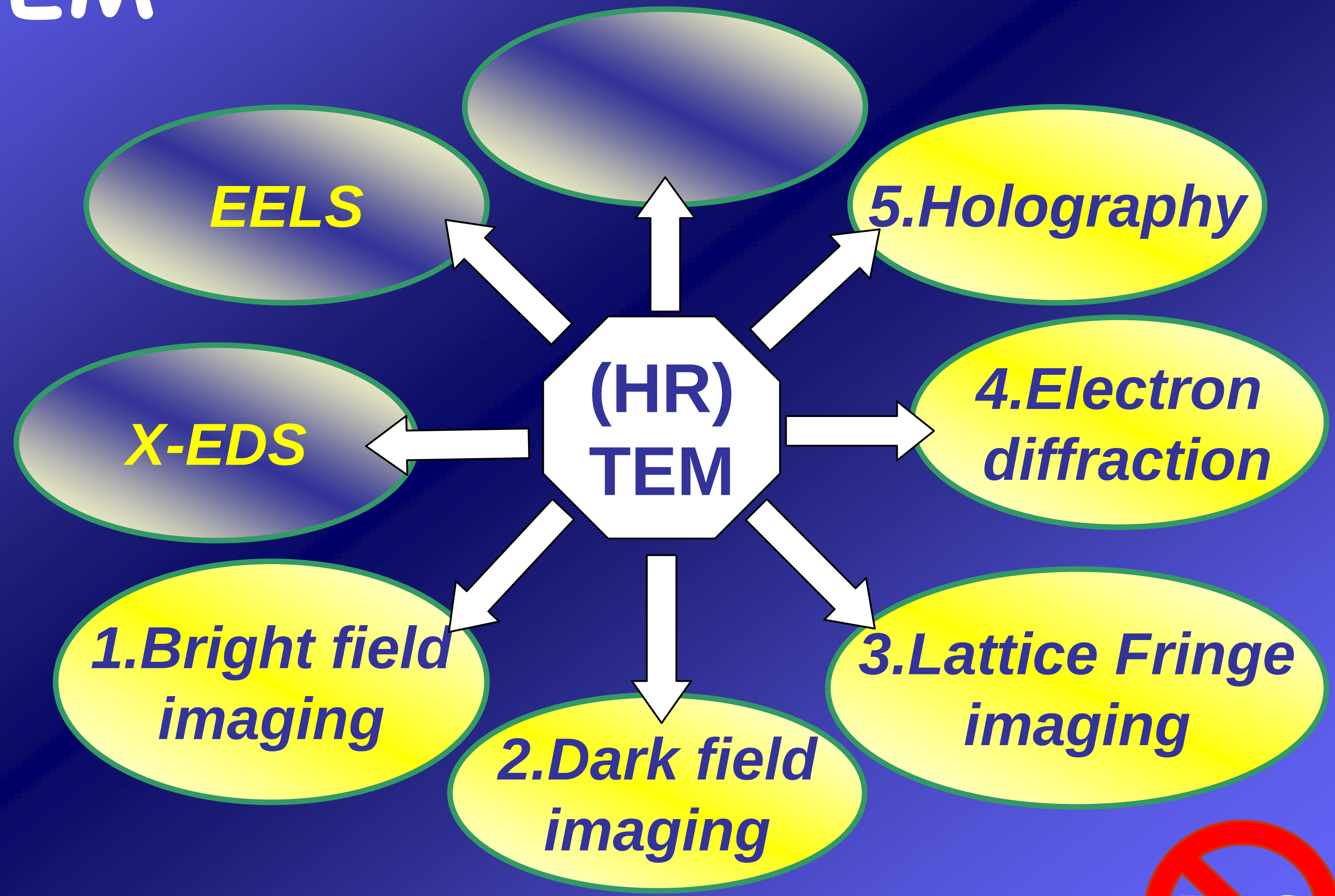
Graphenes as seen through the TEM



FGL (or FGC) = less than 10 graphenes

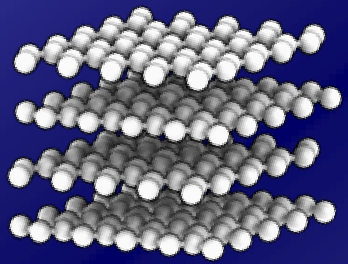
.1.
A BIT about
the POSSIBLE STRUCTURES
of GRAPHENE(S)

Possible stacking sequences (= structure)

AA
(thermodynamically unfavoured, yet possible in FGCs)

ABC
(3 graphenes minimum, thermodynamically unfavoured, yet possible in FGCs and bulk)

AB
(the thermo-dynamically ultimate structure = graphite, as bulk or FGCs)



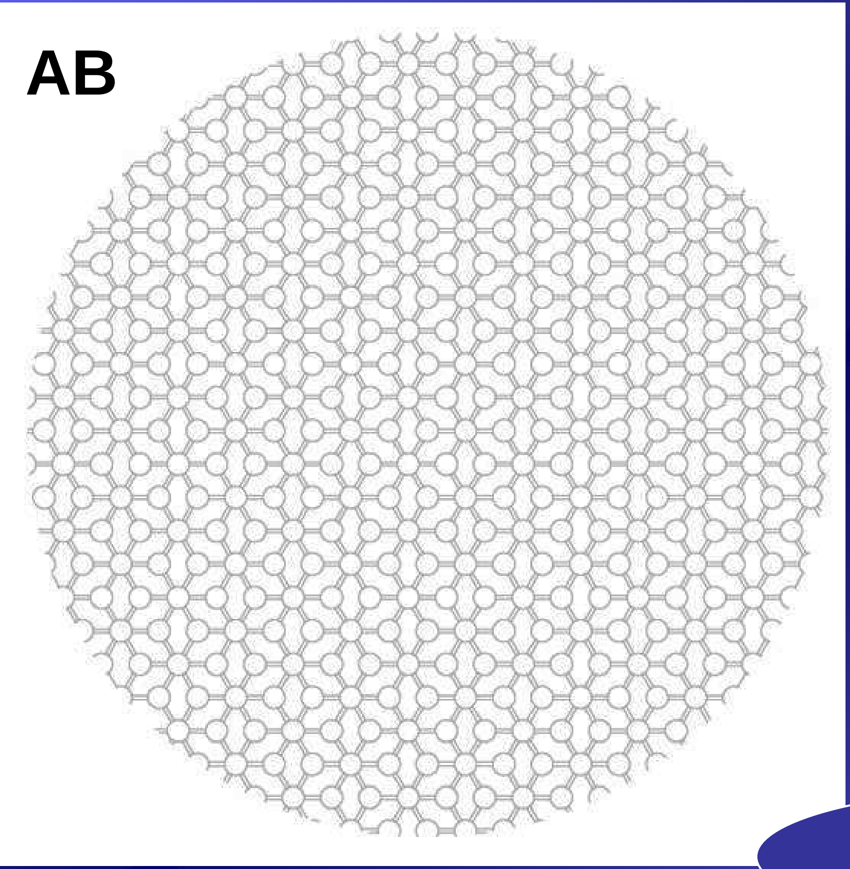
Otherwise: turbostratic *("random" rotation)*

