Deforming Single and Multilayer Graphenes in Tension and Compression

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FORTH/ ICE-HT
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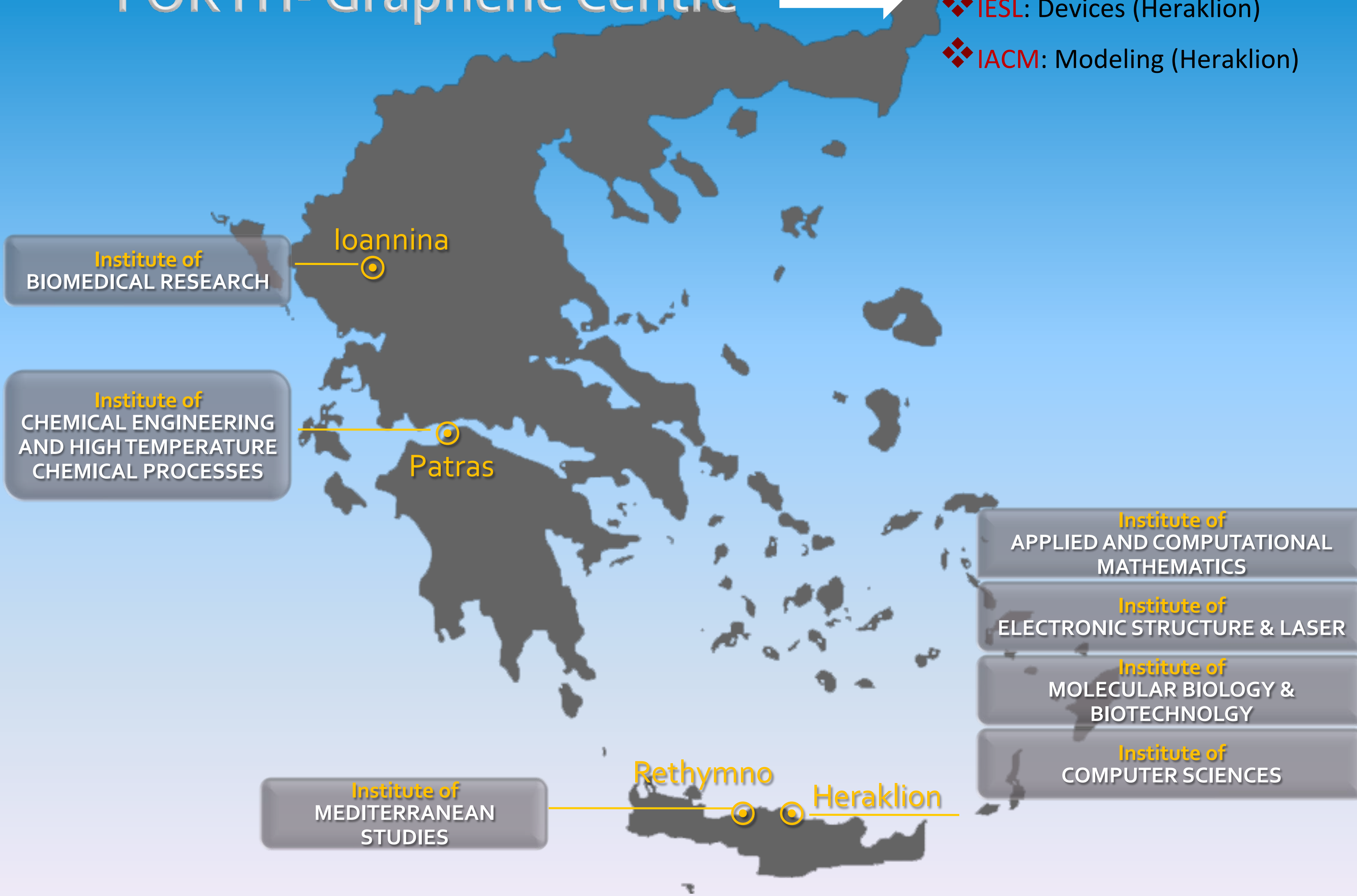
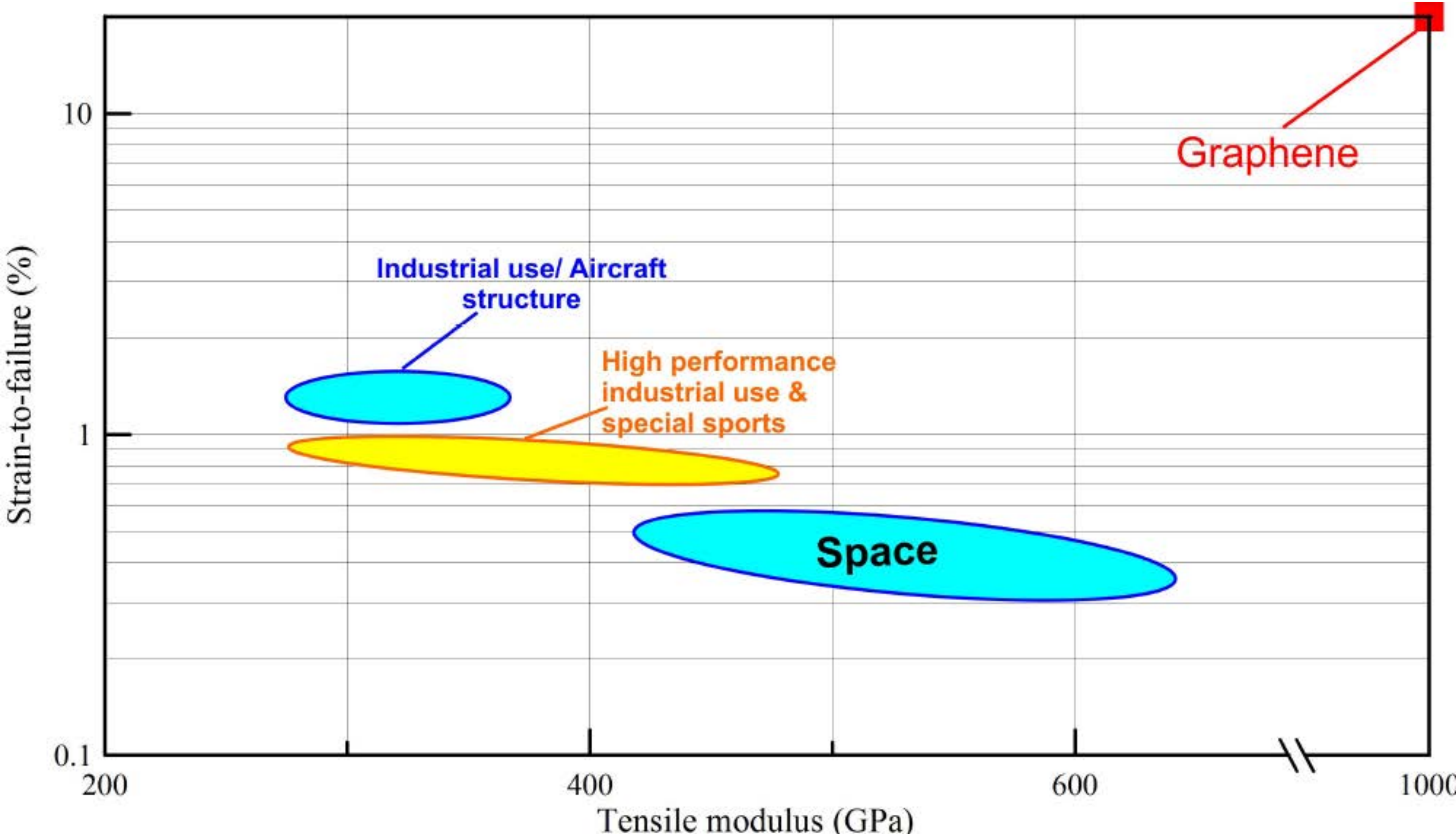
- IESL: Devices (Heraklion)
- IACM: Modeling (Heraklion)



Background

Mechanical behaviour of graphene:

High stiffness, high strength, high ductility (toughness)…



Current Status/ Aims

- A great deal of modeling work (*ab initio* & other) has been accomplished (*NB. large diversity of values*).

Progress towards verification:

- Relative little experimental work (mainly bending) for freely-suspended flakes

- Axial deformation in tension (up to 1.5%) and compression (up to failure) has been accomplished on flexed beams in combination with simultaneous Raman measurements

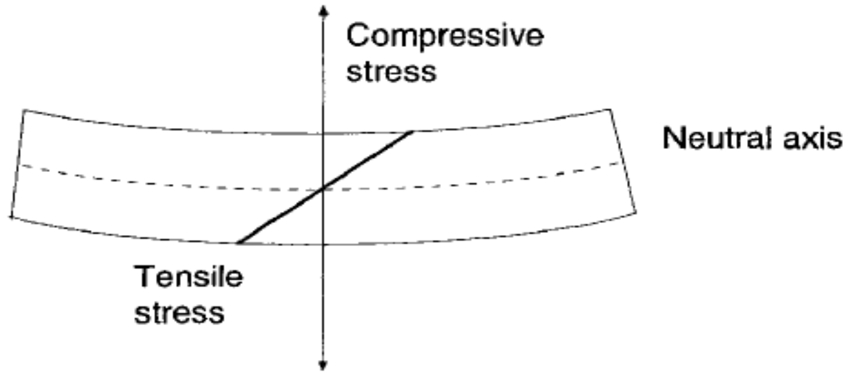
Bending Experiments

Plate vs Membrane Analysis

How should we treat graphene?

- ***Membranes*** exhibit zero bending stiffness (*NB. graphene exhibits a finite value of κ*). They can only sustain tensile loads; their inability to sustain compressive loads leads to wrinkling.

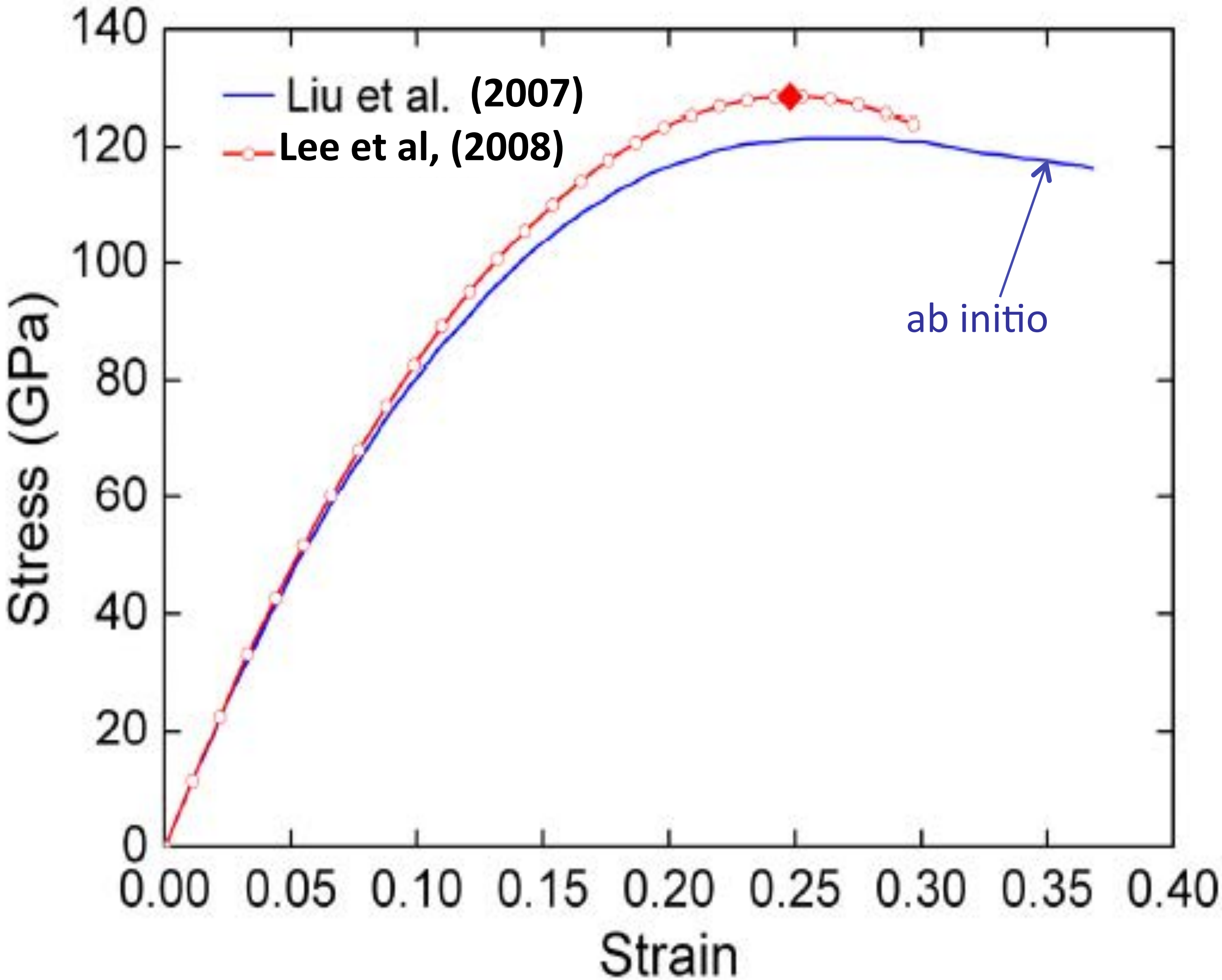
- ***Plates*** have finite thicknesses that normally give rise to internal stress/ strain distribution during bending. The deflection of the mid-plane is small compared to thickness.



