The Structure of suspended Graphene Membranes

Jannik C. Meyer[1,(2)], A. K. Geim[3], M. I. Katsnelson[4], K. S. Novoselov[3], T. J. Booth[3], D. Obergfell[2], S. Roth[2], C. Girit[1], A. Zettl[1]

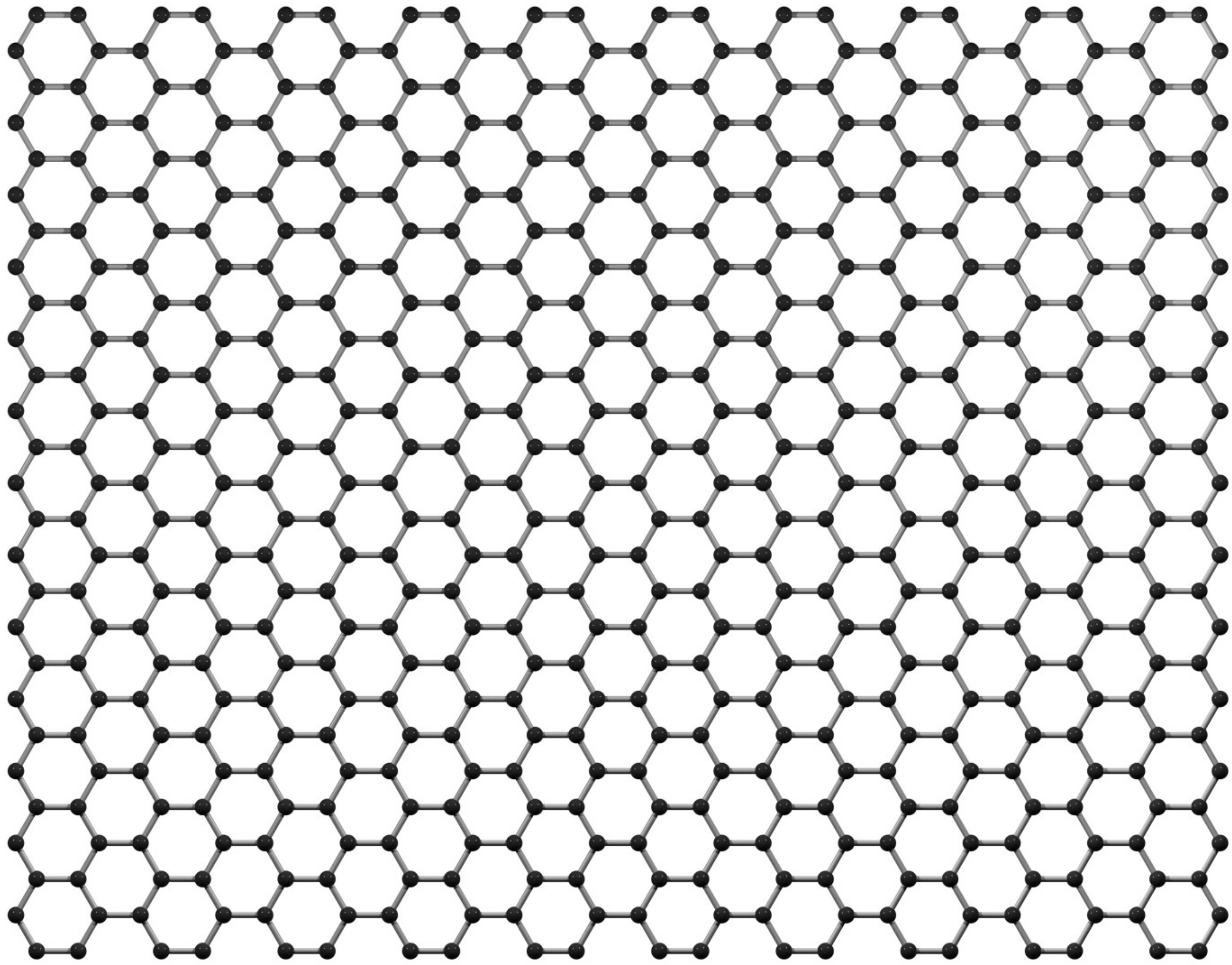
1) Physics Department, University of California, Berkeley and Materials Science Deptartment, Lawrence Berkeley National Laboratory

2) Max Planck Institute for solid state research, Stuttgart, Germany

3) Manchester Centre for Mesoscience and Nanotechnology, University of Manchester, United Kingdom

4) Institute for Molecules and Materials, Radboud University of Nijmegen, The Netherlands

Graphene: 1 layer of a graphite crystal

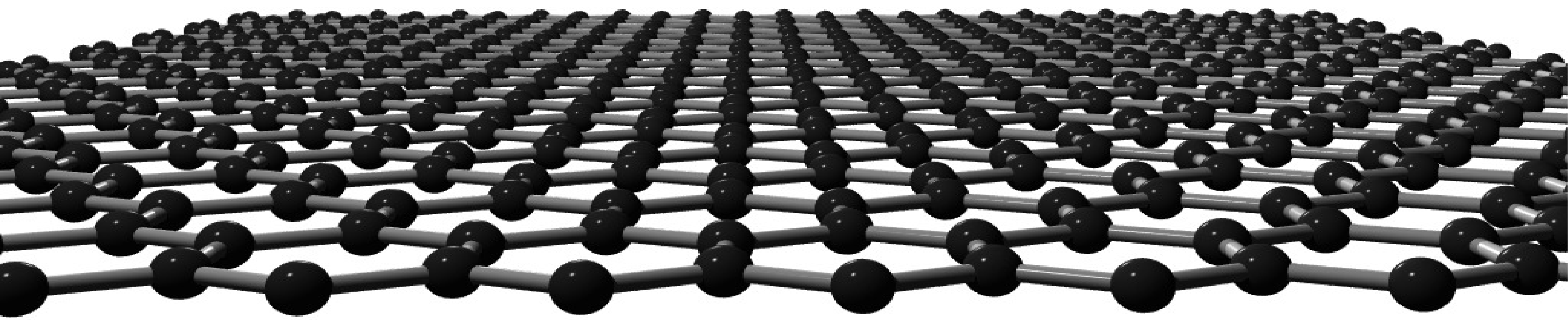


Graphene: 1 layer of a graphite crystal

True 2-D topology

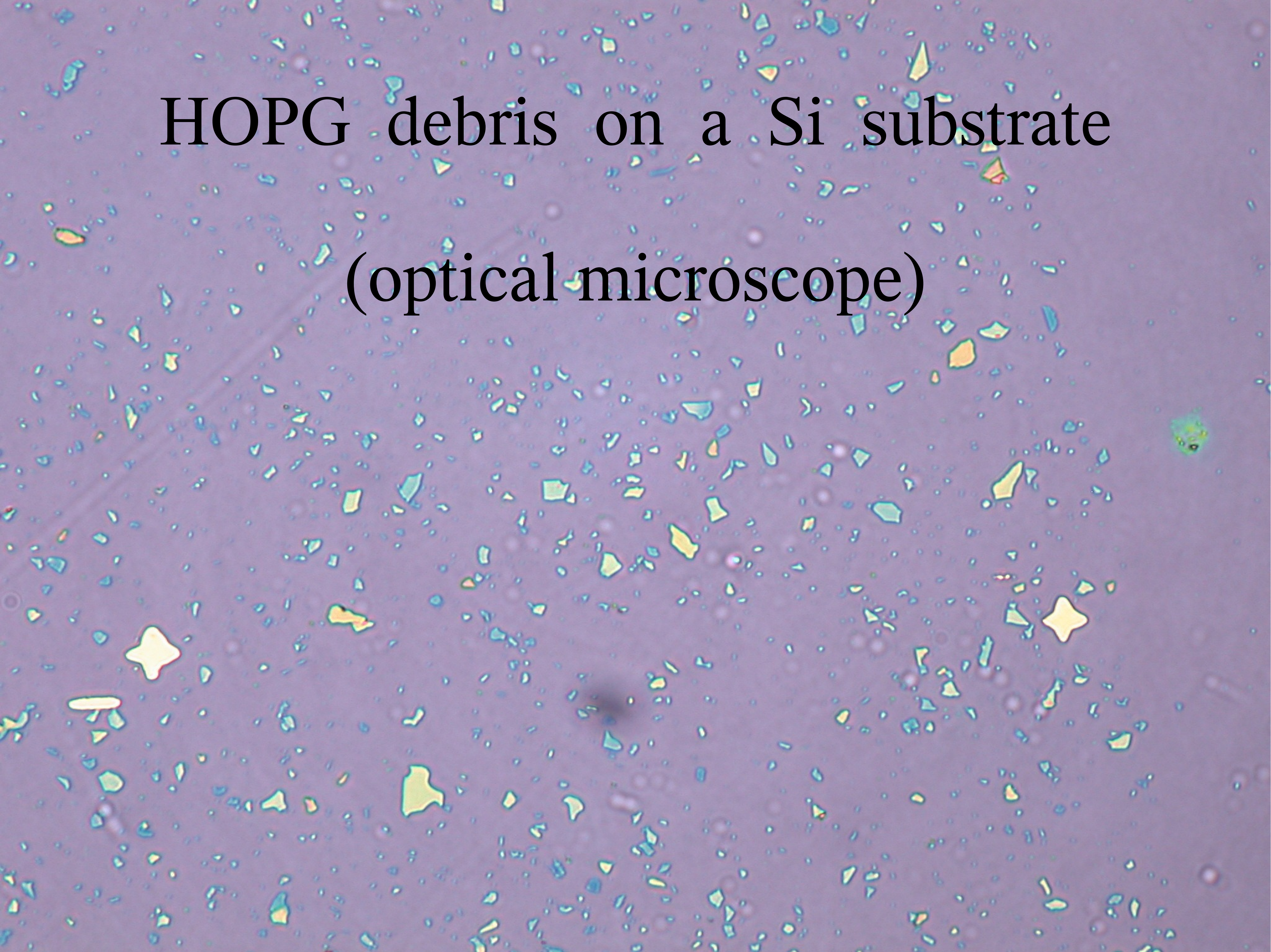
Strong in-plane bonds (sp^2)

only weak (van der Waals) out of plane interaction



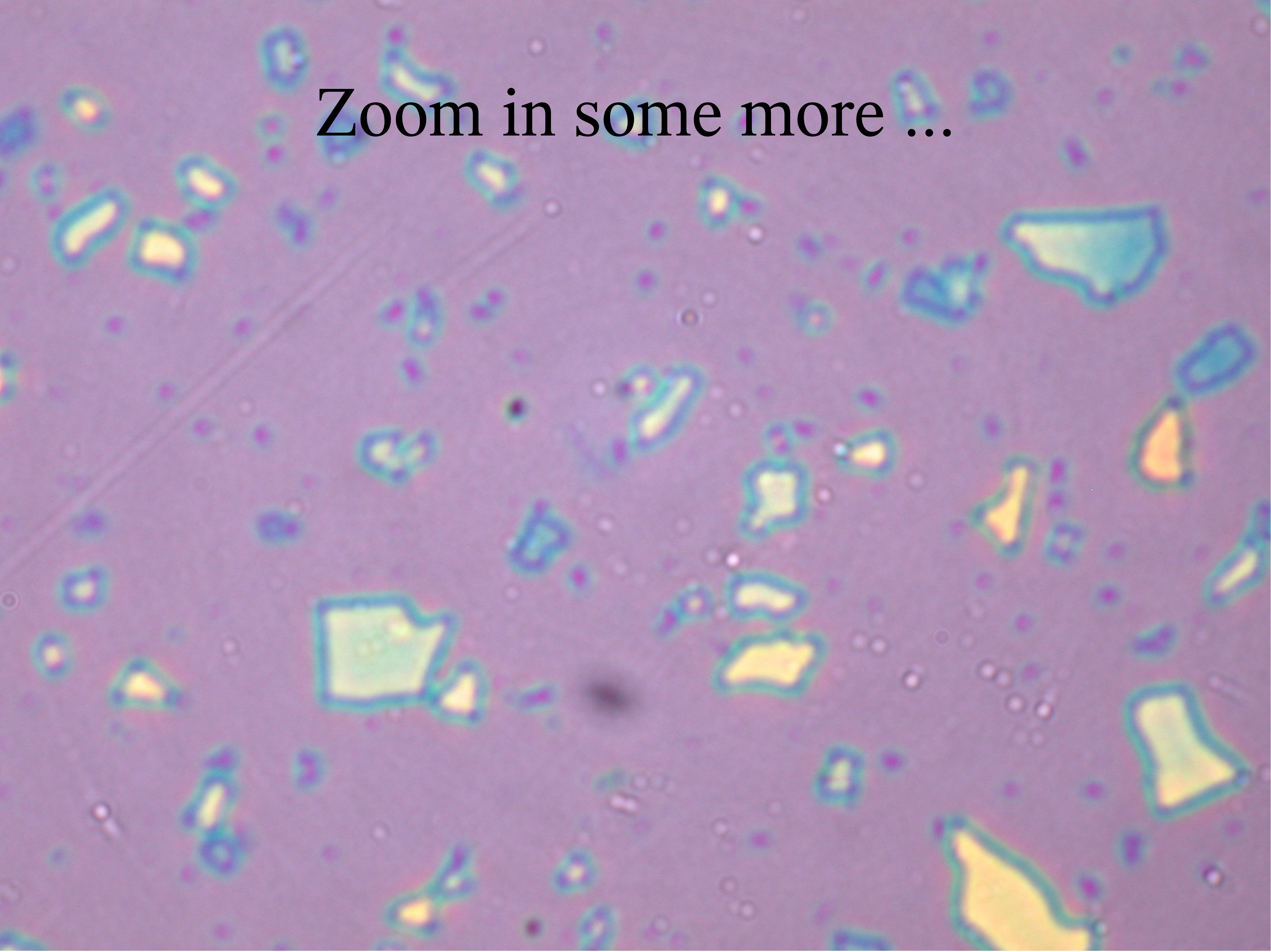
How to make Graphene?

cleave HOPG onto a substrate ...


HOPG debris on a Si substrate
(optical microscope)

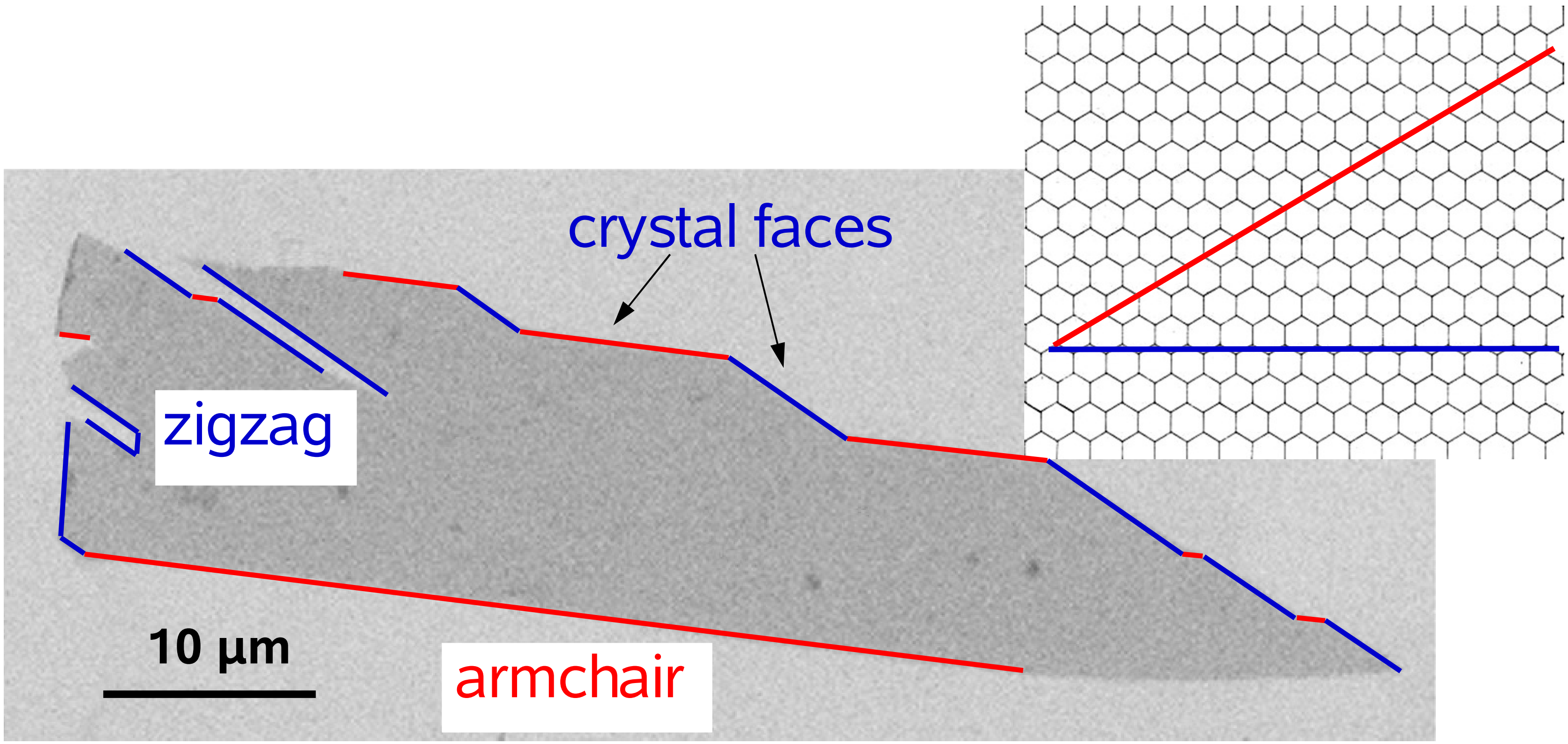

Zoom in ...

Zoom in some more ...




1-layer Graphene !!!

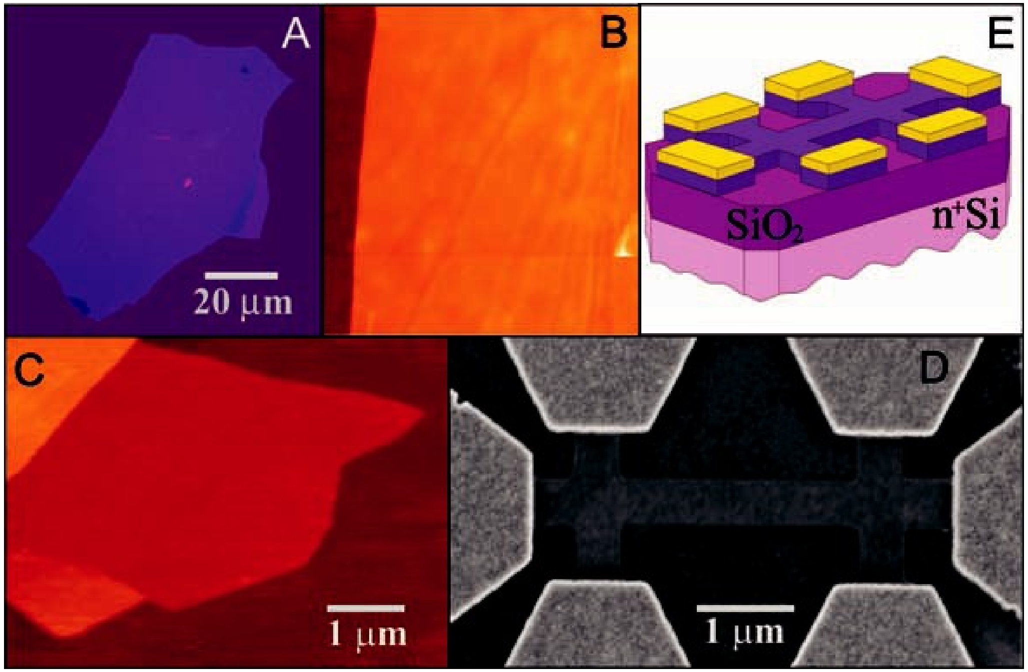
Two Dimensional Crystallites



not just flakes
but graphene crystallites

A. K. Geim, K. S. Novoselov, Nature materials **6** p. 183 (2007)

Recent interest in graphene due to unusual electronic properties:



<- Graphene flake shaped into hall bar

K. S. Novoselov et al., Science **306** p. 666 (2004)

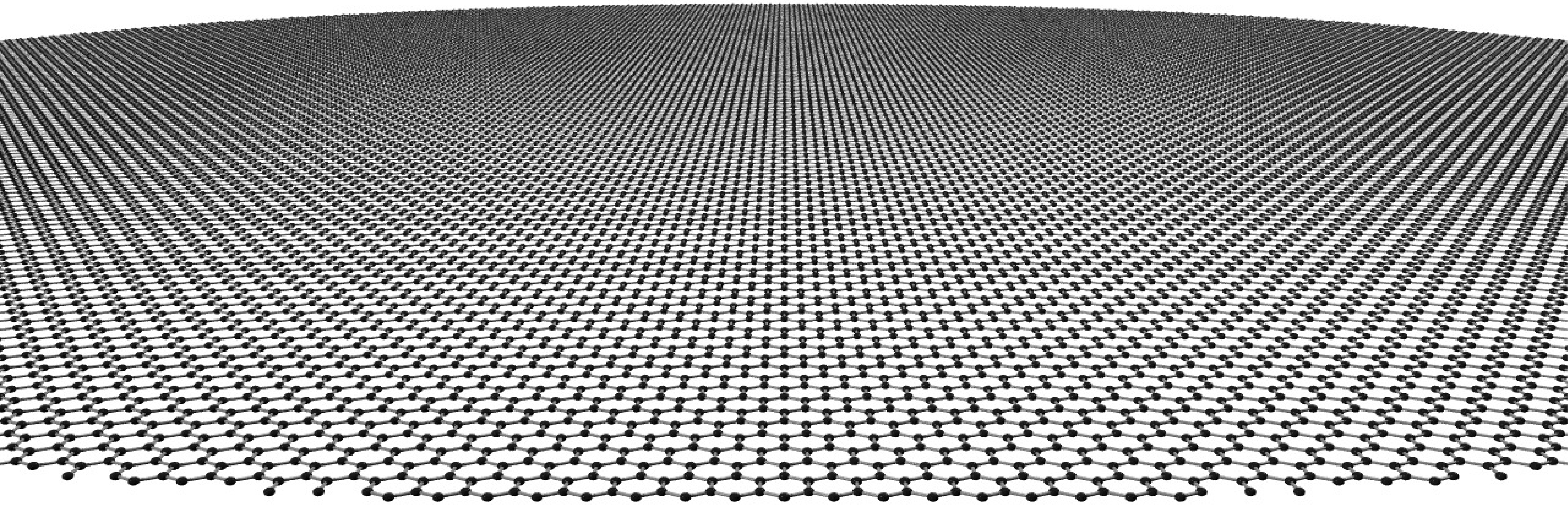
Charge carriers behave like massless relativistic particles.