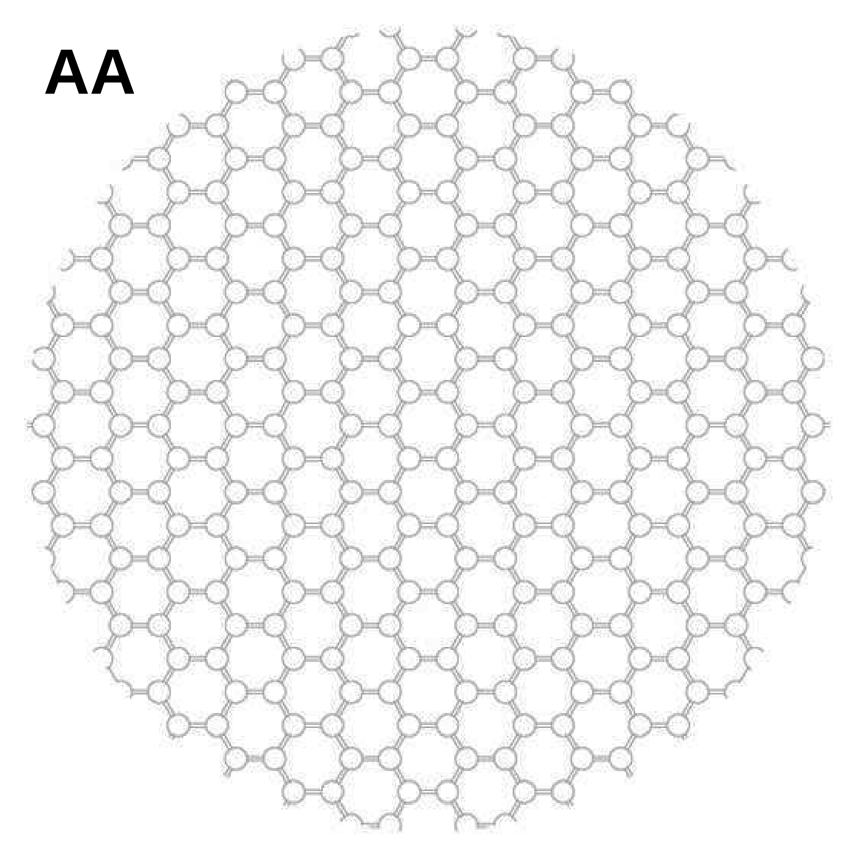
commensurate — selected rotation angles

non commensurate — truly random rotation angles

Dos Santos et al. Phys. Rev. Lett. 99(2007)256802

Top views of various stacking sequences for 2 graphenes

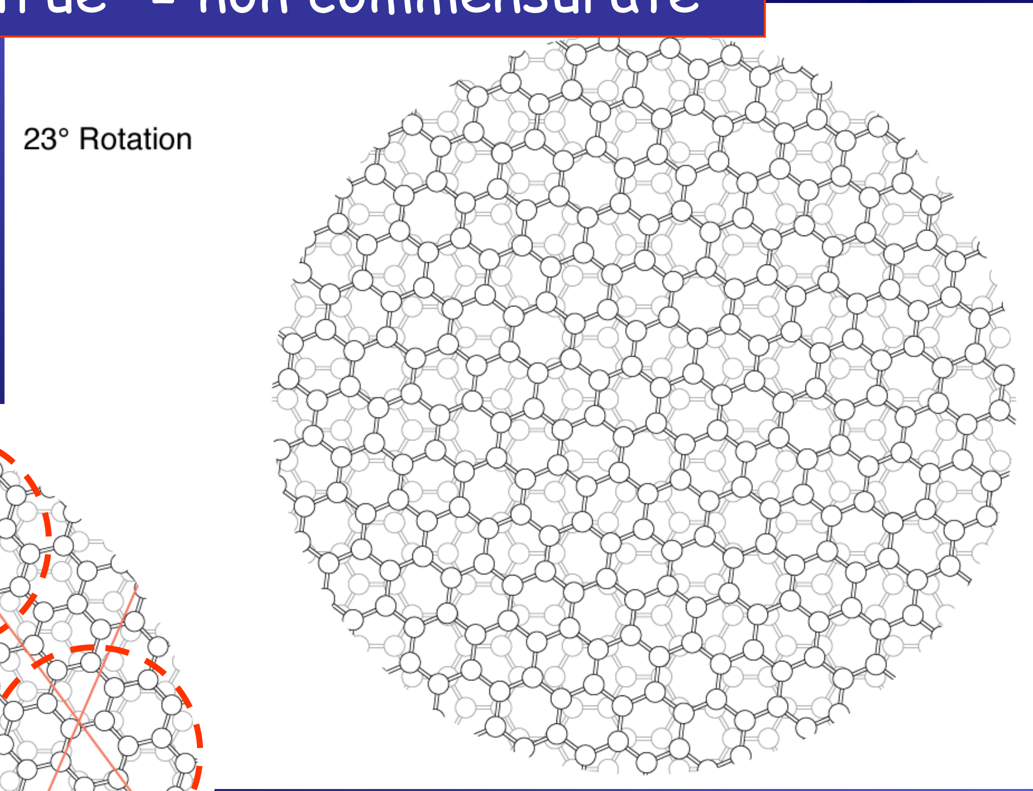




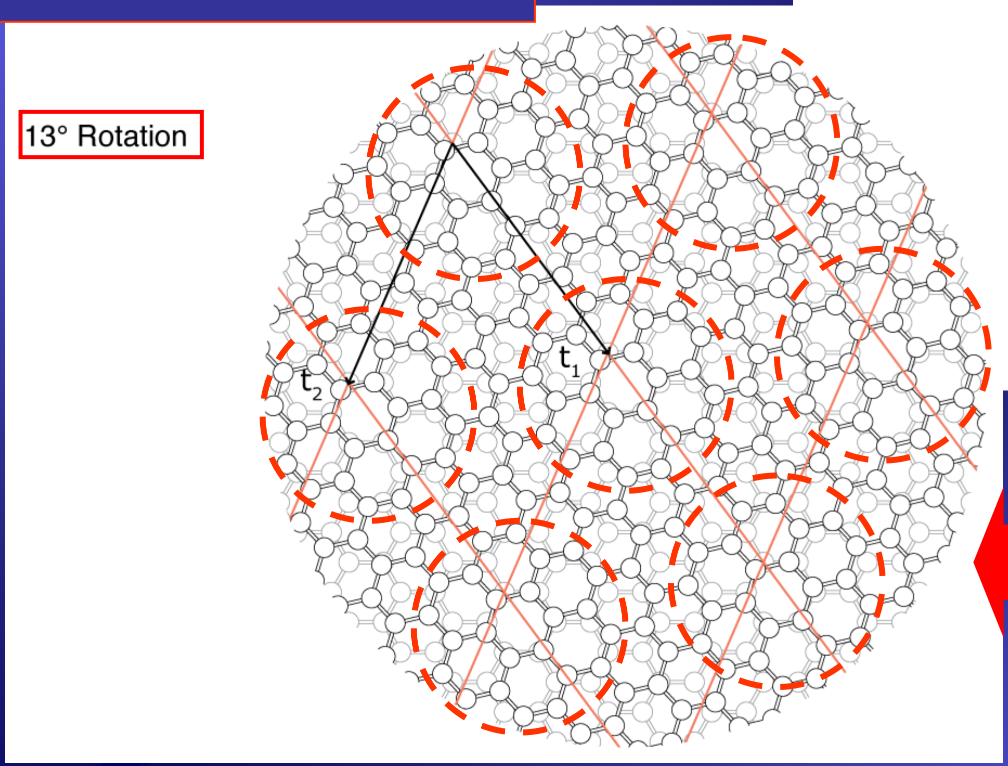
Graphite

Turbostratic

"true" = non commensurate



commensurate



seems to be the only configuration for which each stacked graphenes behave as single (electronically decoupled)

Hass et al., Phys. Rev. Lett. 100(2008)125504

.2.
When GRAPHENE(S) MEET(S) TEM

Standard TEM

. *Bright field imaging*

. *Lattice fringe imaging (+ FFT)*

. *Dark field imaging*

Possible on conventional TEMs

Advanced TEM

. *Atomic resolution*

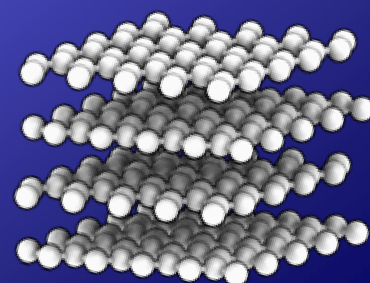
. *Nanodiffraction*

. *Holography*

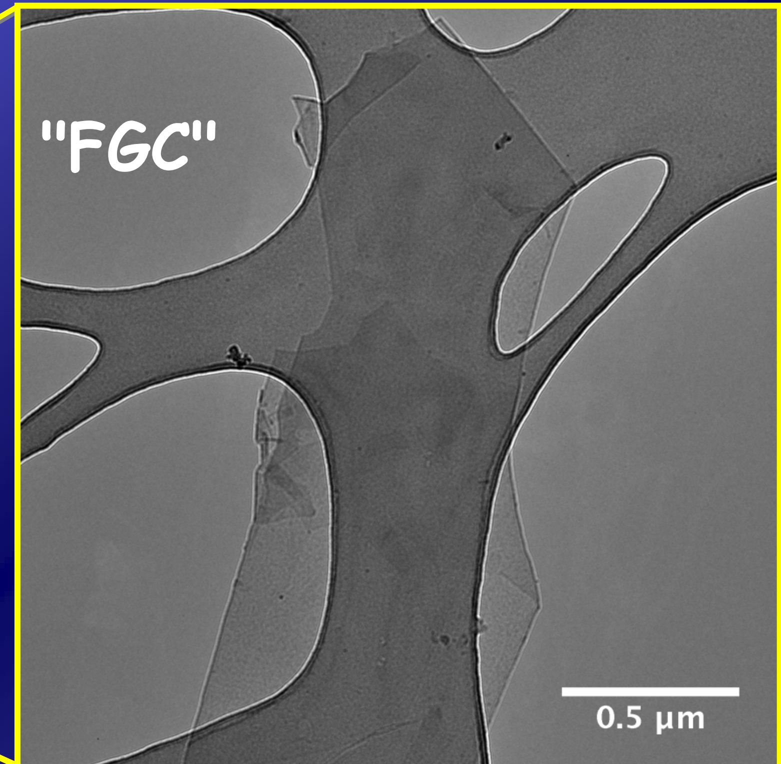
Require specific facilities: Cs corrector, nanoprobe, biprisme…

Graphene(s)

Suspension of graphite flakes



"FGC"

