Biomedical and Biotechnological Applications Research Network

Mechanical Deformation of Graphene

(also a new perspective for the development of stress-sensors)

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Collaborations/ **Acknowledgements**

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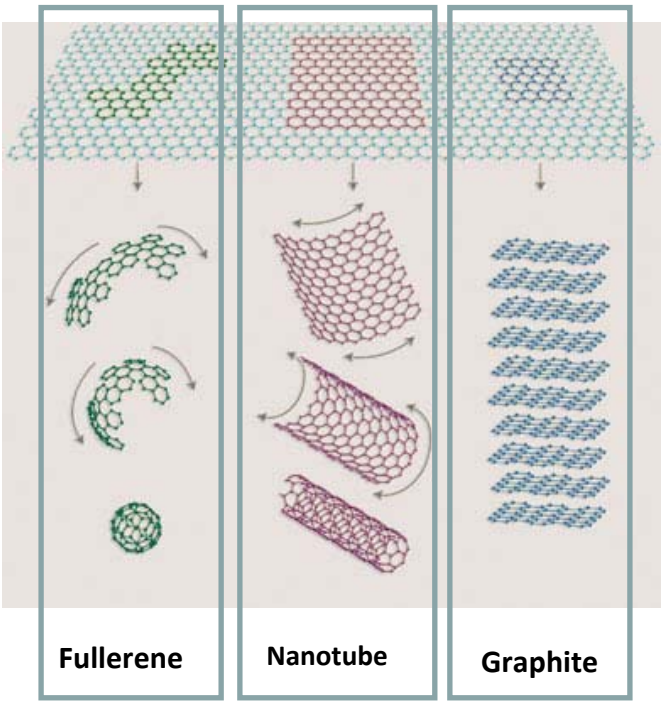
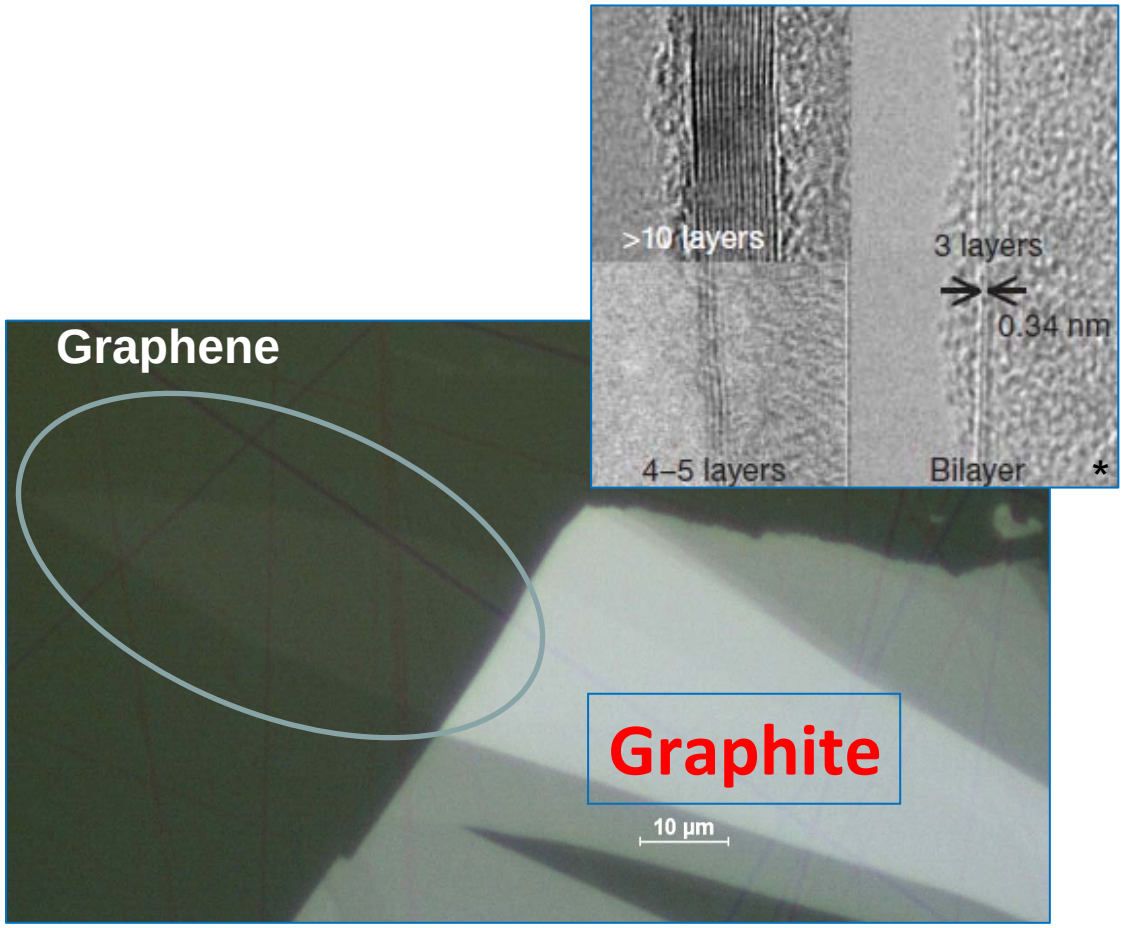
Dr. Otakar Frank (Czech Academy of Sciences)
Prof. Christian Thomsen (TU Berlin)

Graphene: the 2D building block of carbon allotropes





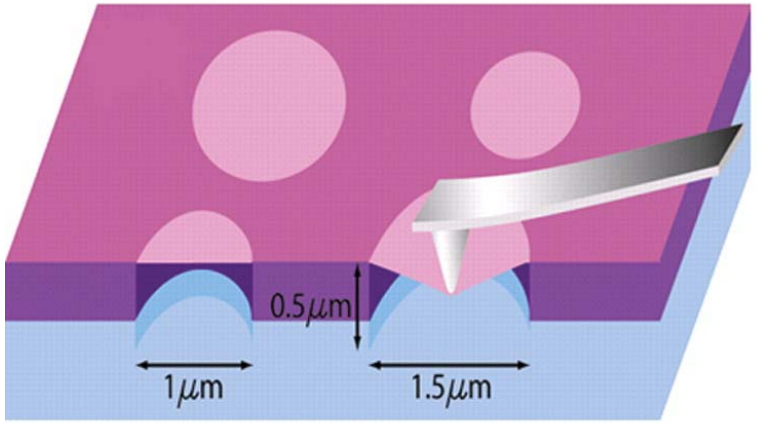
*Tsoukleri et al, Small 2009

*Keun Soo Kim *et al*. Nature, 2009

The rise of Graphene

- High e mobility (~10^5 $cm^2V^{-1}s^{-1}$ at T=300K) and resilience to high current densities (~10^8 A/cm^2) *[Nat. Nanotechnol. 3, 491 (2008)]*
- Ballistic transport even at room temperature *[Nat. Mater. 6, 183 (2007)]*
- Superior thermal conductivity (~$5x10^3$ $Wm^{-1}K^{-1}$ at T=300K) *[Nano Lett. 8, 902 (2008)]*
- Each graphene layer absorbs πα (≈2.3%) of the incident light *[Science 320, 1308 (2008)]*
- Novel quantum Hall physics *[Nature 438, 197 (2005)]*
- Extreme strength (~130 GPa) and modulus (~1TPa) *[Science 321, 385 (2008)]*

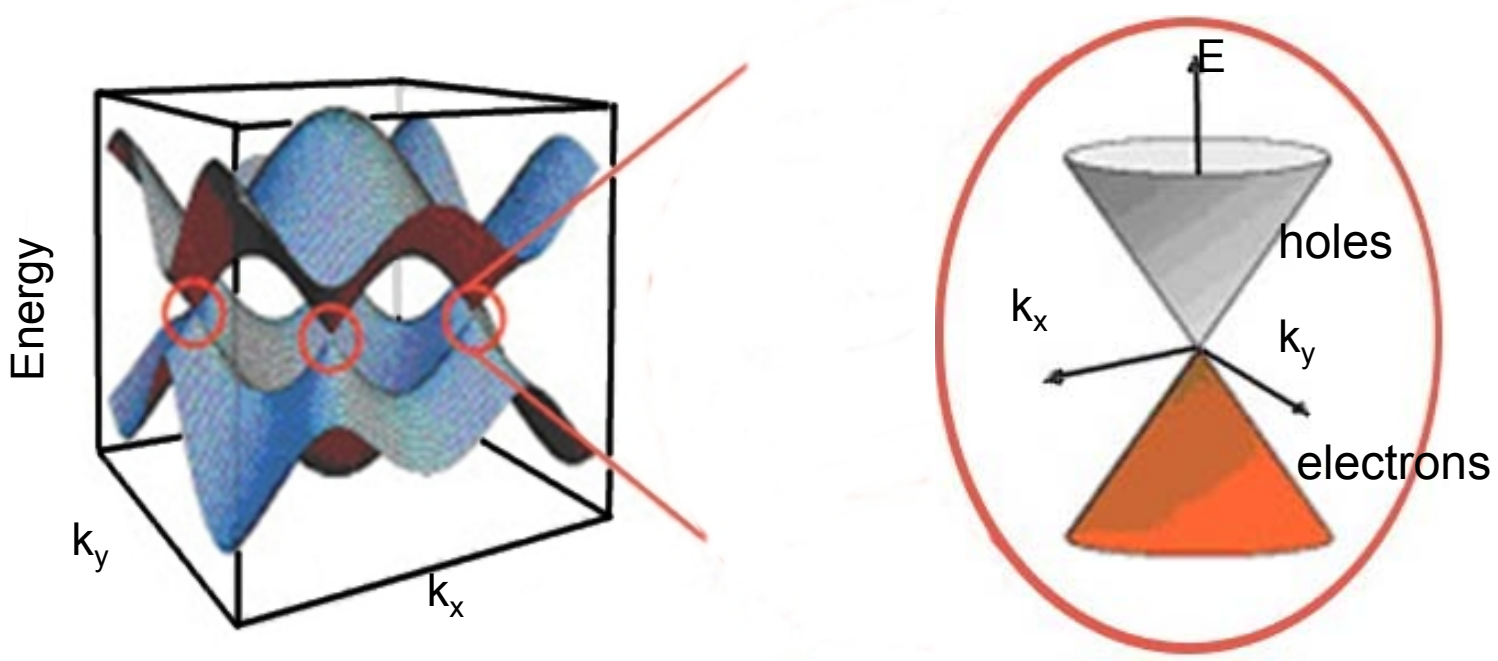
and many others …



Measurement of the mechanical properties of monolayer graphene suspended over open holes onto SiO_2 substrate using AFM nanoidentation [Science (2008)]