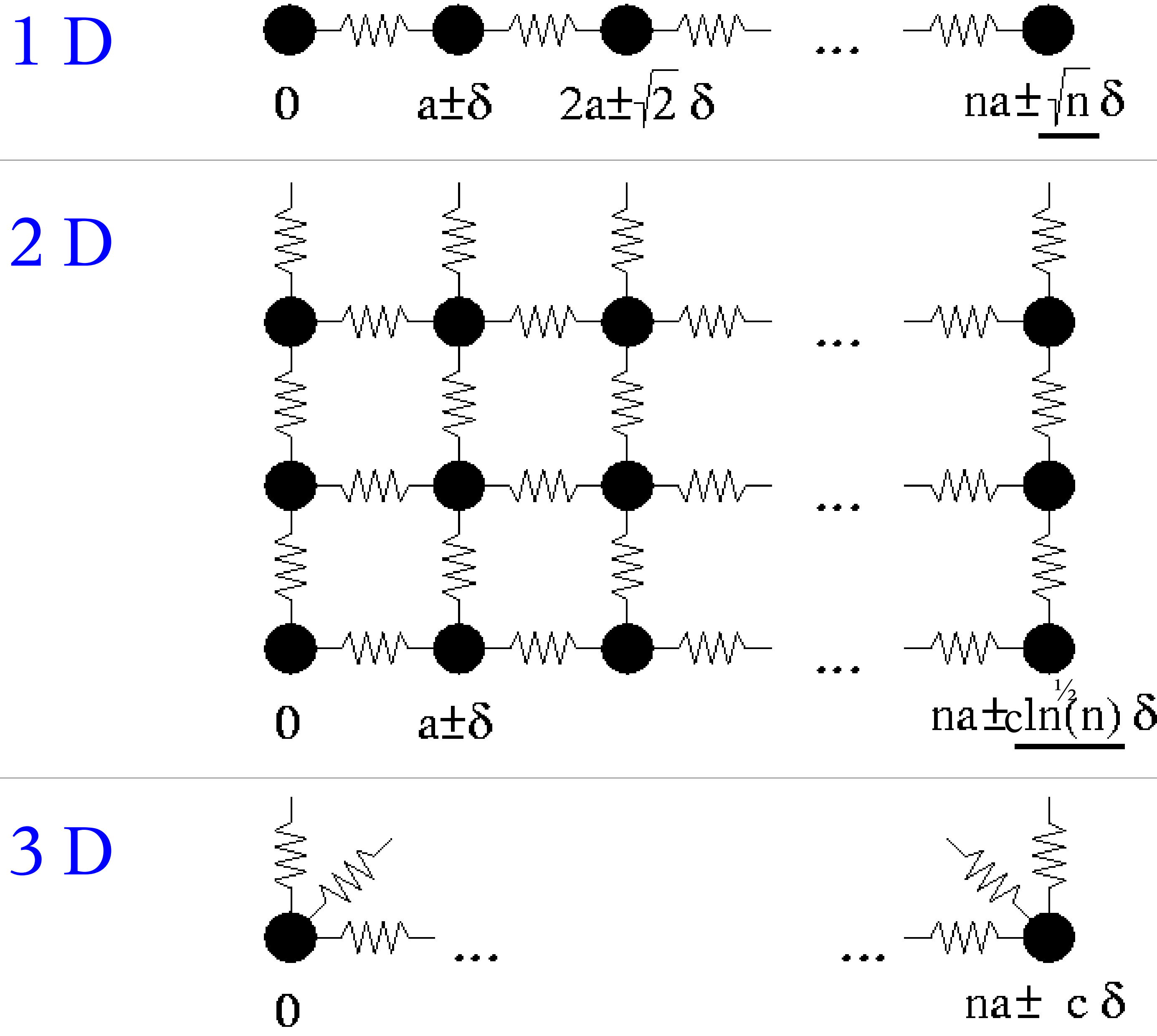
K. S. Novoselov et al., Nature **438**, 198 (2005)
Y. Zhang et al., Nature **438**, 201 (2005)
and many more

Graphene was always supported by a bulk substrate.

Graphene in a “free” state?

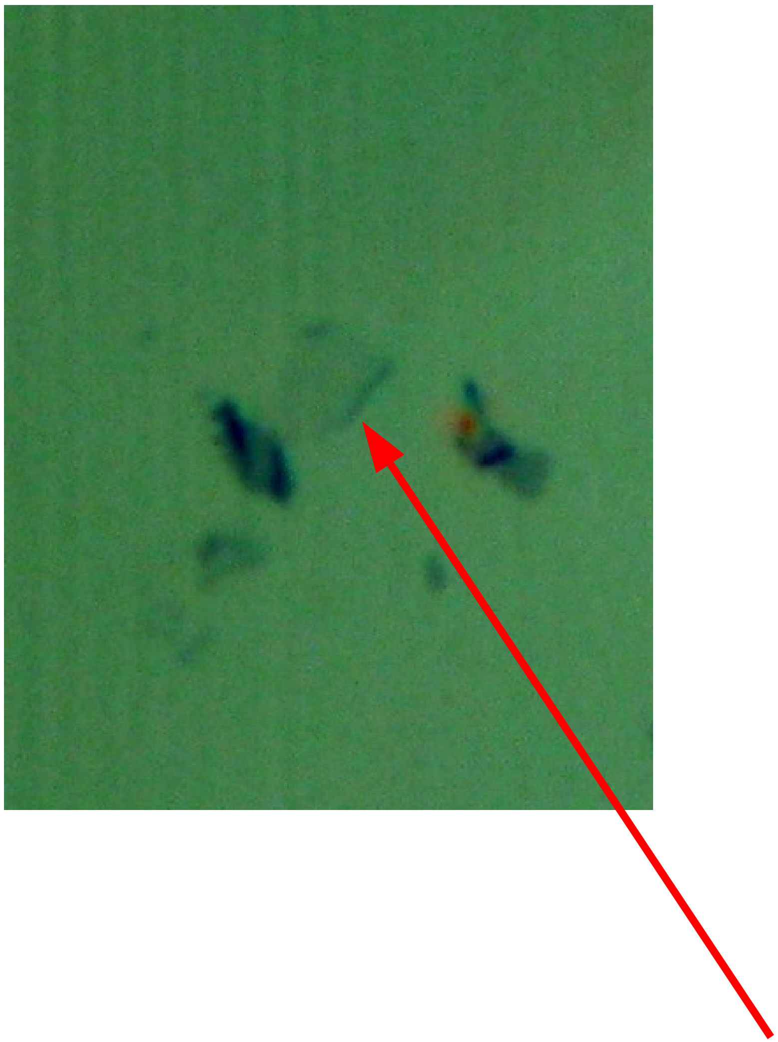
Strictly 2D crystal should not exist
(Peierls, Helv. Phys. Acta 7 (1934) 81-83,
Peierls, Ann. Inst. H. Poincare 5 (1935) 177-222,
Landau, Phys. Z. Sowjet. 11 (1937) 26
Mermin, PRL 17 (1966) 1133, Phys. Rev 176 (1968) 250.)



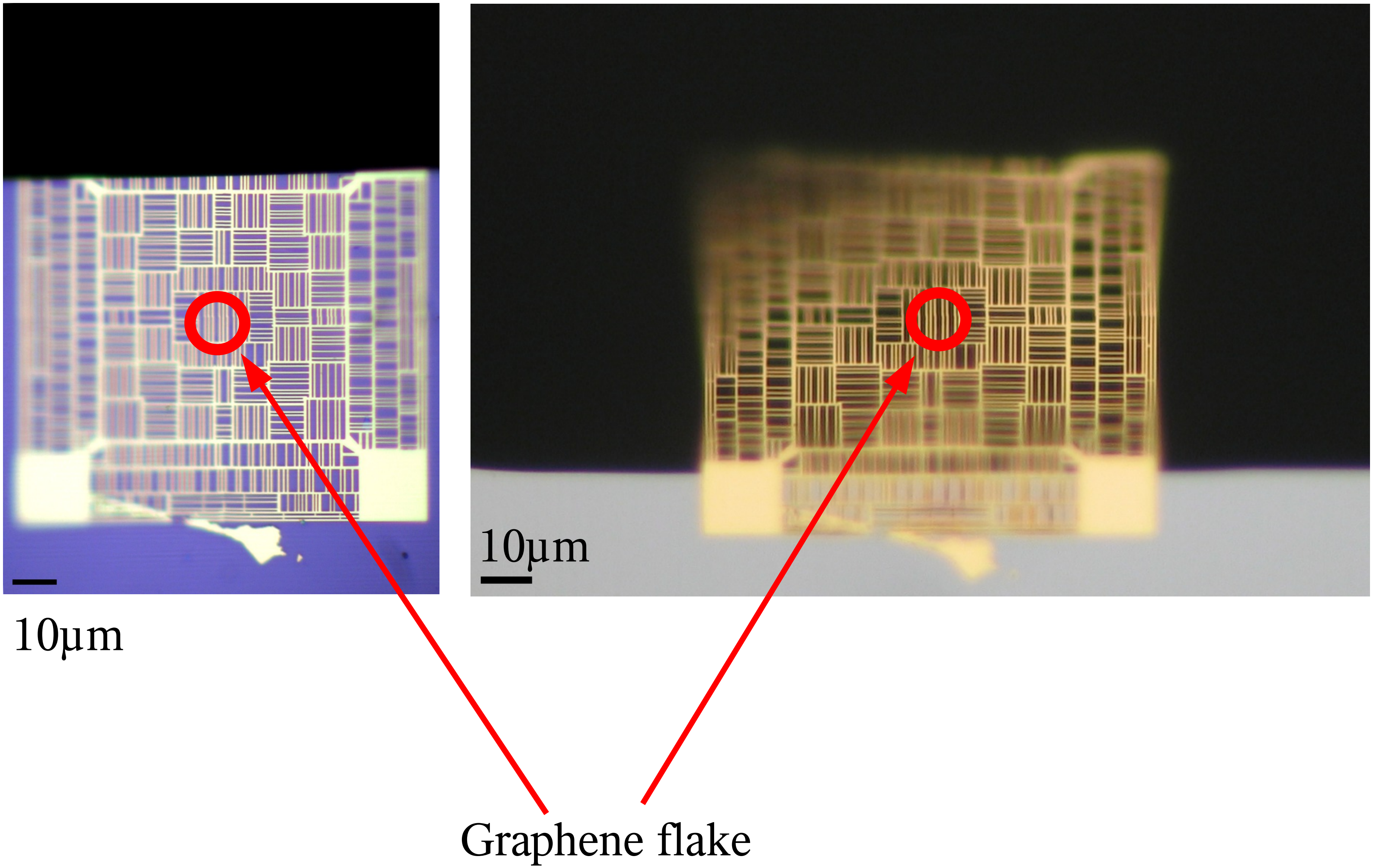


-> “perfect” crystal lattice at T>0 can exist only for D≥3.