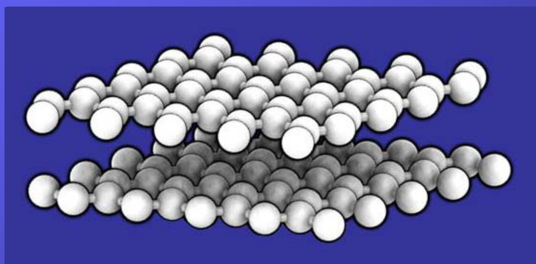


→ **Few-Graphene Crystals**

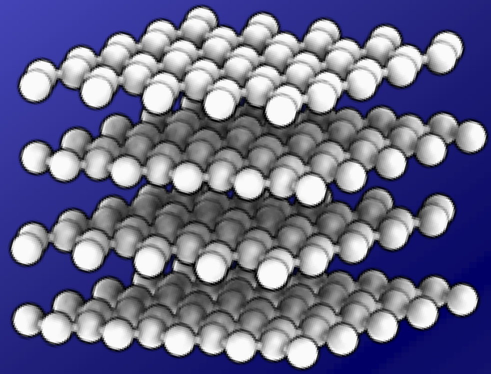
Deposition on TEM grid (Cu + lacey amorphous carbon)

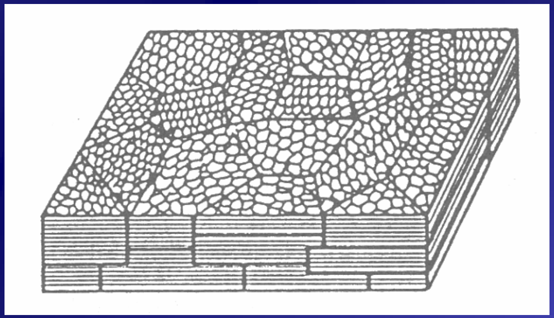
Bright field imaging

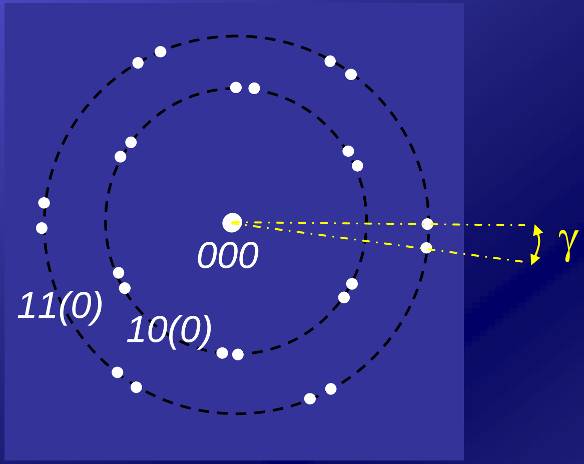
Electron (nano)diffraction

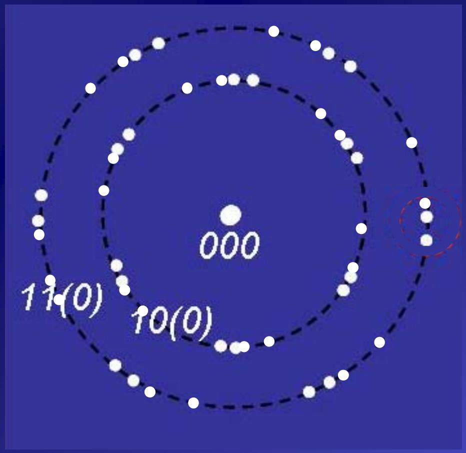


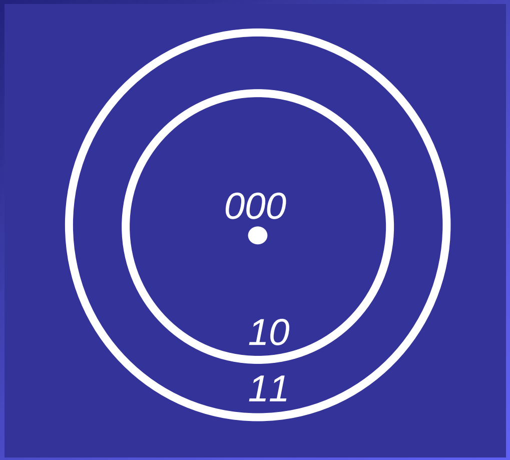
Turbostratic



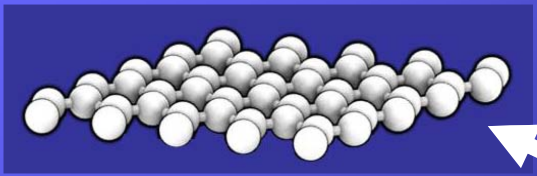






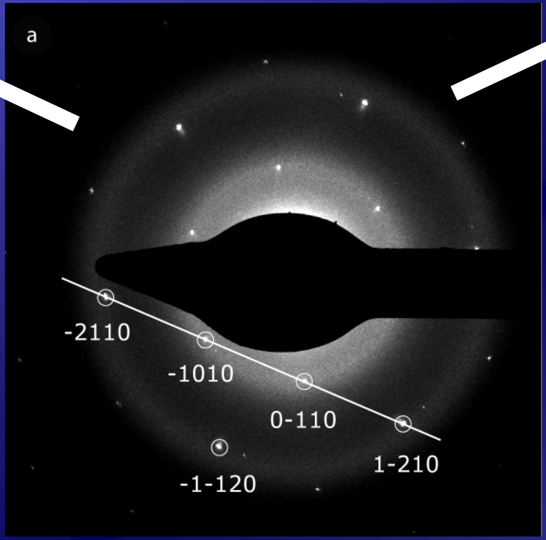


Electron nanodiffraction

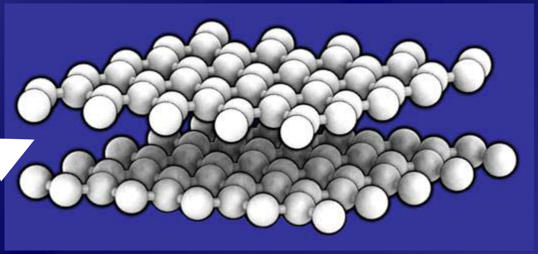


single

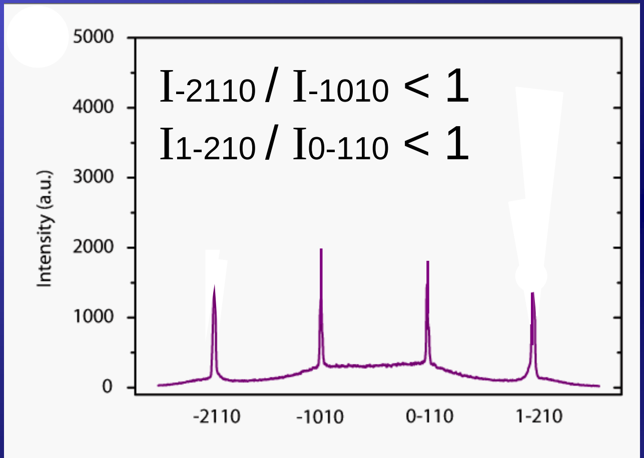
?

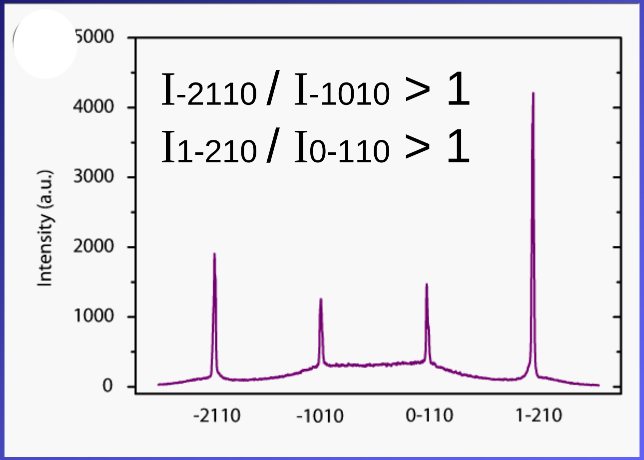


?



graphite (AB)