Physics of Monolayer Graphene

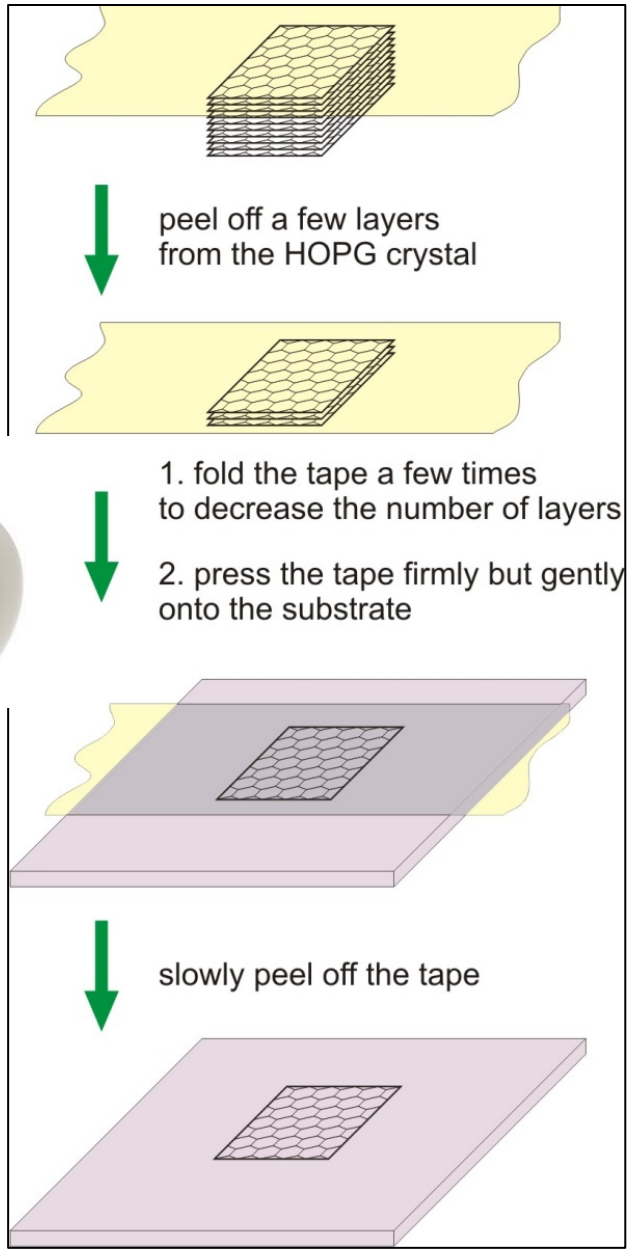
- Perfect crystal quality
- Gapless semiconductor (“semi-metal” ?)



Graphene production (1/2)

I. Mechanical cleavage

- Interlayer van der Waals interaction 2 eV/nm^2
- The force needed to exfoliate graphene ~ 300 nN/mm^2
- Common adhesive tape is sufficient
- Substrate which provides contrast for graphene monolayer is necessary (e.g. SiO_2(300nm)/Si or SU8/PMMA)



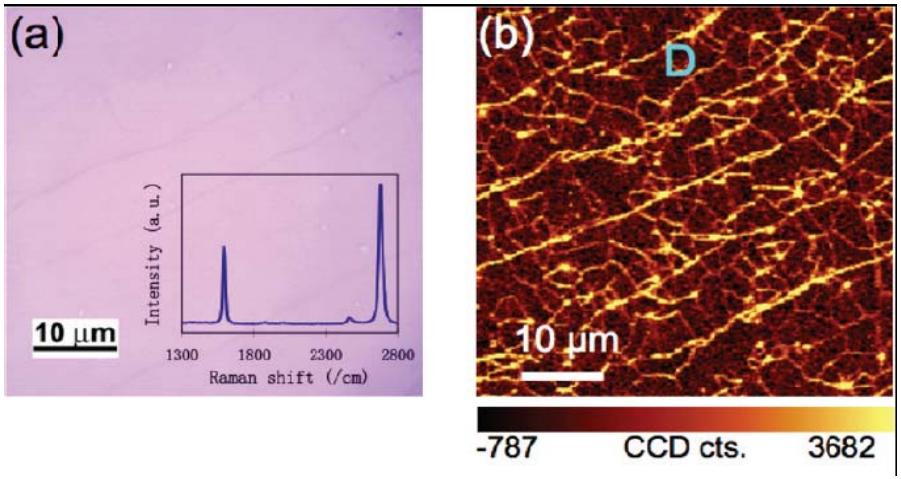
Graphene production (2/2)

II. CVD growth

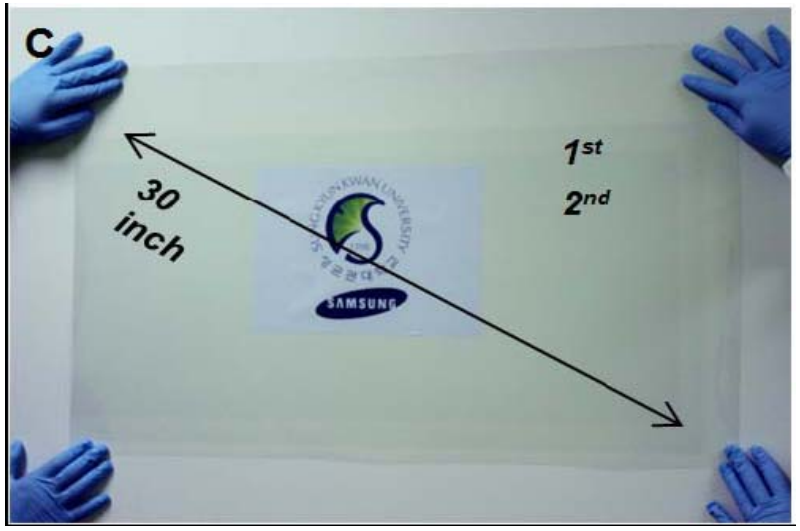
❖Different substrates – Cu, Ni, Pt, Ru, Ir, TiC, TaC

❖ Formation of graphene either by catalytic decomposition of the hydrocarbon gas at the substrate (e.g. Cu), or by dissolution of carbon in the substrate and precipitation of graphene layers upon cooling (e.g. Ni)

❖ CVD on Cu substrate seems to be the most promising at the moment, allowing mass production in the near future



Li *et al.*, Science (2009), Nano Lett. (2009)



Bae *et al.*, *Nature Nanotechnology, DOI: 10.1038*

Rapid Sequencing of Individual DNA Molecules in Graphene Nanogaps

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18111 Nordho Street, Northridge, CA 91330-8268
(Dated: October 20, 2008)

I propose a technique for reading the base sequence of a single DNA molecule using a graphene nanogap.

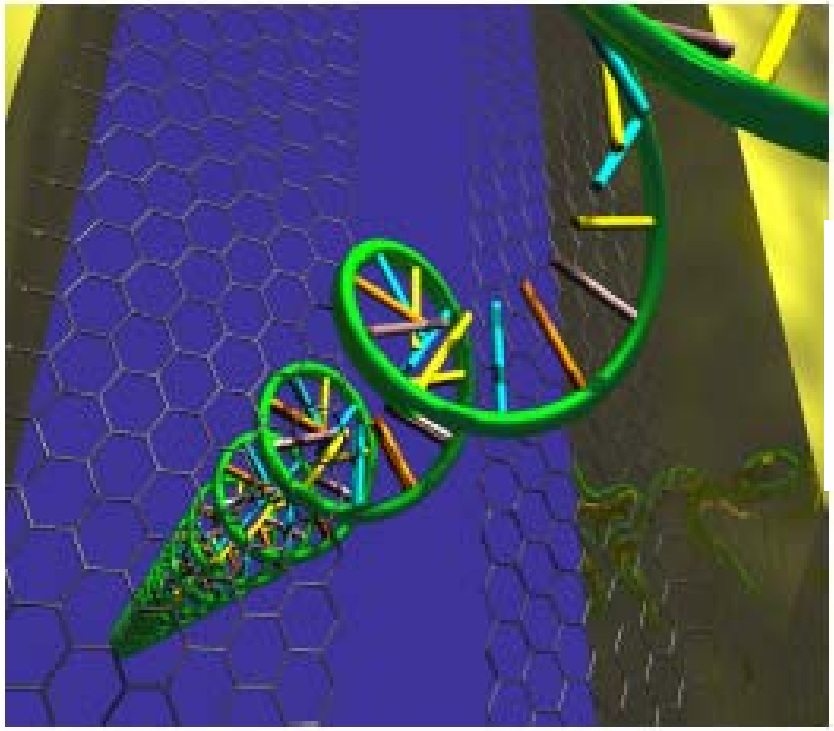

FIG. 1: *The individual bases of a ssDNA molecule (backbone in green, bases in alternating colors) sequentially occupy a gap in graphene (hexagonal lattice) while translocating through it. Their conductance is read, revealing the sequence of the molecule. The contacting electrodes to the graphene nanogap (Au, yellow) are on the far left and right side of this image.*