Graphene as a membrane: past bending experiments

❖ to nd

❖ a



Lee et al, *Science*, 2008

Cantilever Mechanics

fin quì dichiarate, non sarà difficile l'intender la ragione, onde auuenga, che vn Prisma, ò Cilindro solido di vetro, acciaio, legno, ò altra materia frangibile, che sospeso per lungo sosterrà gravissimo peso, che gli sia attaccato, mà in trauerso (come poco fà diceuamo) da minor peso assai potrà tal volta essere spezzato, secondo che la sua lunghezza eccederà la sua grossezza. Imperò che figuriamoci il Prisma solido A B, C D fitto in vn muro dalla parte A B, e nell'altra estremità s'intenda la forza del Peso E, (intendendo sempre il muro esser eretto all'Orizonte, & il Prisma, ò Cilindro fitto nel muro ad angoli retti) è manifesto che douendosi spezzare si romperà nel luogo B, doue il taglio del

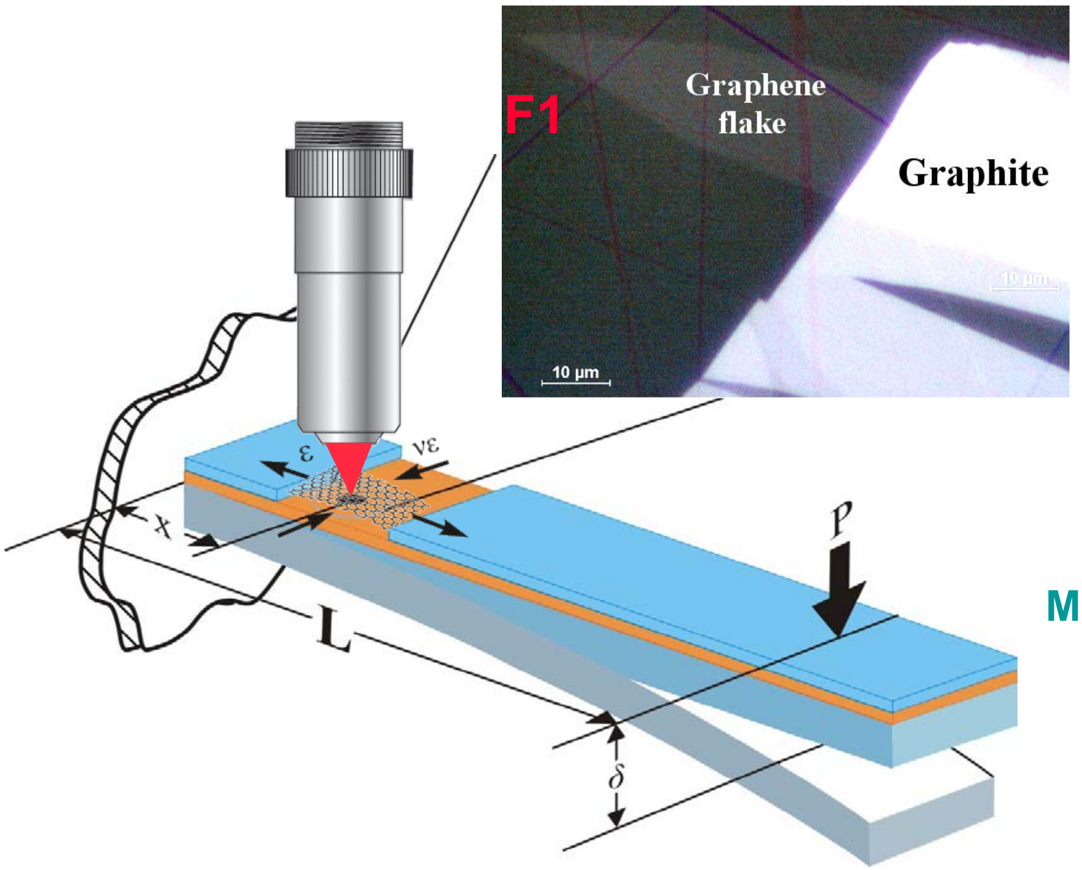
Prop. I.

Galilei, Galileo (1564-1642)
Discorsi e dimostrazioni matematiche, intorno à due nuoue scienze.

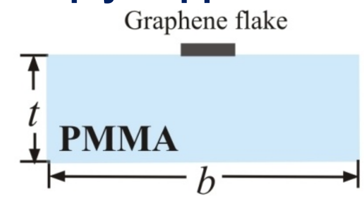
(*tension & compre* … *rements*)

del solido B A e l'altra parte della Leua, nella quale è posta la resistenza, che consiste nello staccamento, che s'hà da fare della parte del solido B D, che è fuor del muro, da quella che è dentro; e per le cose dichiarate il momento della forza posta in C al momento della resistenza che stà nella

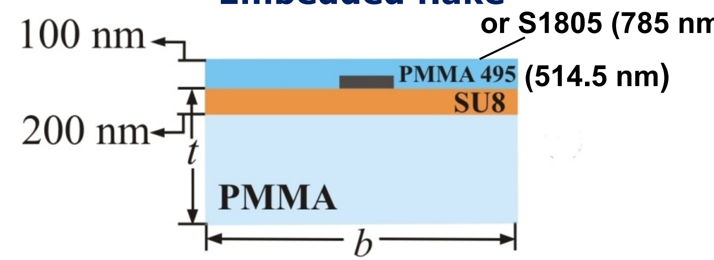
Experimental set-up for application of uniaxial strain



Simply-supported flake



Embedded flake



Mechanical strain at the top of the beam

$$\varepsilon(x) = \frac{3t\delta}{2L^2}\left(1-\frac{x}{L}\right)$$

δ: deflection of the beam neutral axis
L: span of the beam
t : beam thickness

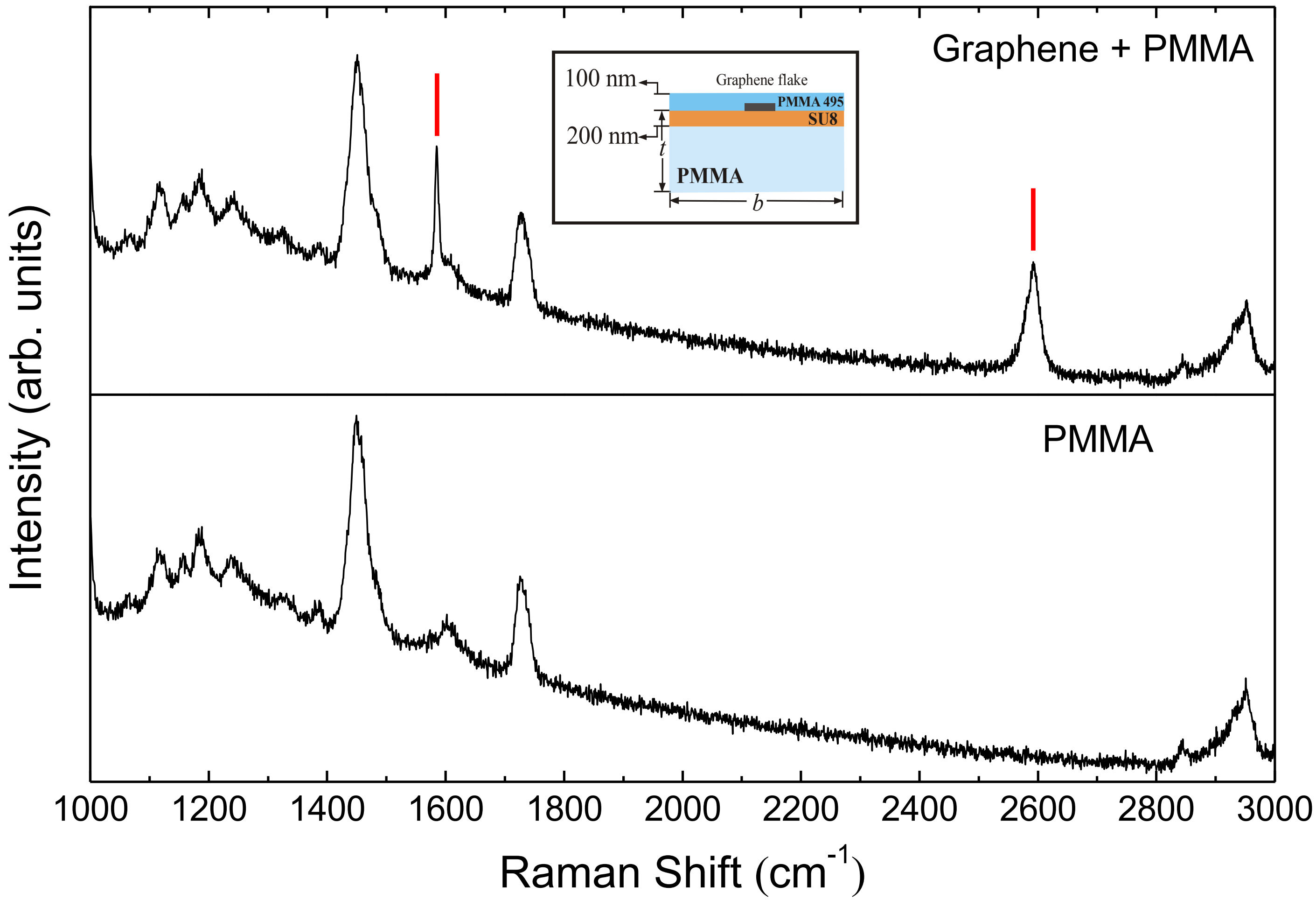
Materials & Geometry

- SU8 photo resist epoxy-based polymer
- PMMA beam substrate (*2.9x12.0x70*) mm^3
- *x* = 10.4 mm and *L* = 70 mm

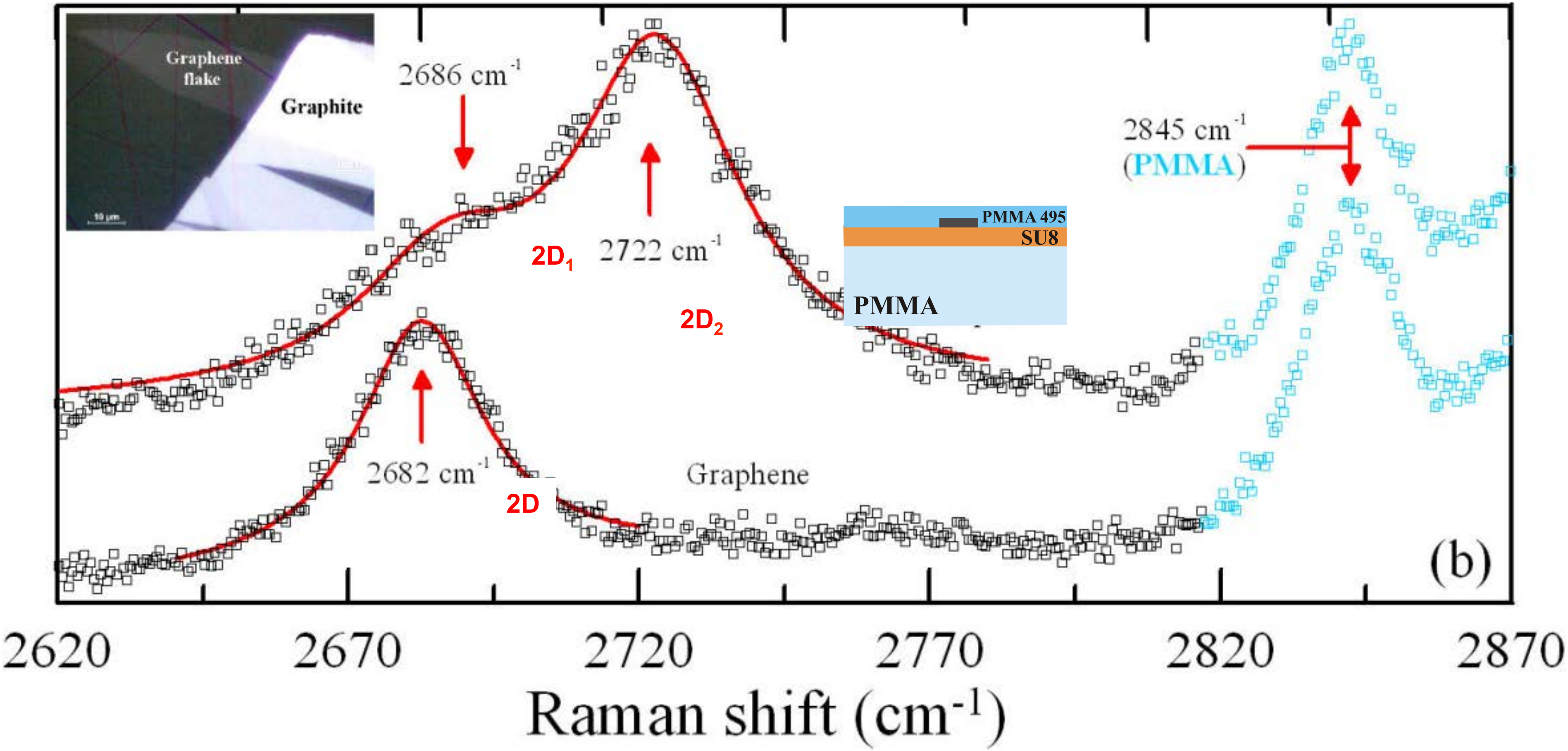
Operating limits:

- L>> $10\delta_{max}$
- -1.5% < ε < 1.5%

Raman Spectra of embedded layer graphene inside PMMA



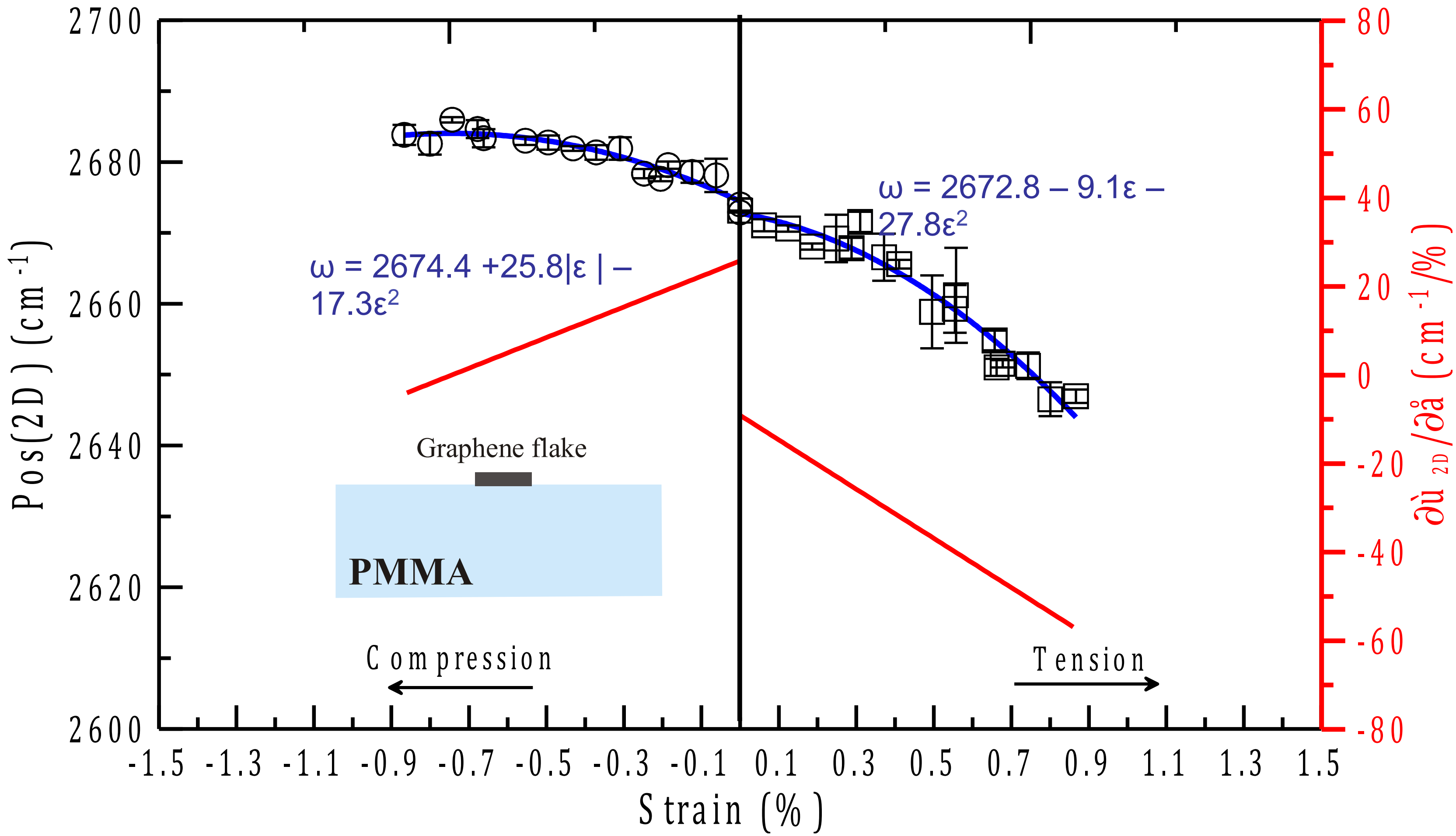
Raman spectra of 2D-peak from embedded graphene flakes and bulk graphite



Tsoukleri et al. *Small* **2009**, 5, 2397]

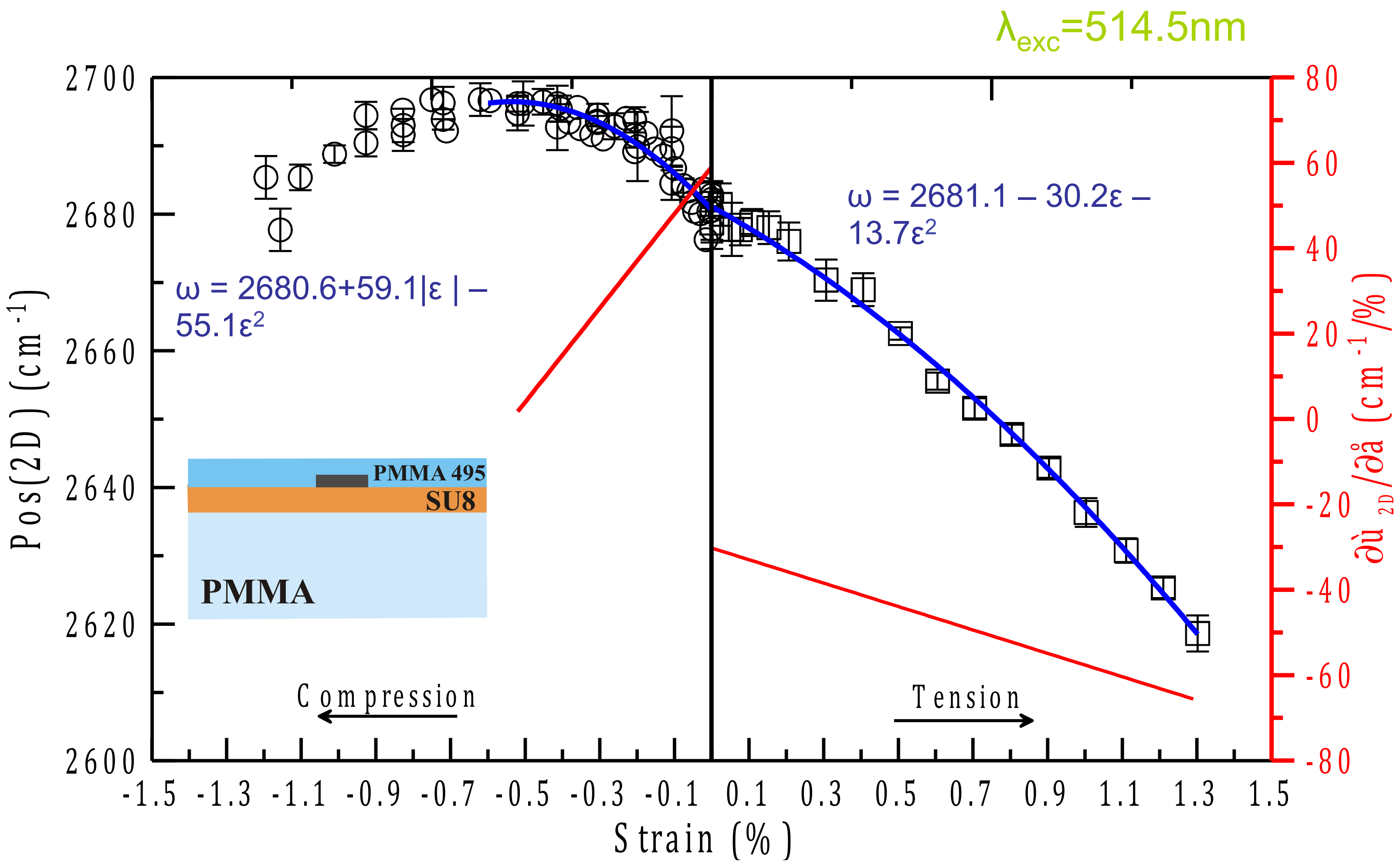
Simply-supported (“bare”) flake

λ_{exc}=514.5nm



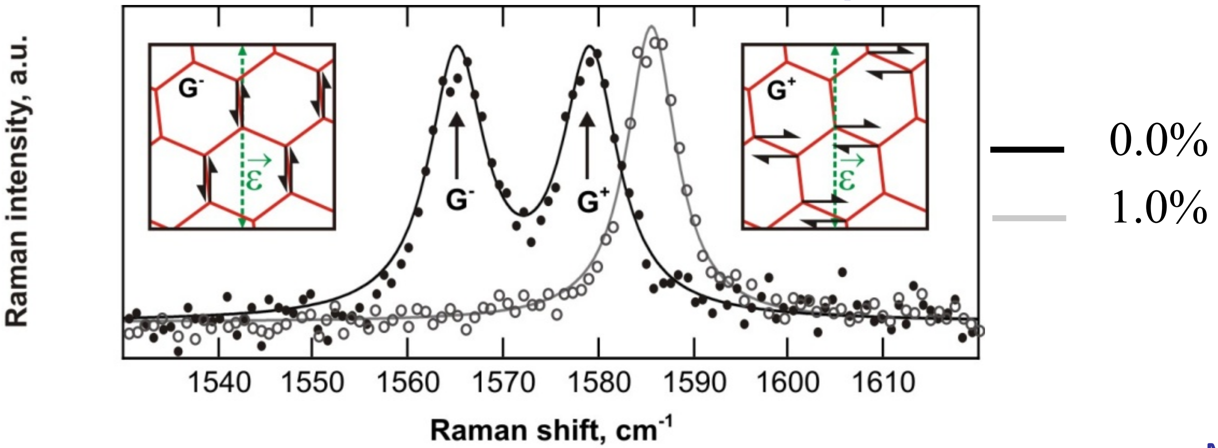
Tsoukleri et al. *Small* **2009**, 5, 2397]

Fully embedded flake



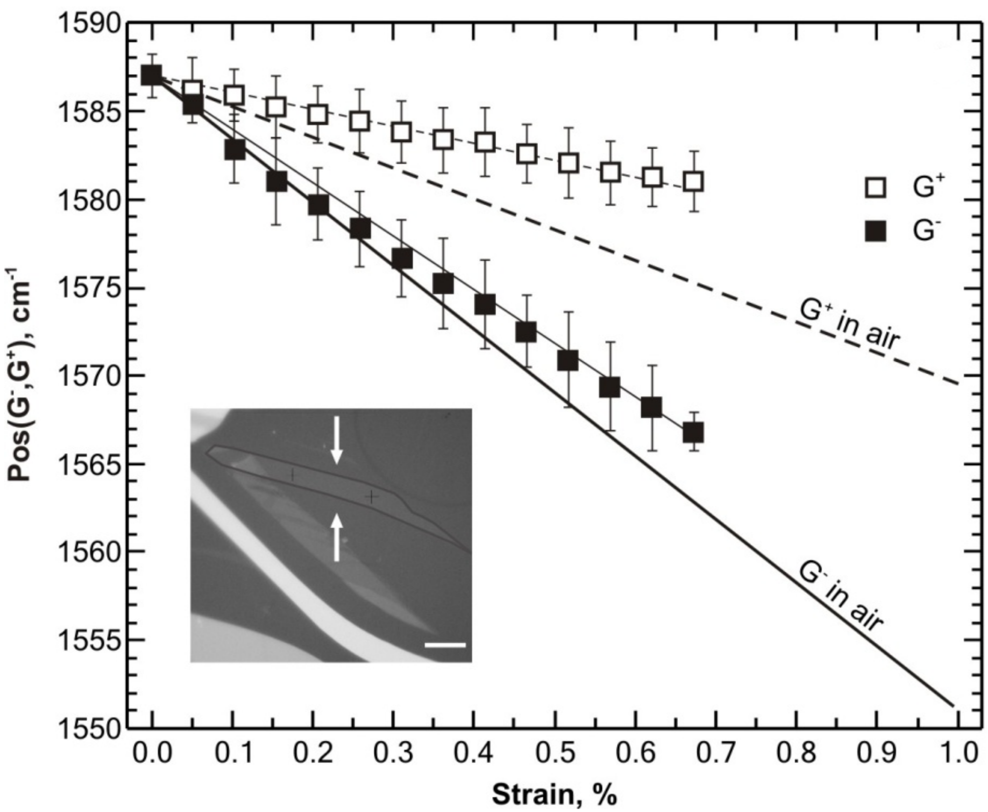
Tsoukleri et al. *Small* **2009**, 5, 2397]

G peak vs. strain (no residual strain)