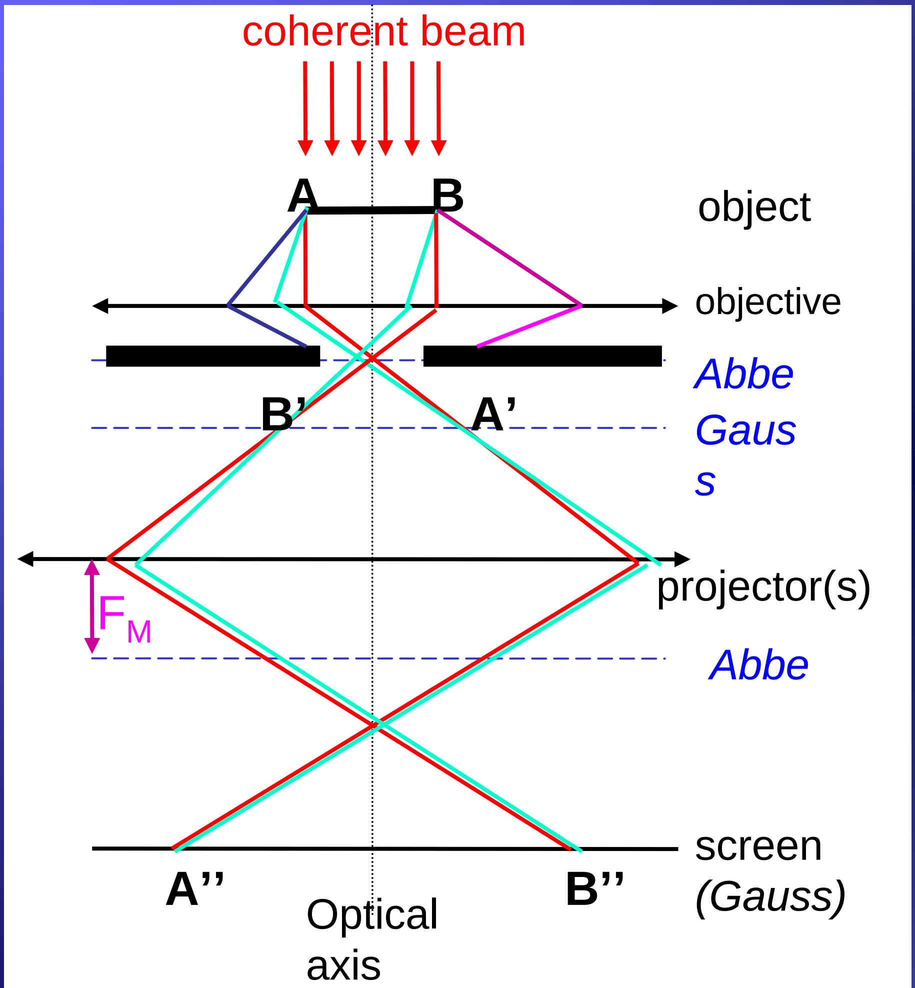


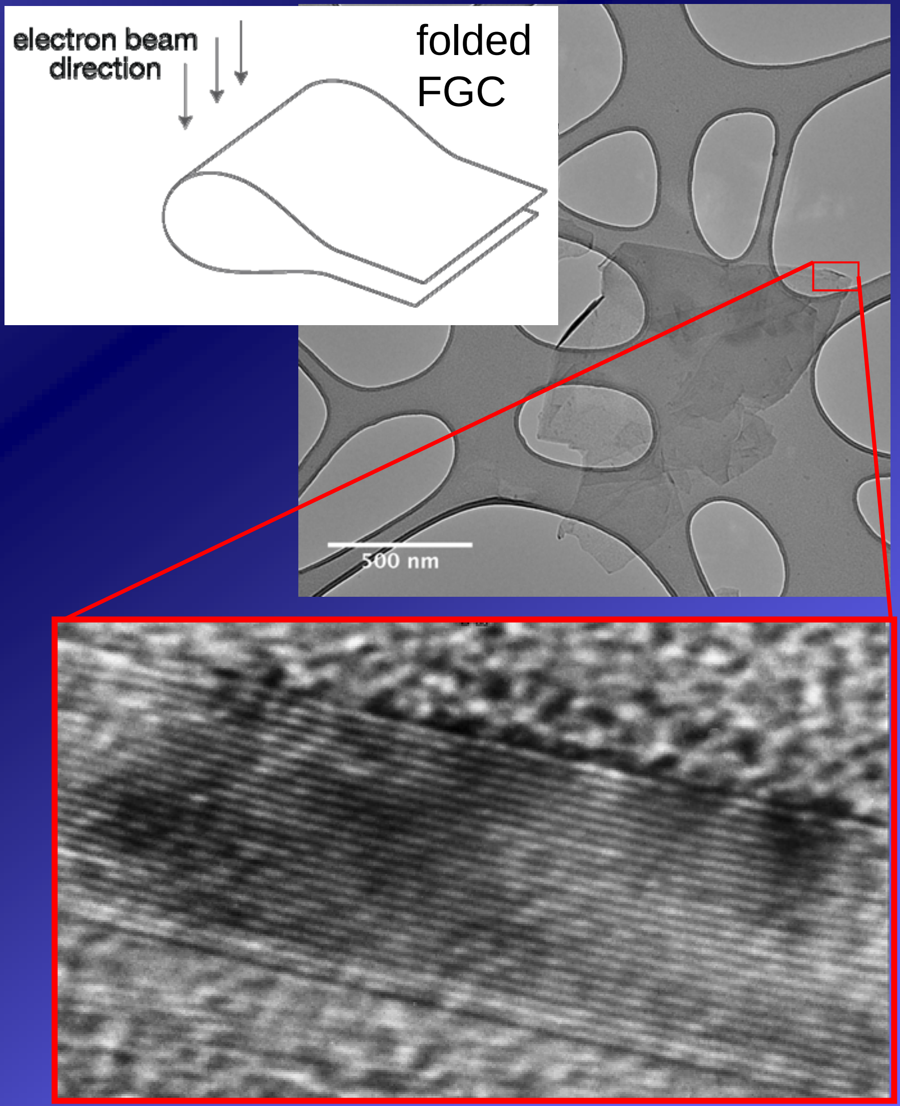


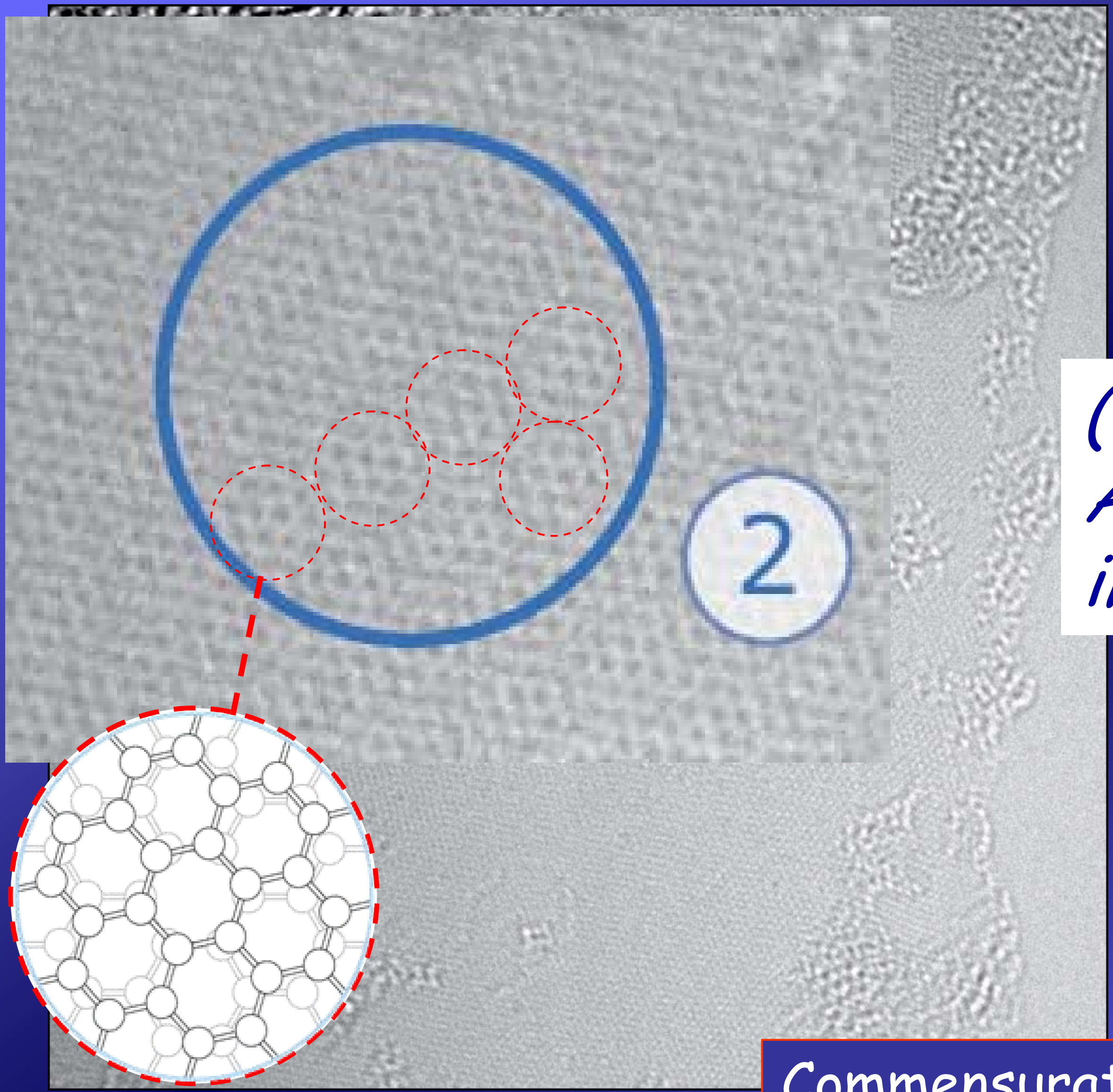
graphene/graphite discrimination

Lattice fringe imaging

Transmission electron microscope = electron interferometer



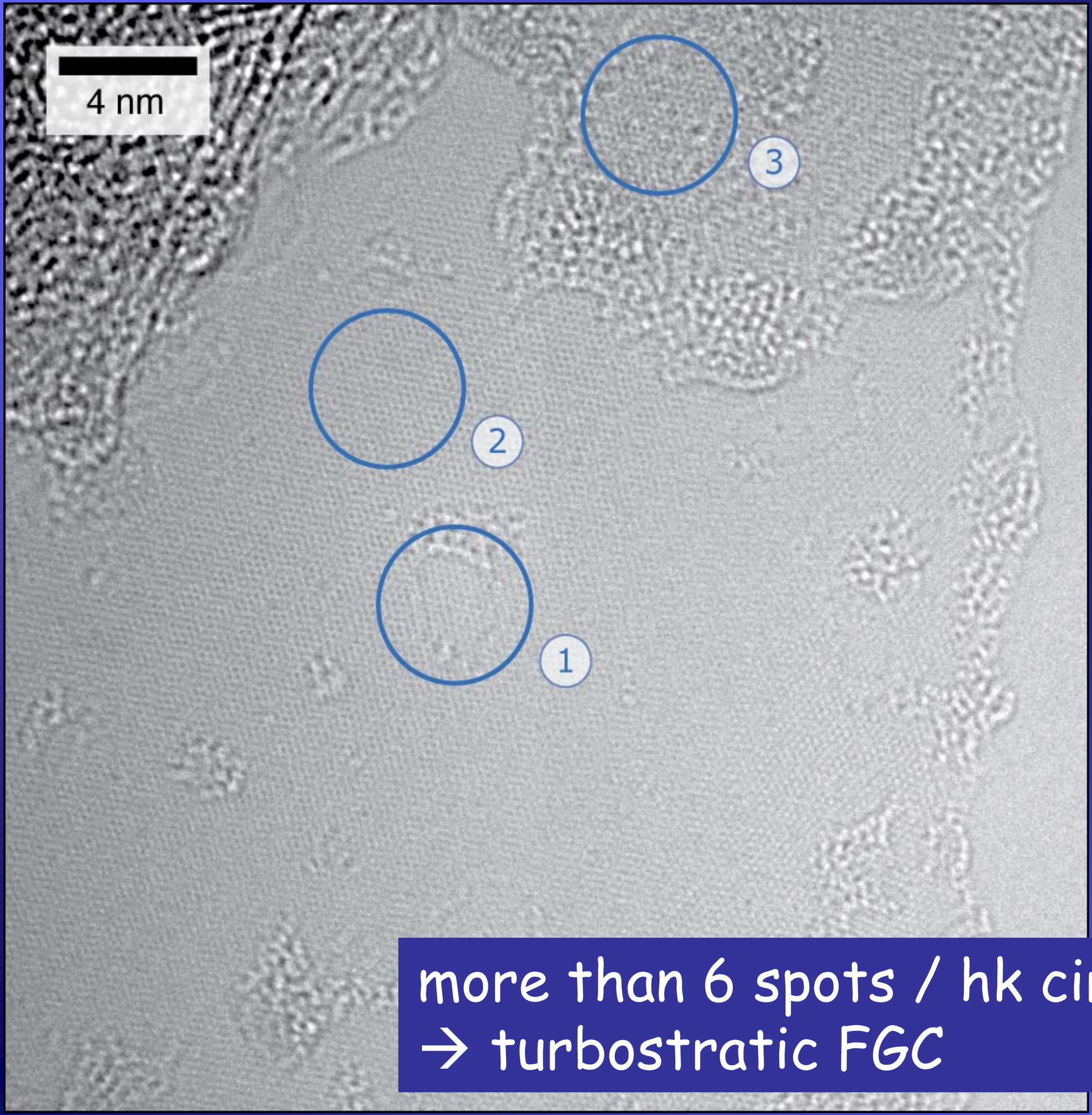


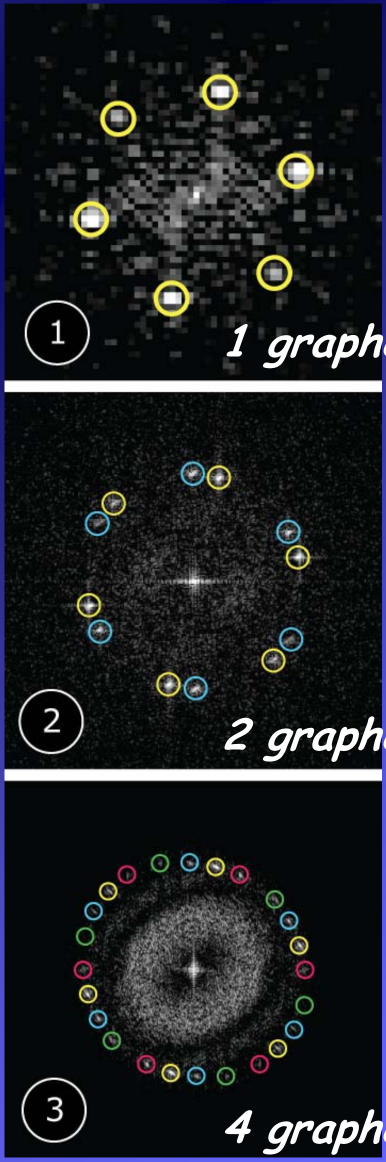