NANO LETTERS

pubs.acs.org/NanoLett

DNA Translocation through Graphene Nanopores

Grégory F. Schneider, Stefan W. Kowalczyk, Victor E. Calado, Grégory Pandraud, Henny W. Zandbergen, Lieven M. K. Vandersypen, and Cees Dekker*

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ABSTRACT Nanopores—nanosized holes that can transport ions and molecules—are very promising devices for genomic screening, in particular DNA sequencing. Solid-state nanopores currently suffer from the drawback, however, that the channel constituting the pore is long, ~100 times the distance between two bases in a DNA molecule (0.5 nm for single-stranded DNA). This paper provides proof of concept that it is possible to realize and use ultrathin nanopores fabricated in graphene monolayers for single-molecule DNA translocation. The pores are obtained by placing a graphene flake over a microsize hole in a silicon nitride membrane and drilling a nanosize hole in the graphene using an electron beam. As individual DNA molecules translocate through the pore, characteristic temporary conductance changes are observed in the ionic current through the nanopore, setting the stage for future single-molecule genomic screening devices.

KEYWORDS Graphene, nanopore, wedging transfer, translocation, DNA, sequencing

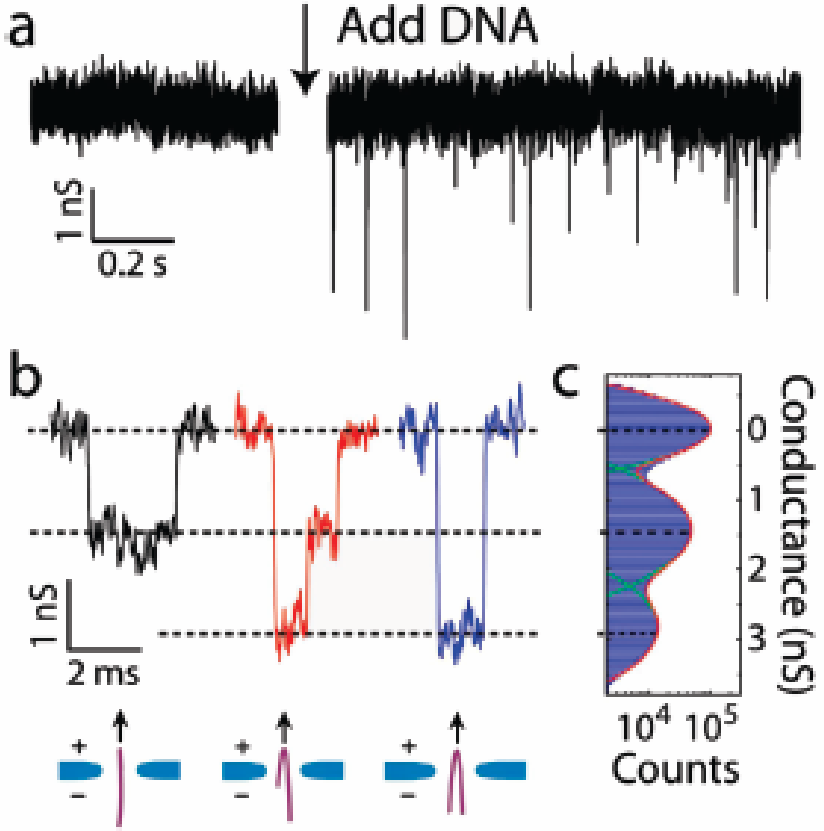


FIGURE 4. DNA translocation through a nanopore in a graphene monolayer. (A) Translocation of 48 kbp double-stranded λ-DNA across a 22 nm nanopore within a graphene monolayer, showing the baseline conductance (left) and blockade events upon addition of DNA (right). (B) Examples of translocation events of nonfolded (black), partially folded (red), and fully folded (blue) DNA molecules recorded at 200 mV in the 22 nm pore represented in Figure 3. (C) Conductance histogram collected from 1222 translocation events, including the open-pore conductance before and after the event.

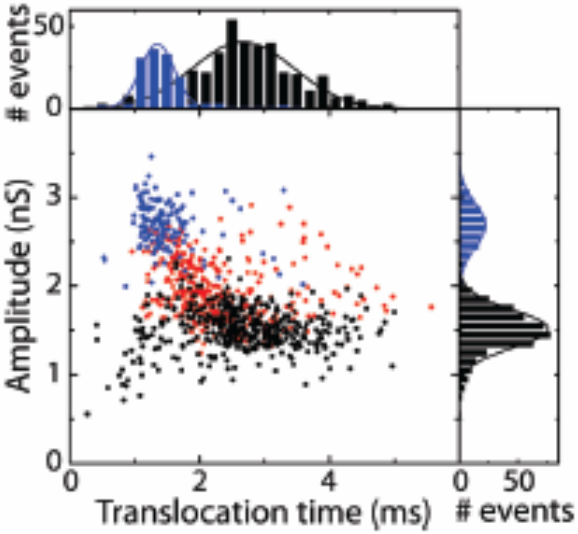
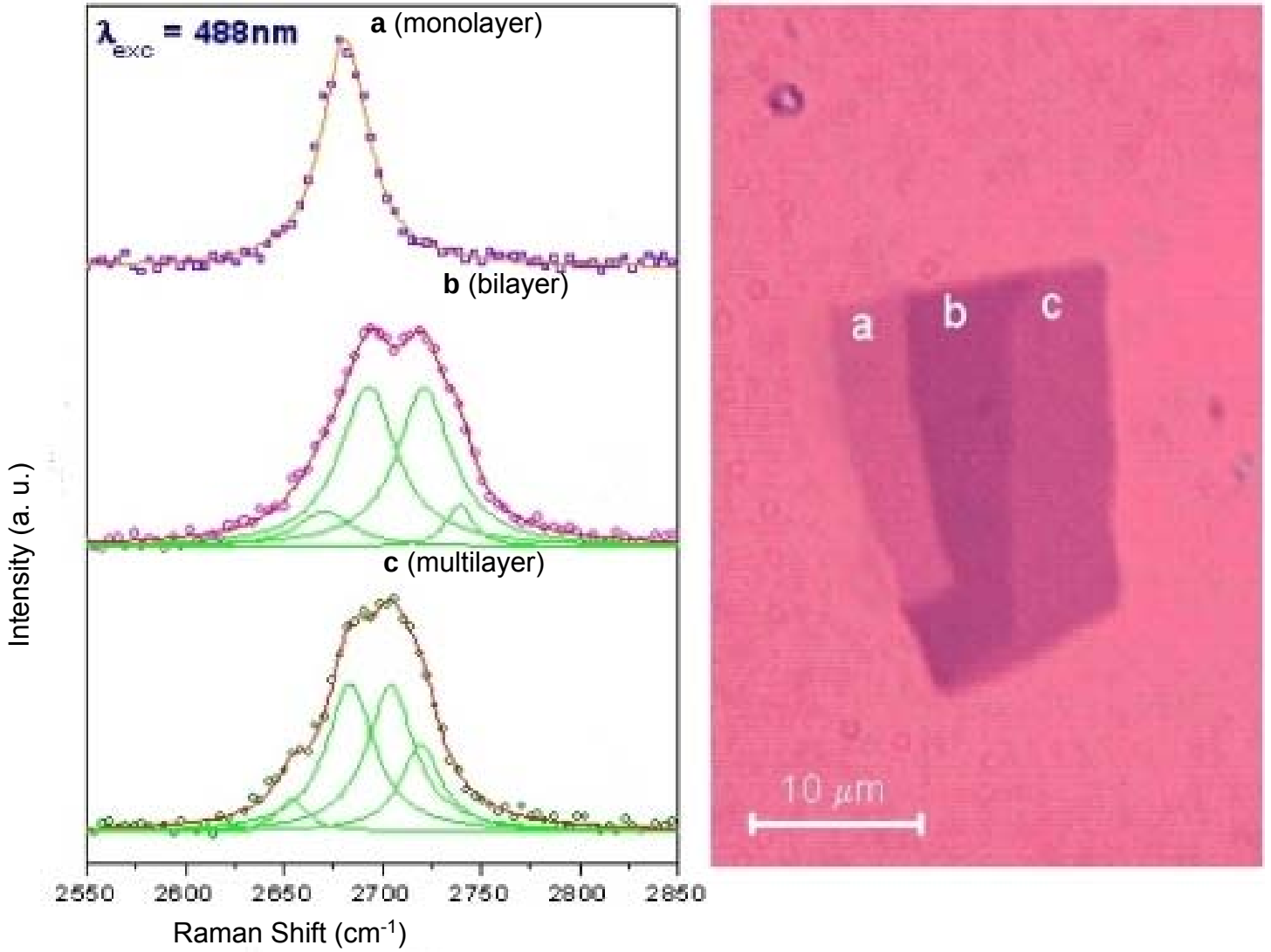
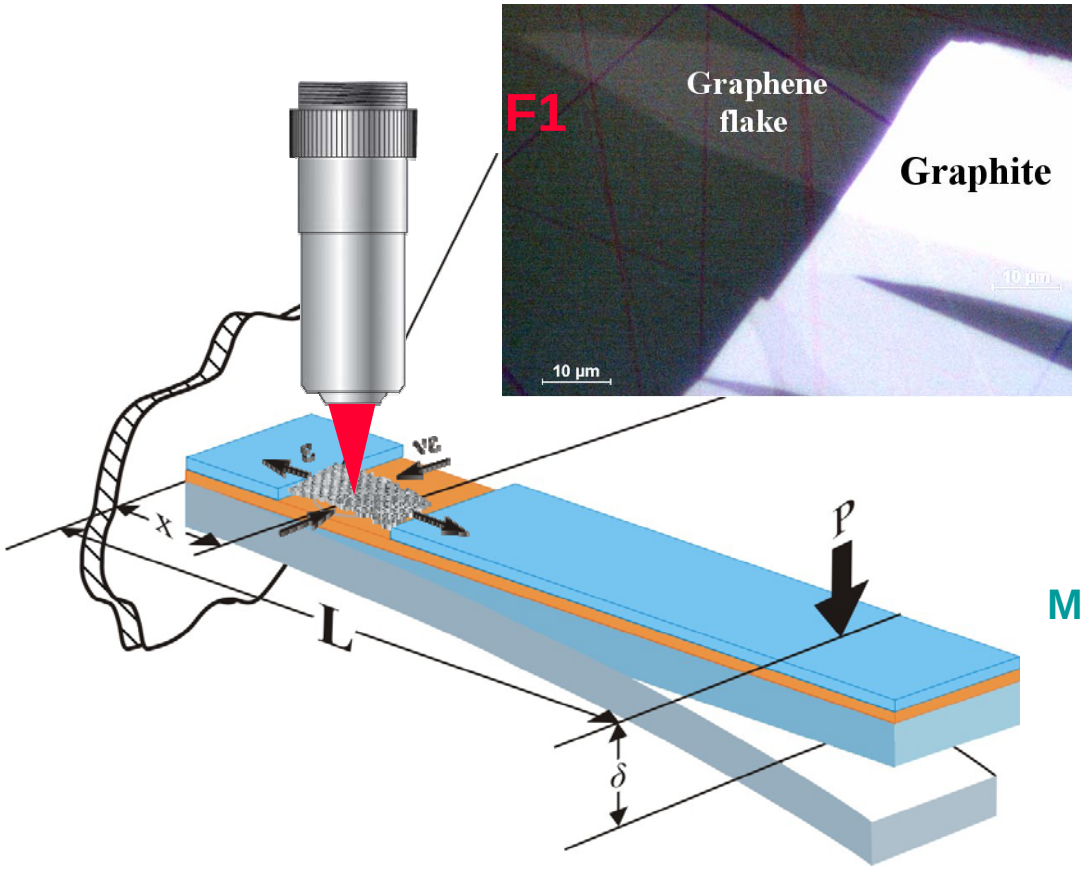