Mohiudin et al, *PRB*, **2009**

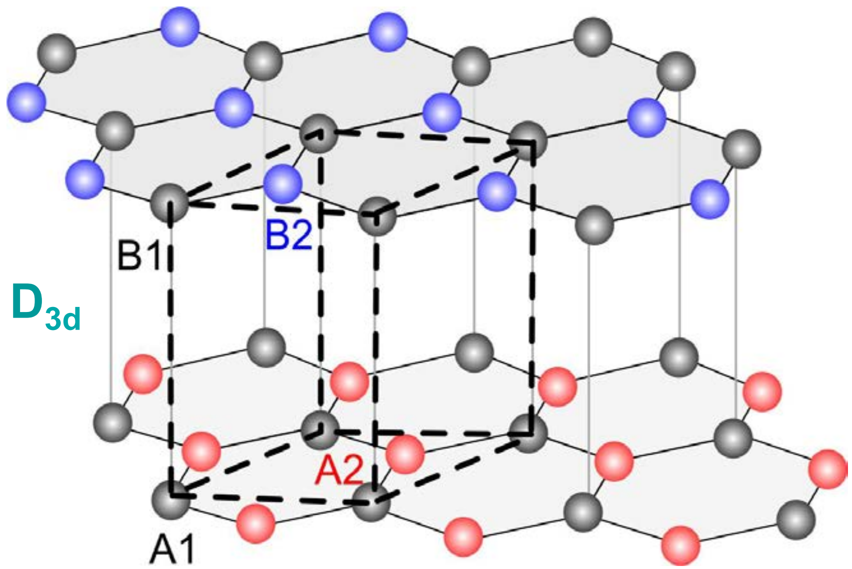
Frank et al, *ACS-Nano*, **2010**

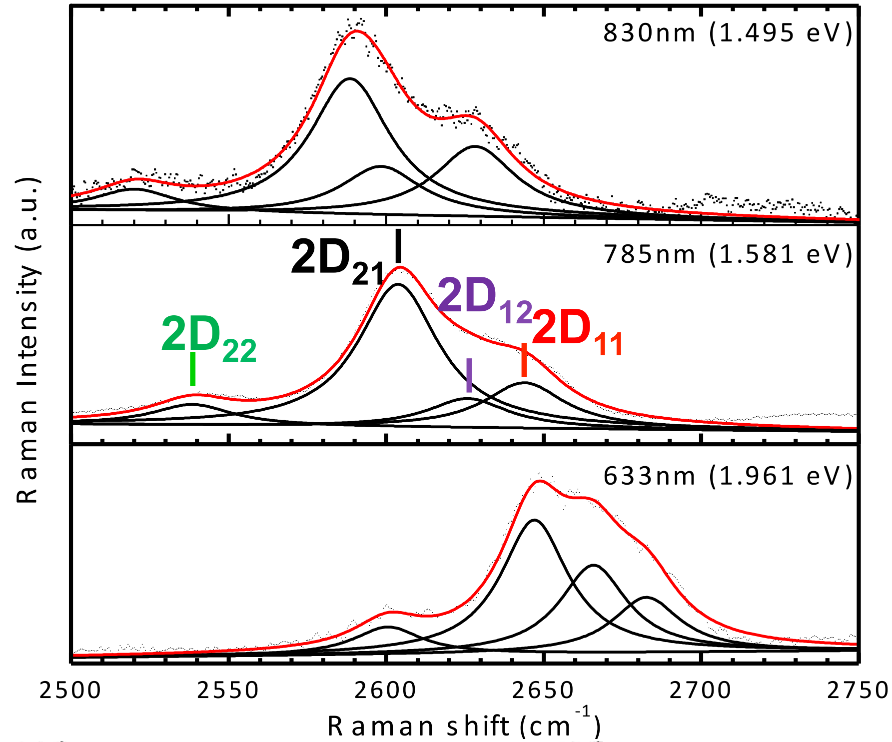


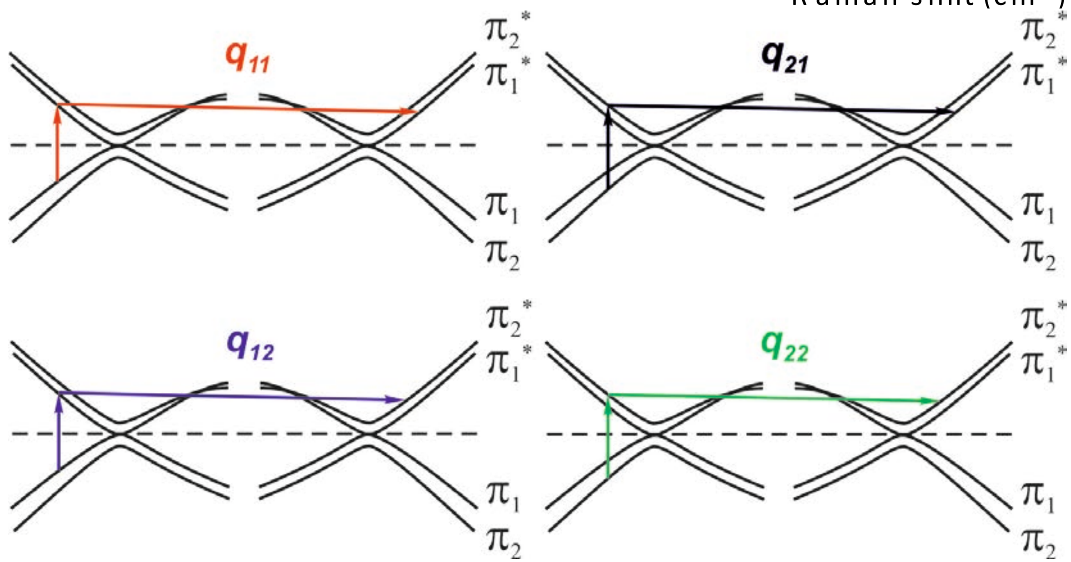
$$\partial \omega_{G^-} / \partial \varepsilon = -36.0\,\mathrm{cm}^{-1}/\%$$

$$\partial \omega_{G+} / \partial \varepsilon = -17.5\,\mathrm{cm}^{-1}/\%$$

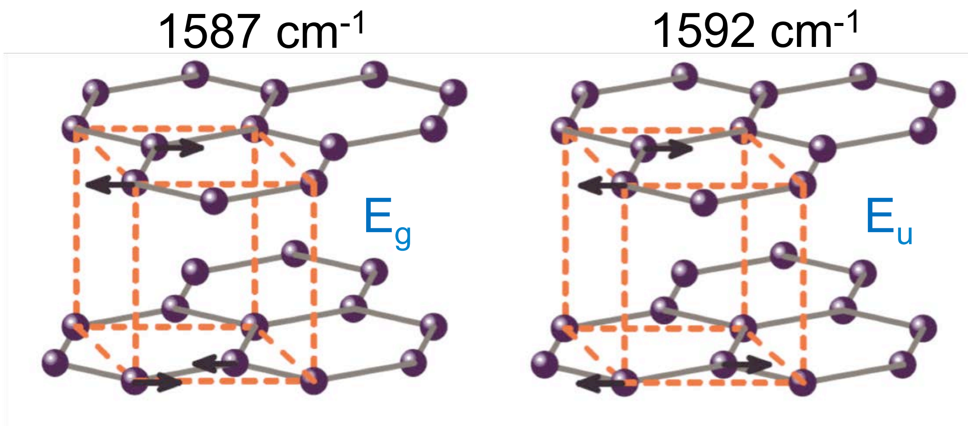
Loading a graphene bilayer



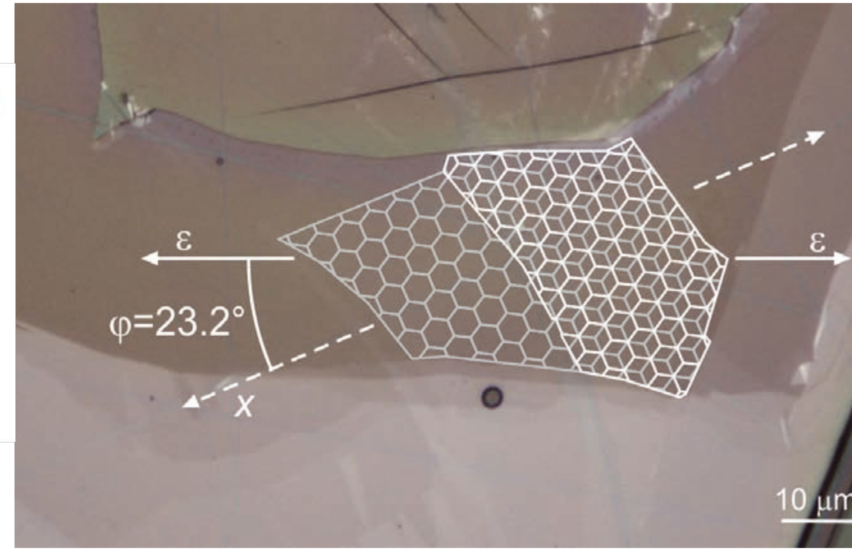


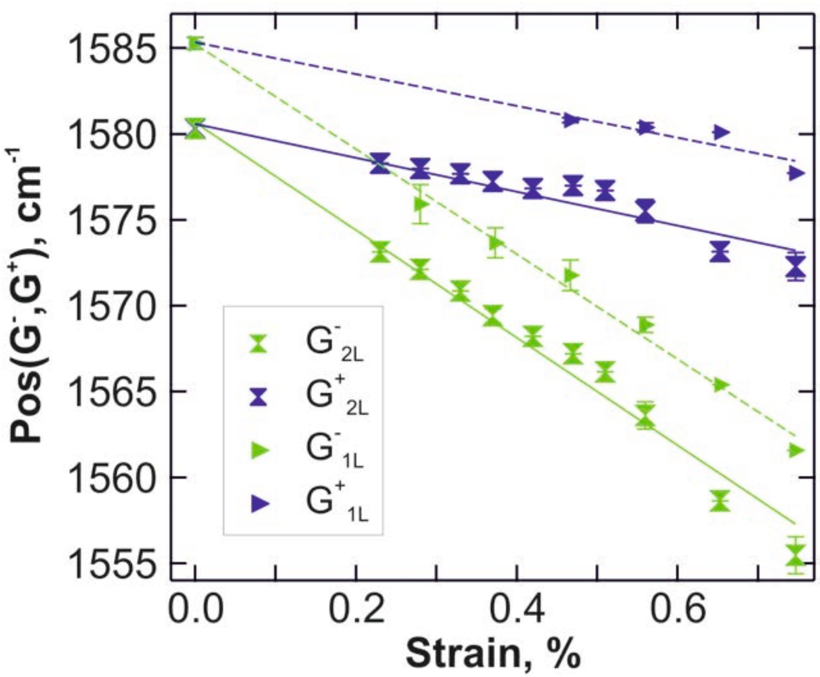


Graphene bilayer under uniaxial tension – G peak



[Yan et al. PRB **77**, 125401 (2009)]



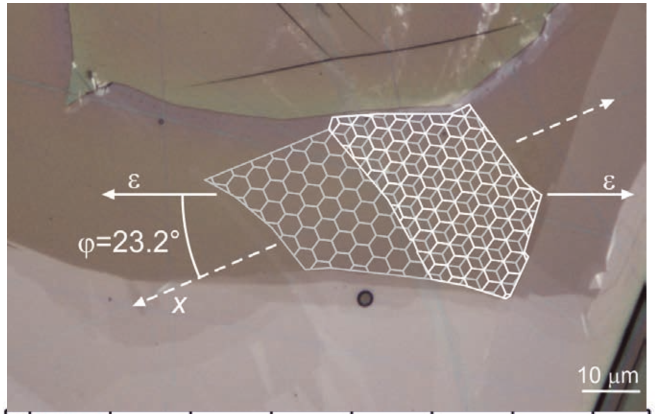


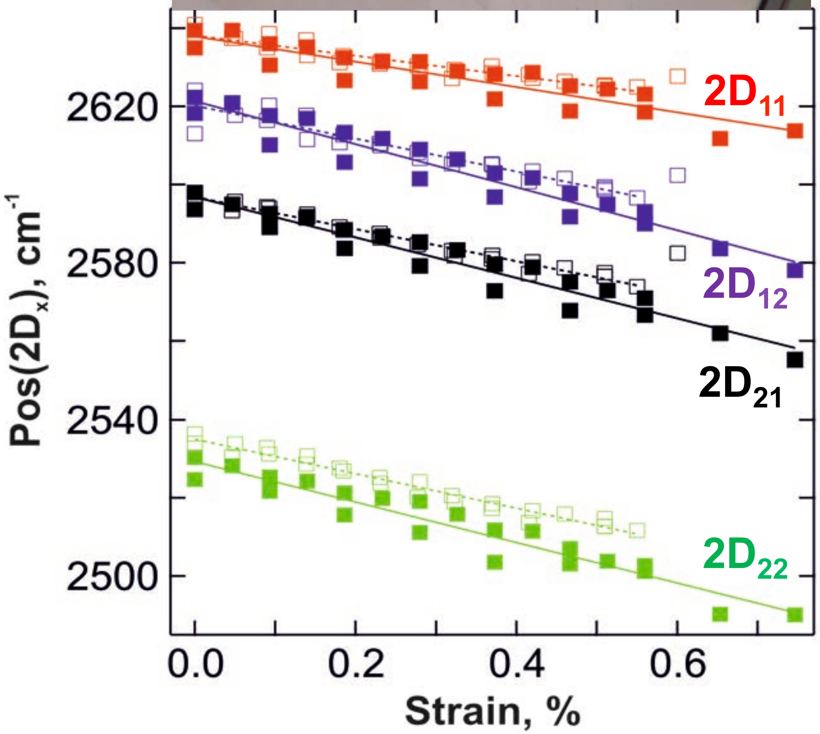
$$\partial\omega_G^+(2L) / \partial\varepsilon = -9.9 \pm 4.9\,\mathrm{cm}^{-1} / \%$$