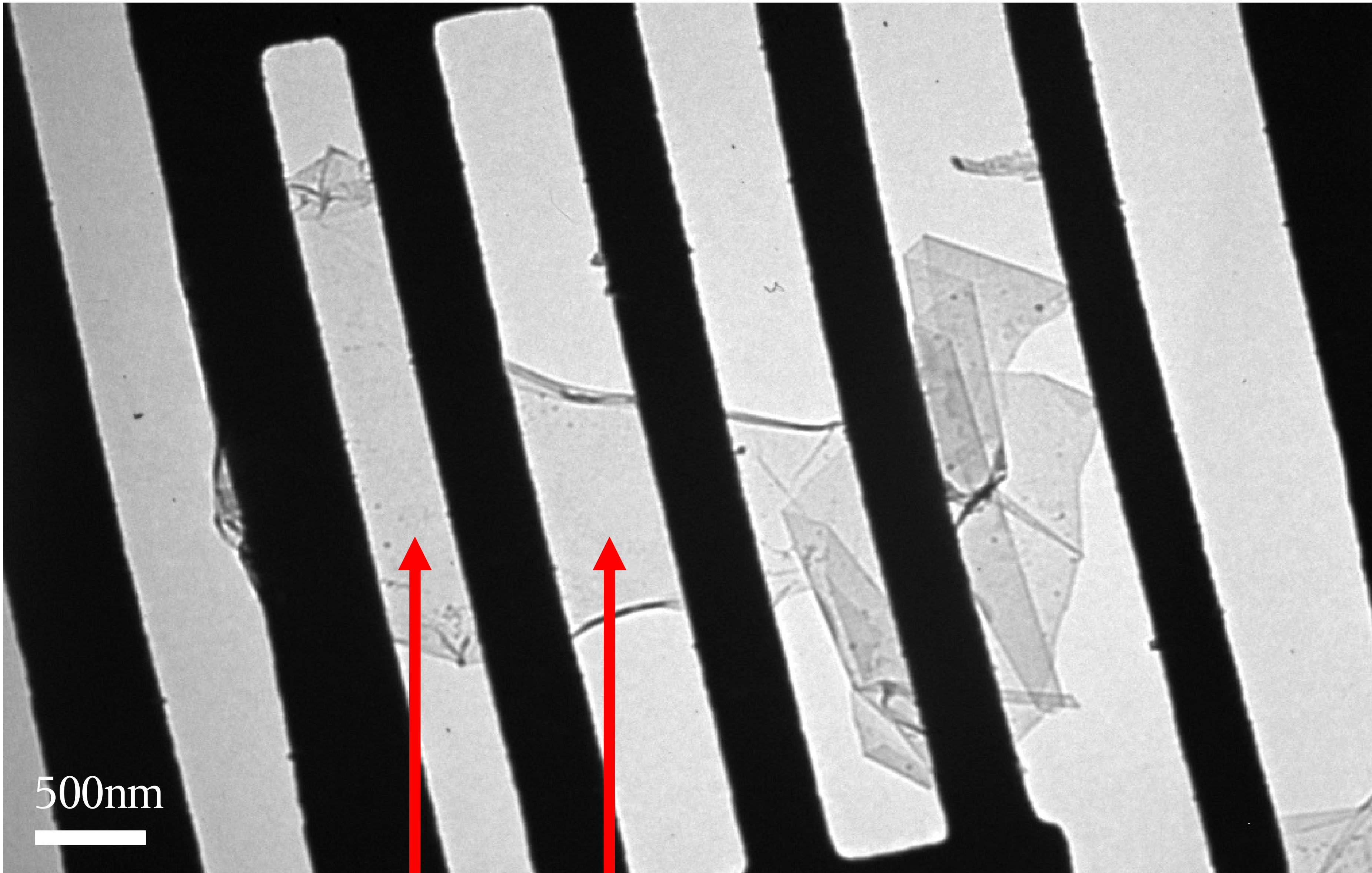
Freely suspended 2D graphene



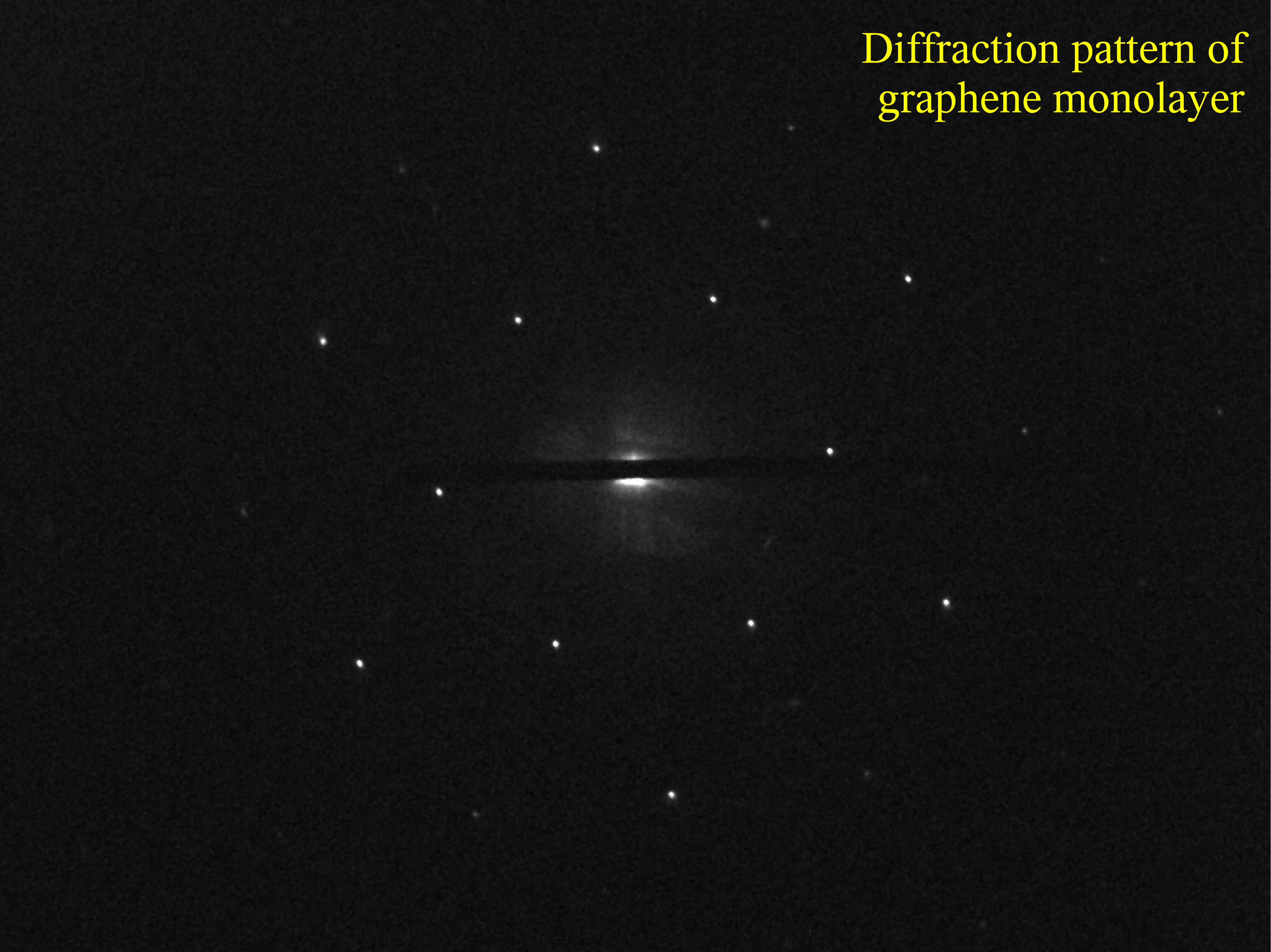
Freely suspended 2D graphene

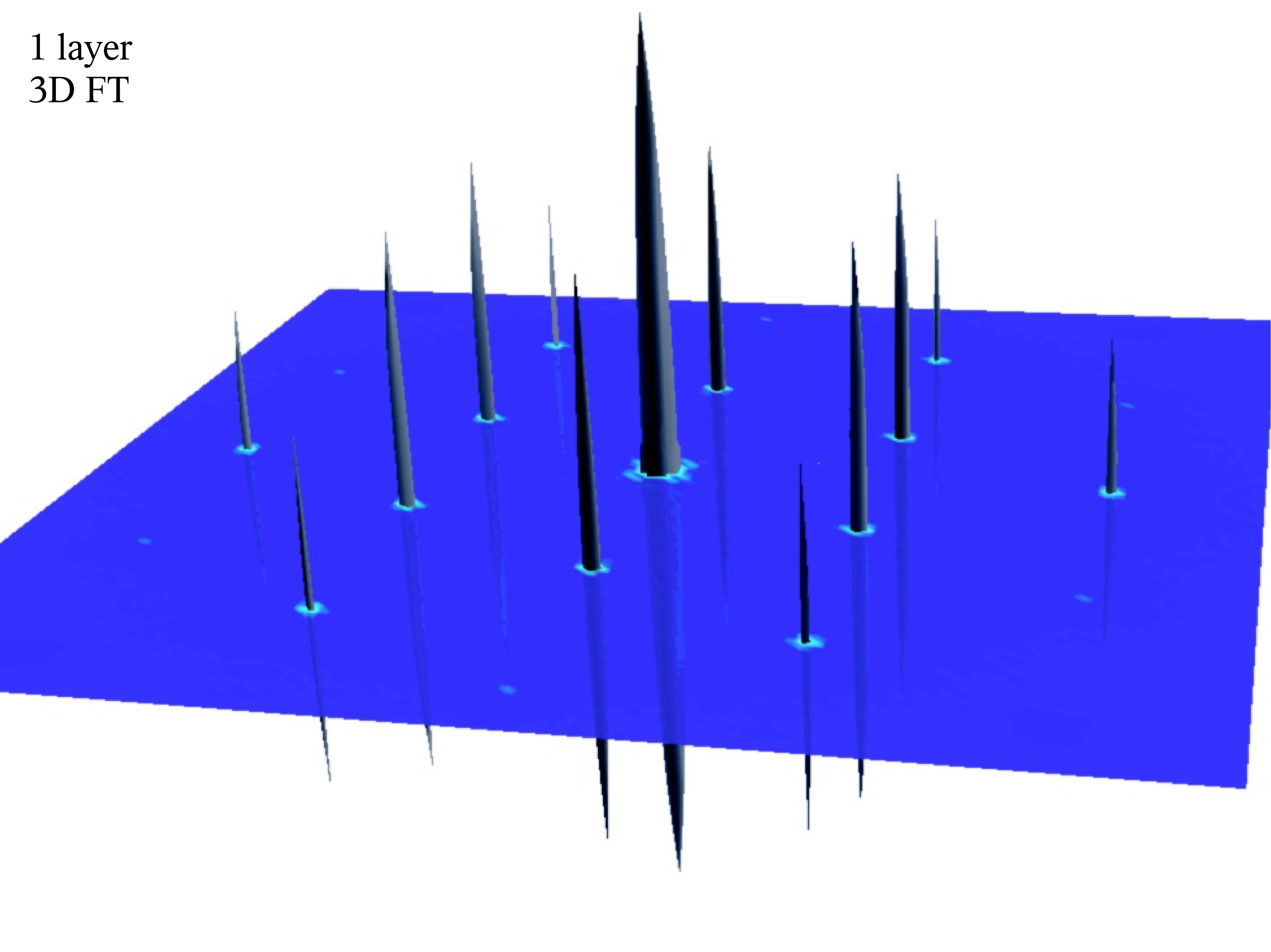


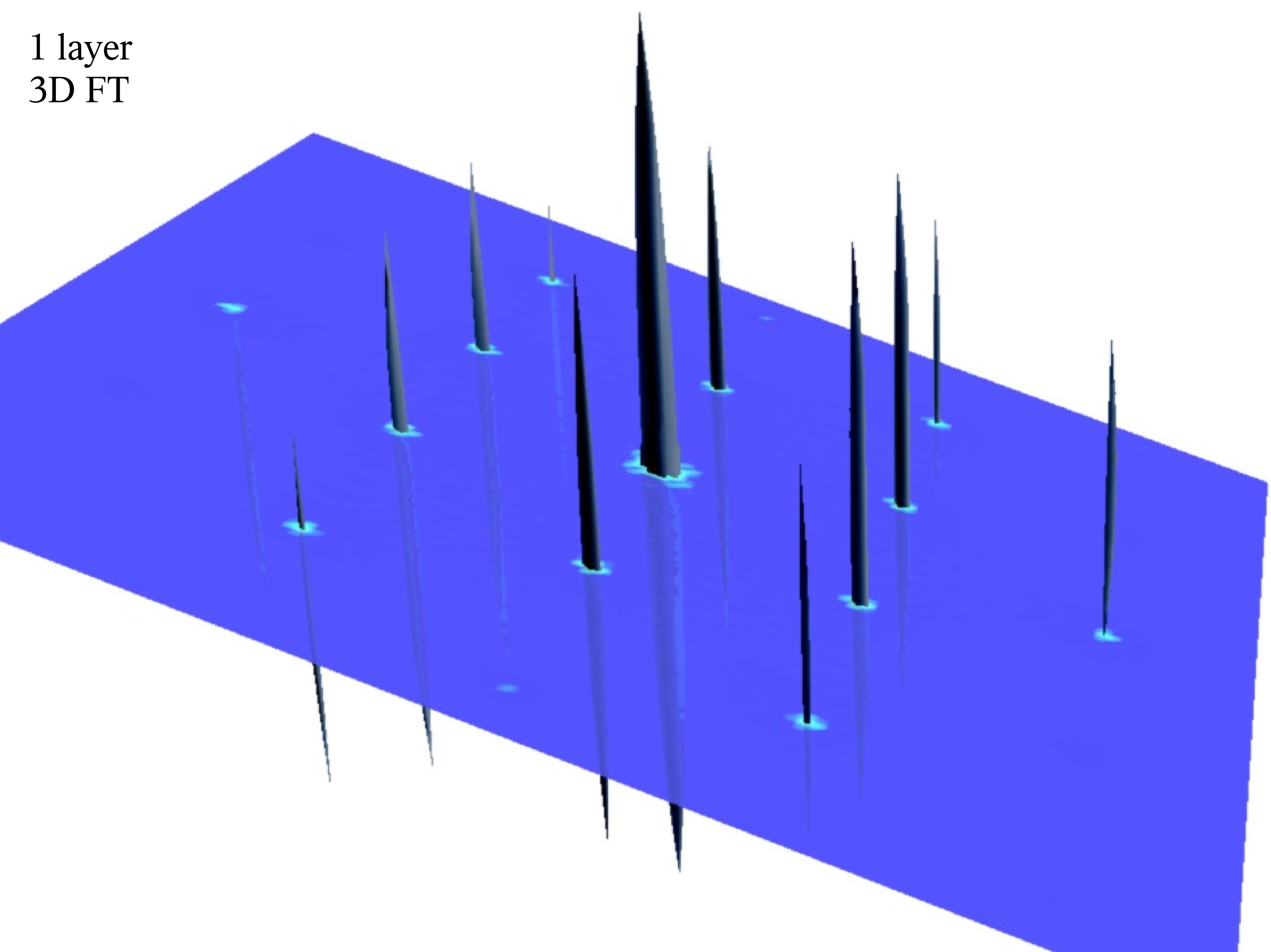
Free-standing graphene sheet

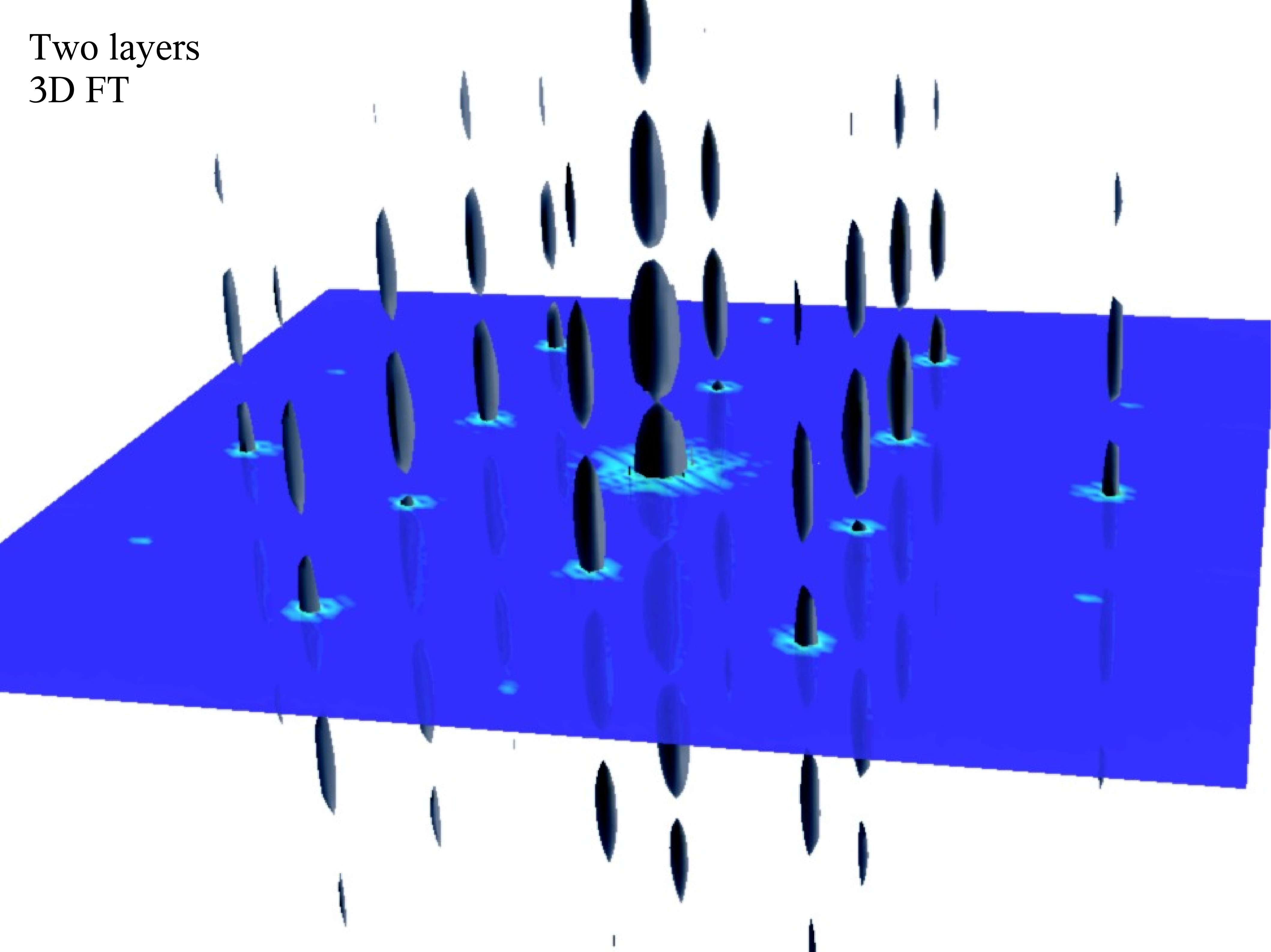


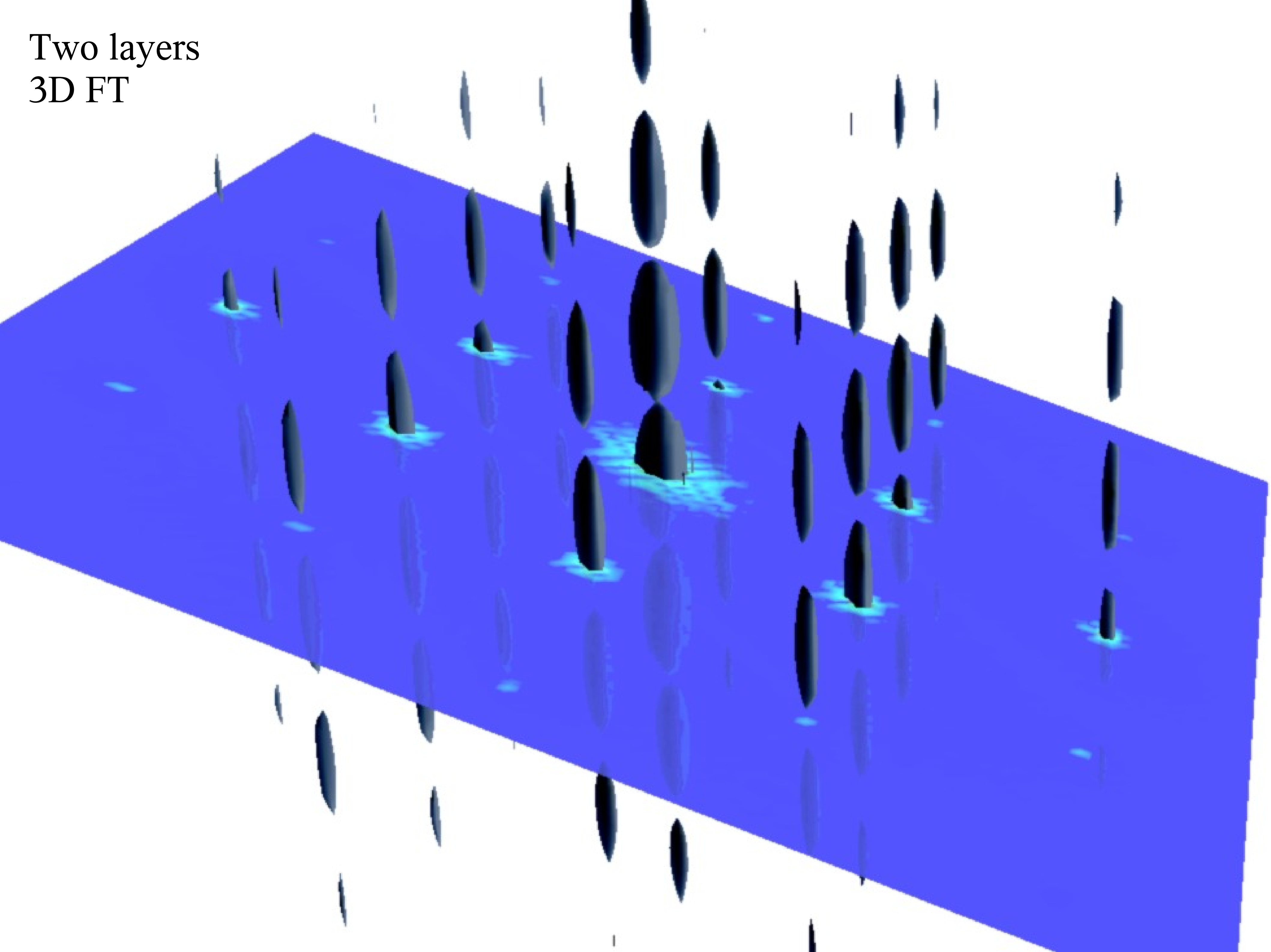
1 layer of graphene !


Diffraction pattern of
graphene monolayer


1 layer
3D FT

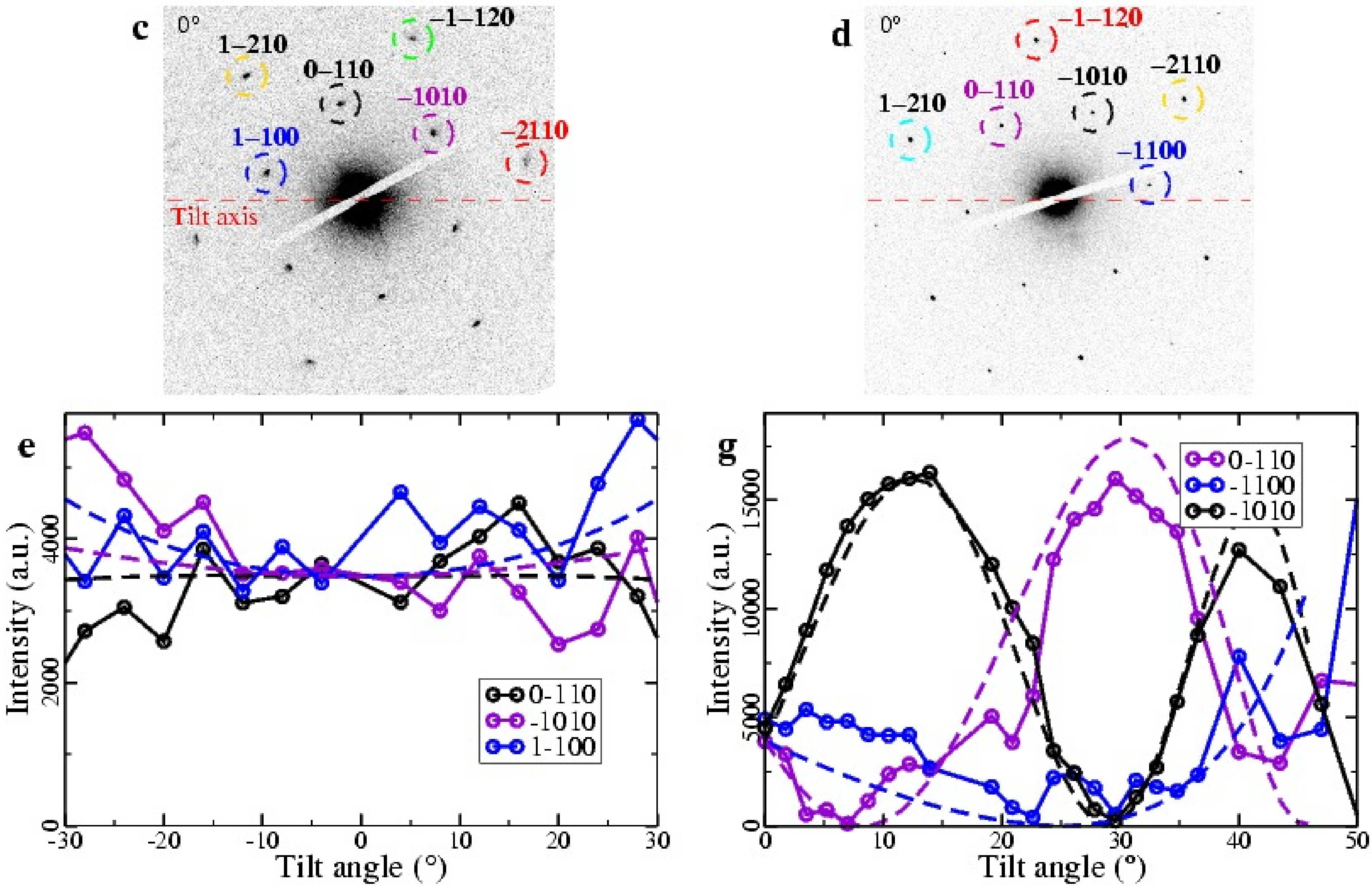

1 layer
3D FT


Two layers
3D FT

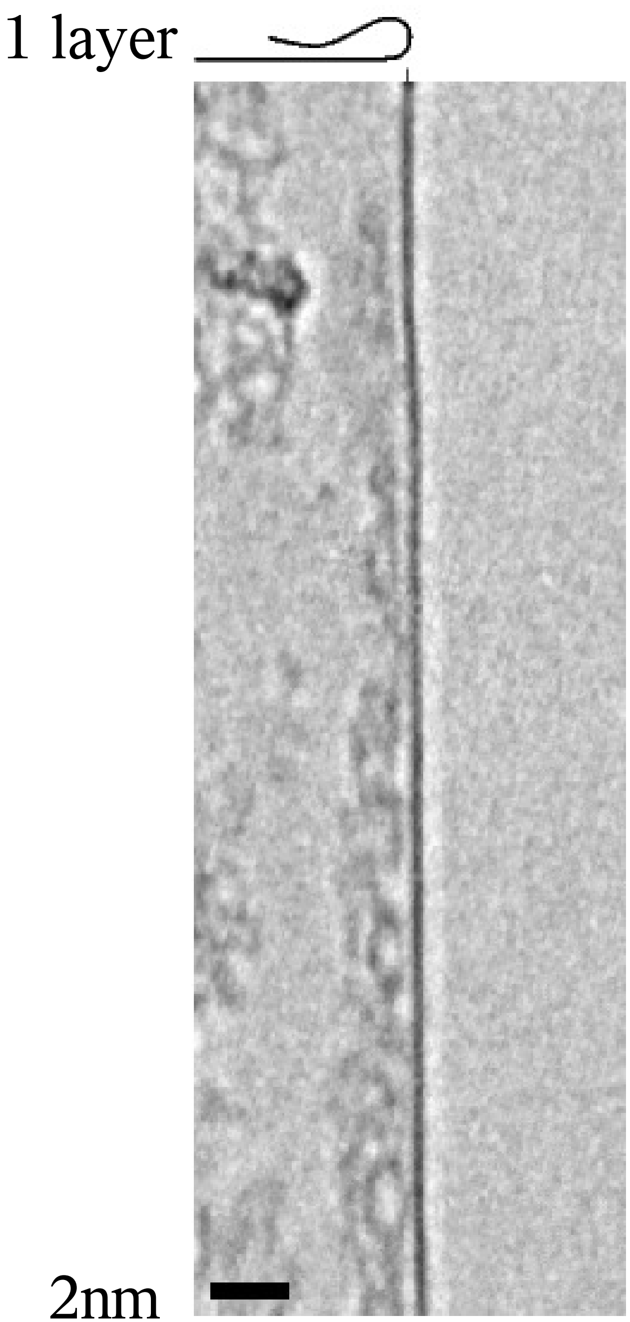

Two layers
3D FT

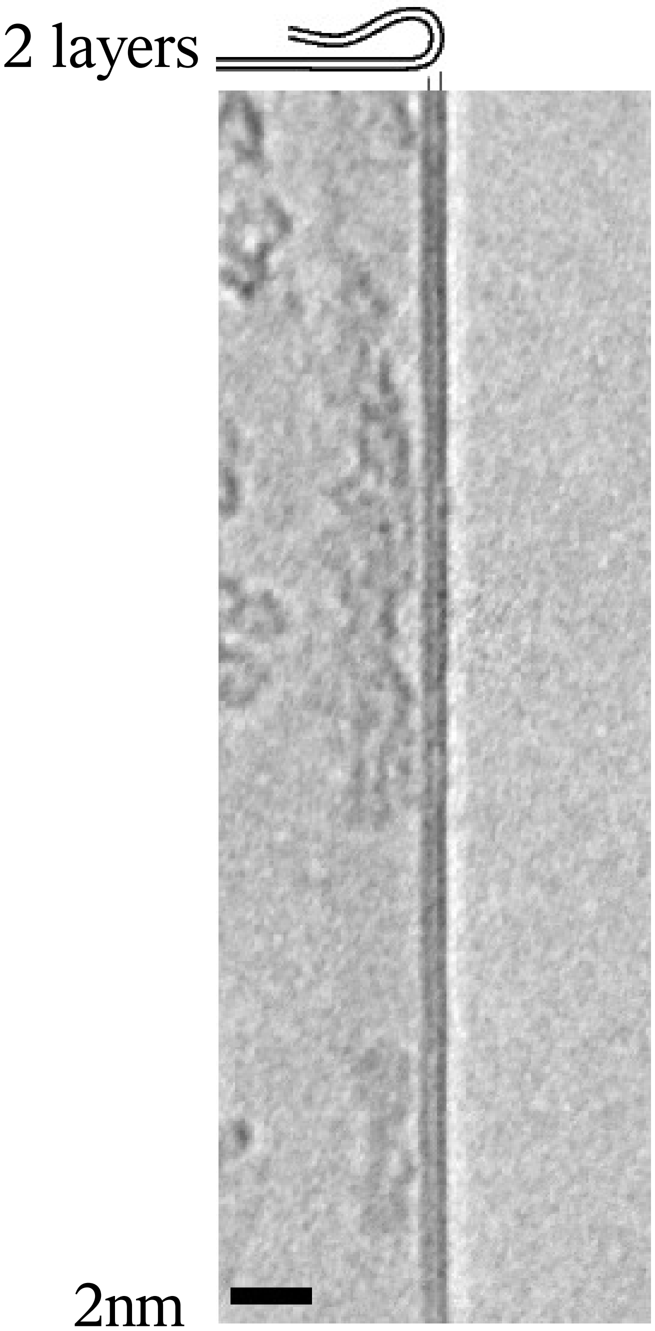
Diffraction intensity variation with tilt angle