FIGURE 5. Scatter diagram of the amplitude of the conductance blockade versus translocation time for DNA translocation through a 22 nm diameter nanopore in a graphene monolayer. The accompanying histograms for the nonfolded and fully folded data are included at the top and the right. Color coding is as Figure 4. Each point in this scatter diagram corresponds to a single translocation event. Applied voltage is 200 mV.

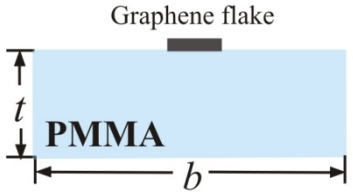
Raman spectroscopy: a unique characterization tool for graphitic materials



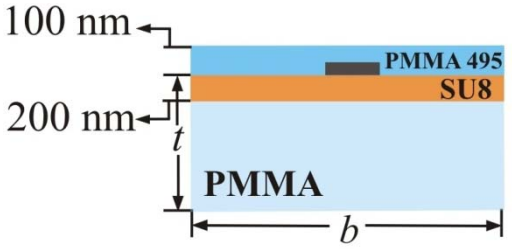
Experimental set-up for application of uniaxial strain



Bare (just attached) flake



Embedded flake



Mechanical strain at the top of the beam

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

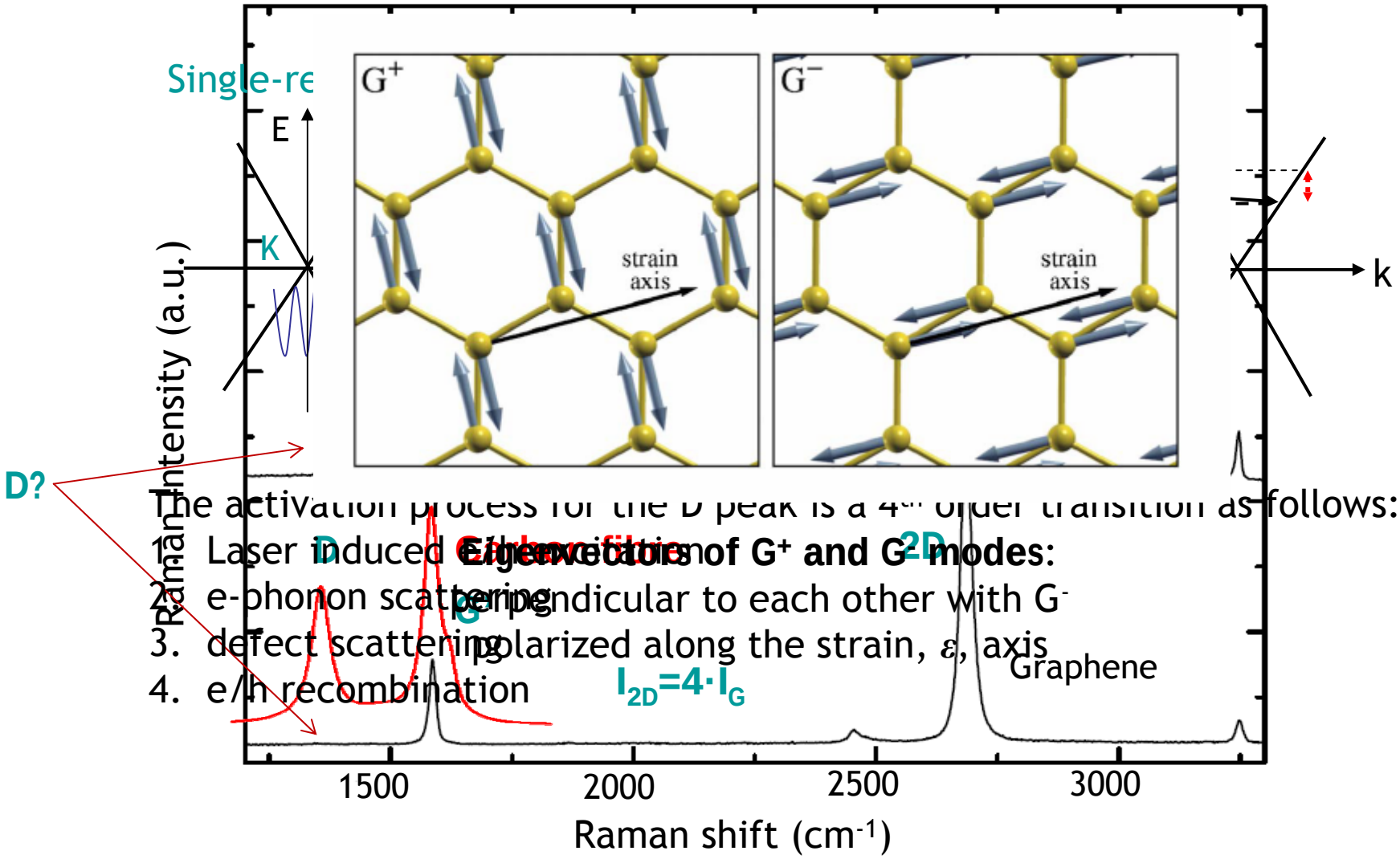
δ: *deflection of the beam neutral axis*
L: *span of the beam*
t : *beam thickness*

Materials & Geometry

- SU8 photo resist epoxy-based polymer
- PMMA beam substrate (*2.9x12.0x70)* mm^3
- *x* = 10.44mm
- *L* = 70 mm

The method is valid for:
$L >> 10\delta_{max}$ and $-1.5\% < \varepsilon < 1.5\%$

Typical Raman spectra



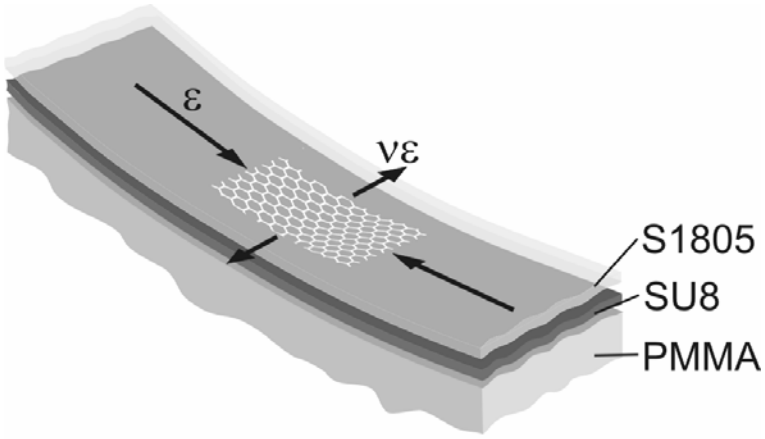
The activation process for the D peak is a 4th order transition as follows:

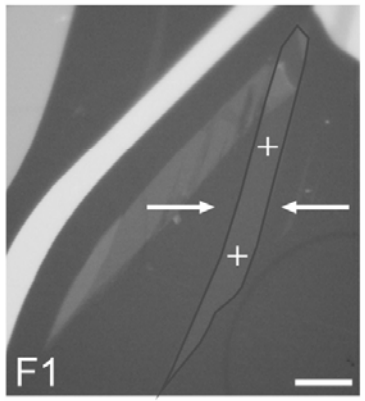
1. Laser induced excitation
2. e-phonon scattering
3. defect scattering
4. e/h recombination

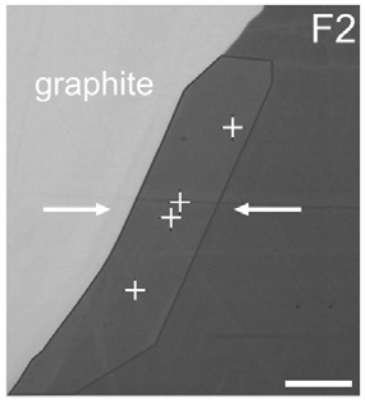
Eigenvectors of G⁺ and G⁻ modes:

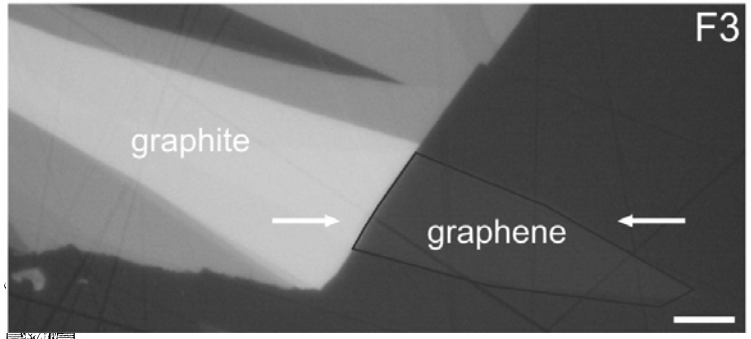
perpendicular to each other with G⁻ polarized along the strain, ε, axis

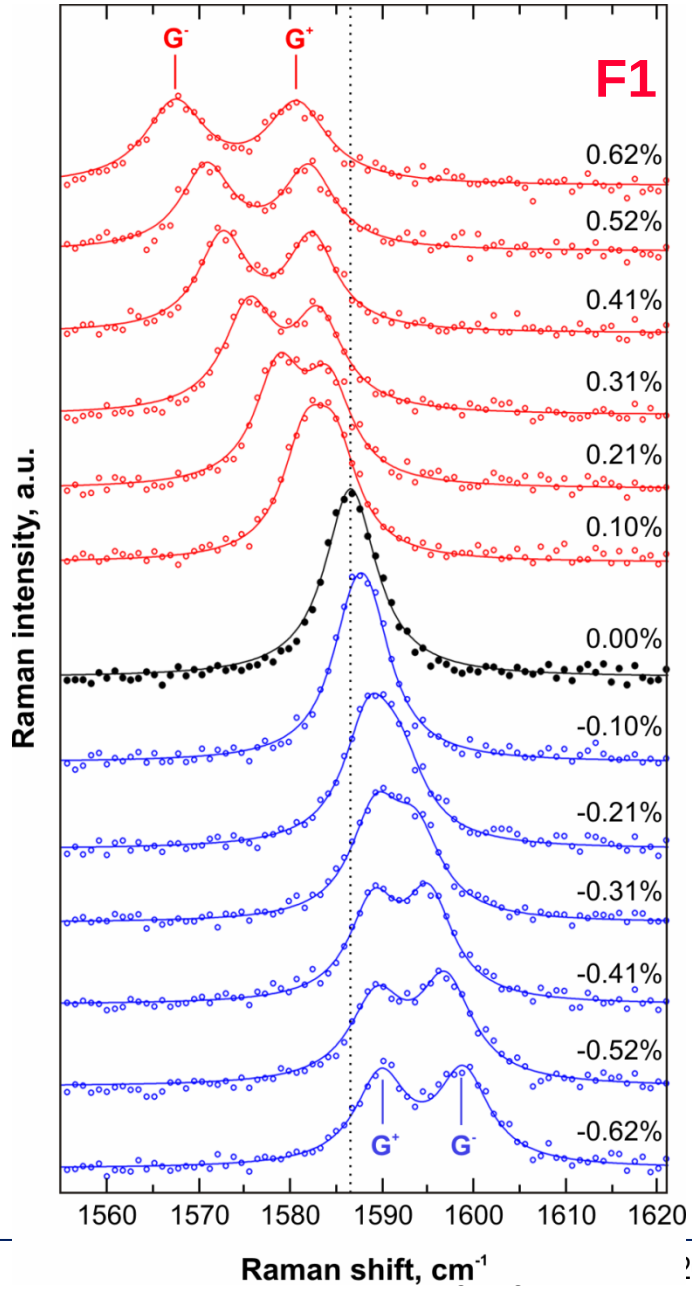
G mode under strain in tension & compression

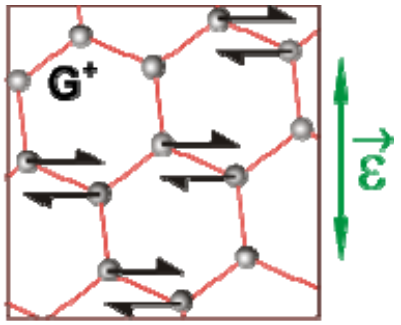


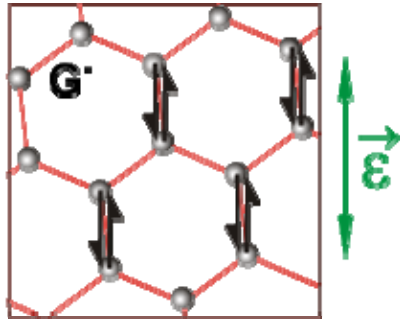




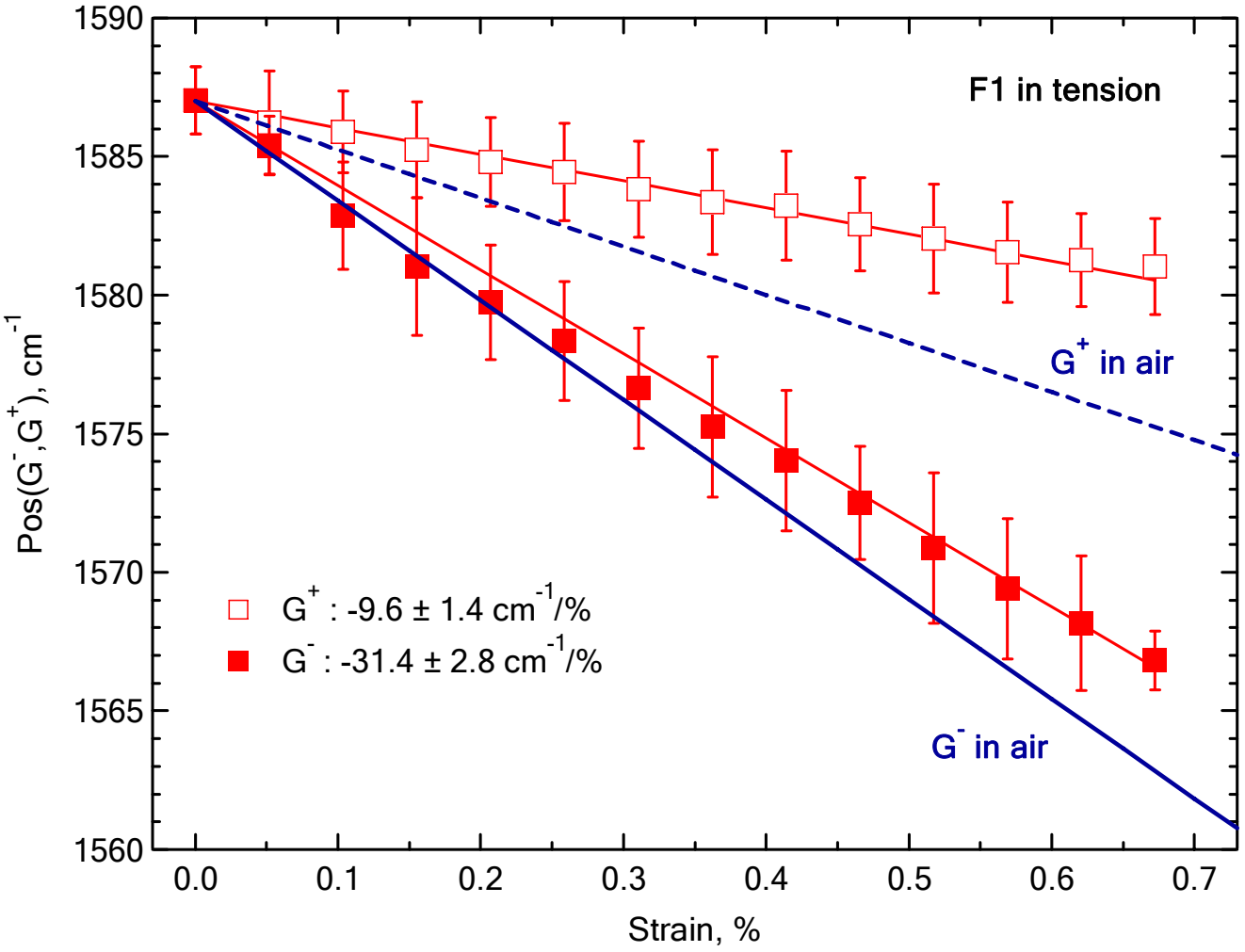








Linear behaviour (no residual strain present)