(Cs-corrected) Atomic resolution imaging

Commensurate (13°), turbostratic FGC

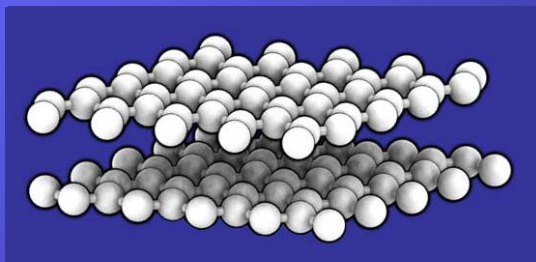
An alternative to (nano)diffraction: *Fourier Transform*



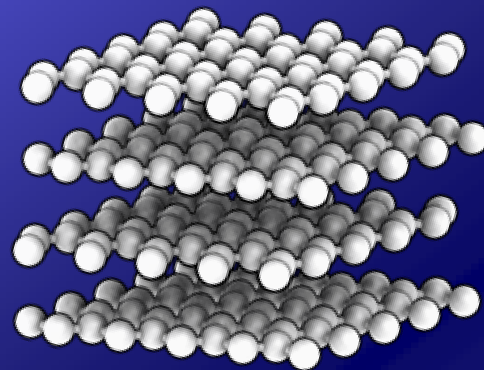


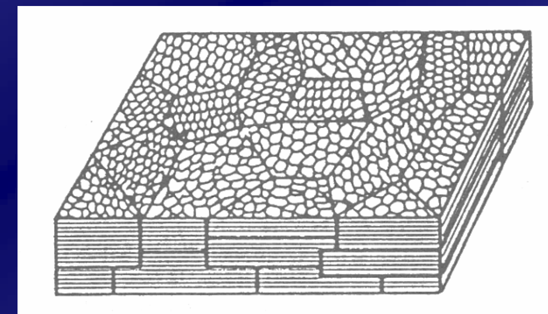
more than 6 spots / hk circle
→ turbostratic FGC