<u>1 layer</u> <u>2 layers</u>

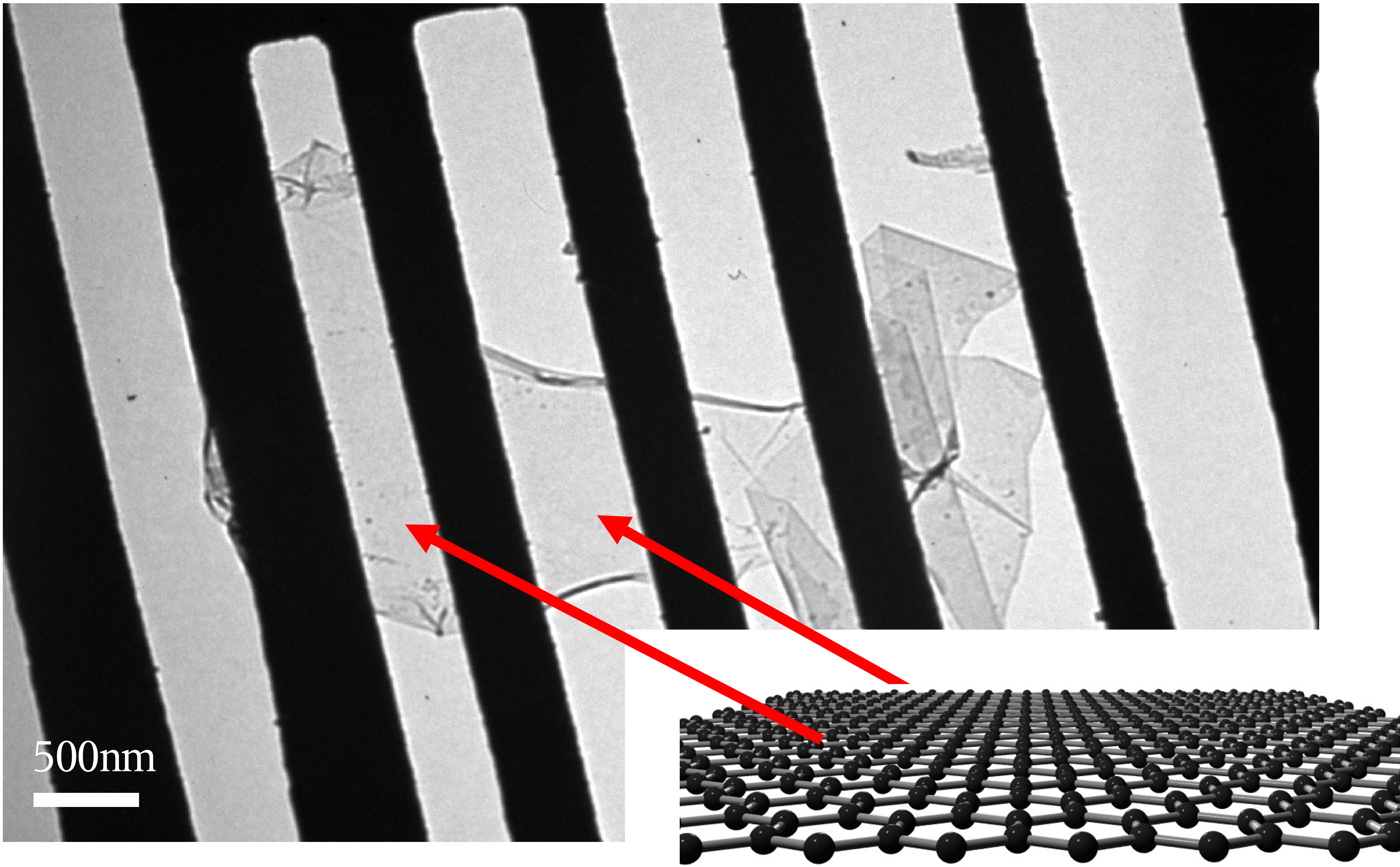


Foldings at edges





Free-standing graphene sheet

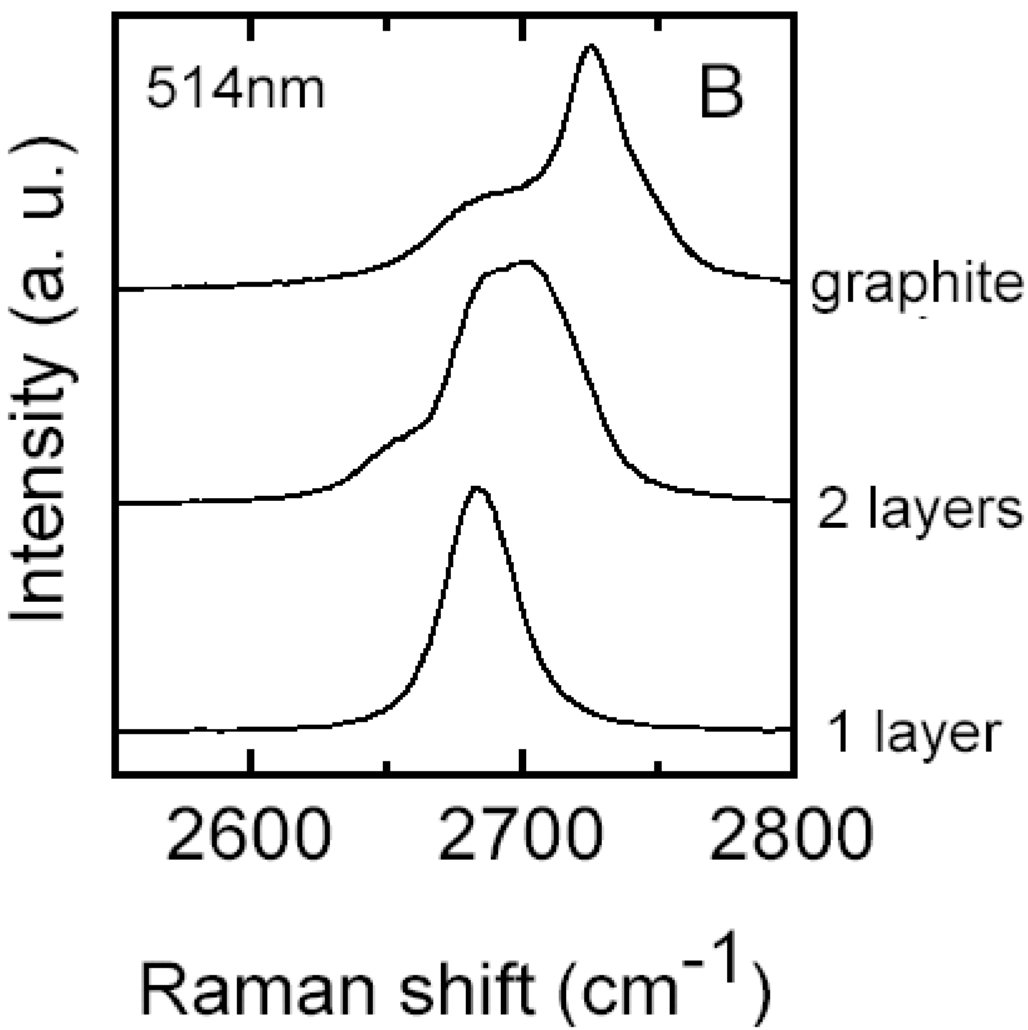


1 layer of graphene !
Free-standing monolayer

J. C. Meyer et al., Nature **446** (2007) 60-63

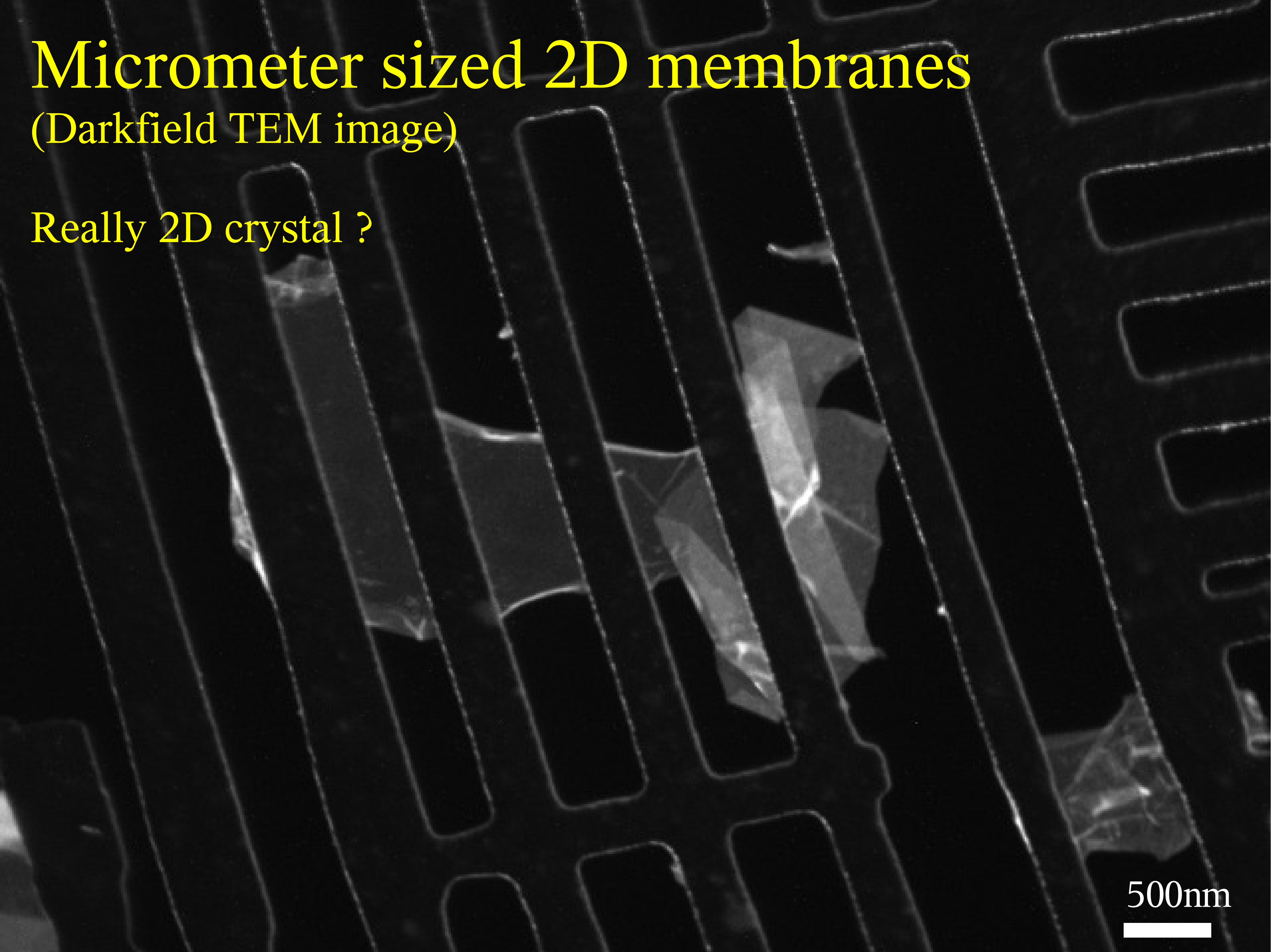
Raman spectroscopy on 1 and 2 layer graphene

Measured on THE SAME sheets as identified by TEM
-> Calibration of the Raman signal vs. number of layers

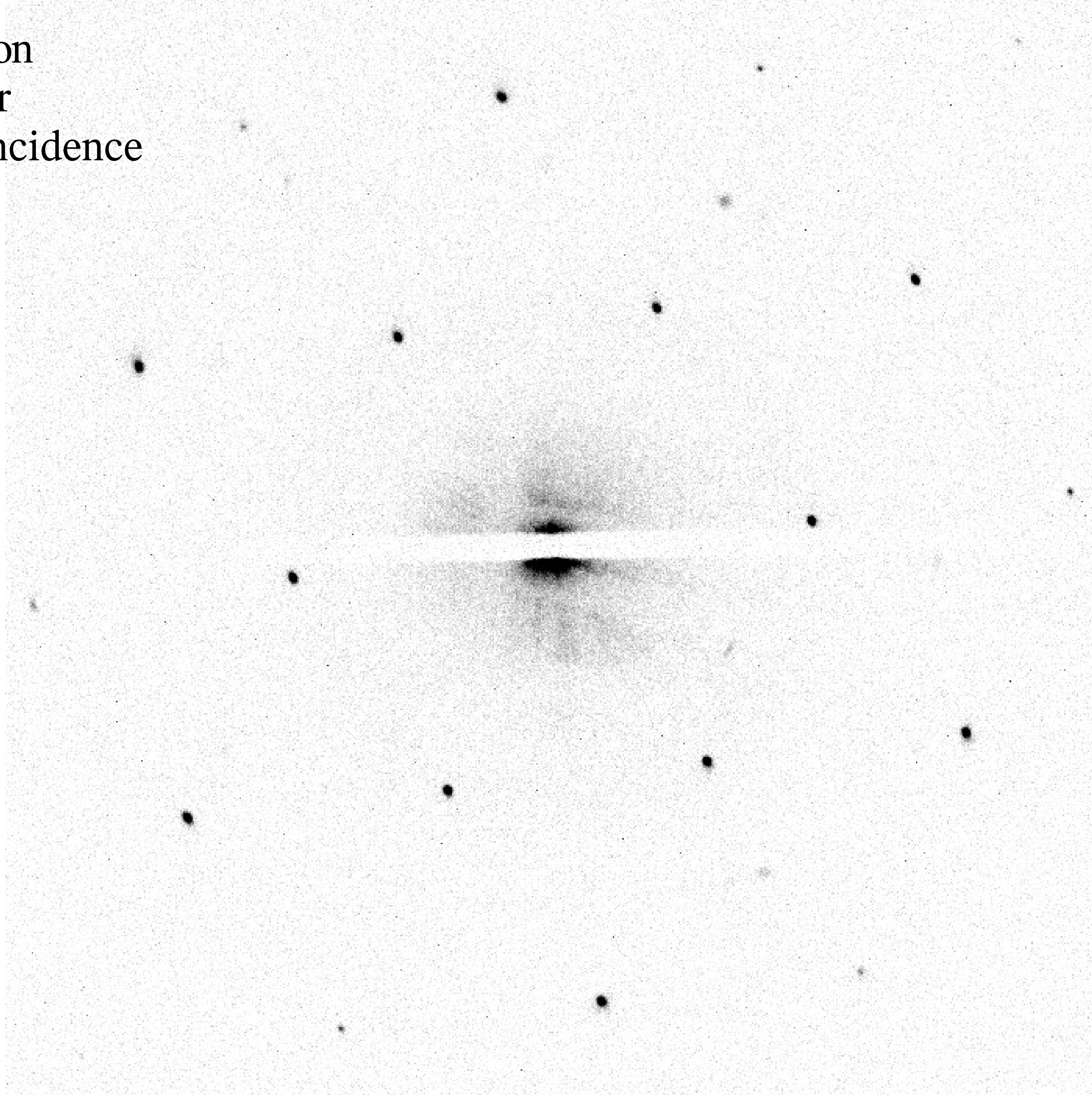


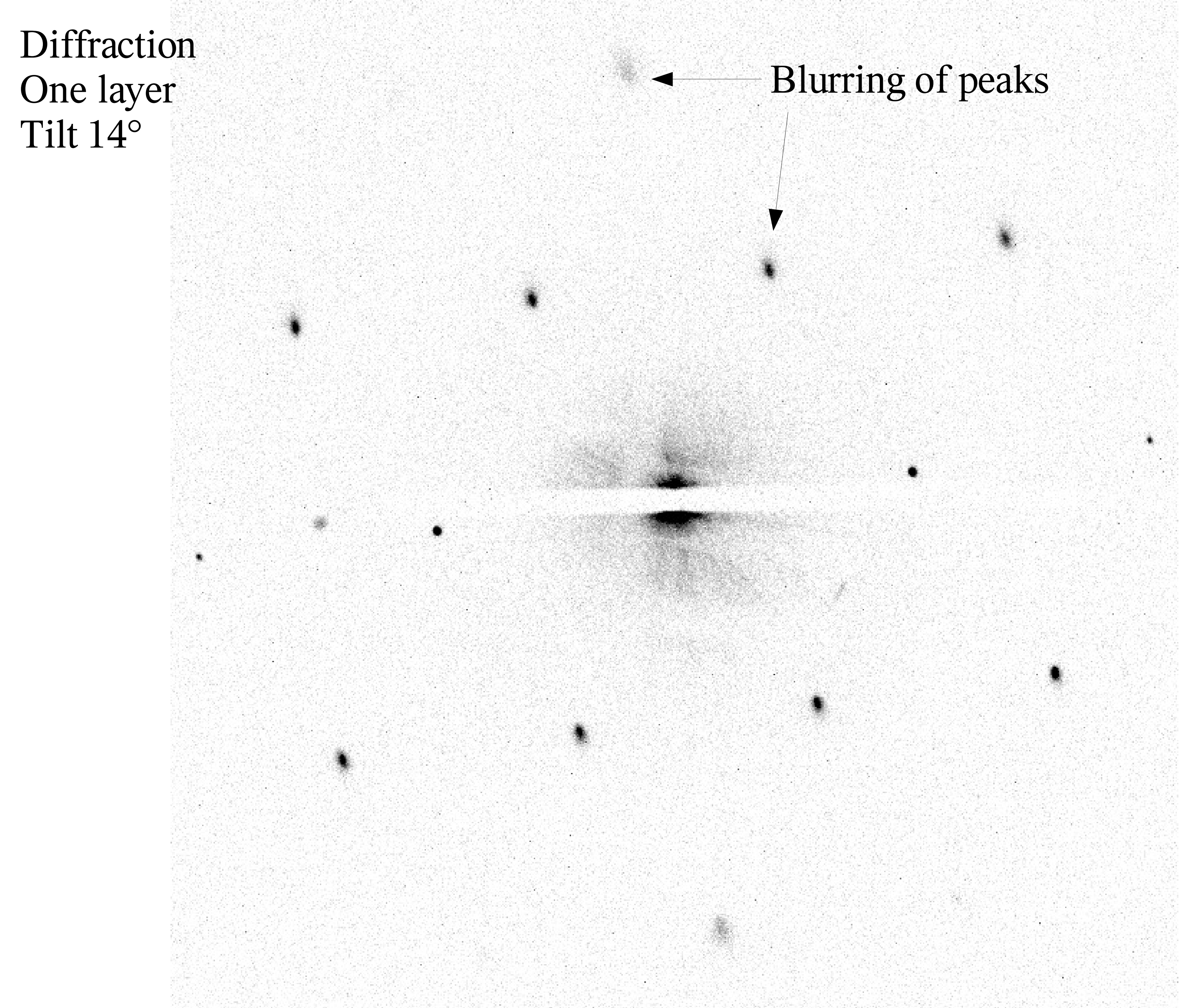
Mono-layer graphene can be unambiguously identified

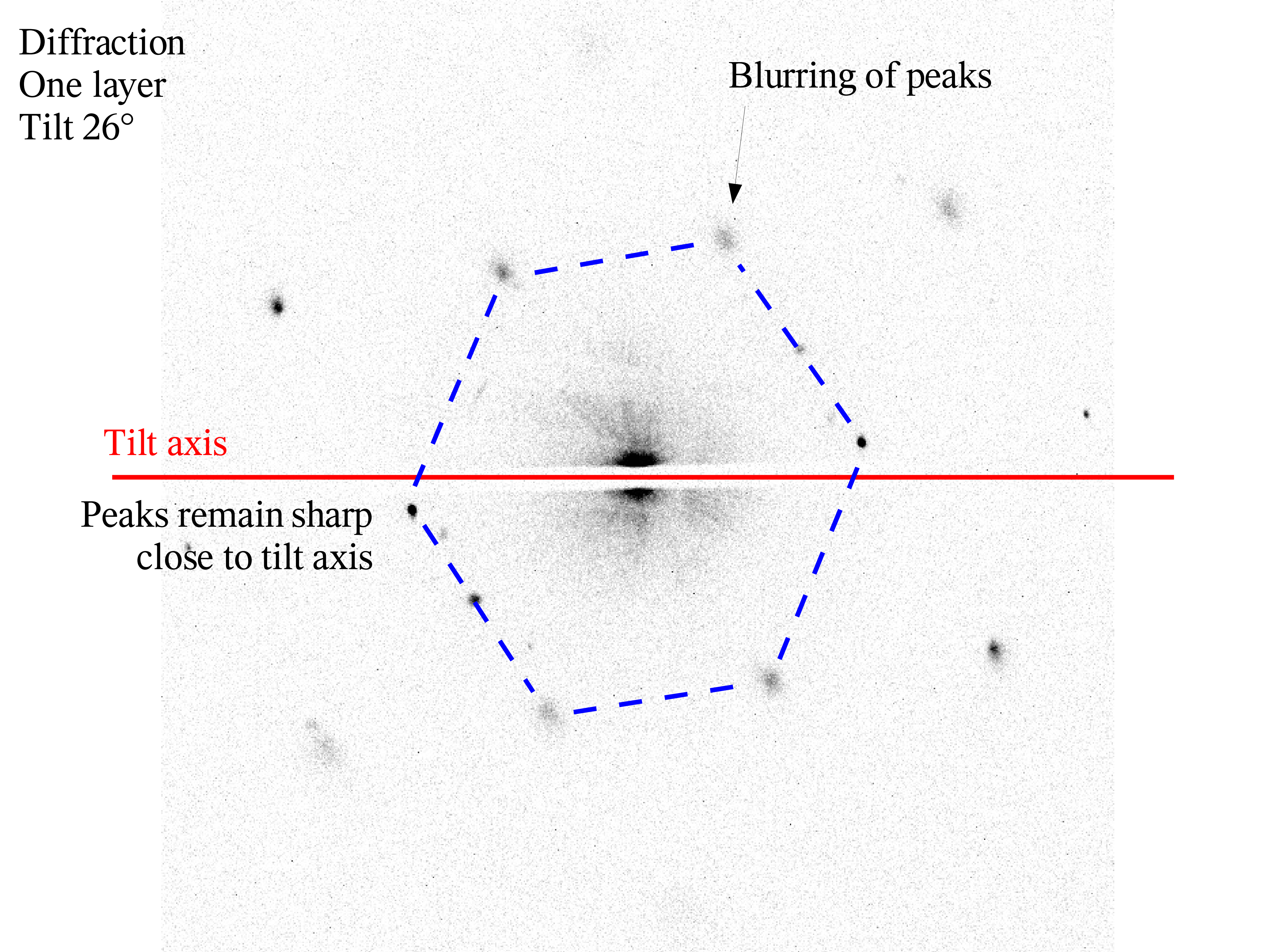
A. C. Ferrari, J. C. Meyer et al., Phys. Rev. Lett. **97**, 187401 (2006)


Micrometer sized 2D membranes
(Darkfield TEM image)
Really 2D crystal ?
500nm

Diffraction
One layer
normal incidence

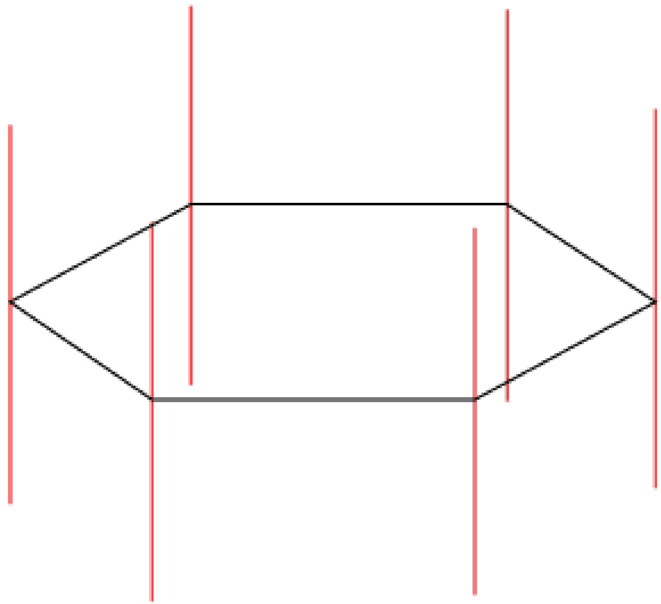



Diffraction
One layer
Tilt 14°
Blurring of peaks

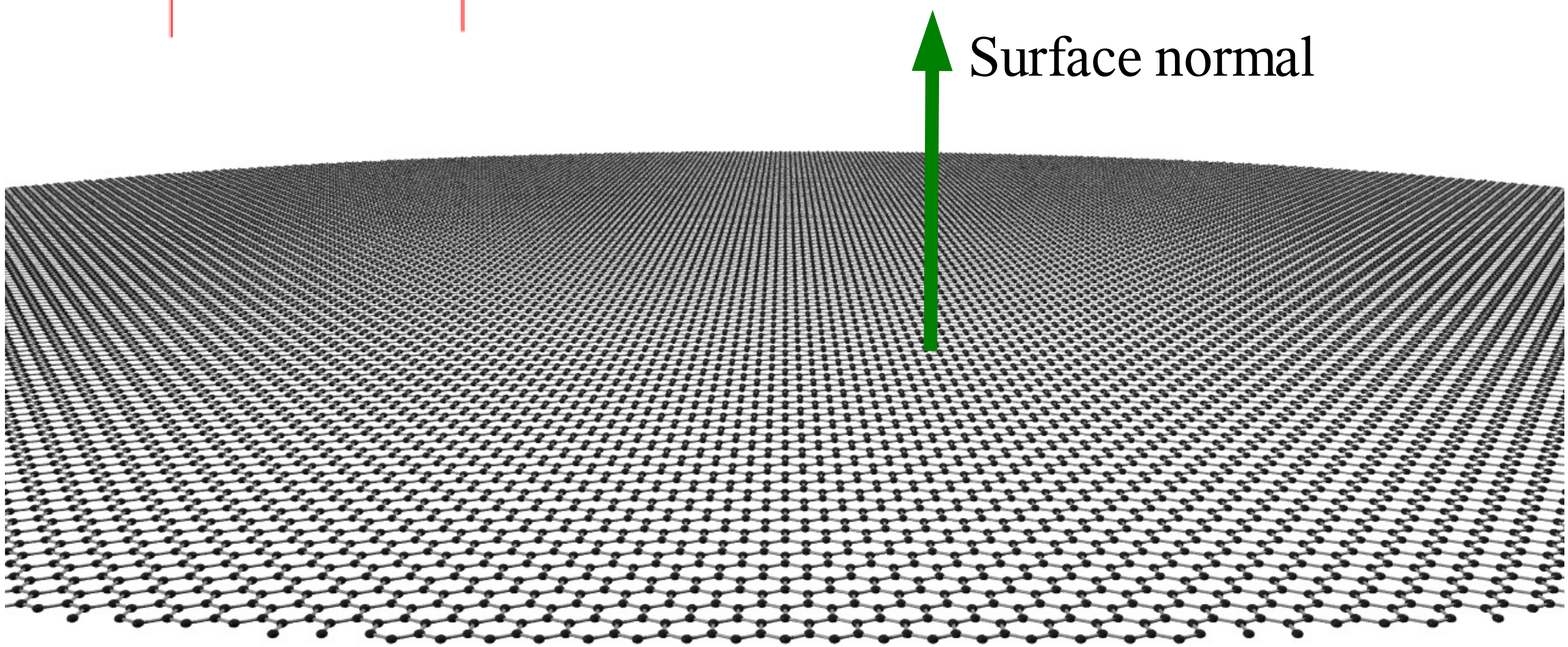


Diffraction
One layer
Tilt 26°
Blurring of peaks
Tilt axis
Peaks remain sharp
close to tilt axis

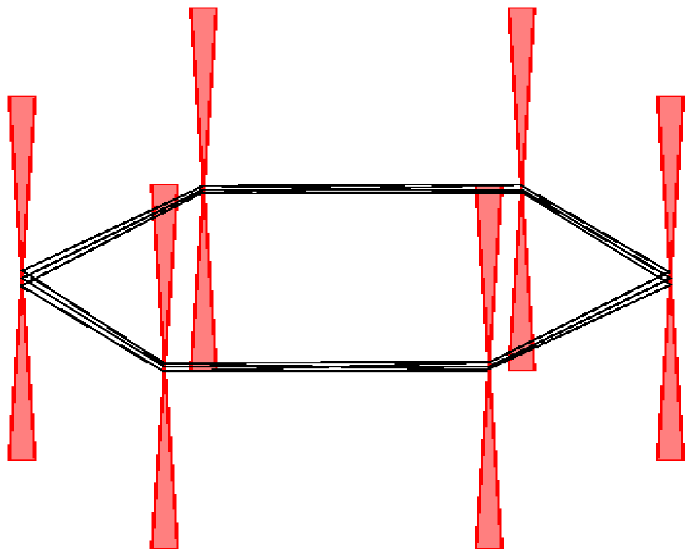
Explanation: Graphene sheet is not flat !