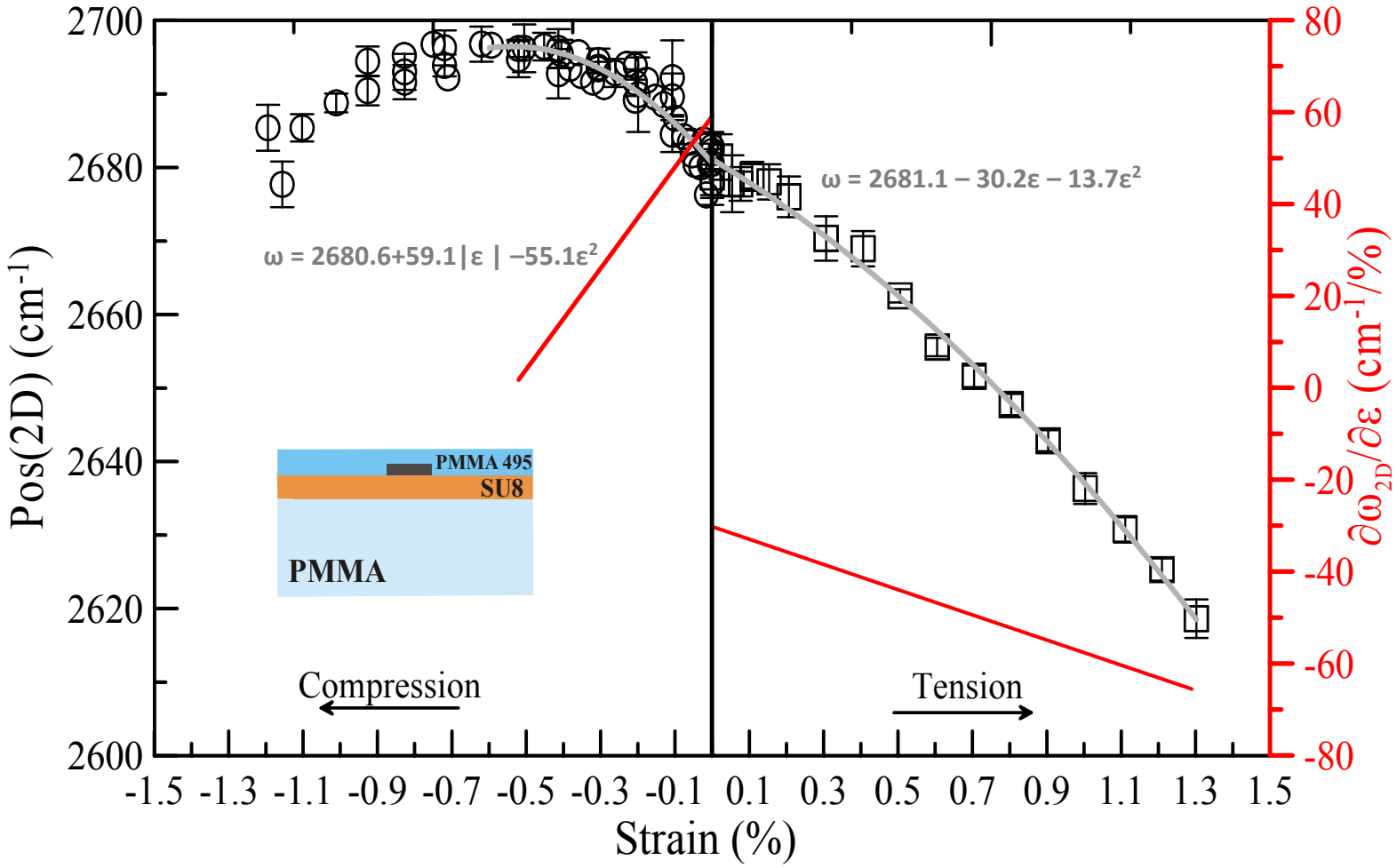


$\partial\omega_{G+} / \partial\varepsilon = -17.5\ \mathrm{cm}^{-1}/\%$

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

Tsoukleri et al, SMALL, 5/21, 2397-02 (2009)
Frank et al, ACS-Nano, 4/6, 3131-38 (2010)]

2D Peak (embedded flakes)



Tsoukleri et al, SMALL, 5/21, 2397-02 (2009)

2D-peak strain sensitivity for various graphitic materials (excluding CNT)

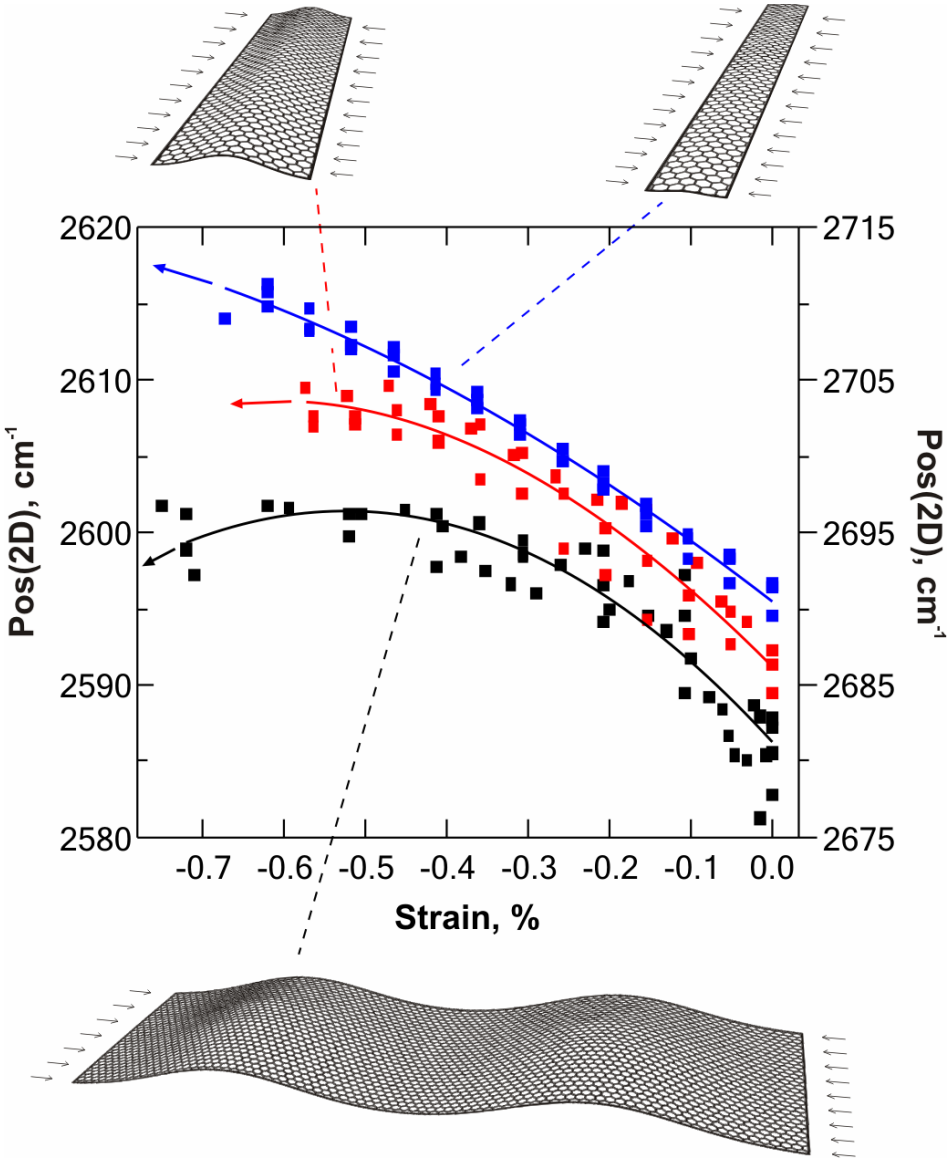
Reference	Maximum Strain Sensitivity (cm^{-1}/ %) for the 2D line in tension		
	Graphene	Graphite	Carbon Fibres
Ni et al (2008) and Yu et al (2008)	-27.8*	-	-
Huang et al (2008)	-21.0*	-	-
Mohiuddin et al (2008)	~-64*	-	-
Galiotis & Batchelder (1988)	-	-	-25
This work	-59.1* +25.8 (compression)*	-1.3/ -2.1*	-
	-65.9** +59.1 (compression)**	-49.0/ -51.0**	

*"Bare" graphene flake or graphite crystal on plastic substrate. For the work reported here, the graphene value was taken at 0.9% strain (Fig.3a).

**"Embedded" graphene flake or graphite crystal within the plastic substrate. The values in tension were taken at 1.3% strain and in compression near the origin (Fig.4 a, b). For the graphite the slopes correspond to the 2690 cm^{-1} ($2D_1$) and 2730 cm^{-1} ($2D_2$) bands, respectively.