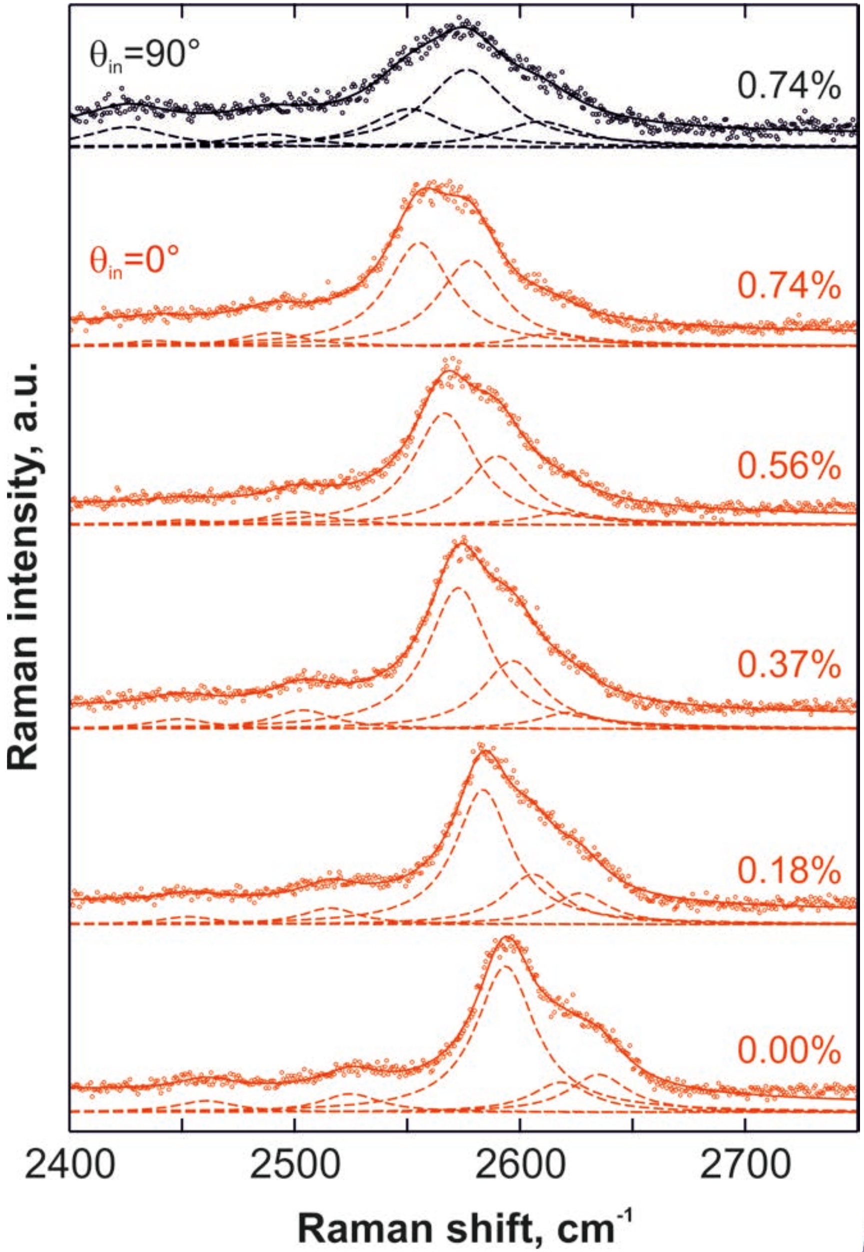
$$\partial\omega_G^-(2L) / \partial\varepsilon = -31.3 \pm 5.4\,\mathrm{cm}^{-1} / \%$$

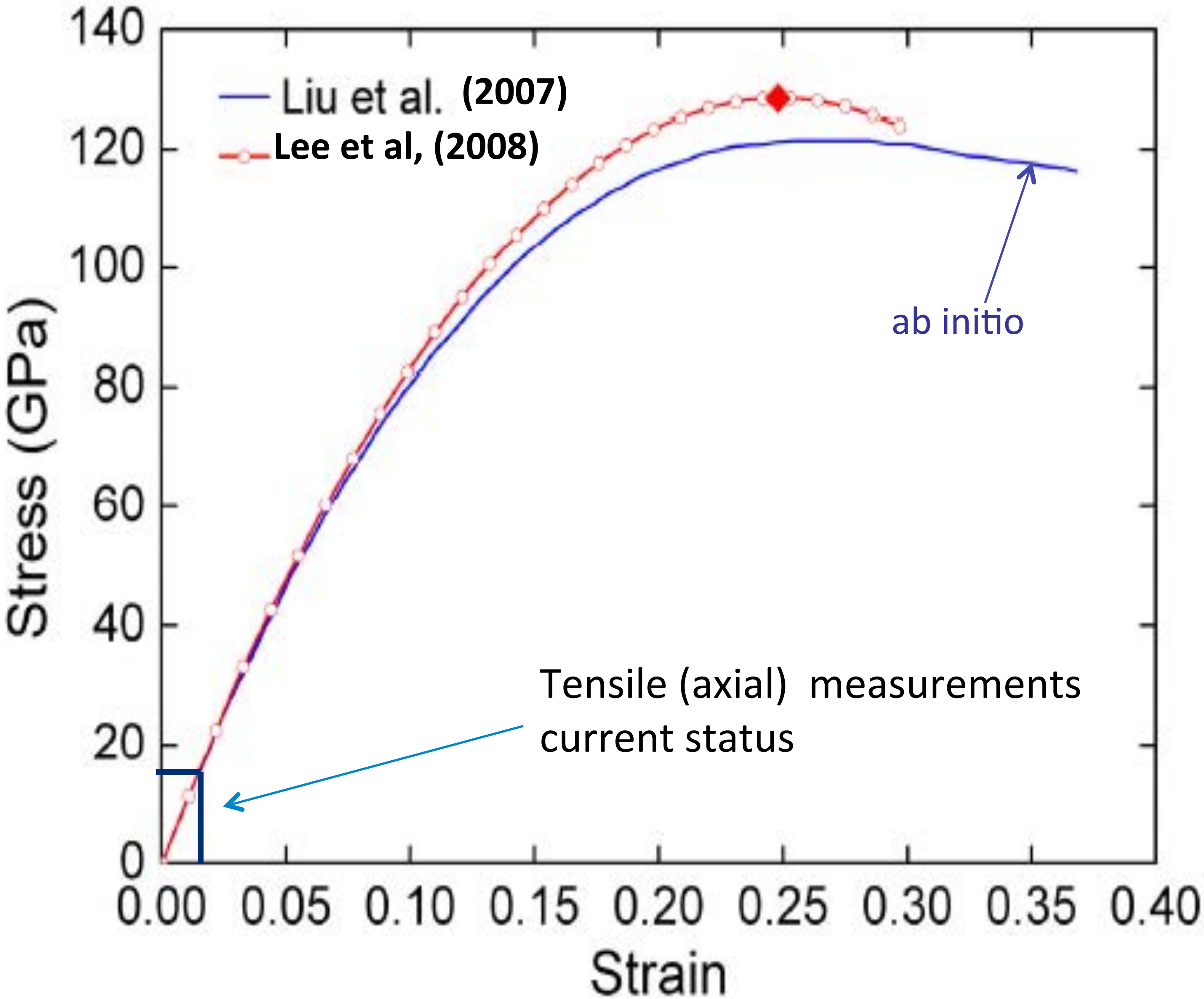
Frank *et al*, to be *submitted*, **2011**

Graphene bilayer under uniaxial tension – 2D peak





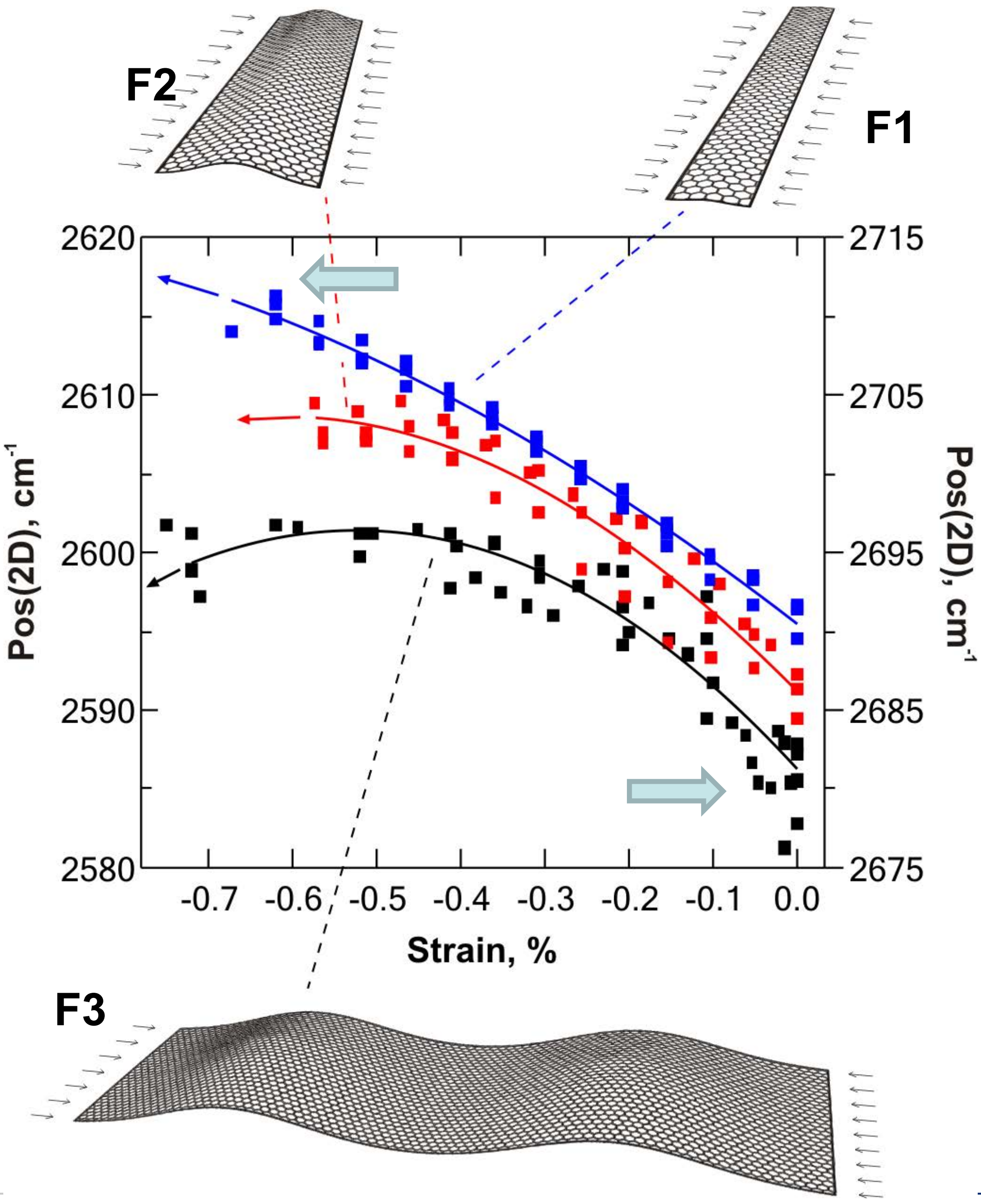



Liu et al. (2007)
Lee et al, (2008)
ab initio
Tensile (axial) measurements
current status
Stress (GPa)
Strain
0
20
40
60
80
100
120
140
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40

Compression

(Measurements & Analysis)

Compression of embedded graphene flakes - 2D band



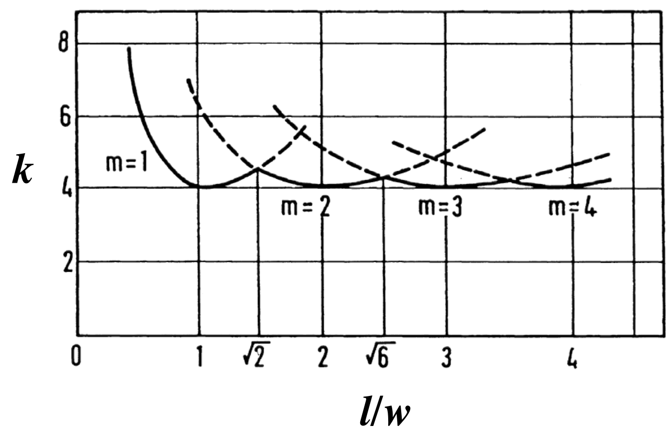
Graphene as a thin plate: critical buckling strain (1/2)

The **critical strain**, ε_c, for the buckling of a rectangular thin plate under uniaxial compression is given by the classical Euler formula:

$$\varepsilon_c = \frac{\pi^2 k}{w^2}\left(\frac{\kappa}{C}\right)$$

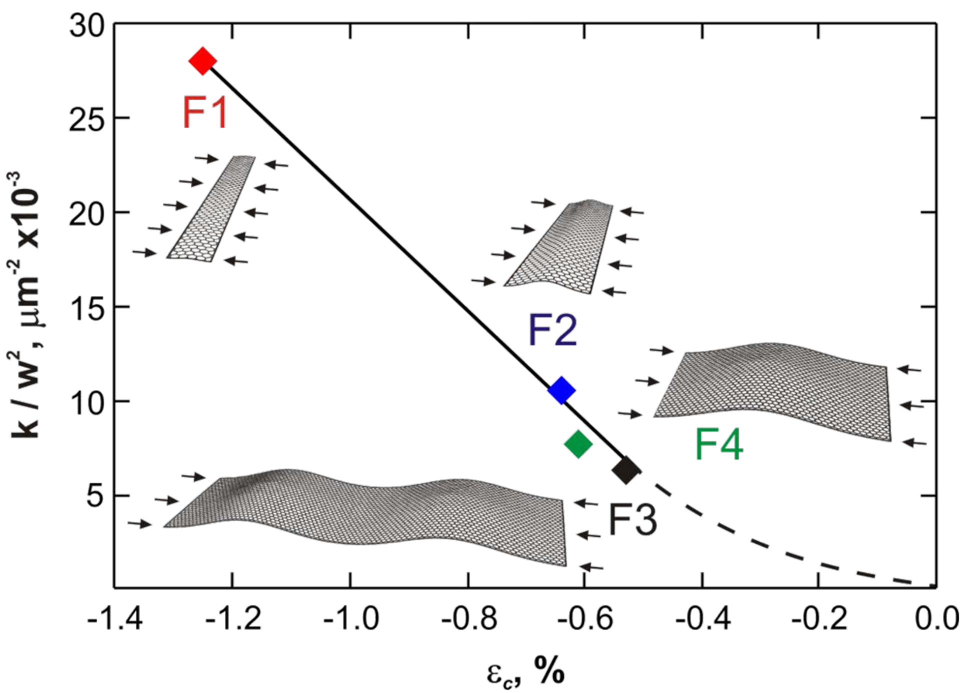
- *l*: length (dimension parallel to strain)
- *w*: width
- *m*: number of half-waves to appear at the critical load
- κ: flexural rigidity, 3.18 GPa nm^3=20 eV[1]
- *C*: tension rigidity, 340 GPa nm[1]

$$k = \left(\frac{mw}{l} + \frac{l}{mw}\right)^2$$



For a layer of atomic thickness in air, $\varepsilon_c \approx 10^{-9}$ (1 nanostrain)