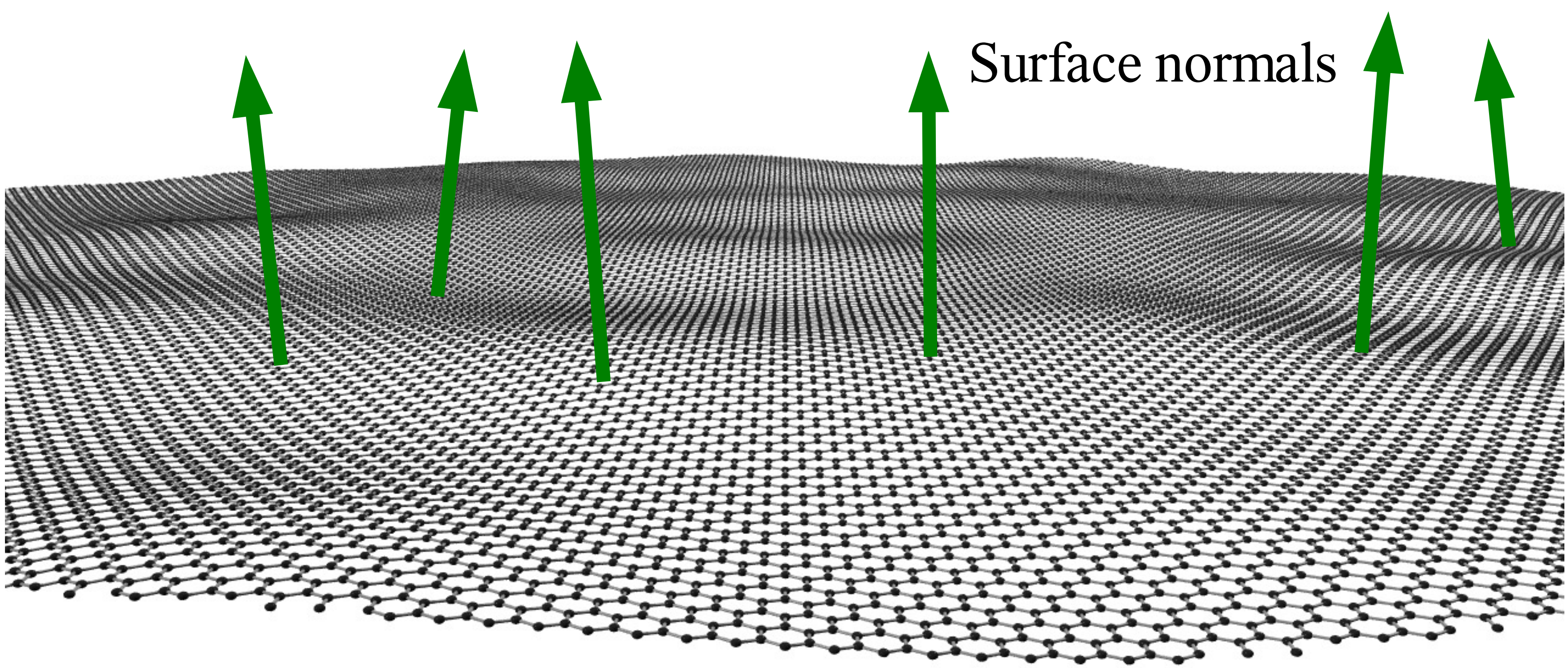
Flat sheet: Nonzero intensities on rods in reciprocal space

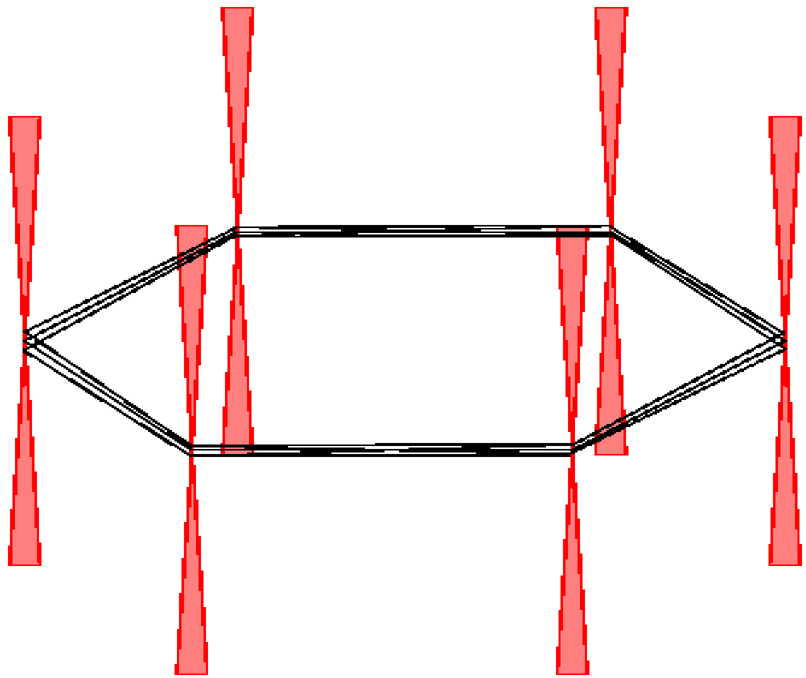


Explanation: Graphene sheet is not flat !

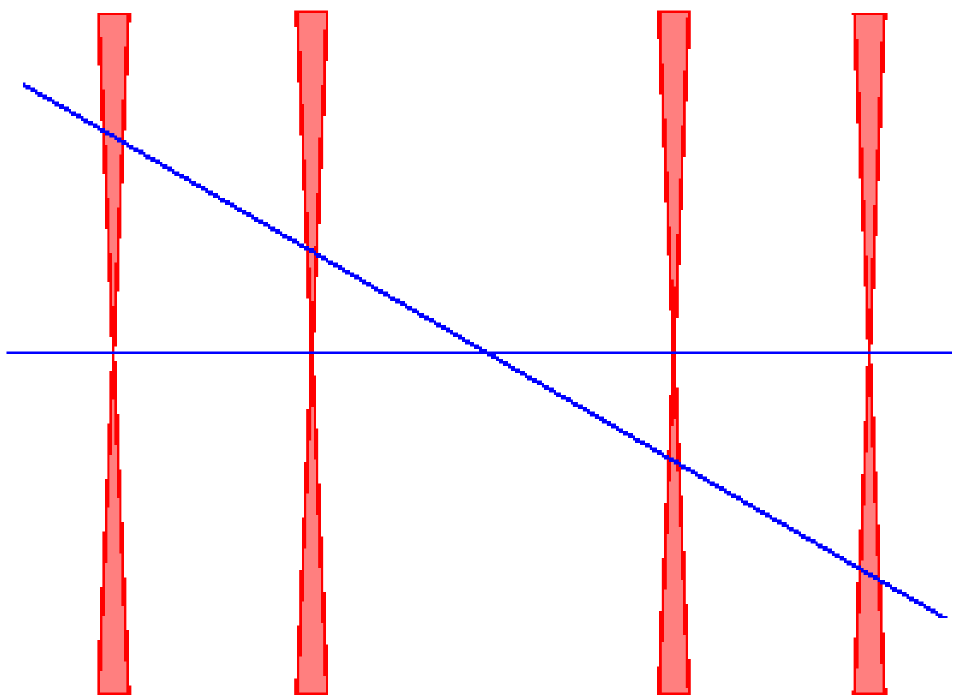


Curved sheet: Incoherent superposition of many slightly tilted contributions (small variation in surface normal)





Non-zero intensities on a cone in reciprocal space



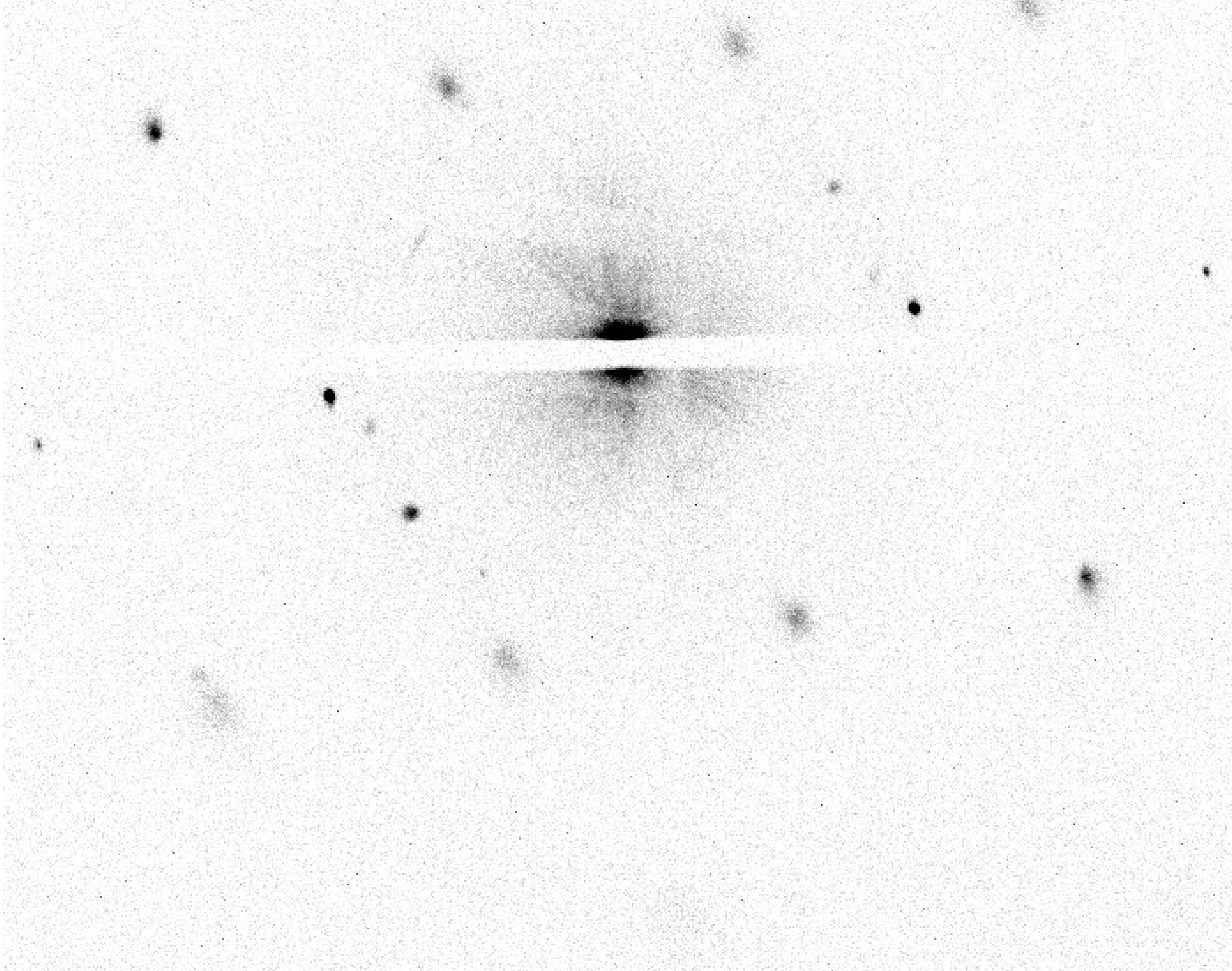
Blue line = slice of Fourier space (section of Ewald sphere) for diff-pattern.

Normal incidence: Sharp peaks (if angle variations are small)

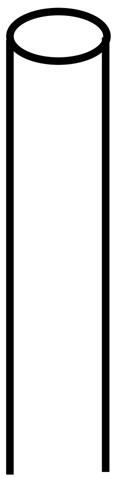
Tilted incidence: Blur visible

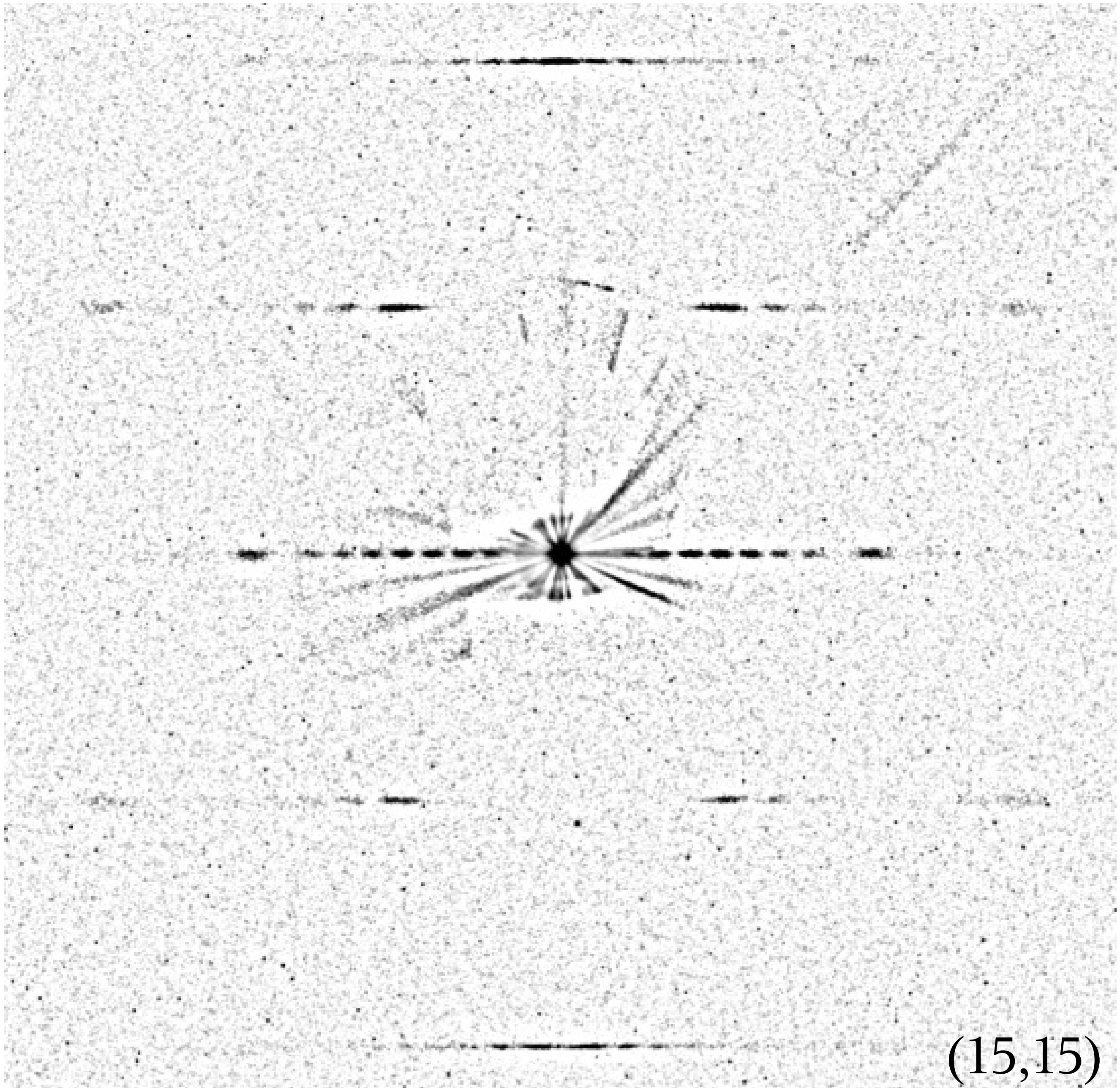
Blur of peaks is **isotropic**; peaks are well fitted by gaussians.

Rigid membrane
can **not** be curved in two directions



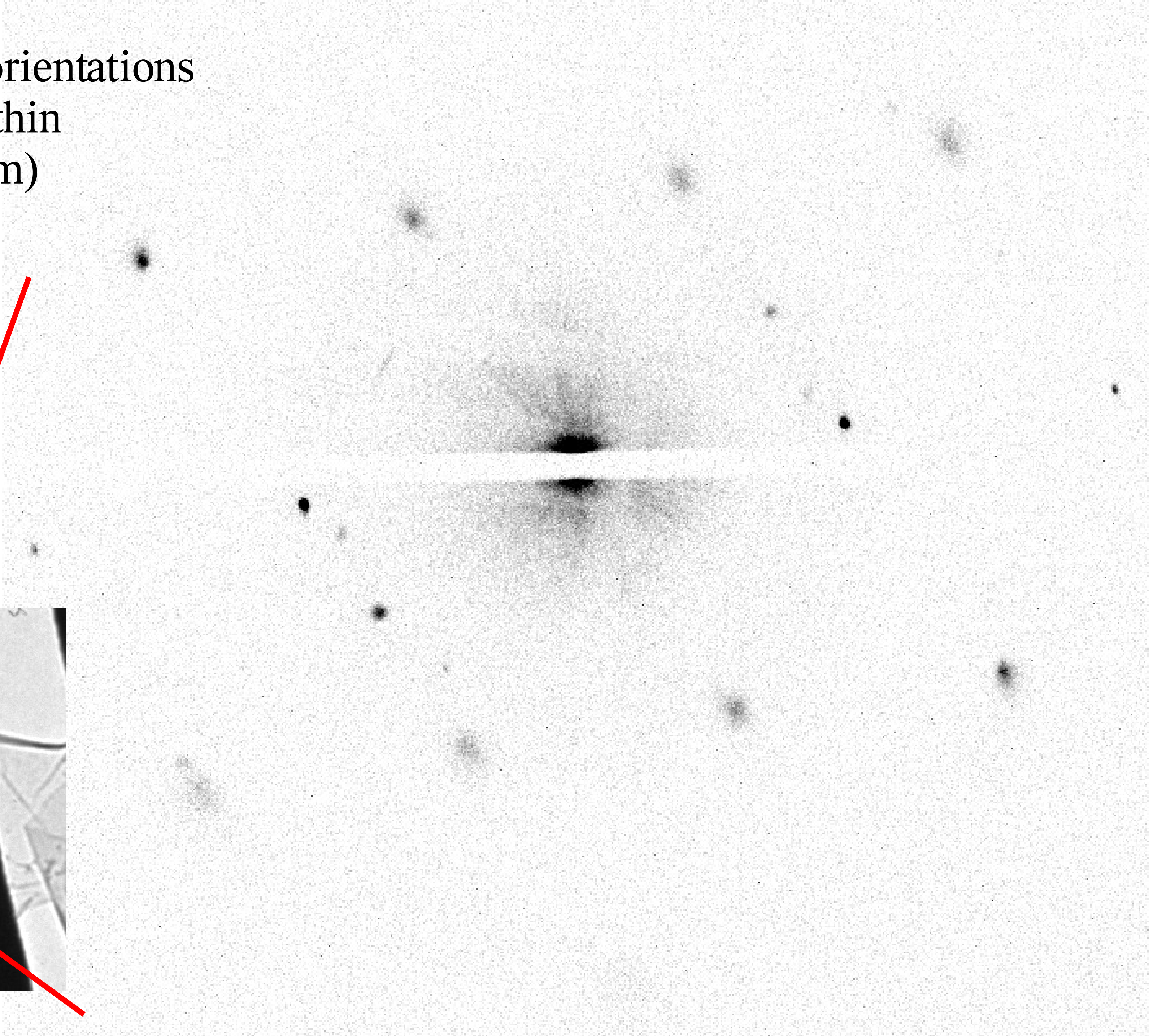
Single-walled carbon nanotube (SWNT) diffraction pattern for comparison: cylinder shape -> peaks spread into line

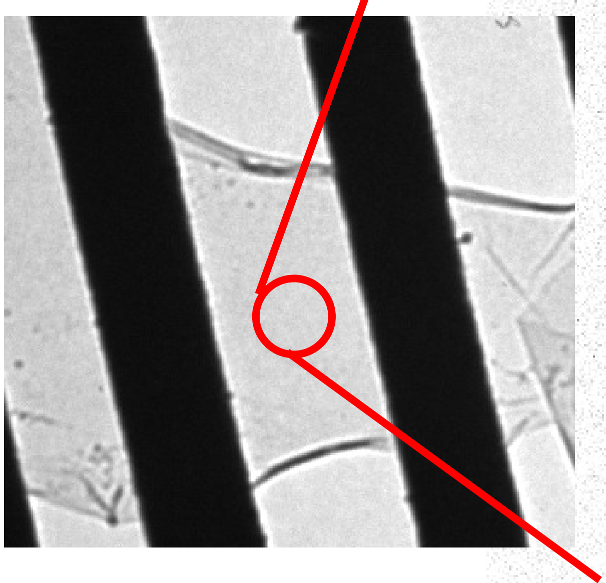




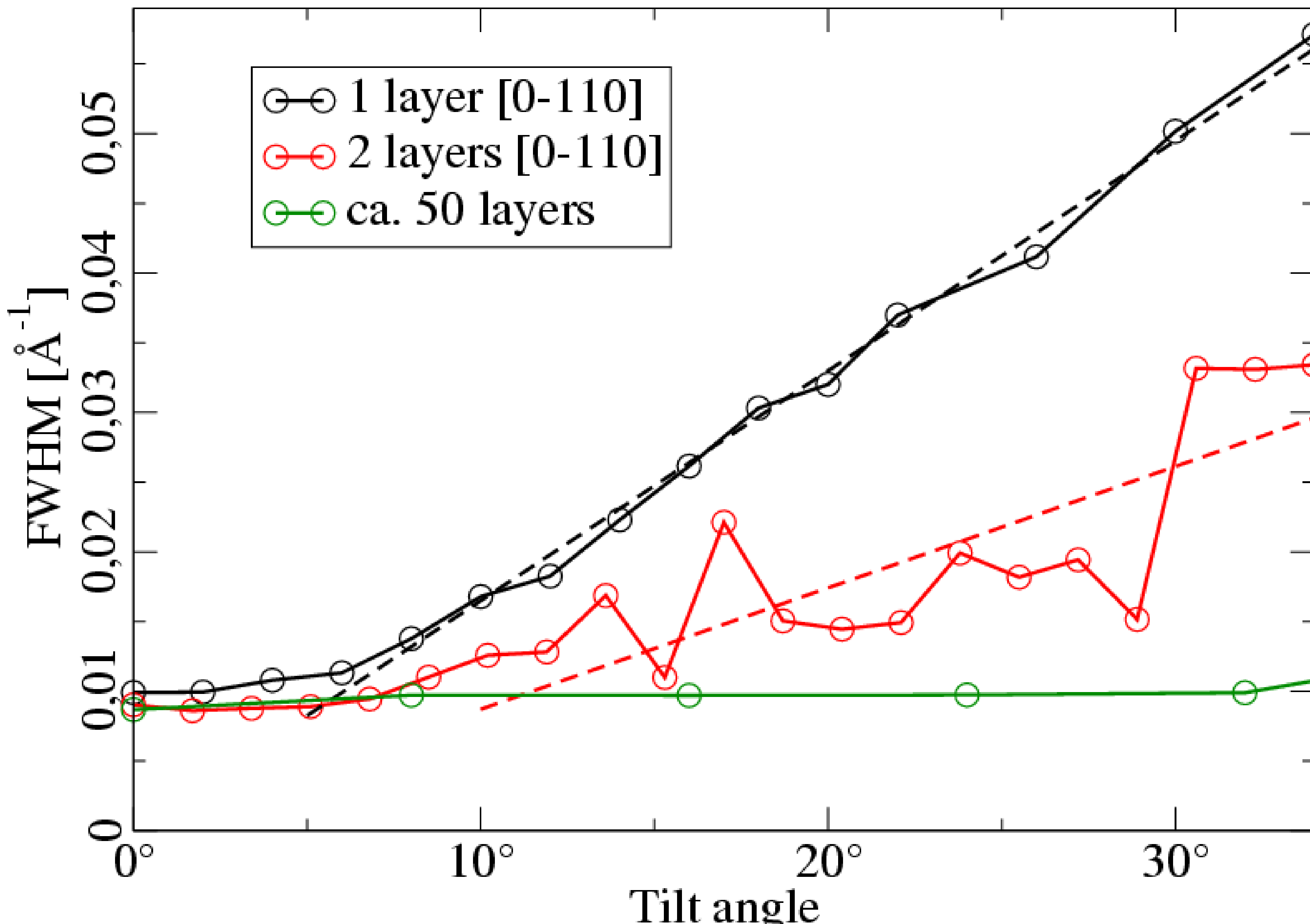
Blur of peaks is **isotropic**; peaks are well fitted by gaussians.