Tsoukleri et al, SMALL, 5/21, 2397-02 (2009)

Compression of graphene flakes - 2D peak



Critical buckling strain of graphene

$$\varepsilon_c \propto \frac{k}{w^2}$$

Euler formula for thin shells

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

l – length (dimension parallel to strain)
w – width
m – number of half-waves to appear at the critical load

Sample	ε_c (%) *	k / w^2 (μm^{-2})	*k*	*l* (μm)	*w* (μm)
F1	-1.25	0.028	89.12	**6**	**56**
F2	-0.64	0.011	22.71	**11**	**50**
F3	-0.53	0.006	4.02	**56**	**25**

*ε_c determined from the 2nd order polynomials as maxima

Critical buckling strain of graphene *(considered as a "thin shell")*

The ratio of flexural, *D*, to tension, *C*, rigidities for uniaxial tension and bending is given by (*h*= the thickness of the plate/ shell) :

$$\frac{D}{C} = \frac{h^2}{12}$$

The **critical strain**, ε_c, for the buckling of a rectangular thin shell under uniaxial compression is given by

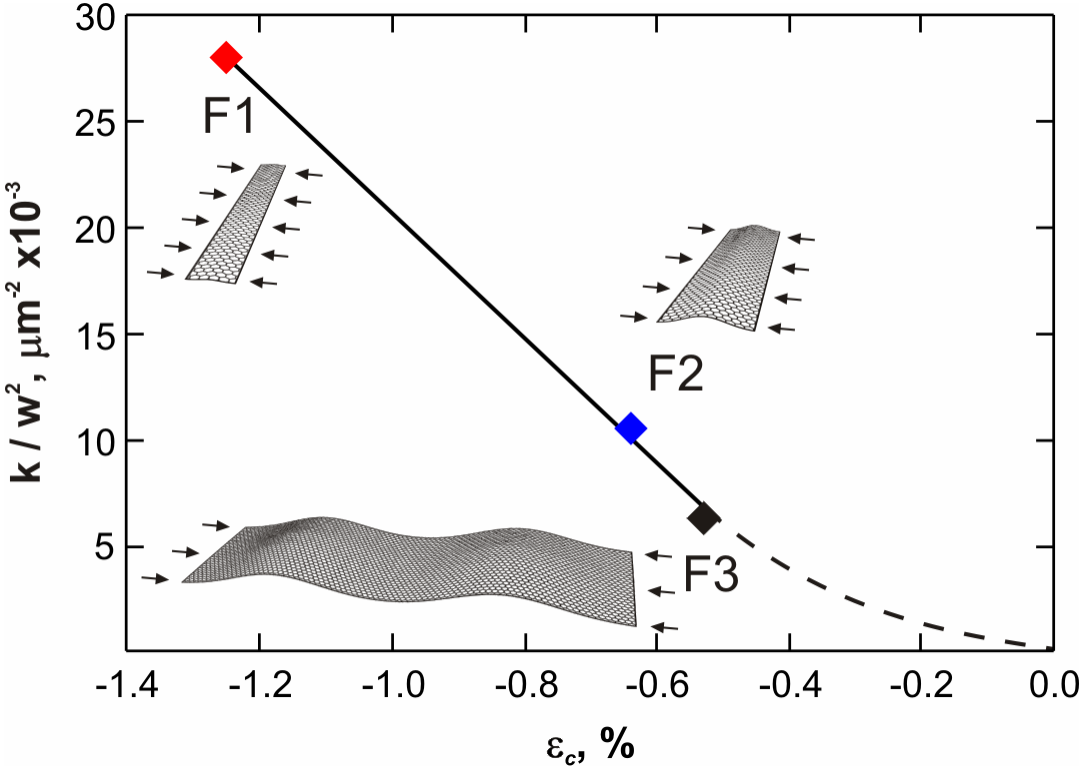
$$\varepsilon_c = \frac{\pi^2 k}{w^2}\left(\frac{D}{C}\right)$$

where *w* is the width of the flake and *k* is a geometric term. The tension rigidity is *C*=340 GPa nm (experimental) and flexural rigidity, D=3.18 GPa nm^3.

For an infinitely thin layer in air, critical buckling strain yields only $\approx 10^{-9}$

- The observed ε_c value of the embedded flake F1 (0.64%) is remarkably high compared to the suspended one. This can be attributed to the support provided by the polymer matrix.

Results



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

slope

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

Linear dependence: Euler regime still applies for the embedded flake!

For supported (embedded) flake:

$$\varepsilon_c^{\,embedded} = \frac{k}{w^2}\frac{D^*\pi^2}{C}, \quad D^* = 12\ \text{MPa}\ \mu m^3$$

The modified flexural rigidity in the presence of the polymer is 6 orders of magnitude higher than for the suspended in air !!!

Analytical Treatment…

(towards the development of a universal stress sensor)

Analytical (1/3)

The secular equation for E_{2g} mode of graphene under strain is given by:

$$\begin{vmatrix} A\varepsilon_{xx} + B\varepsilon_{yy} - \lambda & (A-B)\varepsilon_{xy} \\ (A-B)\varepsilon_{xy} & B\varepsilon_{xx} + A\varepsilon_{yy} - \lambda \end{vmatrix} = 0$$

Solving analytically and ignoring terms higher that ε^2:

$$\mathrm{A} = \frac{2\omega_0 \left(\frac{\partial \omega_{G^-}}{\partial \varepsilon} + \nu \frac{\partial \omega_{G^+}}{\partial \varepsilon} \right)}{1-\nu^2}$$

$$\mathrm{B} = 2\omega_0 \frac{\partial \omega_{G^+}}{\partial \varepsilon} + \nu \mathrm{A}$$

Deformation potentials:

$$A = -1.23 \times 10^7 \,\mathrm{cm}^{-2}$$

$$B = -7.16 \times 10^6 \,\mathrm{cm}^{-2}$$

Analytical (2/3)

For uniaxial stress in graphene, the resulting strains are given by

$$\varepsilon_{xx} = \varepsilon = S_{11}\sigma$$
$$\varepsilon_{yy} = -\nu\varepsilon = S_{12}\sigma$$

or equivalently

$$\varepsilon = S_{11}\sigma$$
$$\nu = -\frac{S_{12}\sigma}{\varepsilon}$$

From the analysis earlier we obtain:

$$\frac{\partial\omega_{G^-}}{\partial\sigma} = \frac{(AS_{11} + BS_{12})}{2\omega_0}$$
$$\frac{\partial\omega_{G^+}}{\partial\sigma} = \frac{(AS_{12} + BS_{11})}{2\omega_0}$$

For

$$S_{11}^{graphene} = 1/E_{11}^{graphene} = 1.00\ \text{TPa}^{-1}$$
$$S_{12}^{graphene} = 1/E_{12}^{graphite} = -0.16\ \text{TPa}^{-1}$$

$$\frac{\partial\omega_{G^-}}{\partial\sigma} = -3.5\ \text{cm}^{-1}\ \text{GPa}^{-1}$$
$$\frac{\partial\omega_{G^+}}{\partial\sigma} = -1.6\ \text{cm}^{-1}\ \text{GPa}^{-1}$$

Analytical (3/3)

If both components contribute equally to the measured Raman shift then:

$$\Delta\omega_G = \left(\frac{\Delta\omega_{G^+} + \Delta\omega_{G^-}}{2} \right) = \left[\frac{(A+B)(S_{11}+S_{12})}{4\omega_0} \right] \sigma \approx \left[\frac{S_{11}(A+B)}{4\omega_0} \right] \sigma$$

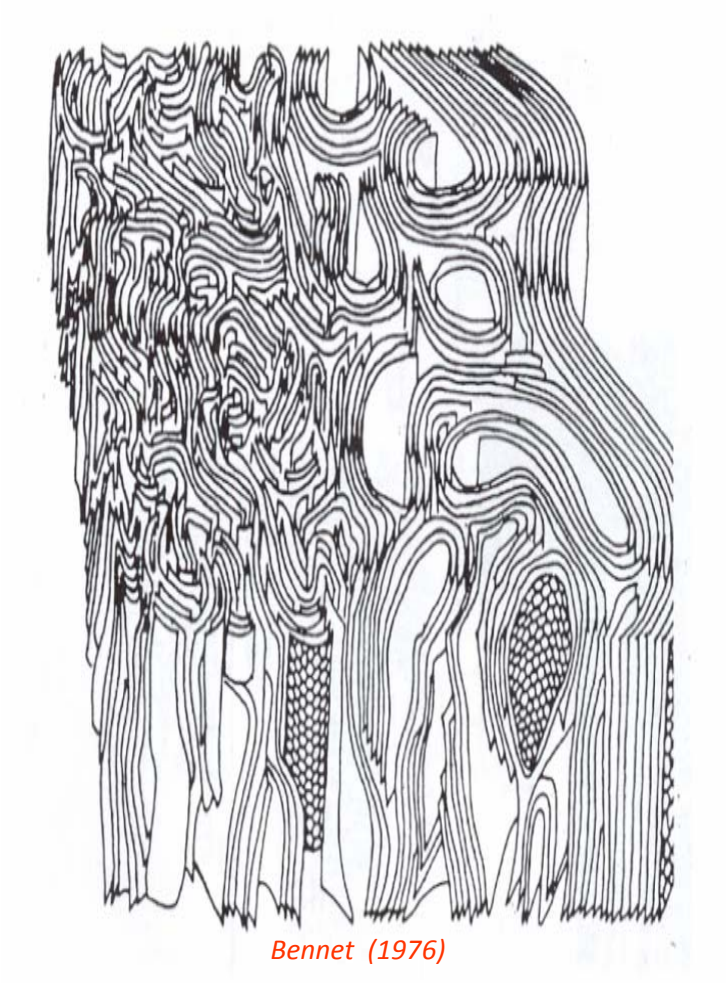
The theoretical value of the expression in brackets is:

$$\sim -5\omega_0^{-1}(\mathrm{cm}^{-1}\mathrm{MPa}^{-1})$$

The universal value of our graphene-based stress sensor !