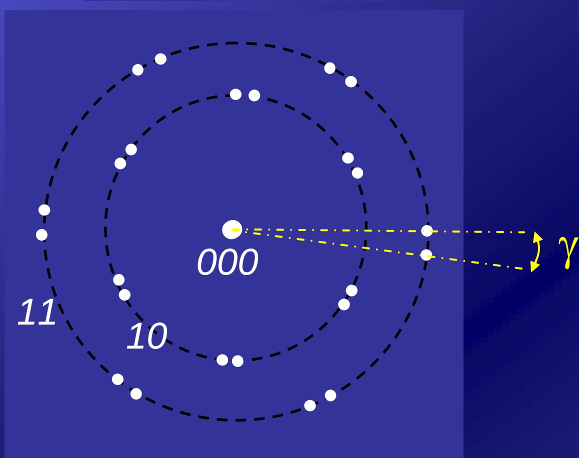
Dark field imaging

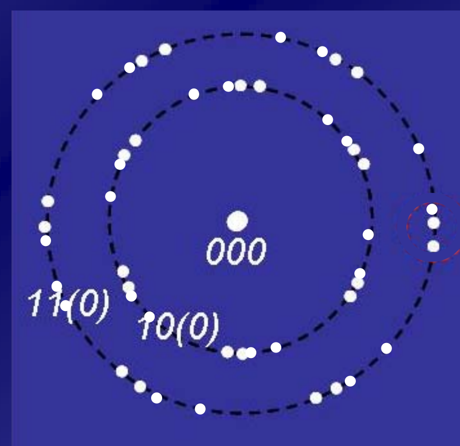


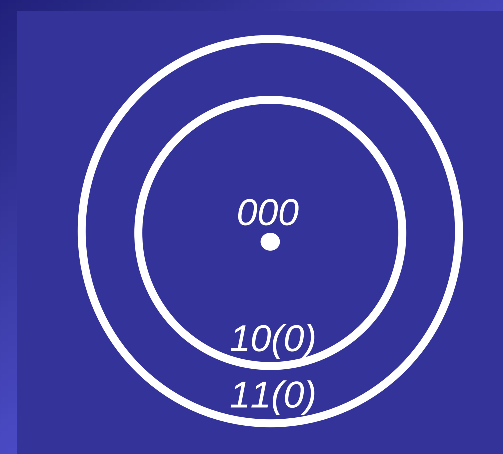
Turbostratic







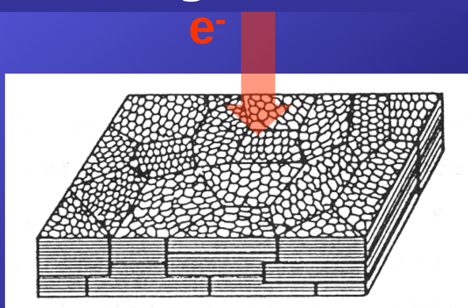


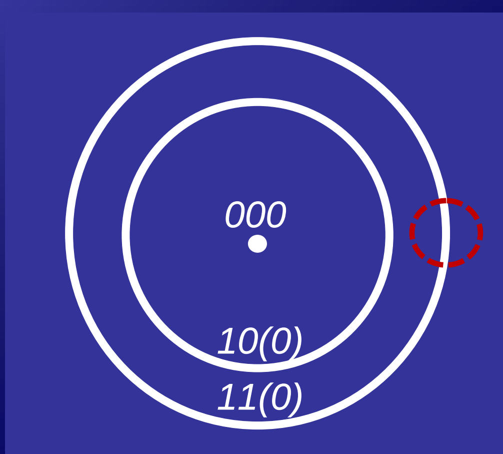


Selected area electron diffraction (SAED)

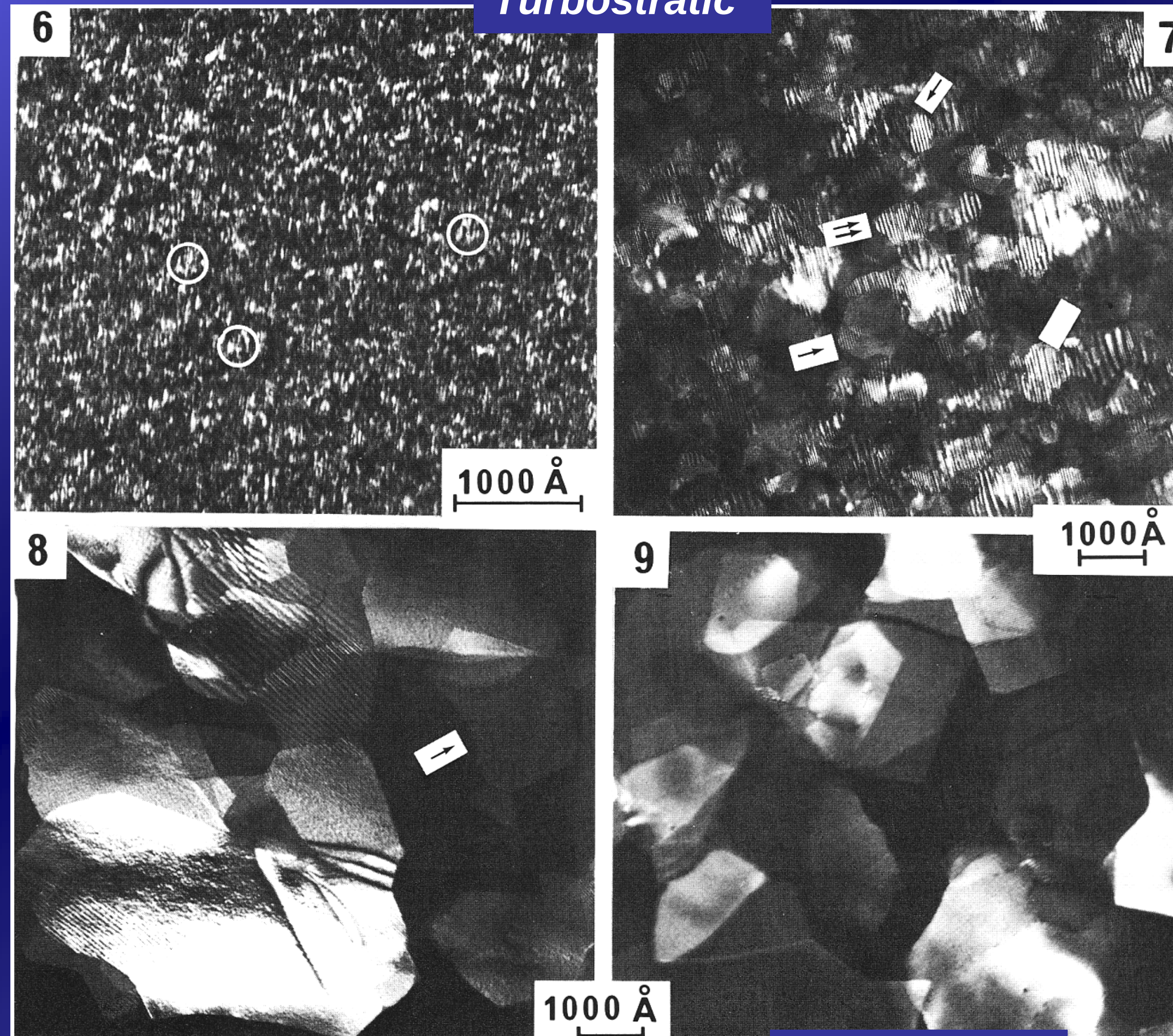
Dark field imaging

Mosaic ("patchwork") configuration





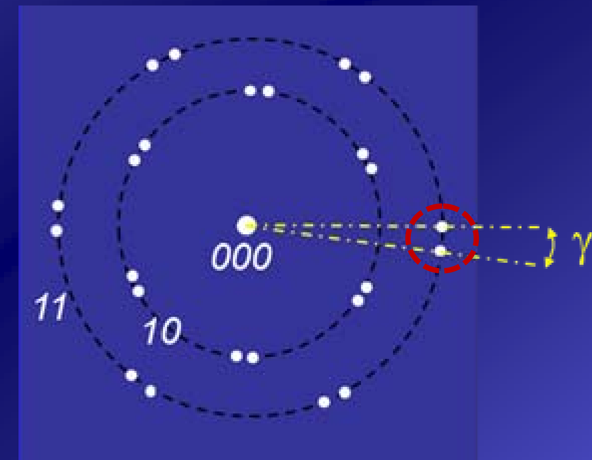
Turbostratic



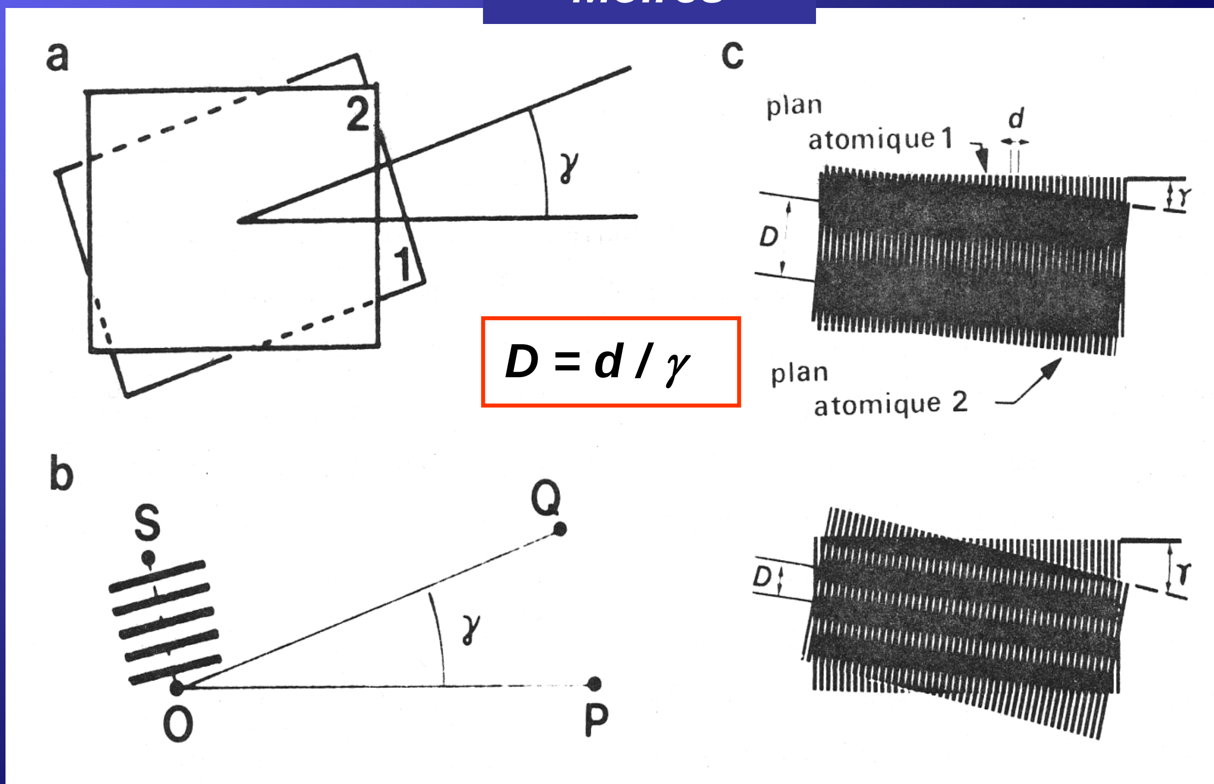
Graphitised (ABAB)

