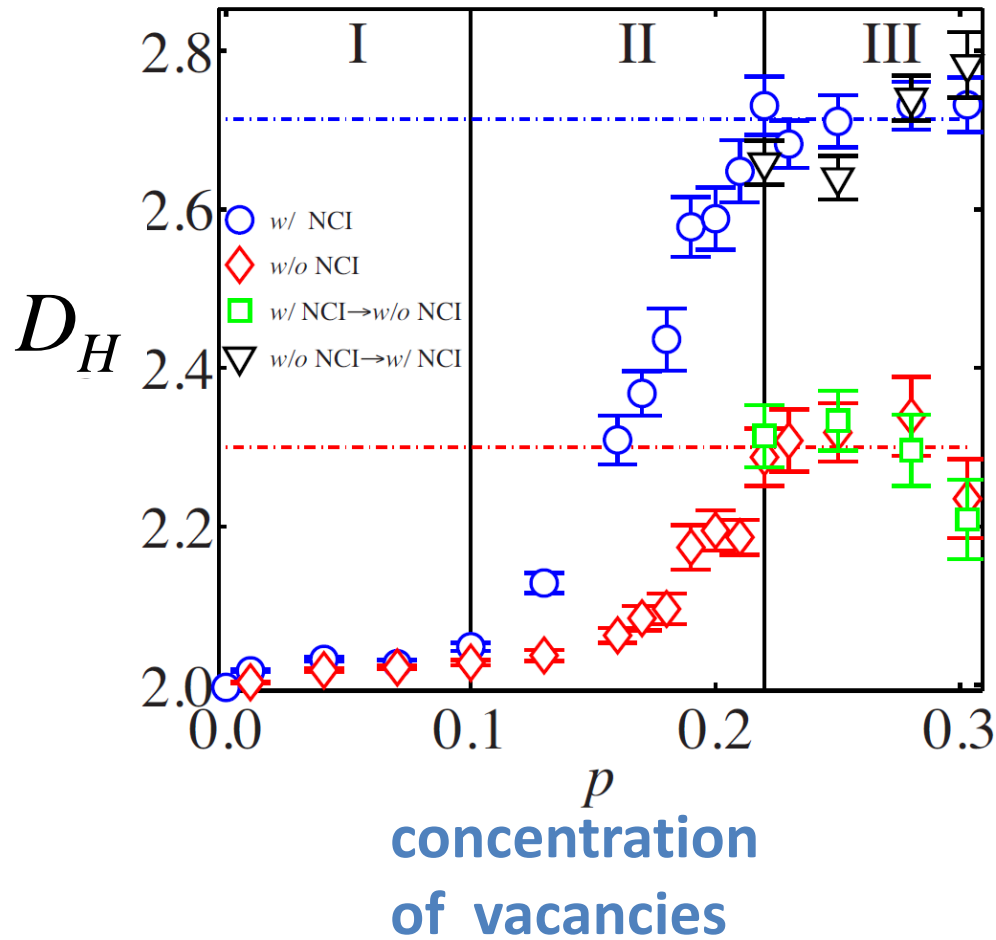
Disorder-induced crumpling



Giordanelli, Mendoza, Andrade, Gomes, Herrmann, Scientific Reports (2016)

Pristine graphene membranes were damaged by adding random vacancies and carbon-hydrogen bonds.

Fractal dimension of crumpled graphene



$$D_H^{clean} = \frac{2}{1 - \eta / 2}$$

$\downarrow (\eta \rightarrow \eta / 4)$

$$D_H^{dis} = \frac{2}{1 - \eta / 8} \approx 2.2$$

for $\eta \approx 0.8$

Interesting theoretical problems to be solved:

1) Bubbles on the substrate

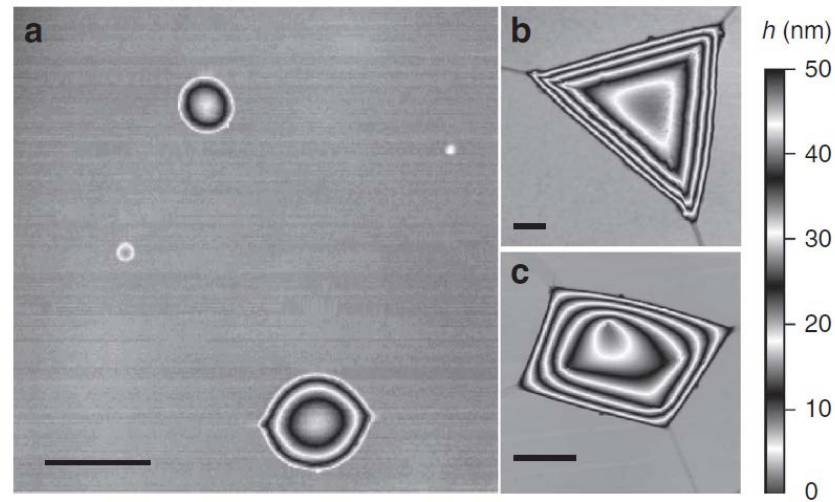


Figure 1 | Graphene bubbles. (a-c) AFM images of graphene bubbles of different shapes. Scale bars, 500 nm (a); 100 nm (b); 500 nm (c). The vertical scale on the right indicates the height of the bubbles.