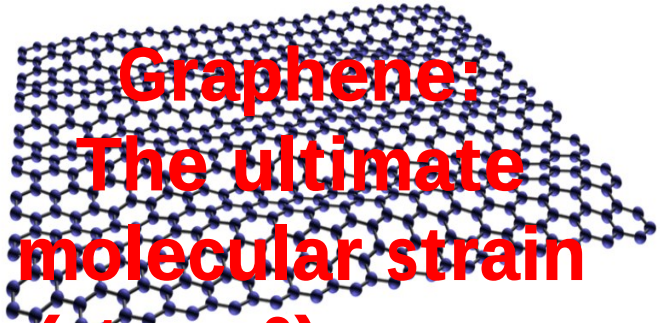
Stress sensors

Carbon fibres (microscale)



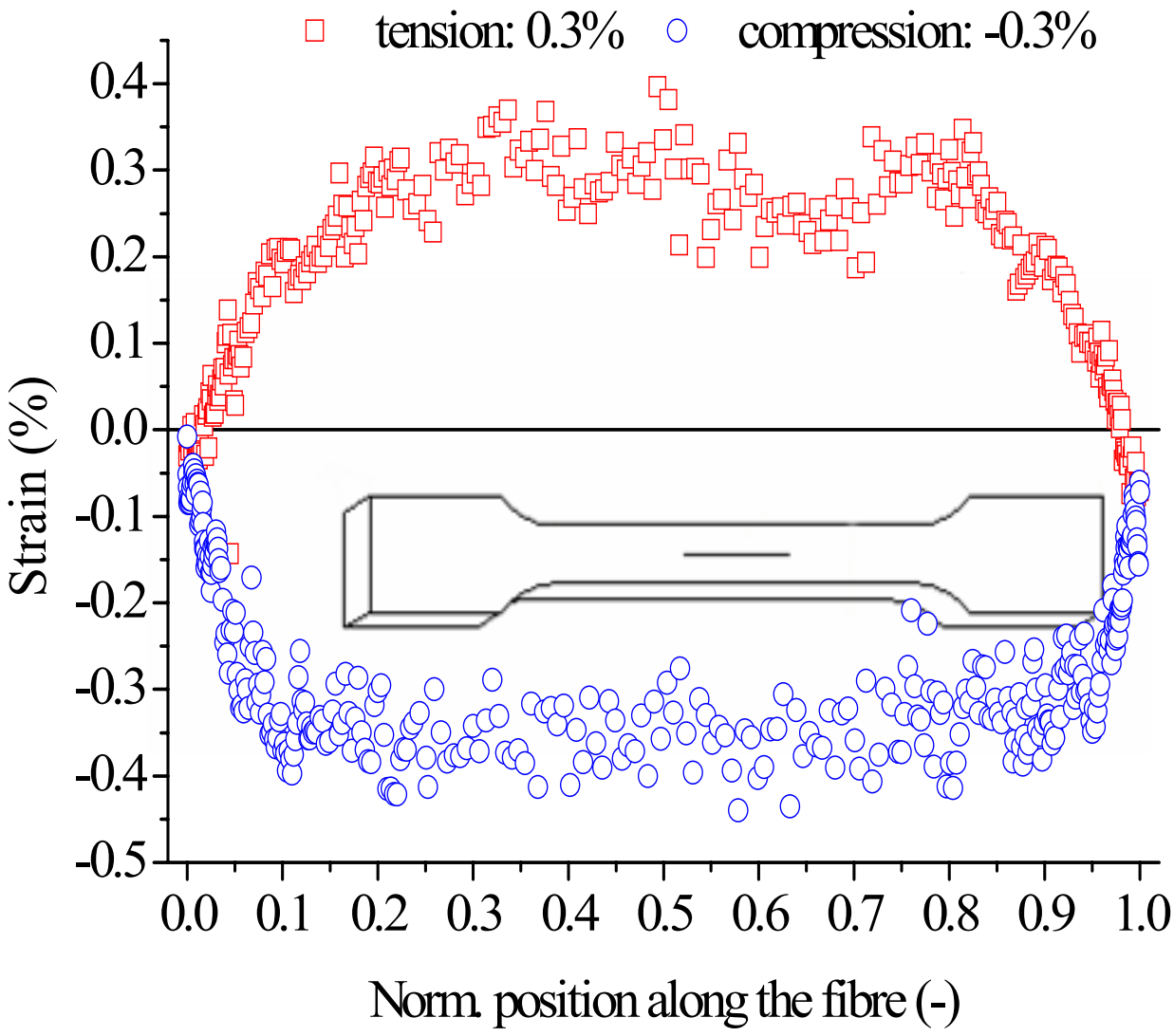
Bennet (1976)

Graphene (nanoscale)



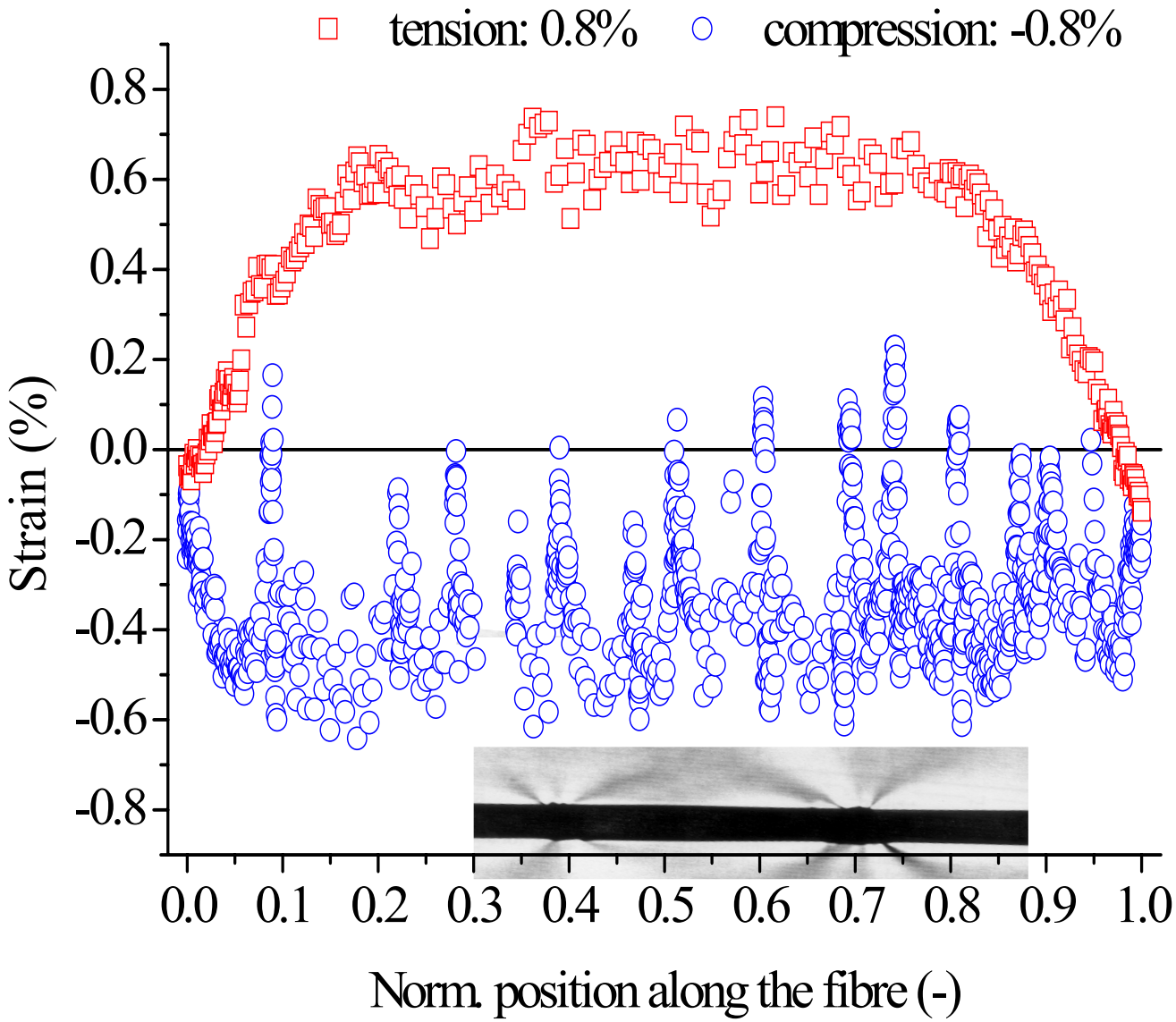
Graphene: The ultimate molecular strain (stress?) sensor

Strain distribution along a short fibre at ±0.3%



Goutianos et al, Composites-Part A, **35**/4, 461-475 (2004)
Goutianos, Int. J. Solids & Structures, **40**/21, 5521-5538 (2003)

Detection of failure processes



Goutianos et al, Composites-Part A, **35**/4, 461-475 (2004)
Goutianos, Int. J. Solids & Structures, **40**/21, 5521-5538 (2003)

Last Thoughts

- Graphene has great potential for biological and biomedical applications.
- The smallest stress/ strain sensor ever known.
- Any collaborations on this new material within the biotargeting network are very much welcome