(+ Moirés 10(0) or 11(0))

Two identical lattices superimposed with a random rotational angle γ



"Moirés"

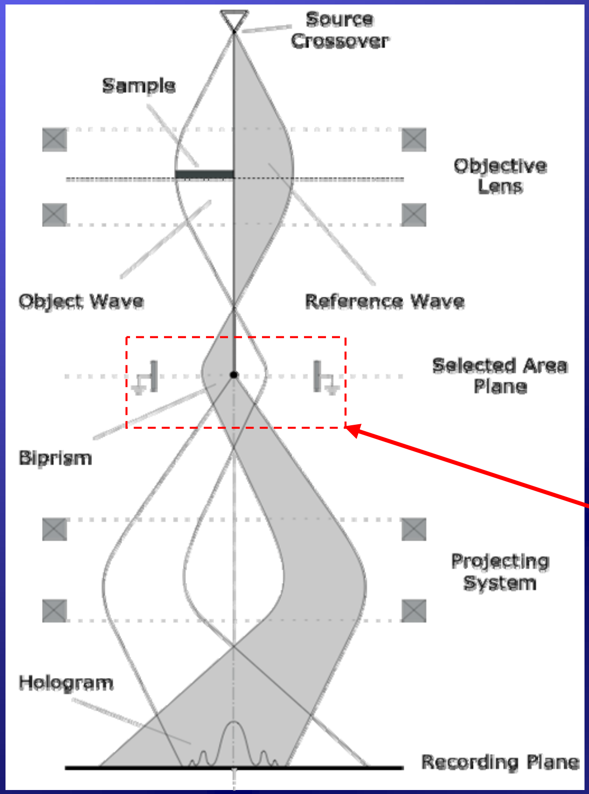


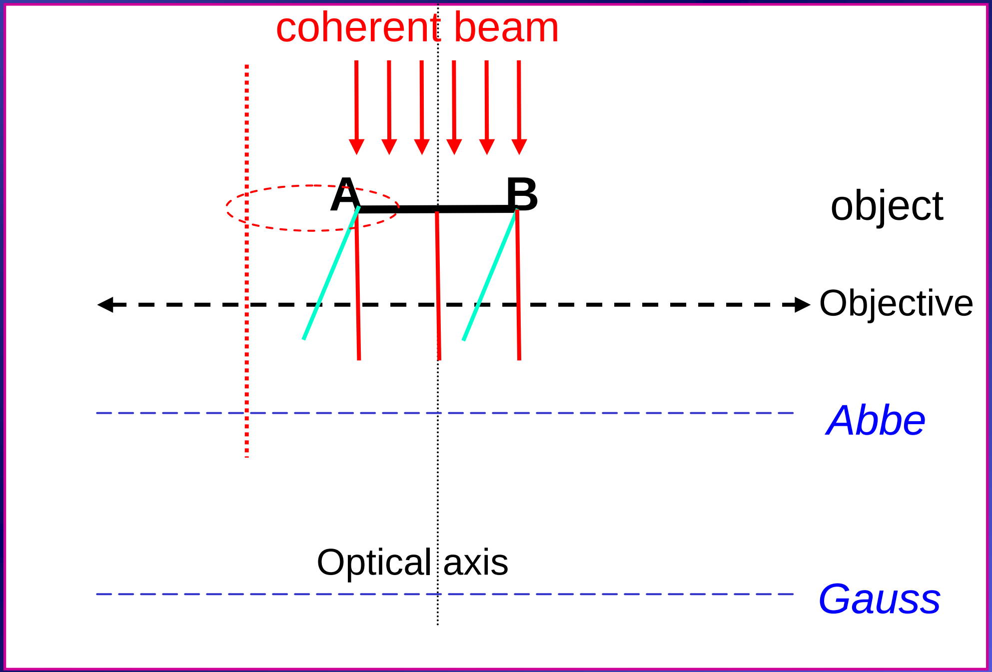
γ increases

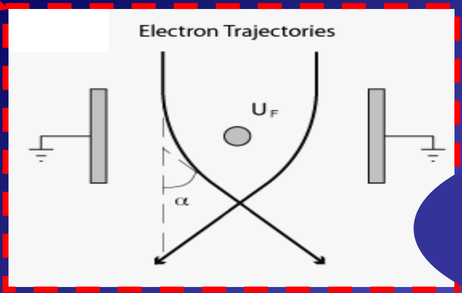
⇩

D decreases

Electron interferometry mode #2: Electron holography



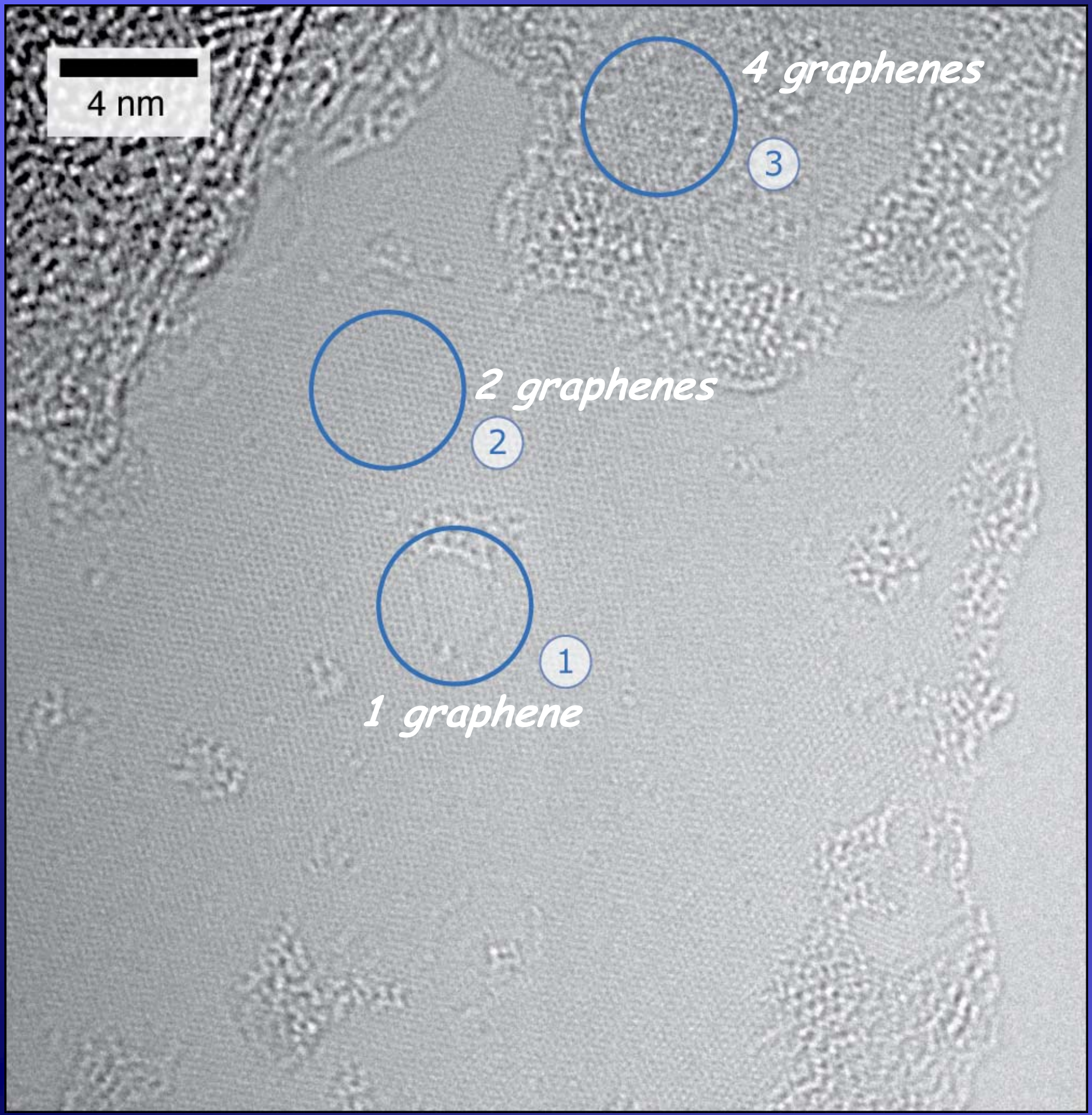




Electrostatic biprism

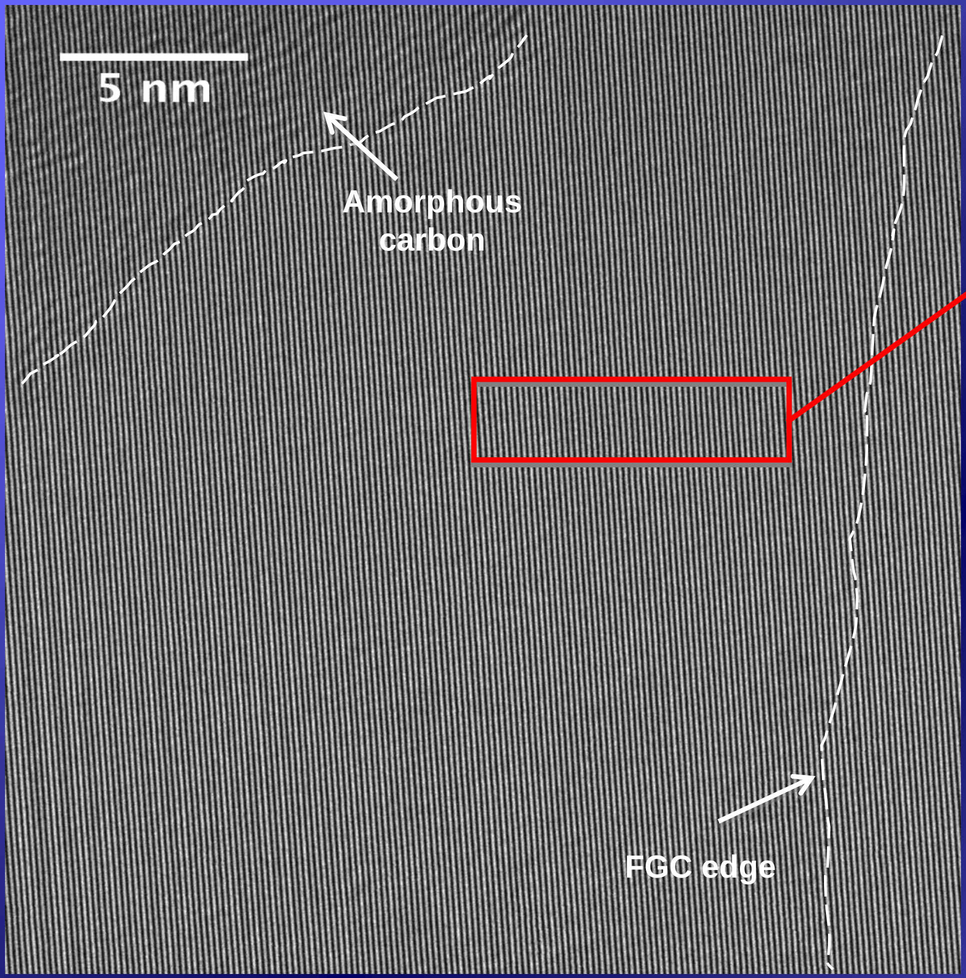