Graphene as a thin plate: critical buckling strain (2/2)



$$\frac{k}{w^2} = a\varepsilon_c + b$$

slope

$$a = -0.03\ \mu\text{m}^{-2}$$

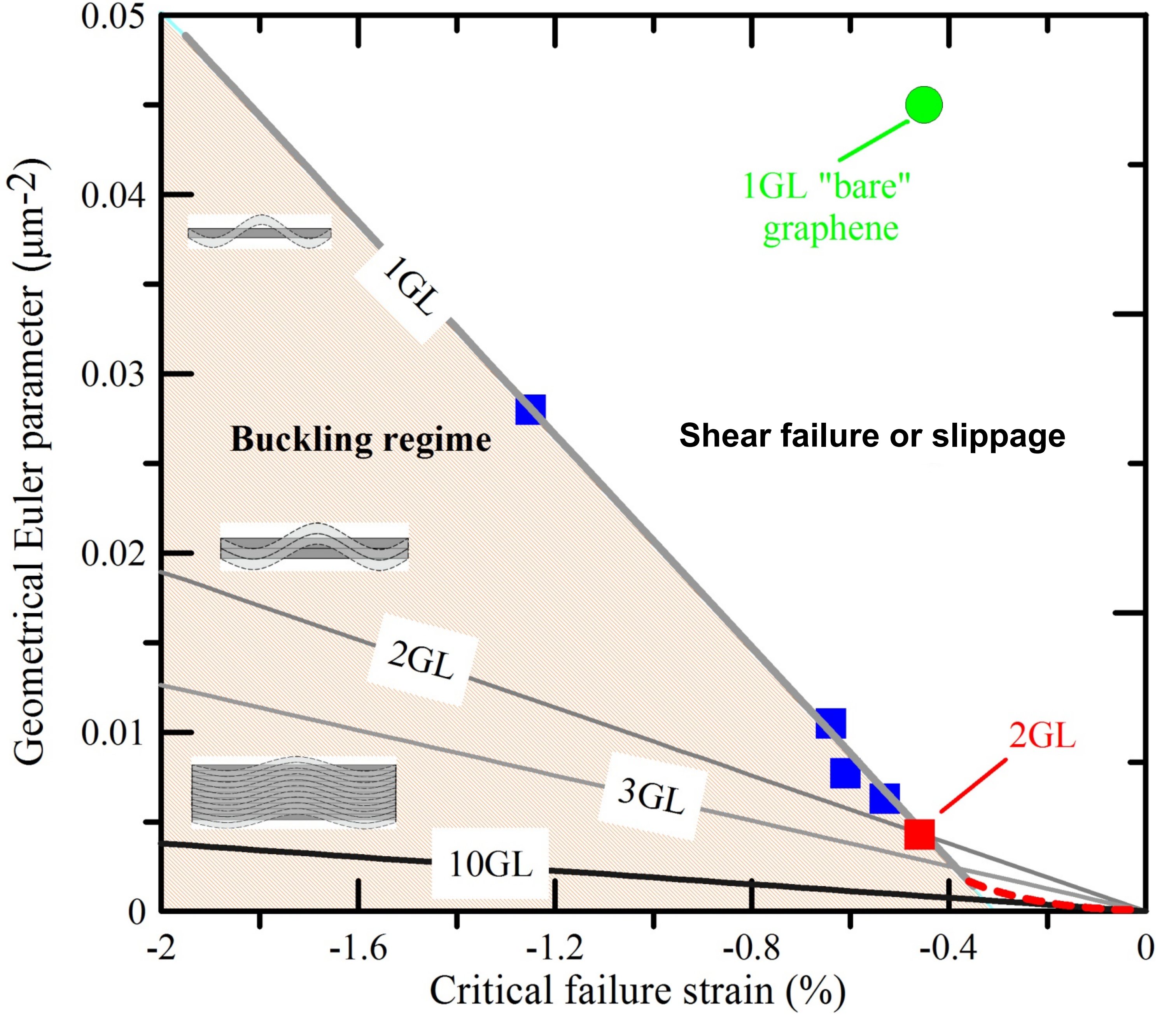
Euler regime applies for k> 0.05 μm^{-2}

– For freely suspended flake in air: $\kappa = 3.18\ \text{GPa}\ nm^3 \sim 20\ \text{eV}$

– For embedded flake:

$$\varepsilon_c^{\ embedded} = \frac{k}{w^2}\frac{\kappa_{embedded}\pi^2}{C},$$

$$\kappa_{embedded} = 1.2\times10^7\ \text{GPa nm}^3 \sim 70\ \text{MeV}$$



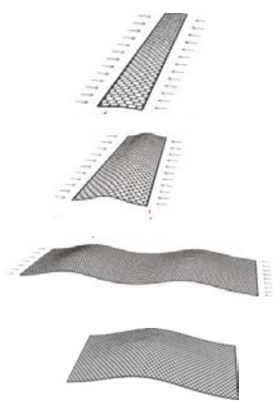
Geometrical Euler parameter (μm-2)
Critical failure strain (%)
0.05
0.04
0.03
0.02
0.01
0
-2
-1.6
-1.2
-0.8
-0.4
0
1GL
2GL
3GL
10GL
Buckling regime
Shear failure or slippage
1GL "bare" graphene
2GL

Bending Stiffness, κ, for h=0.335 nm

Specimen	κ (eV)	κ (Joules)
Free-standing	~20[1]	$\sim 3 * 10^{-18}$
Embedded	$\sim 7 * 10^{7}$ (70 MeV)[2]	$\sim 1 * 10^{-11}$ (10 pJ)
Simply-supported	$\sim 2 * 10^{7}$ (20 MeV)[2]	$\sim 3 * 10^{-12}$ (3 pJ)[3]

[1] Lee et al, *Science*, 2008
[2] Frank et al, *ACS Nano*, 2010
[3] Unpublished Data

Estimation of compression strength



SLG Flake	ε_c (%)[1]	σ_c (GPa)[2]	l (μm)	w (μm)	k	k / w^2 (μm^{-2})
F1	-1.25	**12.5**	**6**	**56**	89.12	0.028
F2	-0.64	**6.4**	**11**	**50**	22.71	0.011
F3	-0.53	**5.3**	**56**	**25**	4.02	0.006
F4	-0.61	**6.1**	**28**	**23**	4.14	0.008

[1] ε_c determined from the 2nd order polynomials as maxima

[2] Assuming a modulus of 1 TPa and a linear relationship

Typical compression strength of carbon fibres (microscale): 2-3 GPa

Stress transfer phenomena in polymer/ graphene composites

Graphene: A powerful stress/ strain sensor

Phonon stress or strain sensitivities:

G peak

$$\left(\frac{\partial \overline{G}}{\partial \sigma}\right)_T \sim -2.7\ (\mathrm{cm}^{-1}\mathrm{GPa}^{-1})$$

$$\left(\frac{\partial \overline{G}}{\partial \varepsilon}\right)_T \sim -2700\ \mathrm{cm}^{-1}$$

2D peak

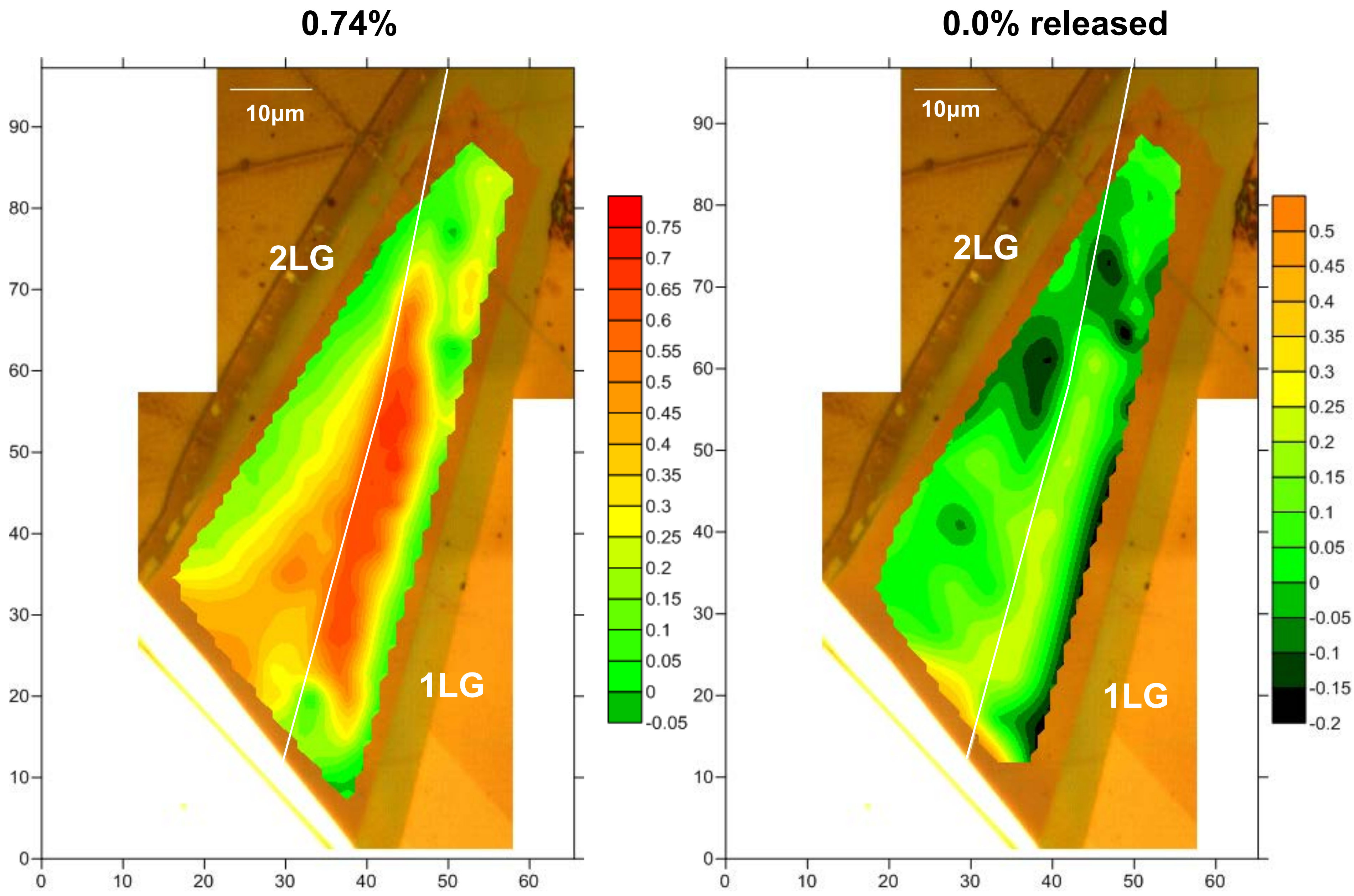
$$\left(\frac{\partial (2D)}{\partial \sigma}\right)_T \sim -6.0\ (\mathrm{cm}^{-1}\mathrm{GPa}^{-1})$$

$$\left(\frac{\partial (2D)}{\partial \varepsilon}\right)_T \sim -6000\ \mathrm{cm}^{-1}$$

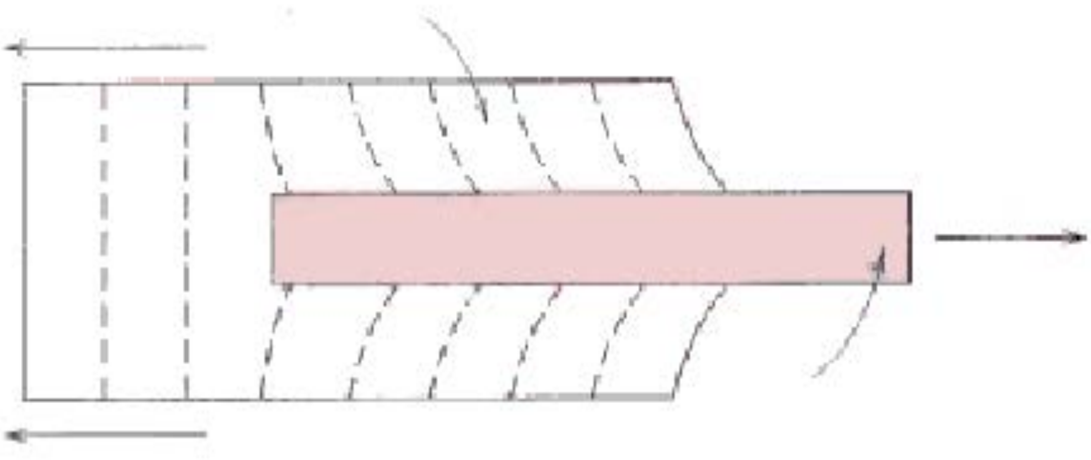
Knowing the wavenumber shift we can resolve the inverse problem i.e. to obtain the values of axial σ and/or ε in graphene composites through the above relations.