**Khestanova, Guinea,
Fumagalli, Geim,
I.V. Grigorieva,
Nature Comm. 2016**

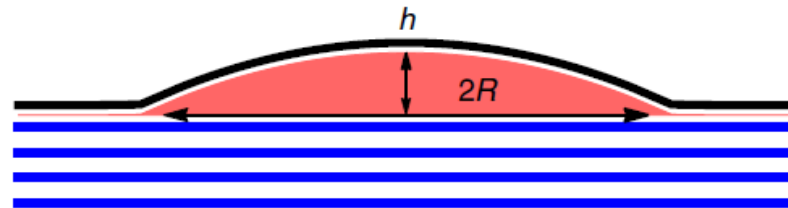
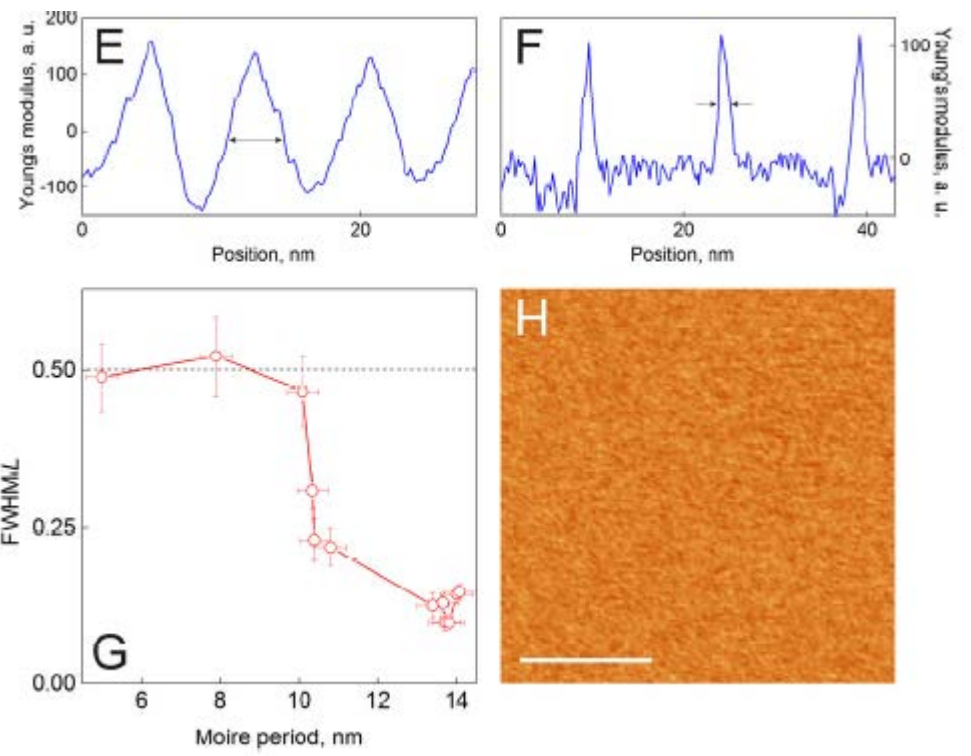
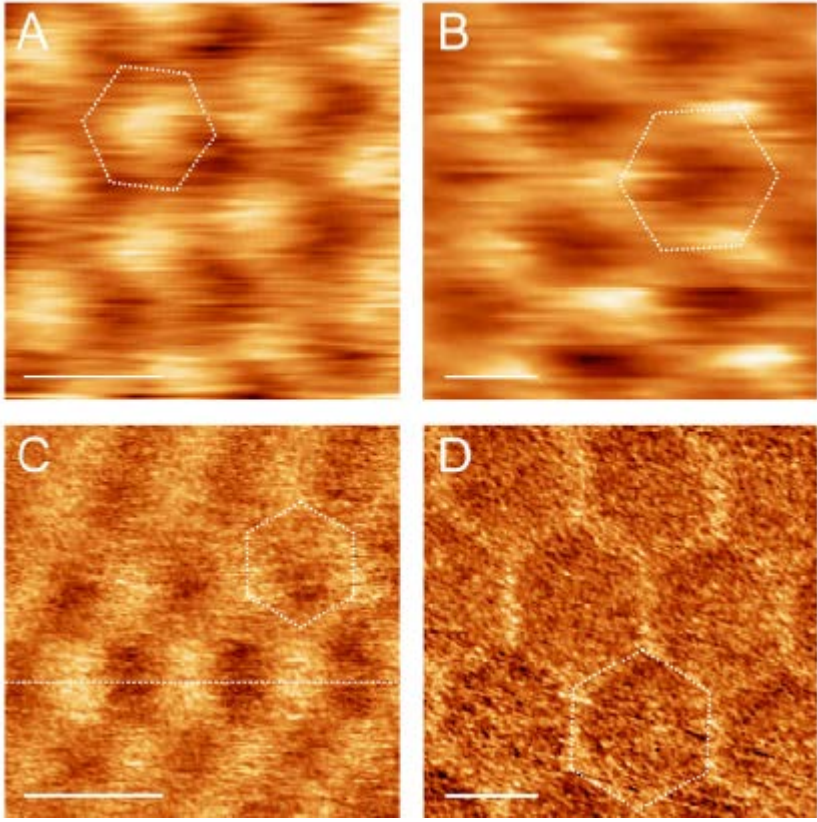


Figure 5 | Sketch of the bubble considered in our theoretical analysis. The bubble is formed by material trapped between a substrate and a 2D layer (graphene).

2) Commensurate-incommensurate transition in graphene on hBN

C. R. Woods et al *Nature Physics* 2014

Moiré patterns



Main results

- Anharmonicity crucially effects elastic properties of graphene → crumpling and buckling transitions
- Stretching of the membrane is non-linear function of tension
- Strong disorder leads to crumpling transition
- Thermal expansion coefficient is negative up to very low temperatures
- Poisson ratio is controlled by applied stress and can change sign