-> many different orientations must be present within a very small (250nm) region



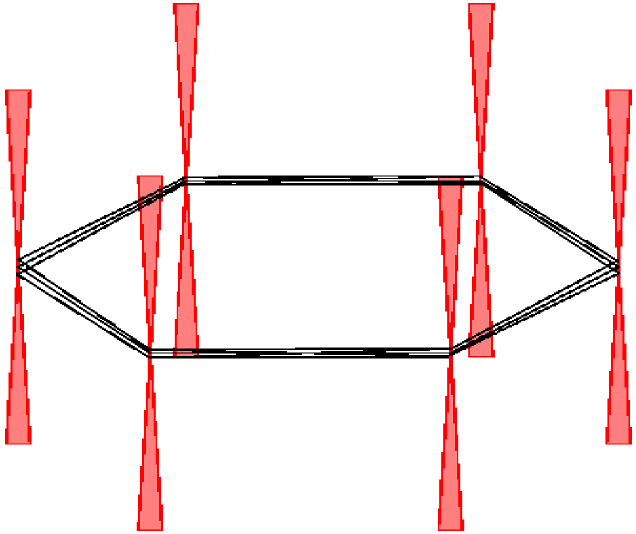


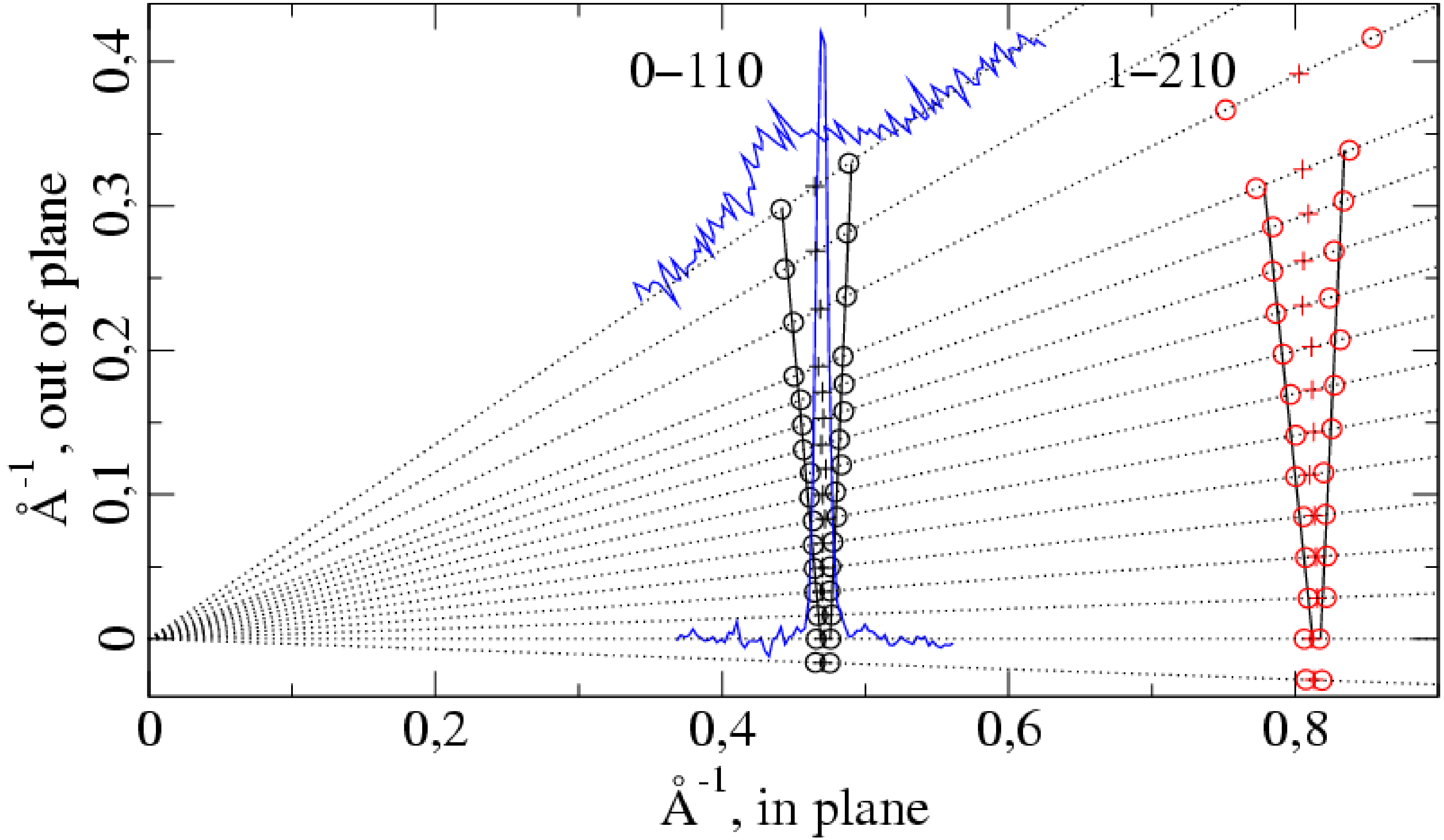
Quantitative Analysis:
Gauss fit to each peak. Analysis width vs. tilt angle.



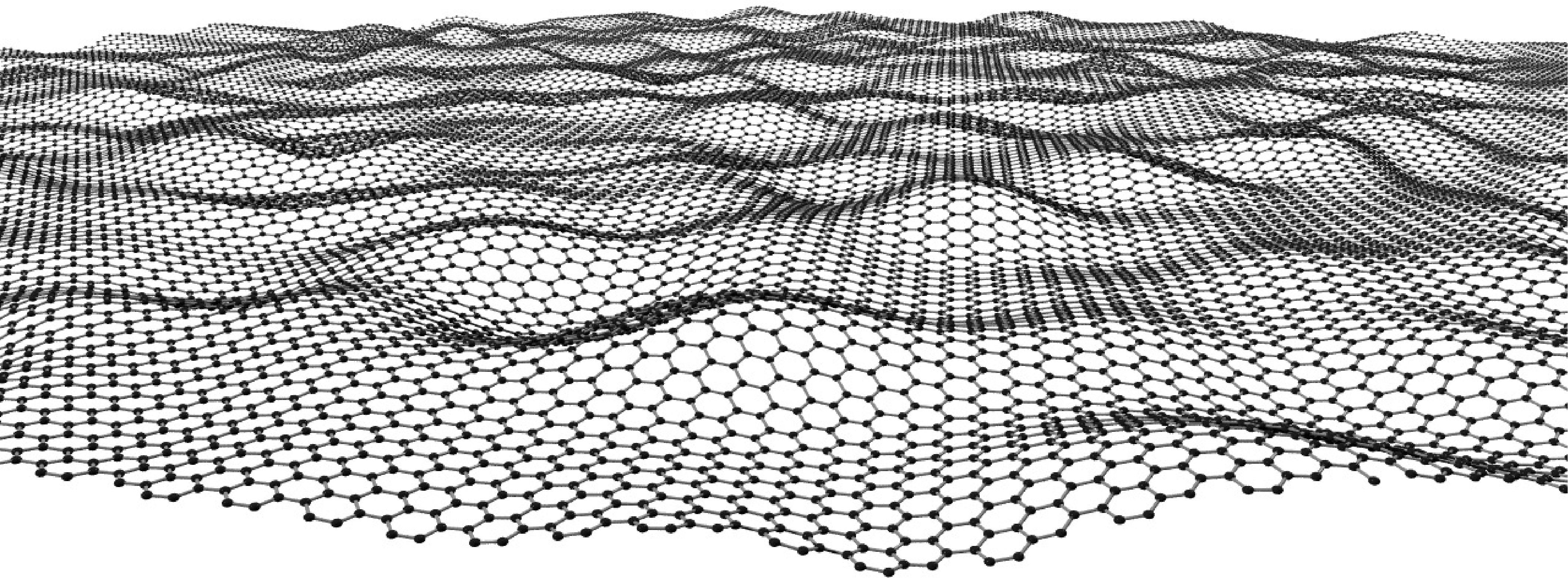
Cones in Fourier space: Peak width vs. incidence angle

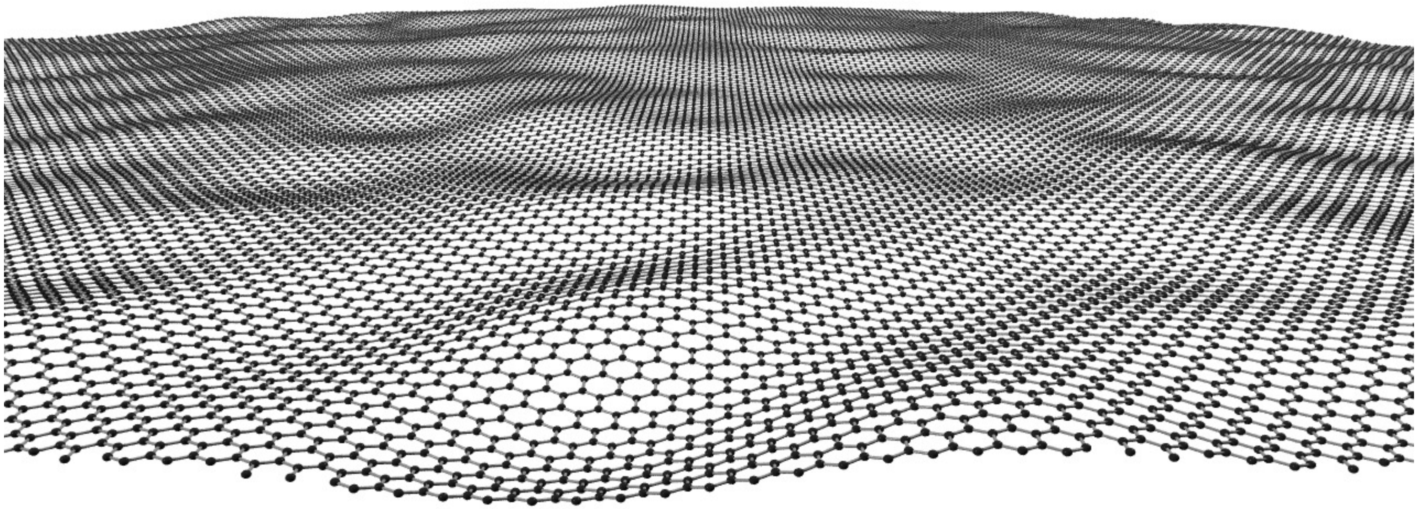
Cone angle is 11° => 5° variation in surface normal



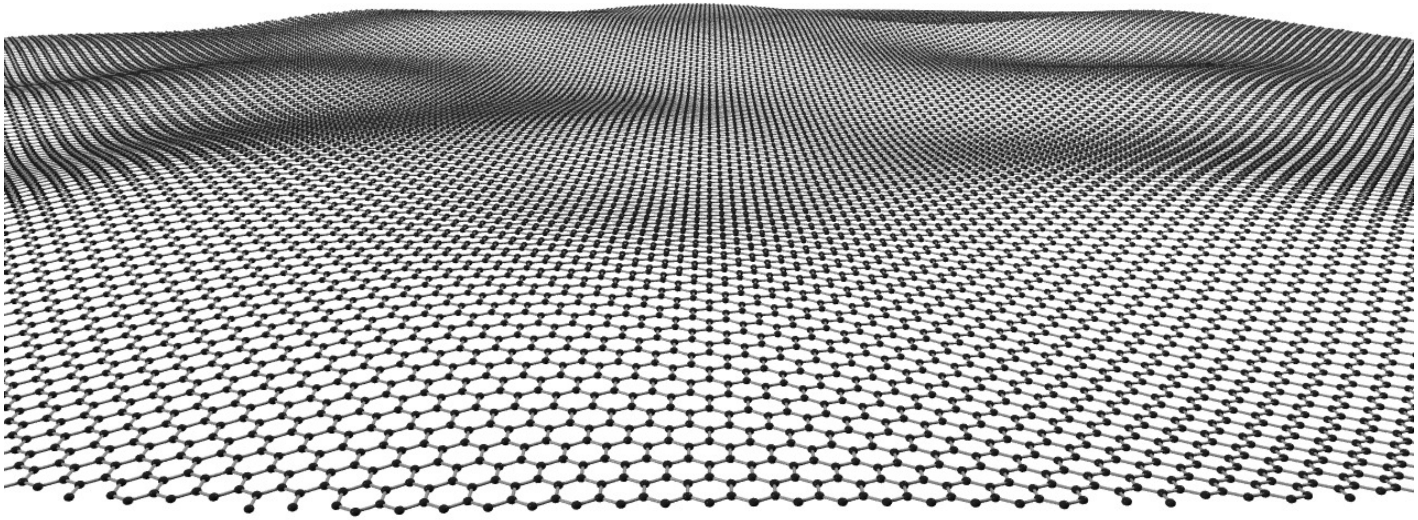


Suspended Graphene sheets are not flat !!!



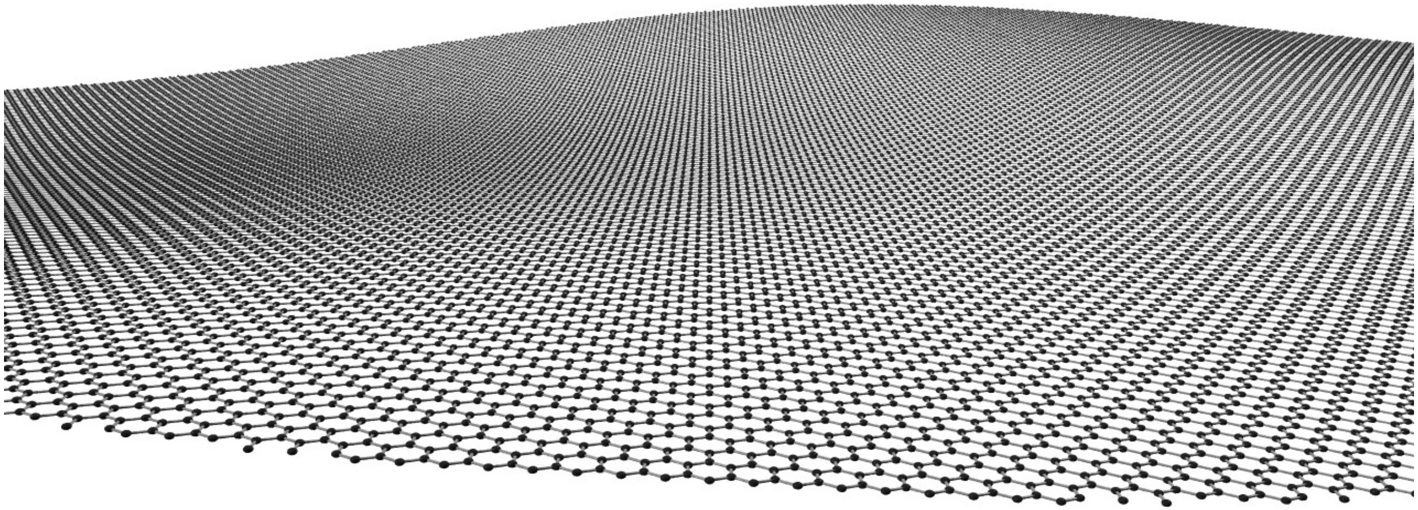


Variations smaller than coherence length of diffracting electrons would not lead to blurring
(=> can be excluded)

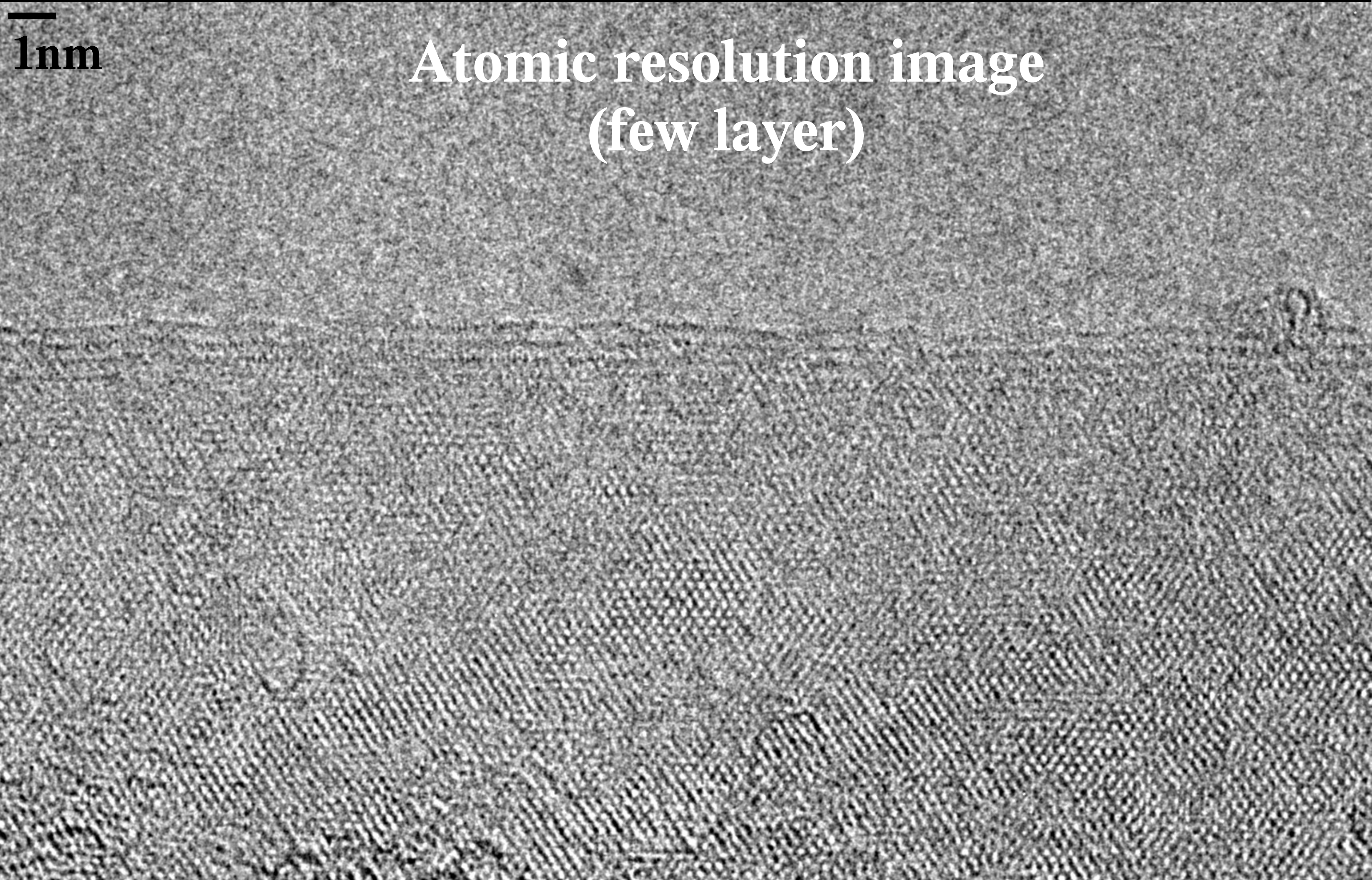


Variations of 5..10nm size, height 0.5-1nm:

Simulations agree with results.



Very large ripples (>=20nm): individual configuration should be visible (which is not the case).

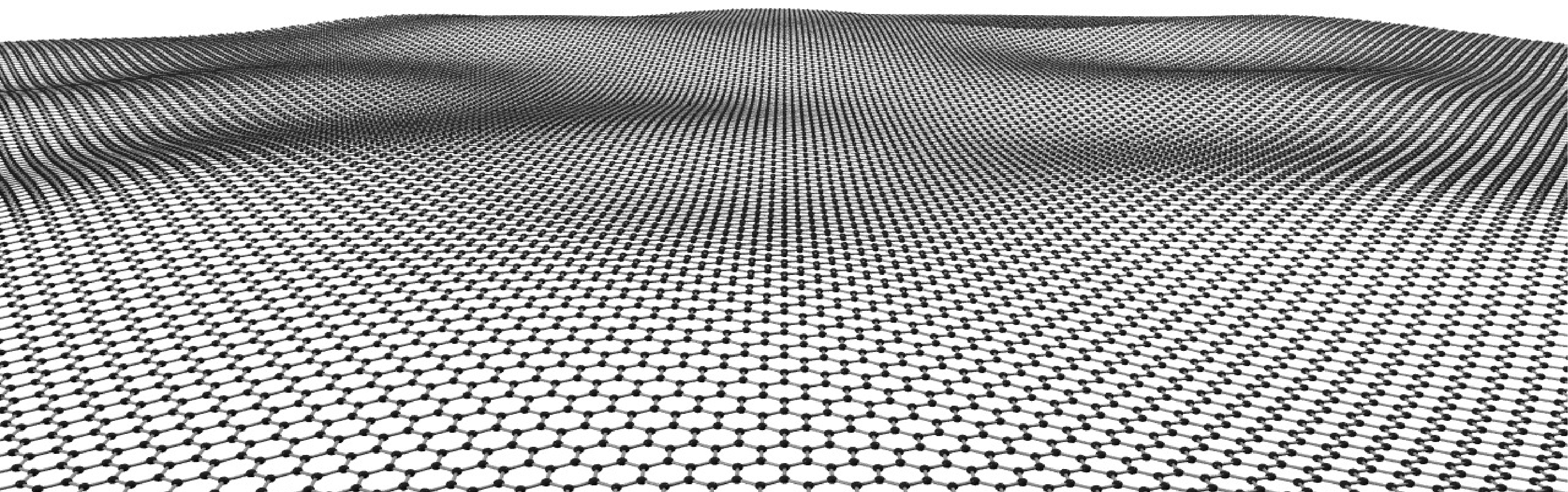

1nm
Atomic resolution image
(few layer)