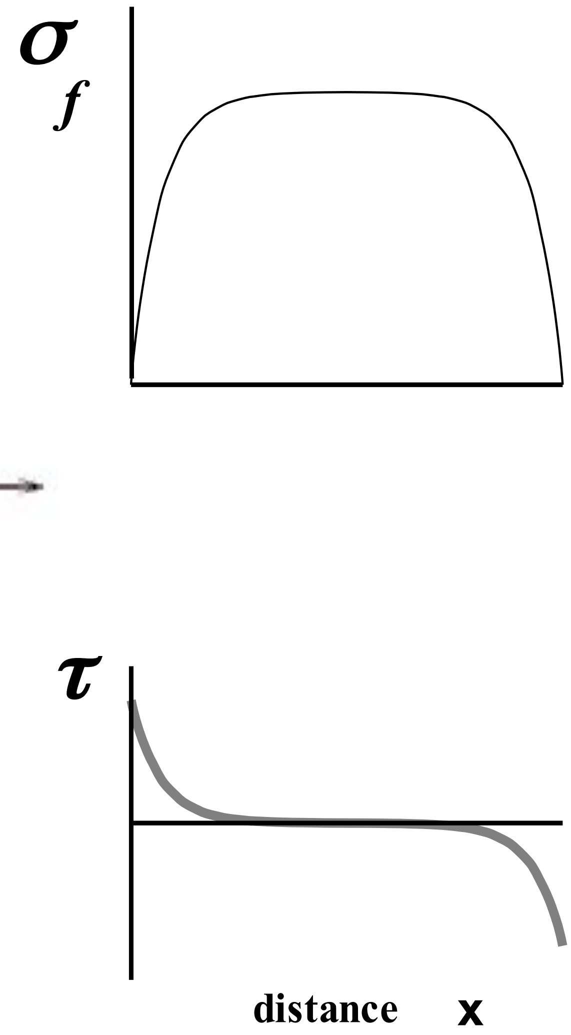
Frank et al, *Nature Comms*,2:255, DOI 10.1038, 2011

Strain maps of graphene flakes embedded into polymers



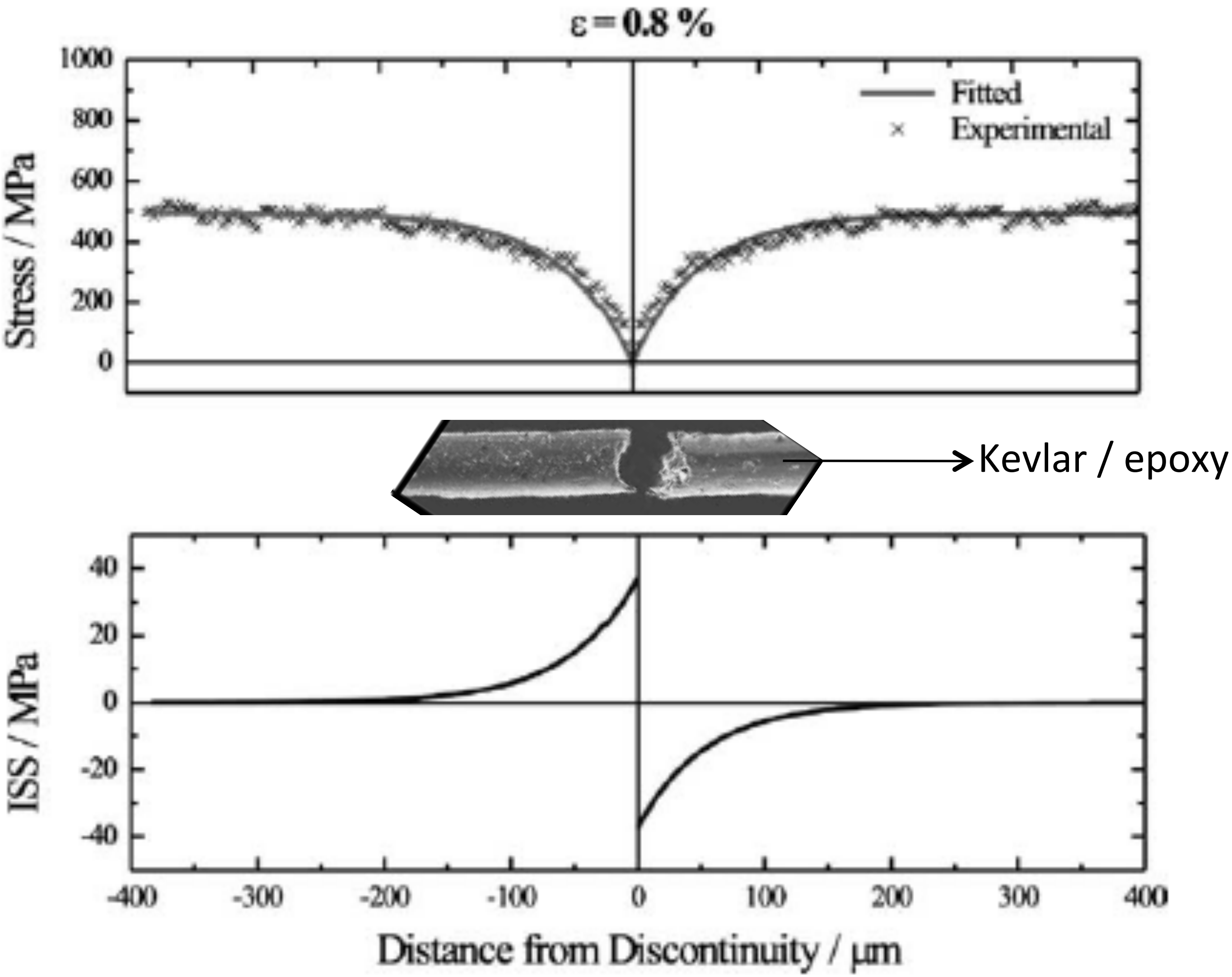
Textbook stuff: Mechanisms of Stress Transfer in Composites





Elastic transfer in polymer composites (1/2)

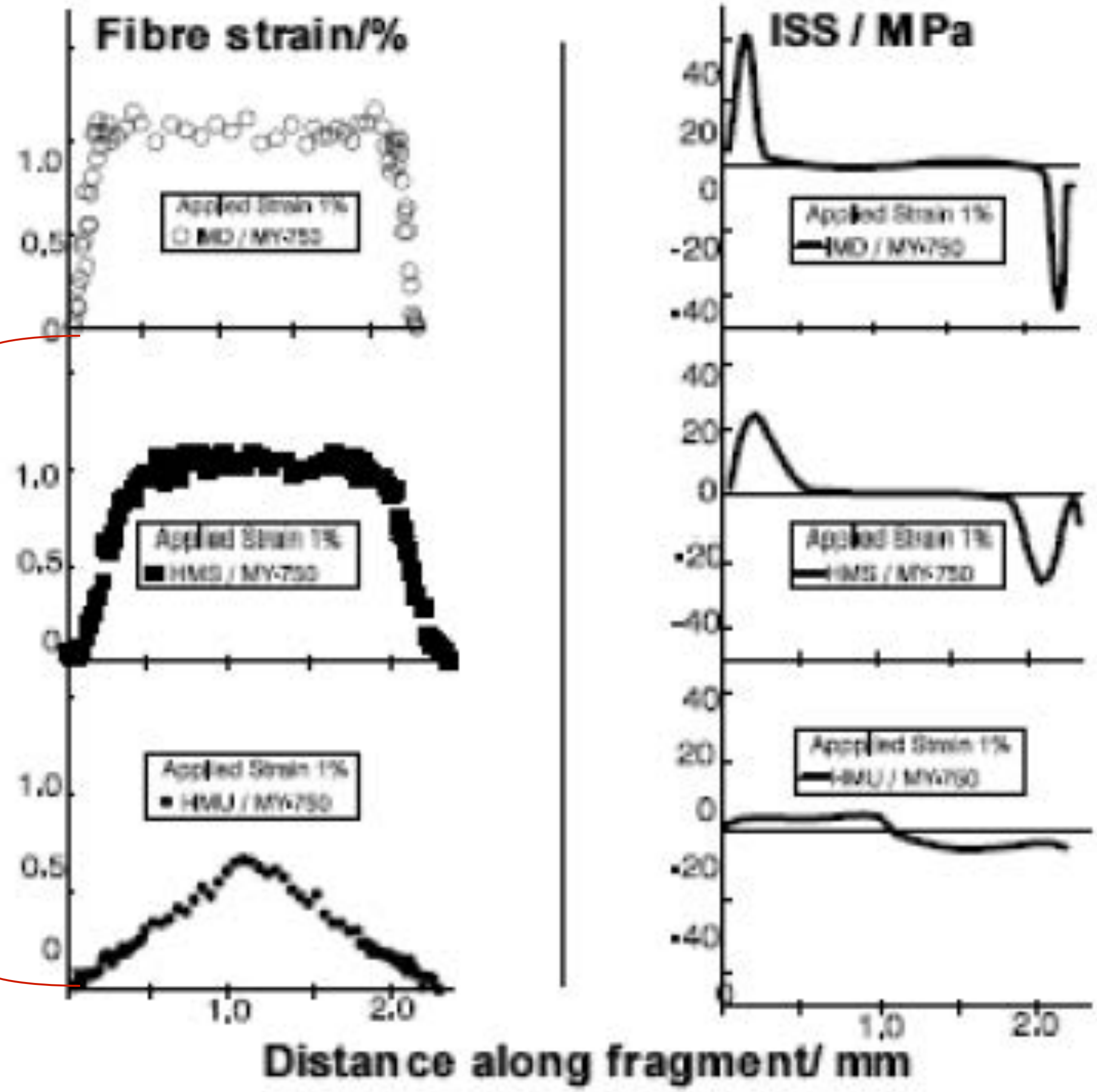
(shear-lag analysis)



Anagnostopoulos et al, Acta Materialia, 53, 2005

Elastic transfer in polymer composites (2/2)

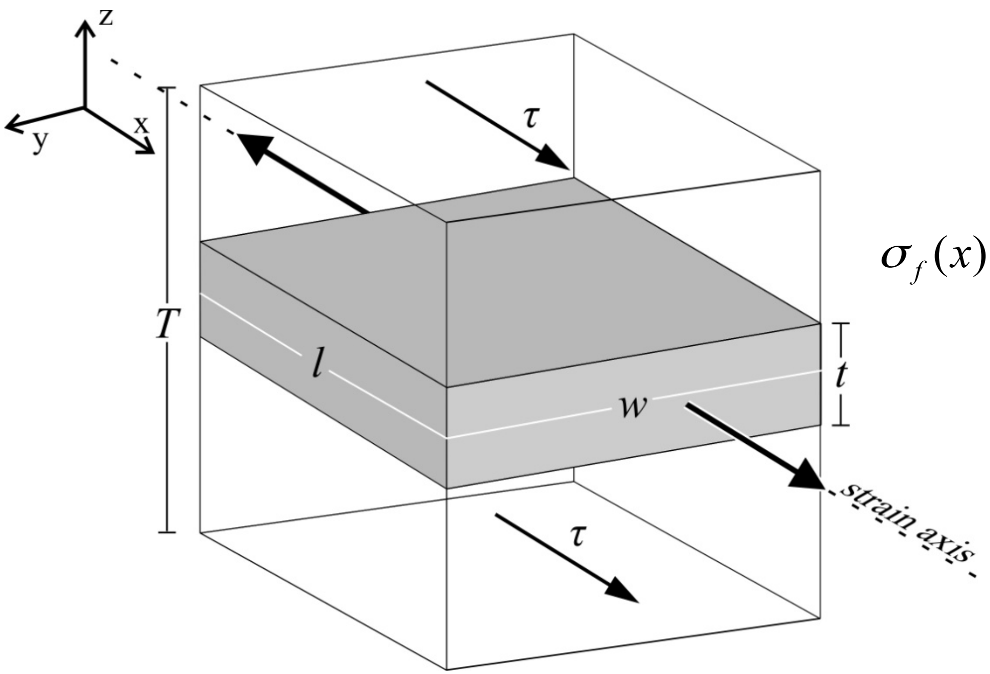
(shear-lag analysis)



Same high-modulus carbon fibre but different oxidative treatment

Melanitis & Galiotis, Proc. of Royal Soc.-A, **440** 379-398, (1993)

Shear lag analysis of graphene flakes embedded into polymers

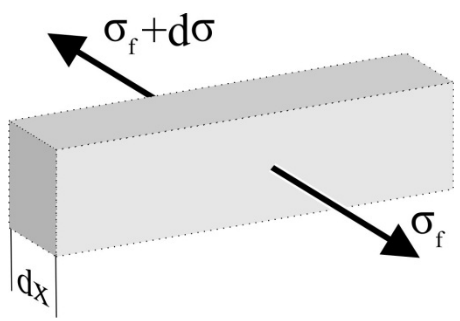


$$\frac{d^2\sigma_f}{dx^2} = \frac{H}{wt}\left(\frac{\sigma_f}{E_f} - \varepsilon\right)$$

$$\sigma_f(x) = E_f \cdot \varepsilon_\infty \cdot \left[1 - \cosh(\beta x) + \tanh\left(\frac{\beta l}{2}\right) \cdot \sinh(\beta x)\right]$$

where

$$H = \frac{wG_{m,T}}{t \ln \frac{T}{t}} \text{ and } \beta = \frac{1}{t}\sqrt{\left(\frac{G_{m,T}}{E_f \ln \frac{T}{t}}\right)}$$