Graphene membranes

<u>Structural modifications</u> of the 2D lattice

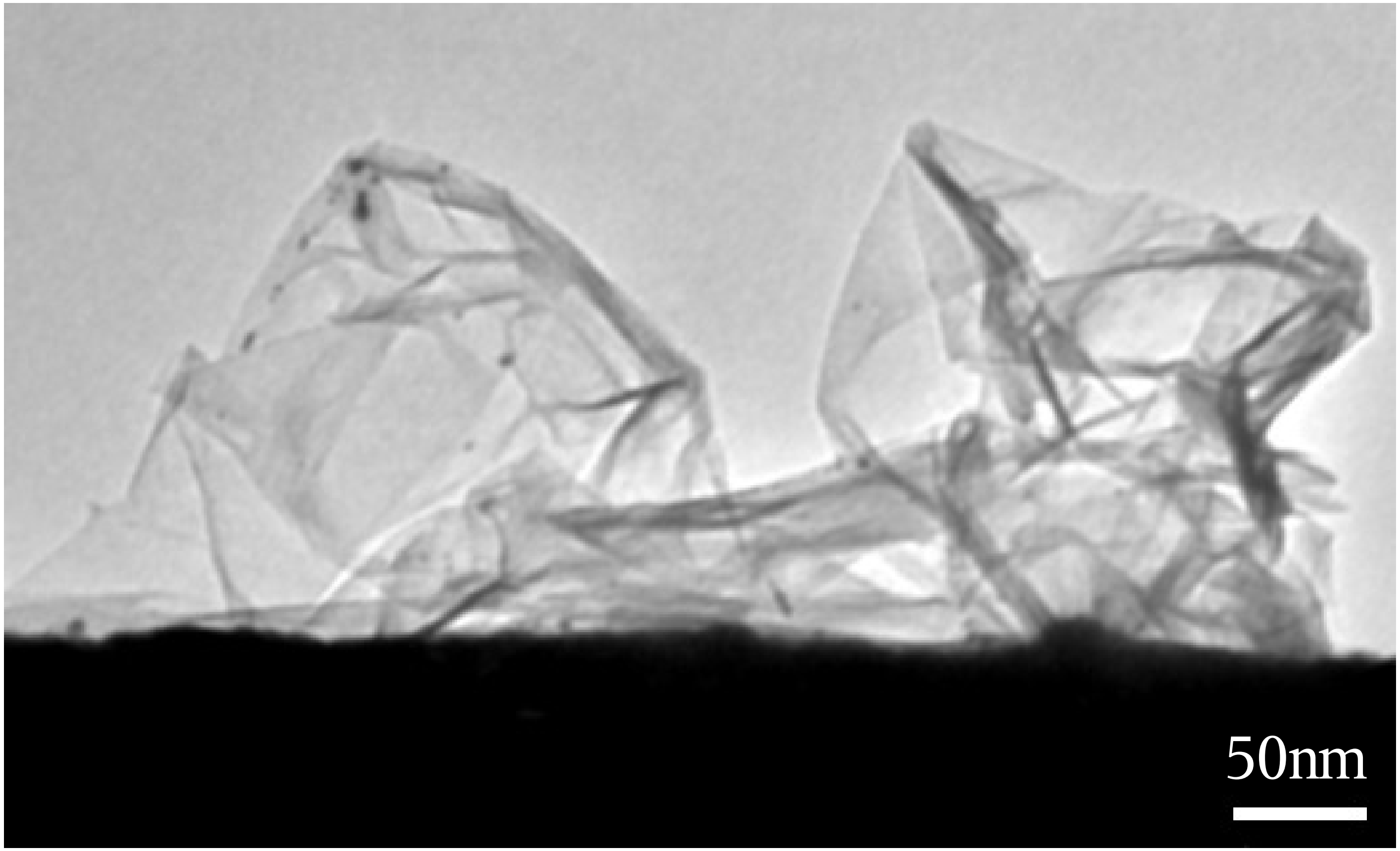
2D membrane is not confined in the 3rd direction

spontaneous, random deformations



Other conformations of graphene

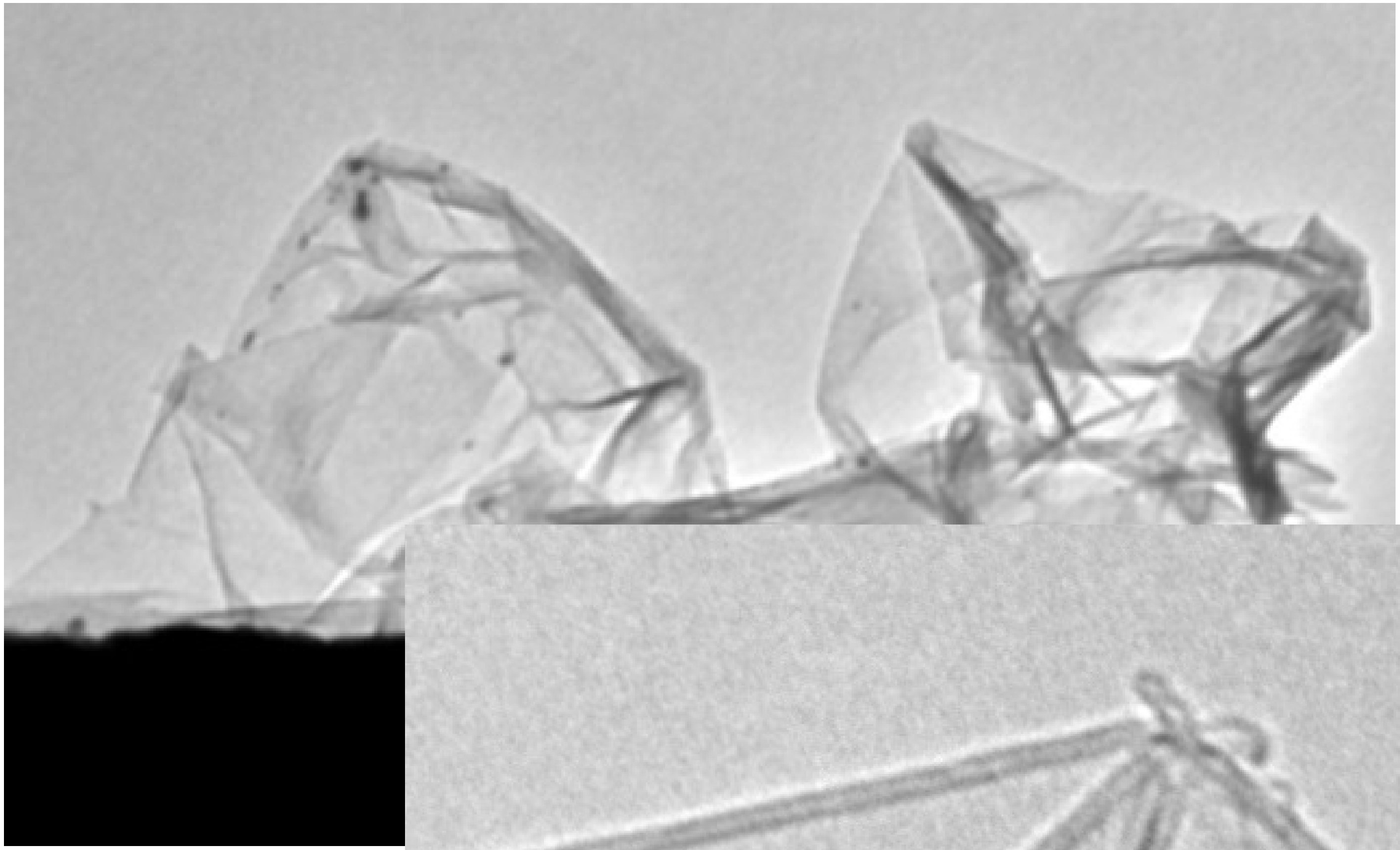
"Crumpled" sheets

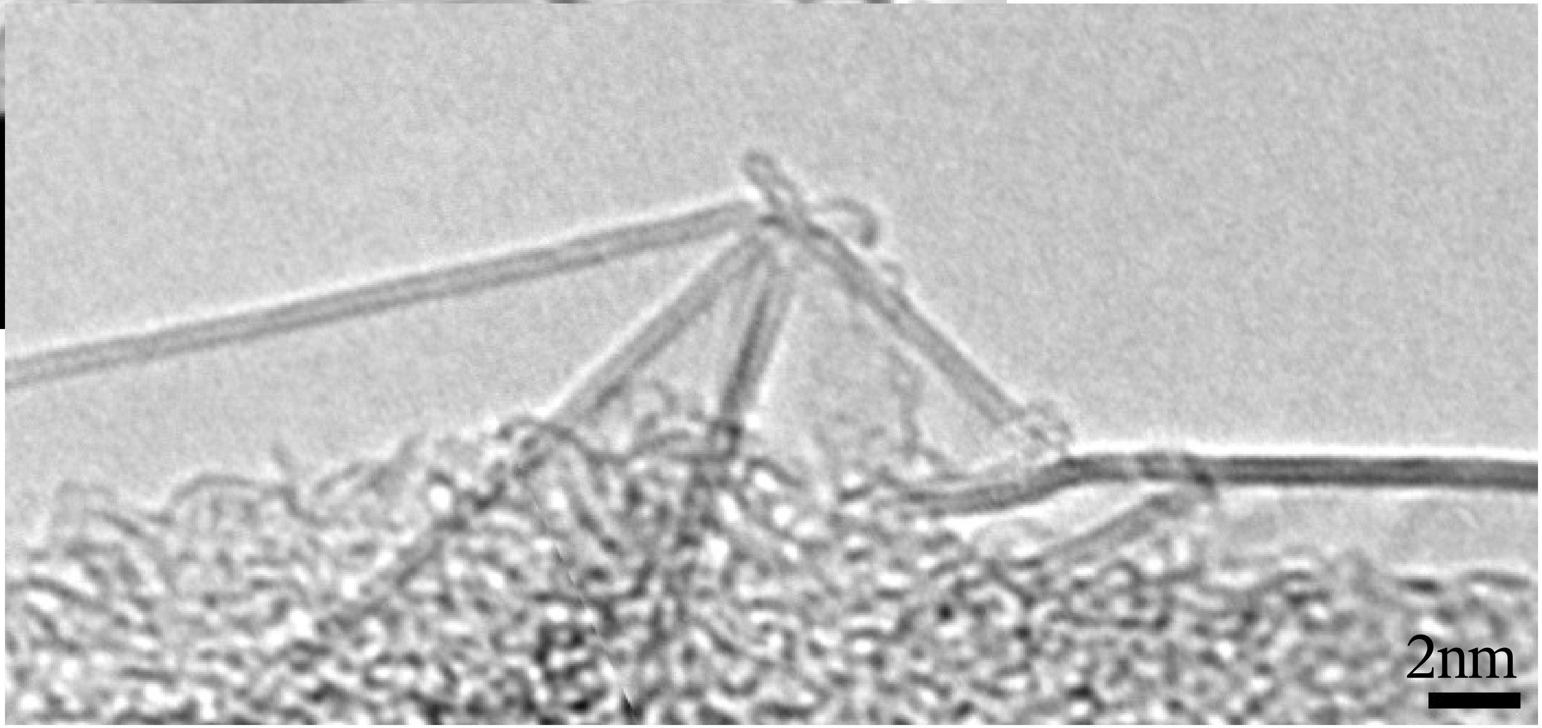


cond-mat/0703033

Other conformations of graphene

"Crumpled" sheets

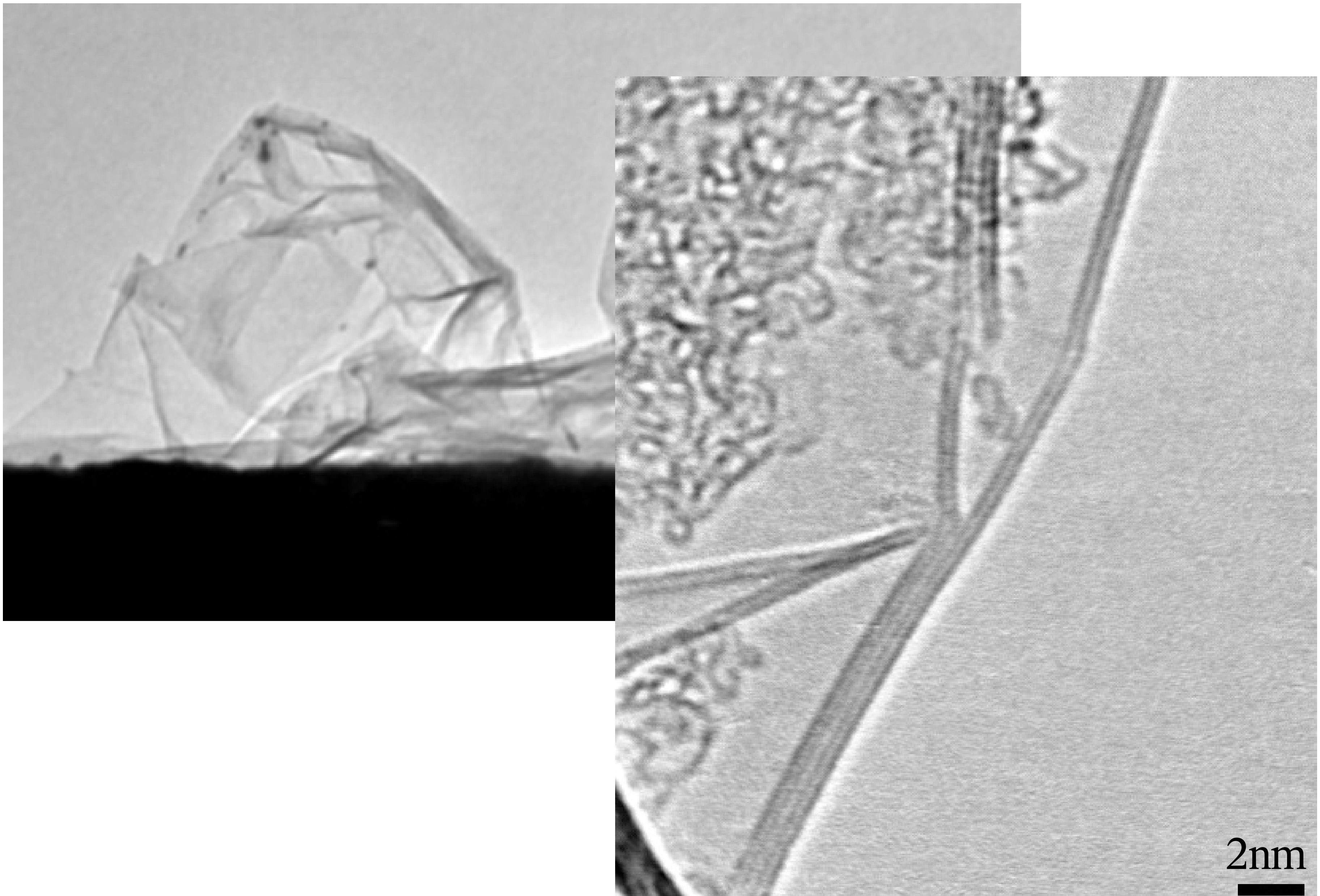




cond-mat/0703033

Other conformations of graphene

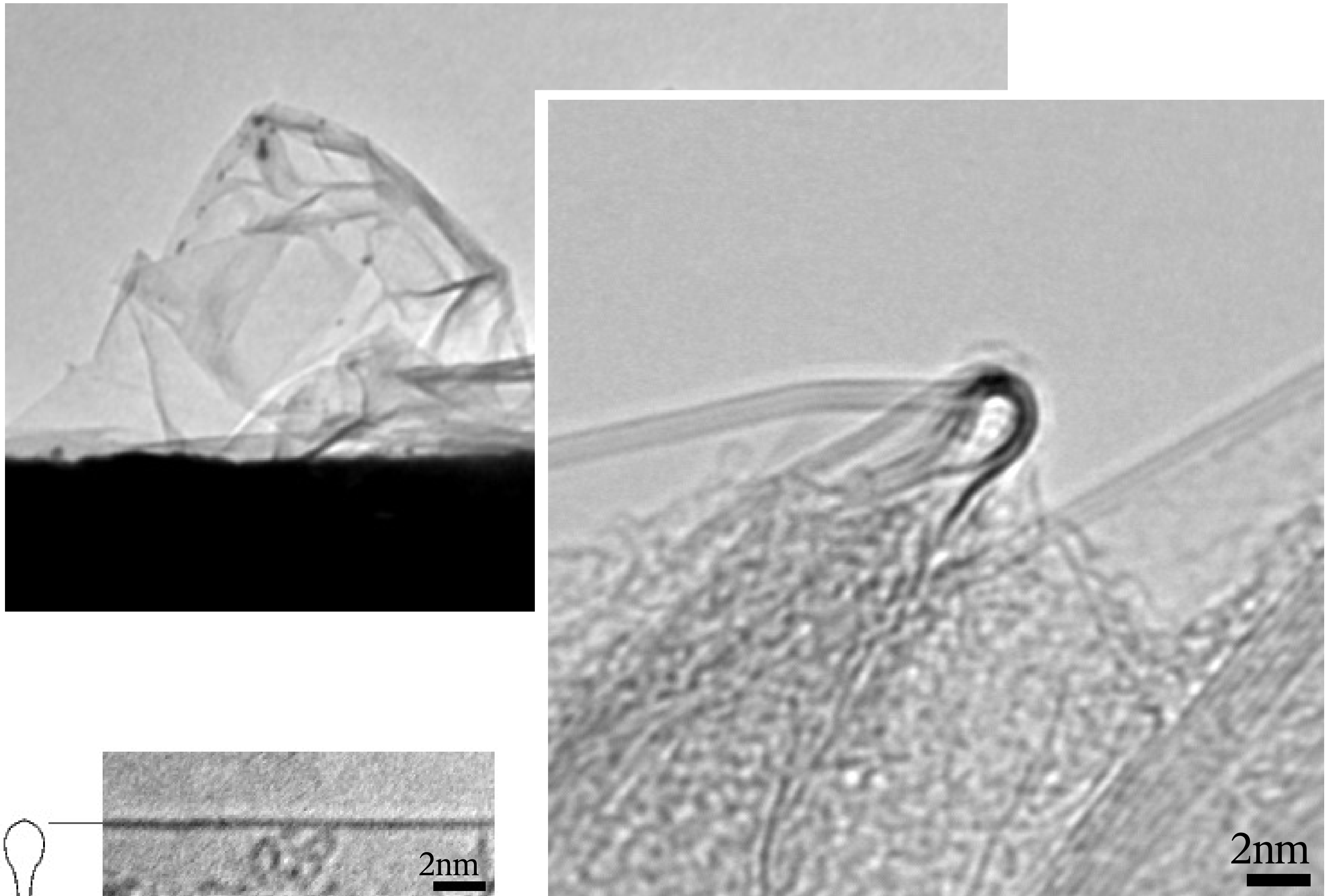
"Crumpled" sheets



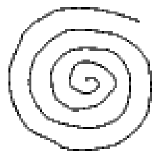
cond-mat/0703033

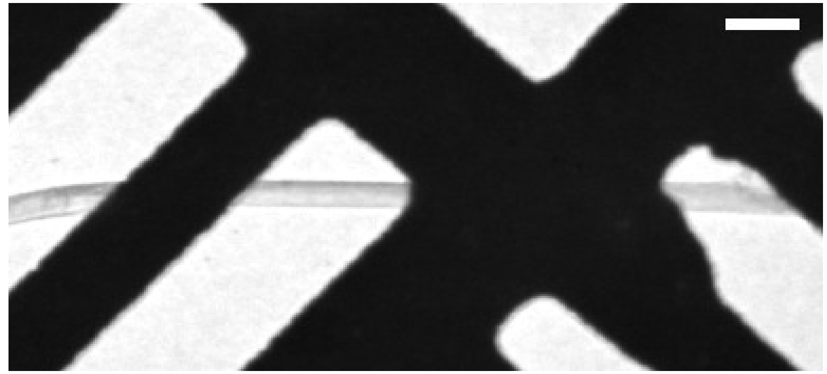
Other conformations of graphene

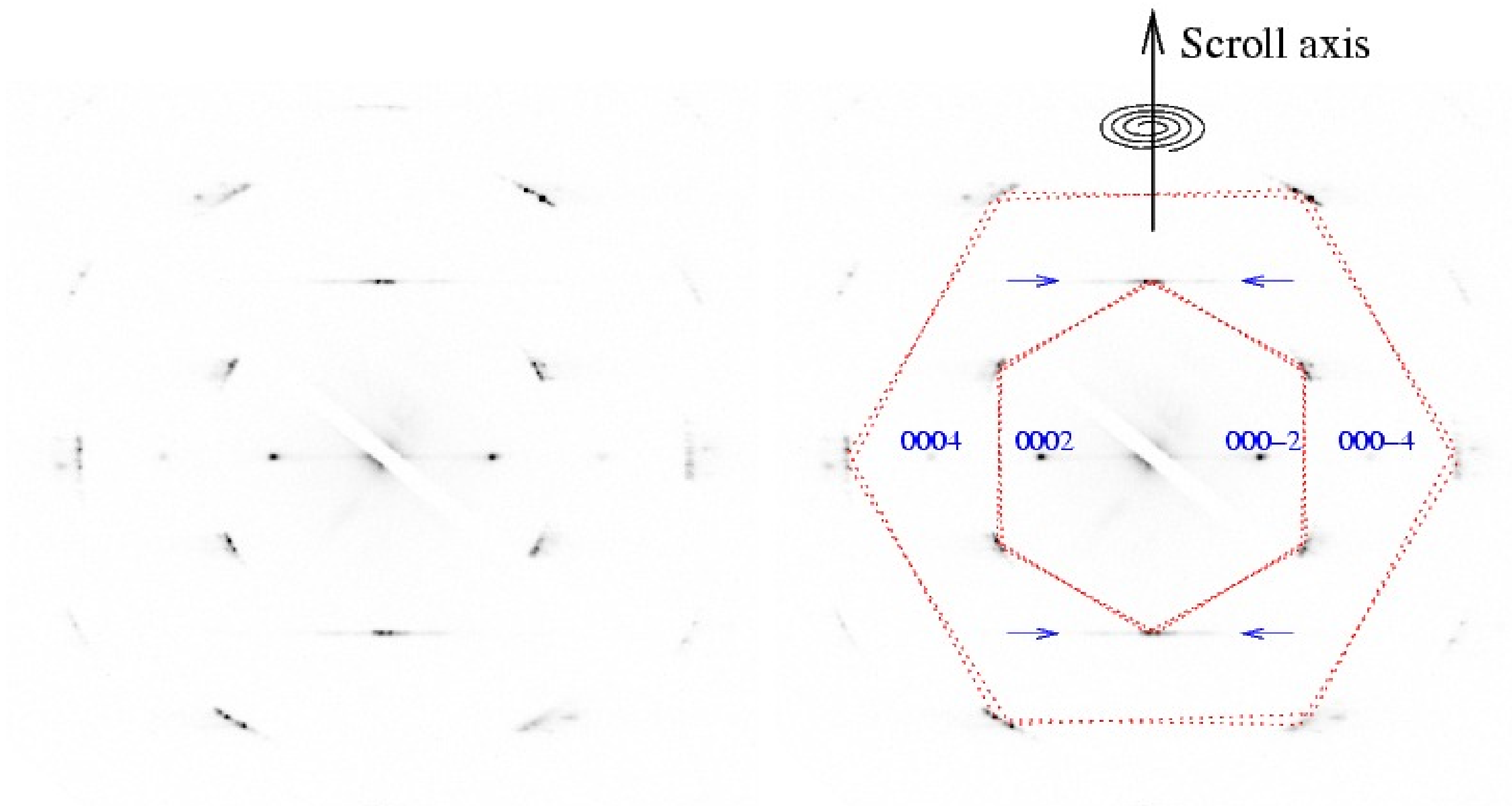
"Crumpled" sheets



Scrolls







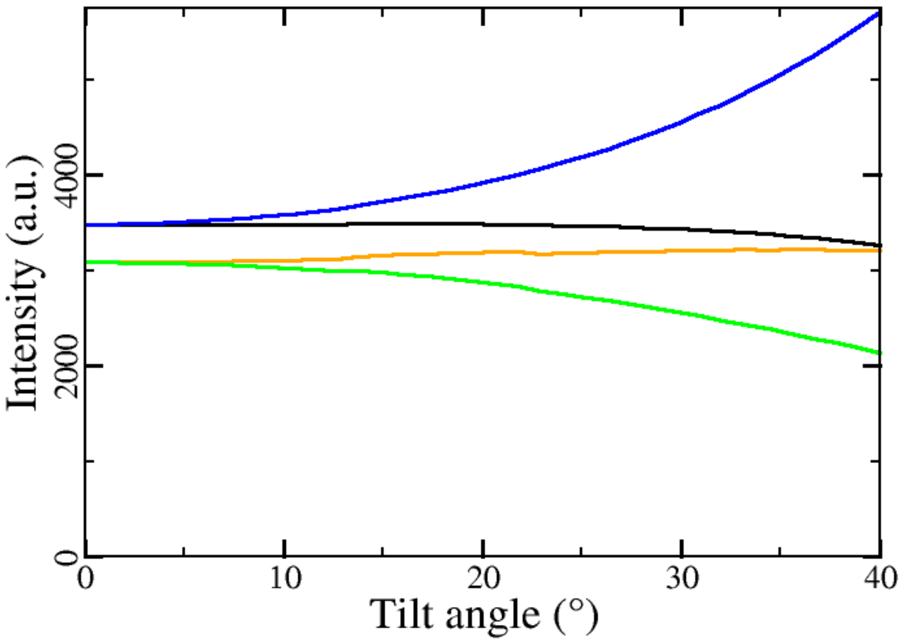
Diffraction pattern of scroll: Very similar to MWNT (but only one orientation).