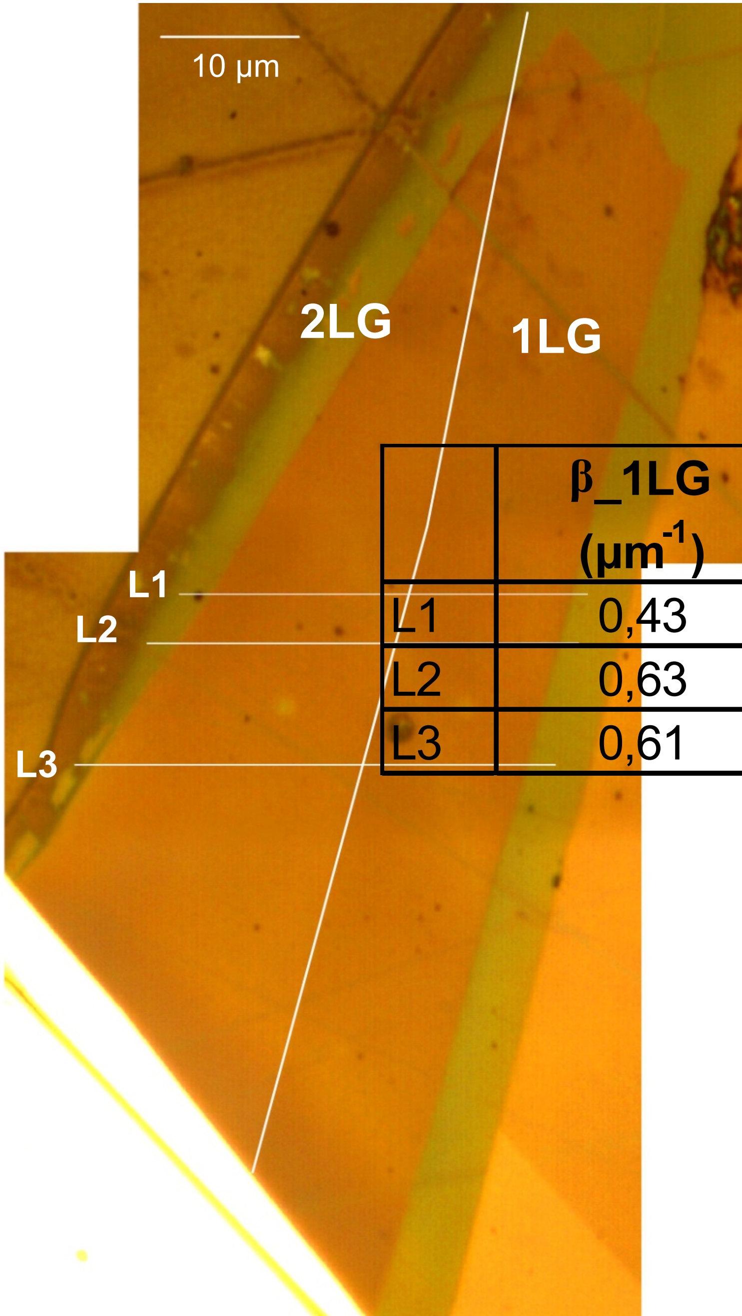
$$\frac{d\sigma_f}{dx} = -\frac{\tau}{t}$$

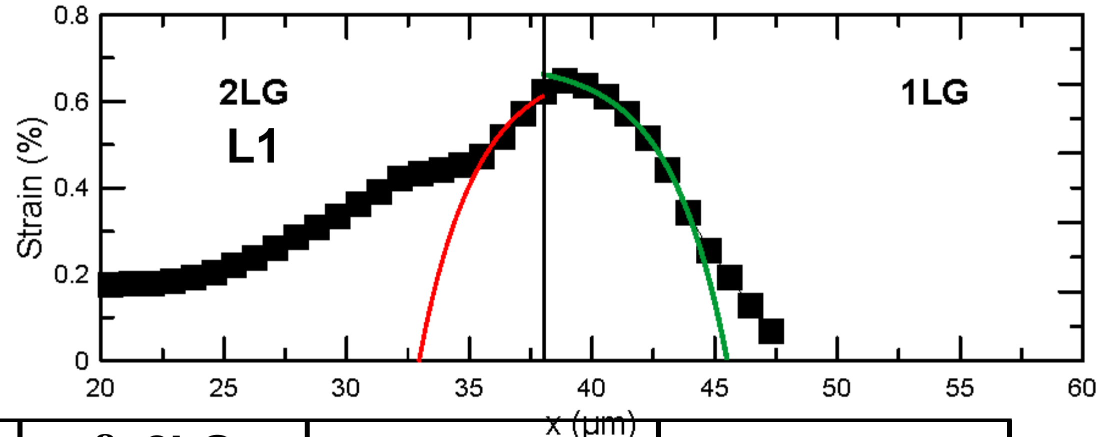
$$\sigma_f(x) \sim \sigma_{f,\infty} \cdot \left[1 - \exp(-\beta x)\right]$$

and

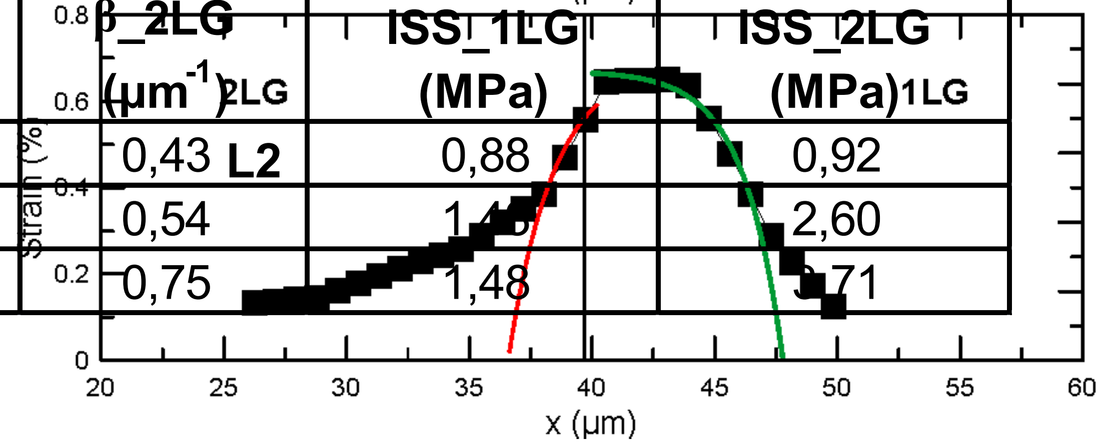
$$\tau \sim -te_{f,\infty} E_f \beta e^{-\beta x}$$

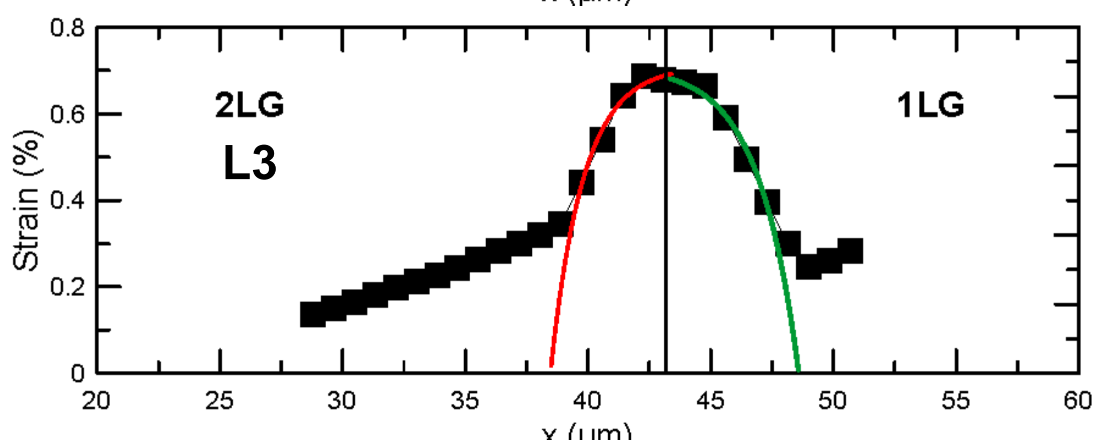
Shear lag analysis of a 1LG/ 2LG graphene flake in PMMA



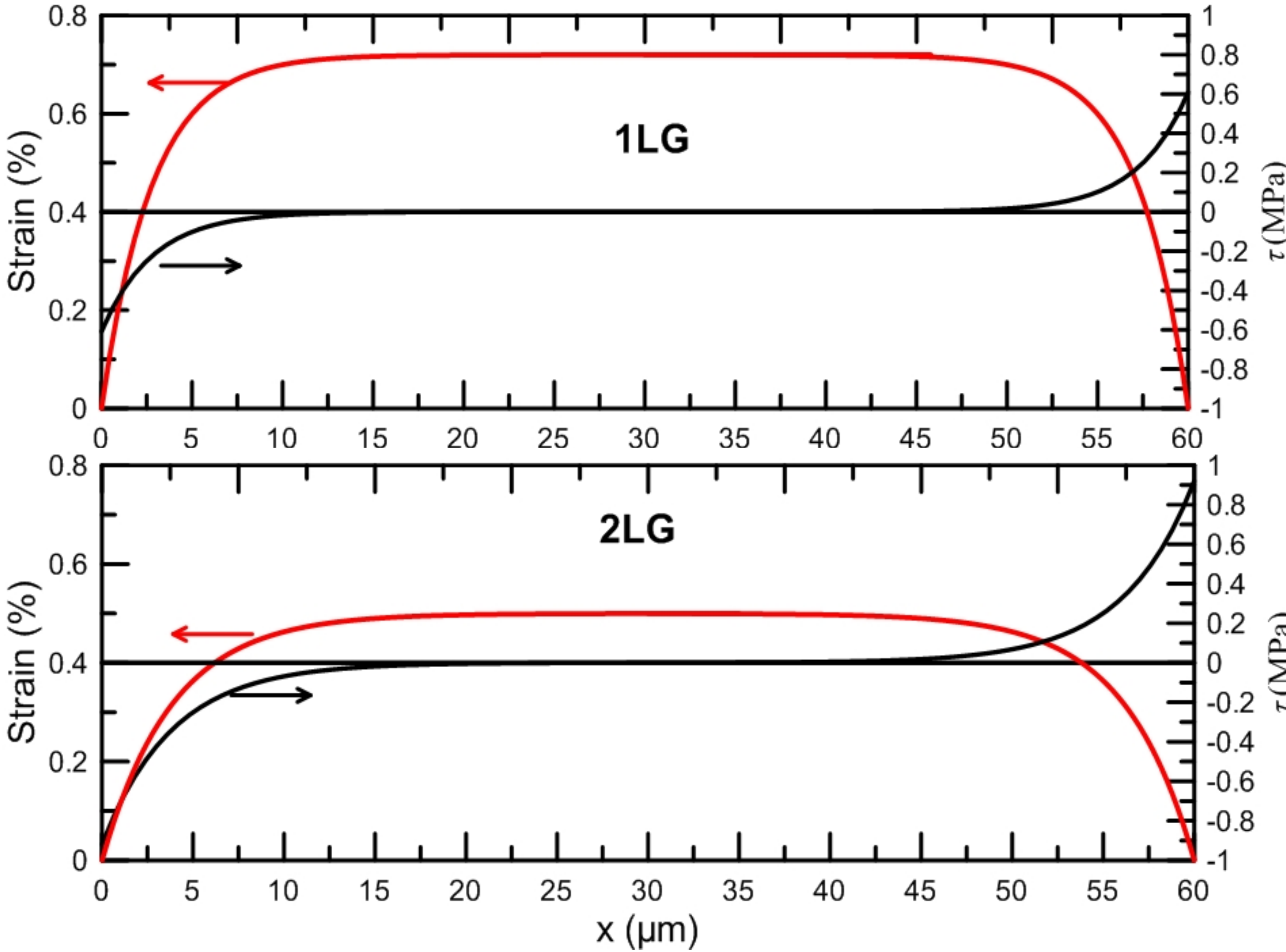


	β_1LG (μm^{-1})	β_2LG (μm^{-1})	ISS_1LG (MPa)	ISS_2LG (MPa)
L1	0,43	0,43	0,88	0,92
L2	0,63	0,54	1,4[illegible]	2,60
L3	0,61	0,75	1,48	3,71





Axial & Interfacial shear stress distributions



Conclusions

- Experiments on purely axial loading of graphene in tension have not been performed as yet.
- If no residual strain is present the phonon vs. strain relatinonship in tension is linear at least up to ~1.5%.
- In compression, the observed phonon relaxation is indicative of failure initiation. The obtained values of critical strain to failure for monolayer graphene agree well with Euler buckling analysis.
- The stress transfer from a polymer matrix to graphenes (1LG &2LG) seems to proceed along macroscopic principles (shear-lag).
- Pristine graphenes exhibit poor interfacial strength in PMMA matrices. Attention should be exercised when measurements are made near the flake edges.

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- Prof. A. Geim (Univ. Manchester, UK)

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- GRAPHENE CENTRE (FORTH)

Graphene bilayer under uniaxial tension – 2D band

	λ= 785 nm		λ= 633 nm	
	ω_{2D} [cm^{-1}]	$\partial\omega_{2D}/\partial\varepsilon$ [cm^{-1}/%]	ω_{2D} [cm^{-1}]	$\partial\omega_{2D}/\partial\varepsilon$ [cm^{-1}/%]
$2D_{11}$	2637.9±2.5	-32.3±6.7	2688.0±2.2	-57.5±7.3
$2D_{12}$	2621.3±2.7	-55.0±7.0	2671.0±2.5	-57.6±8.4
$2D_{21}$	2596.8±2.8	-51.7±6.2	2651.0±1.3	-54.8±4.4
$2D_{22}$	2529.3±2.6	-51.8±6.9	2603.1±1.6	-45.6±5.4