In analogy to CNT, this is a “Zigzag scroll”

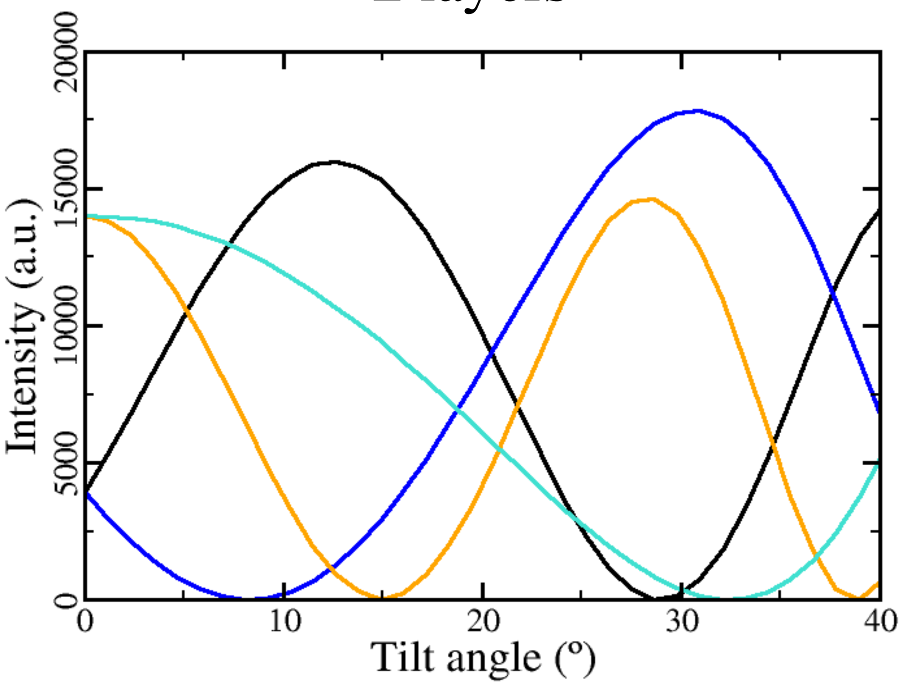
Direct visualization of graphene ripples

Variation of diffracted intensities with tilt angle

1 layer



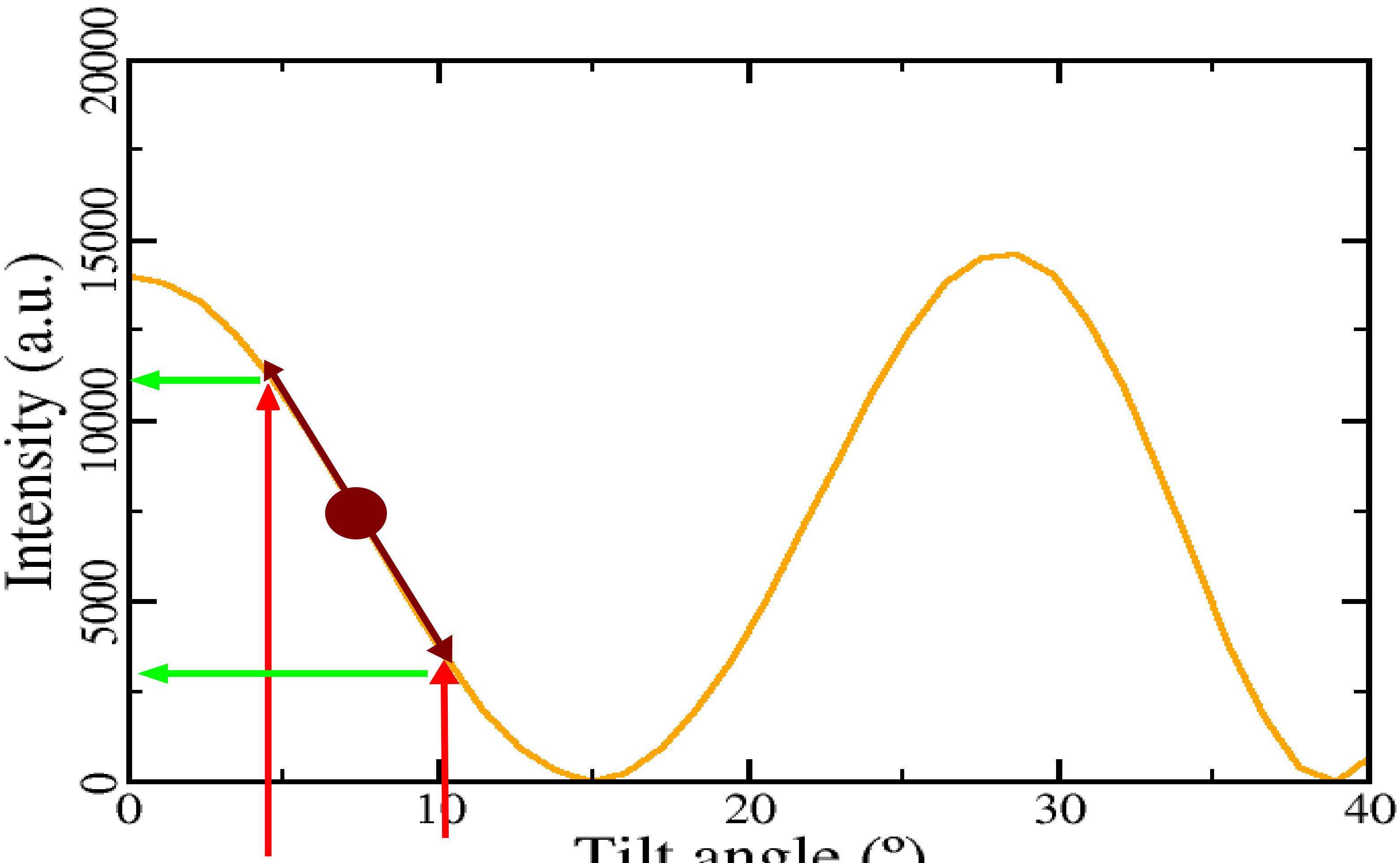
2 layers



Direct visualization of graphene ripples

Variation of diffracted intensities with tilt angle

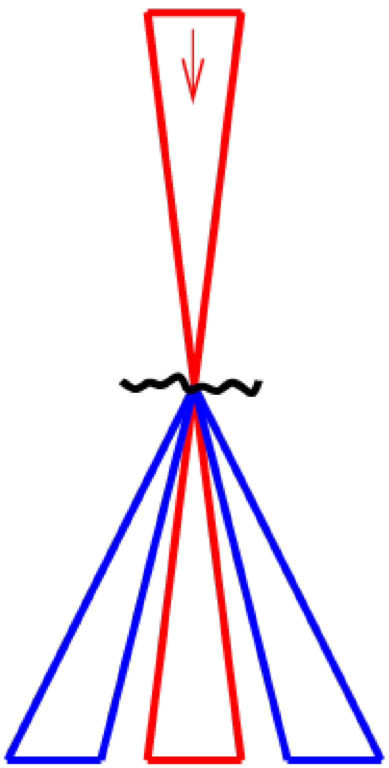
2 layers

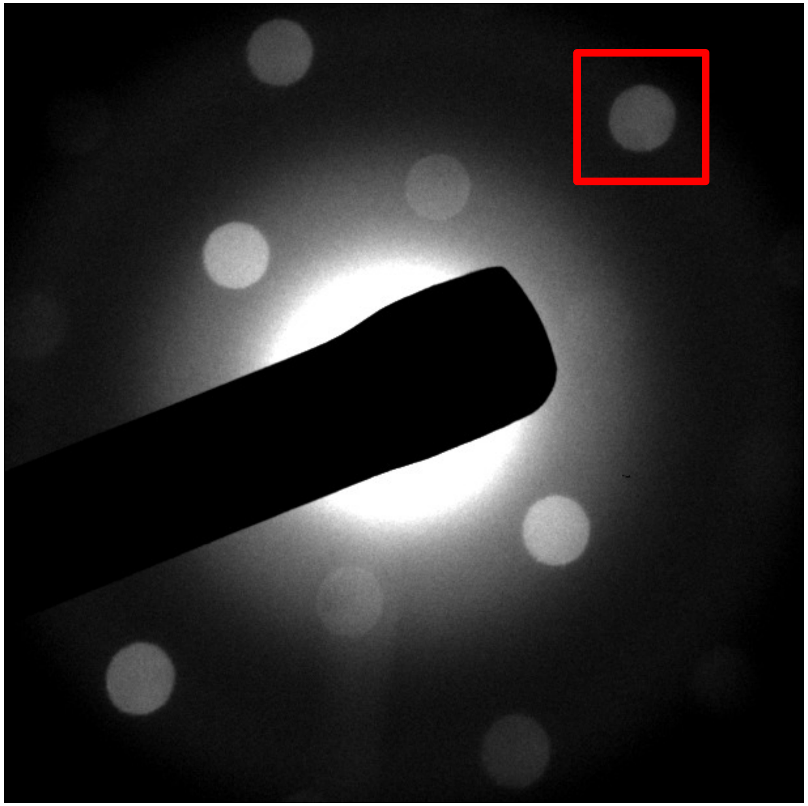


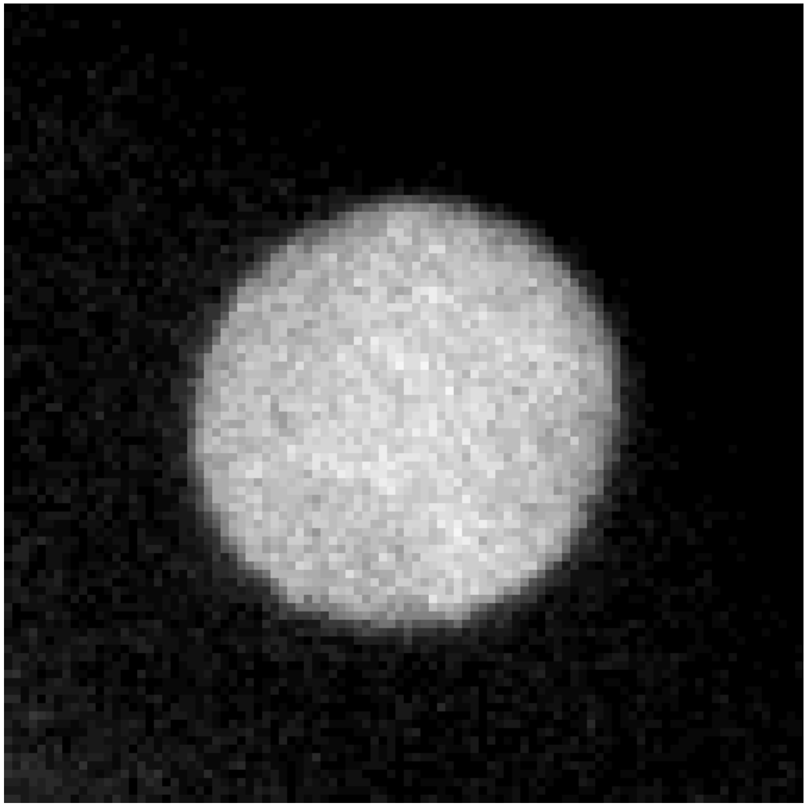
Direct visualization of graphene ripples

Convergent beam electron diffraction (CBED)

focus on sample



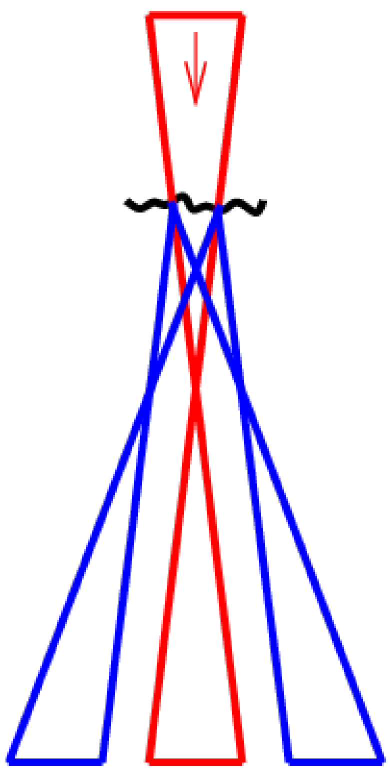


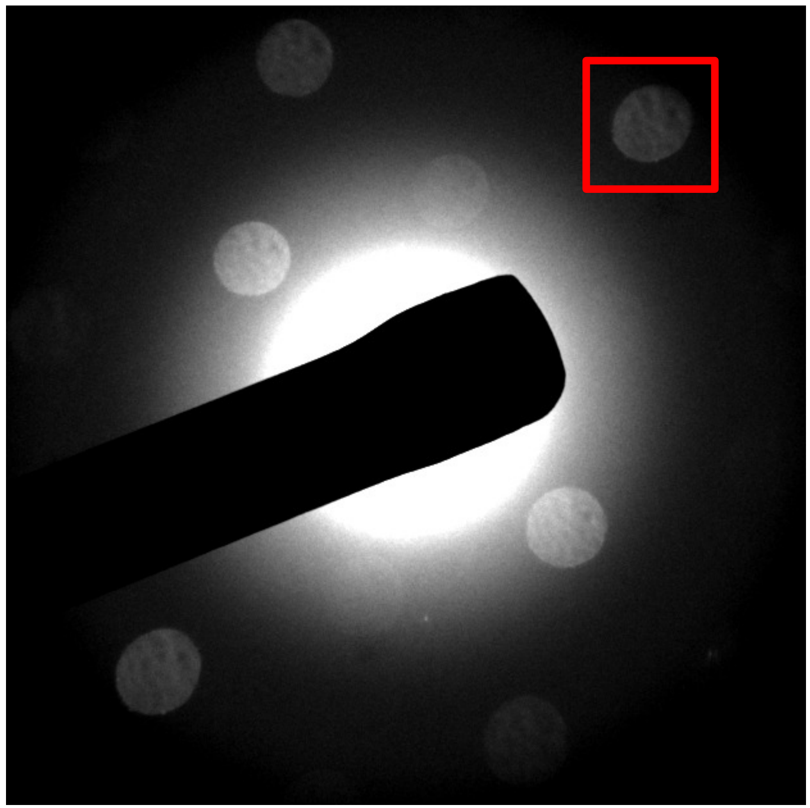


cond-mat/0703033

Direct visualization of graphene ripples

Convergent beam electron diffraction (CBED)
spot focus below/above sample:
Image of sample area in each spot

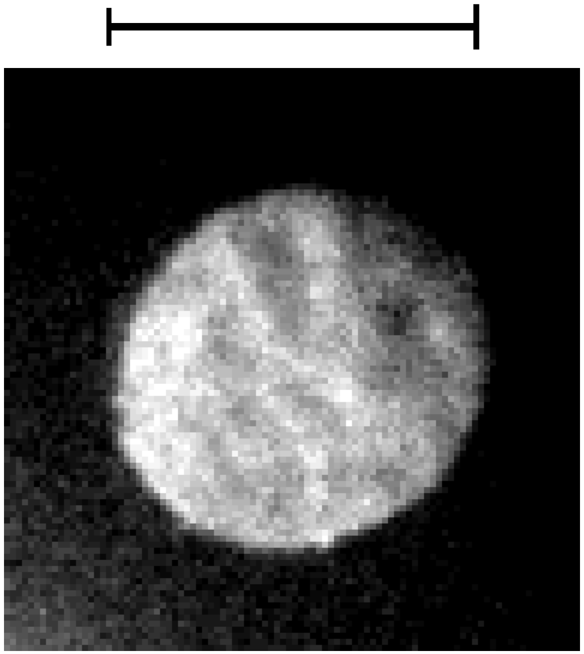




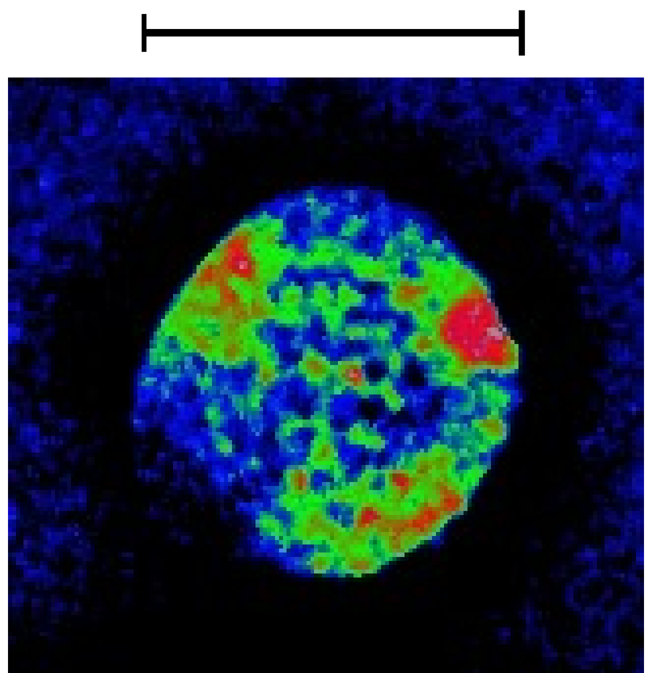
cond-mat/0703033

Direct visualization of graphene ripples

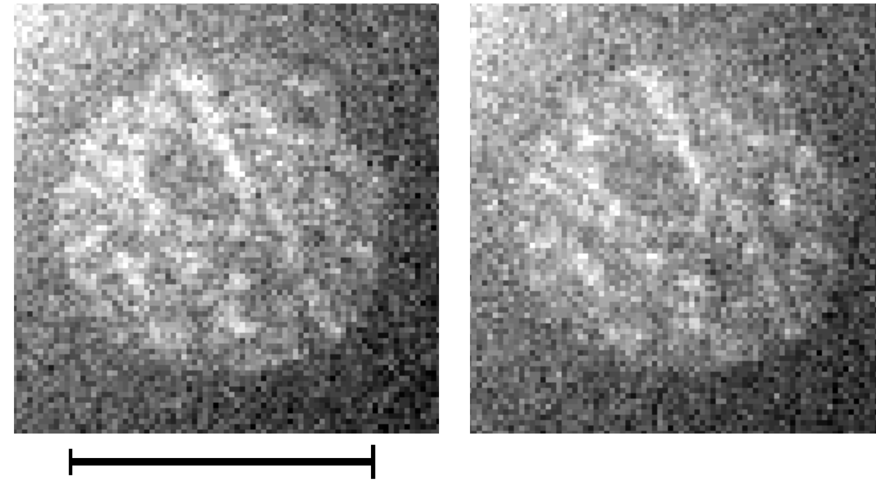
150nm



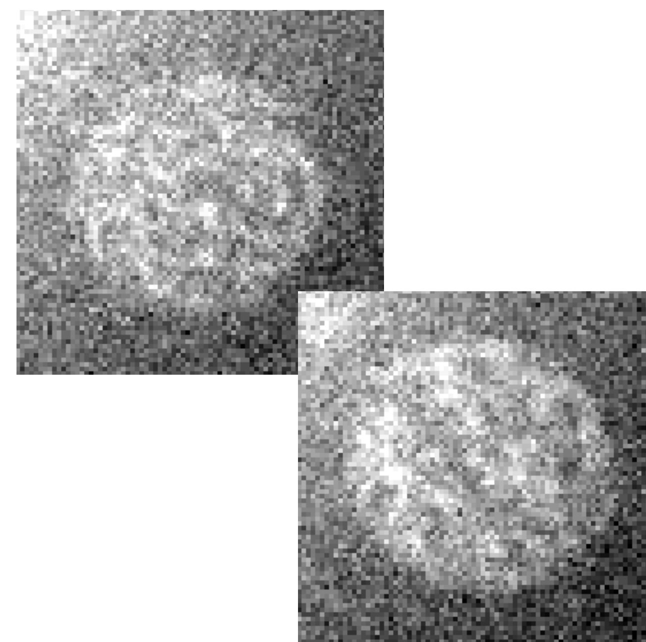
300nm



Repeated exposure of same area



150nm



cond-mat/0703033

Conclusions for "almost free" graphene (membrane attached at the edges):

- Not a strictly 2D crystal: Out of plane deformations.

- Apart from curvature, crystallinity is well preserved (within curved surface):

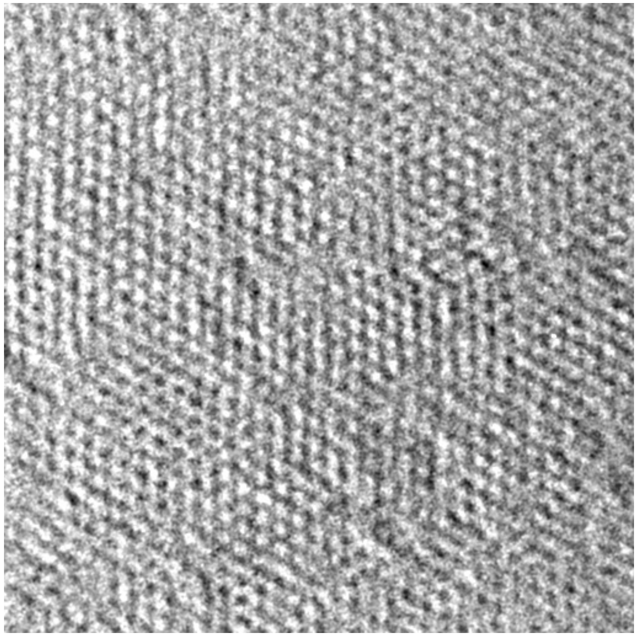
  Sharp diffraction peaks at normal incidence (projected positions are on a lattice).

  No indication of dislocations or disclinations (~ one per ripple would be needed for alternative explanation of deformations)

Conclusions for "almost free" graphene (membrane attached at the edges):

- Ripples may stabilize the membrane (reduce thermal vibrations)

- Scrolls and folded graphene appears during preparation of membranes (nearly flat sheet only meta-stable, with supporting frame?)



-> More experiments and calculations for this particular system are needed.

Potential applications

- Support film for TEM: Individual molecules may become visible
- Electronic applications (to be measured) – but no influcence from substrate
- Gas filter (squeeze atoms through benzene rings?)
- ...

Summary & Conclusions

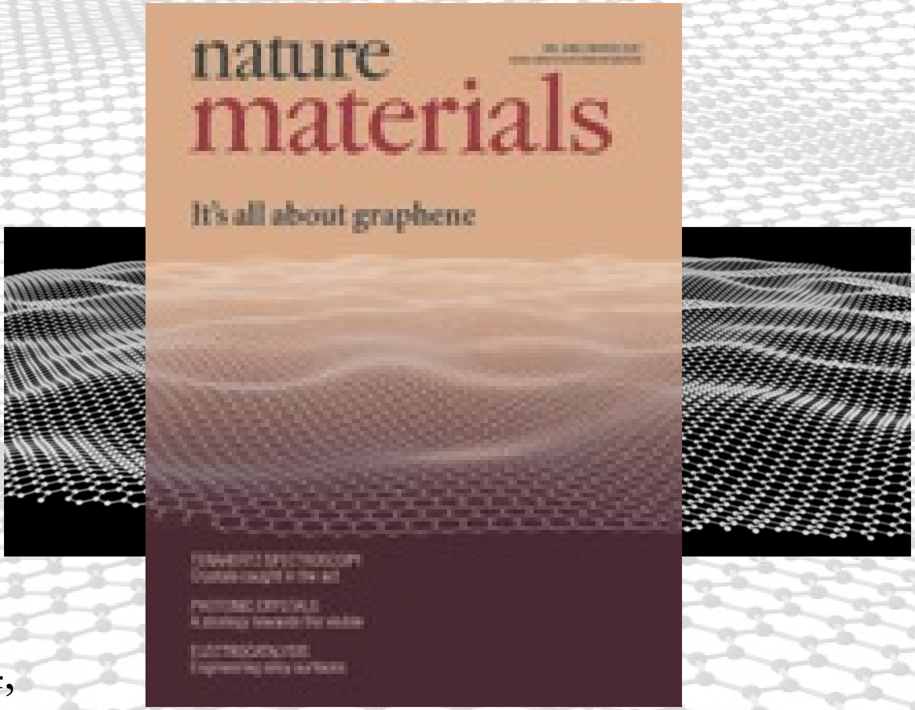
<u>Free standing graphene</u>
Thinnest possible membrane: 1 layer of carbon

Structural modifications of a 2D membrane:

Suspended graphene is not flat
curvature ~10nm lateral, ~1nm in height

Crumpled and scrolled graphene

Huge potential for further research and applications of ultra-thin membranes



<u>Financial support:</u> DOE Contract No. DE-AC-03-76SF00098, NSF Grant N. EEC-0435914, EU project CANAPE, the EPSRC (UK), Royal Society, and FOM (Netherlands).