metal wire,
Voltage
+20 to 200 V

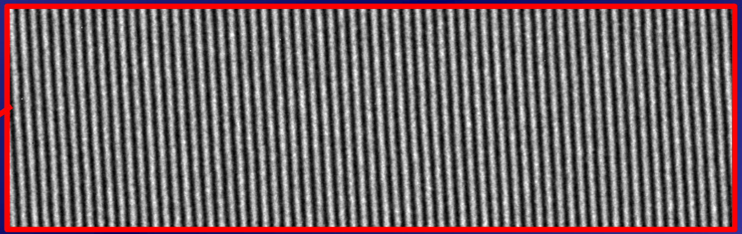
Electron holography on thicker FGL, with variable number of graphenes

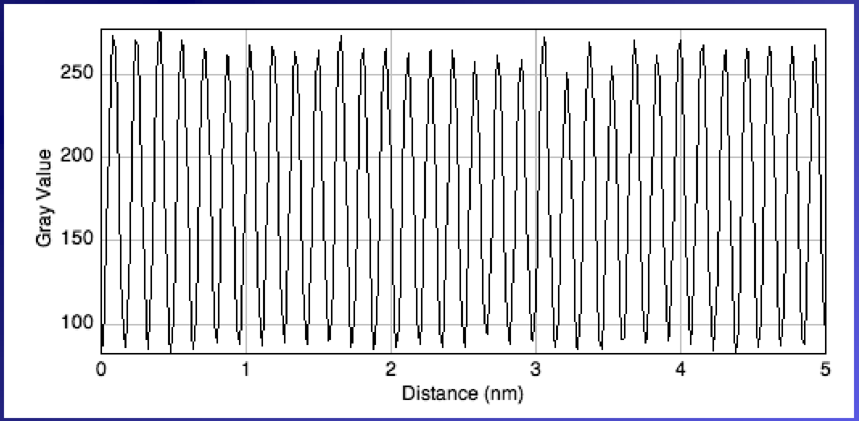


Turbostratic, commensurate (13°)

Resulting hologram



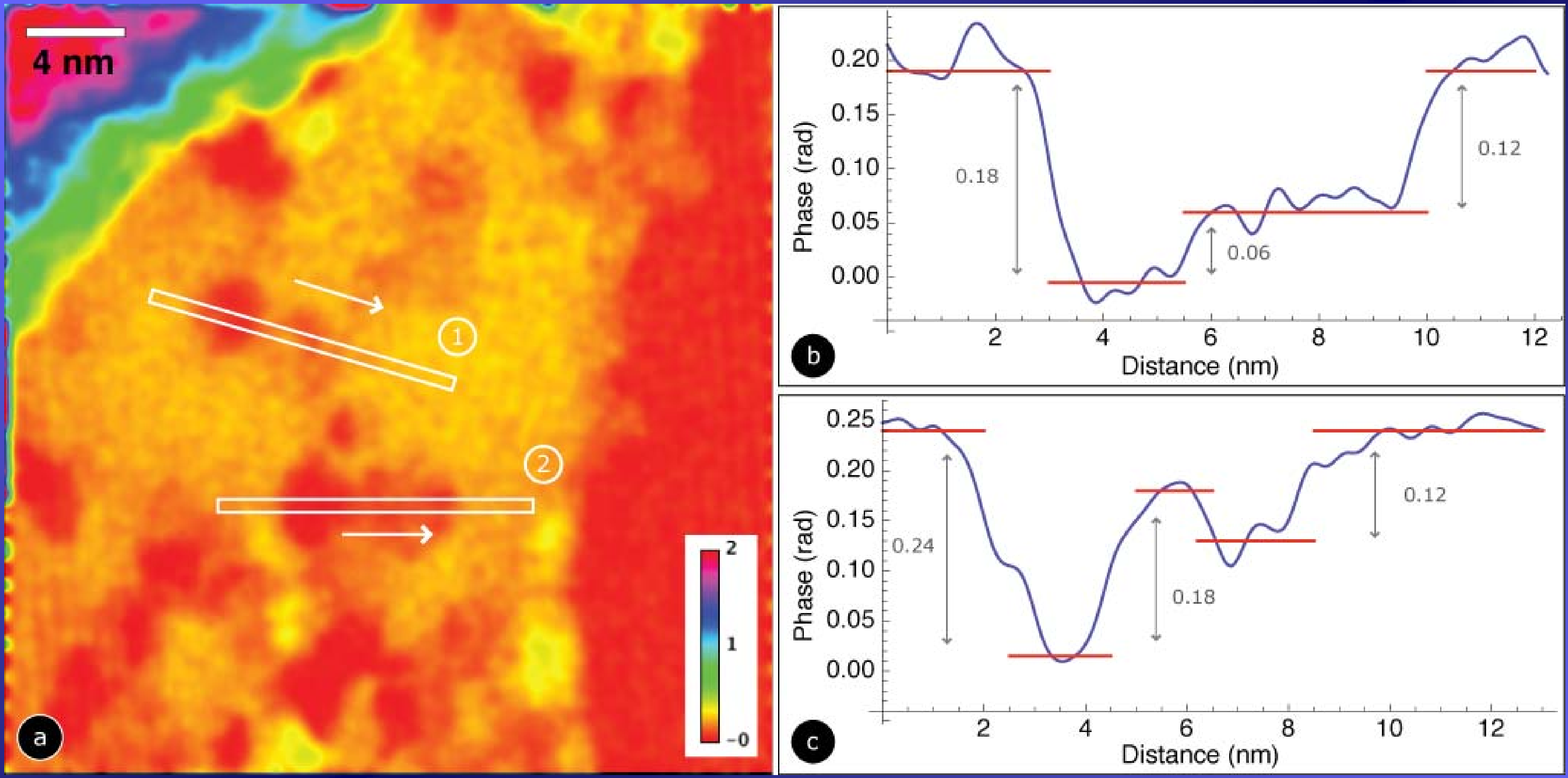




Accelerating voltage: 100 kV
Fringe spacing: 0.15 nm
Fringe contrast: 55%
Biprisme voltage: 160 V

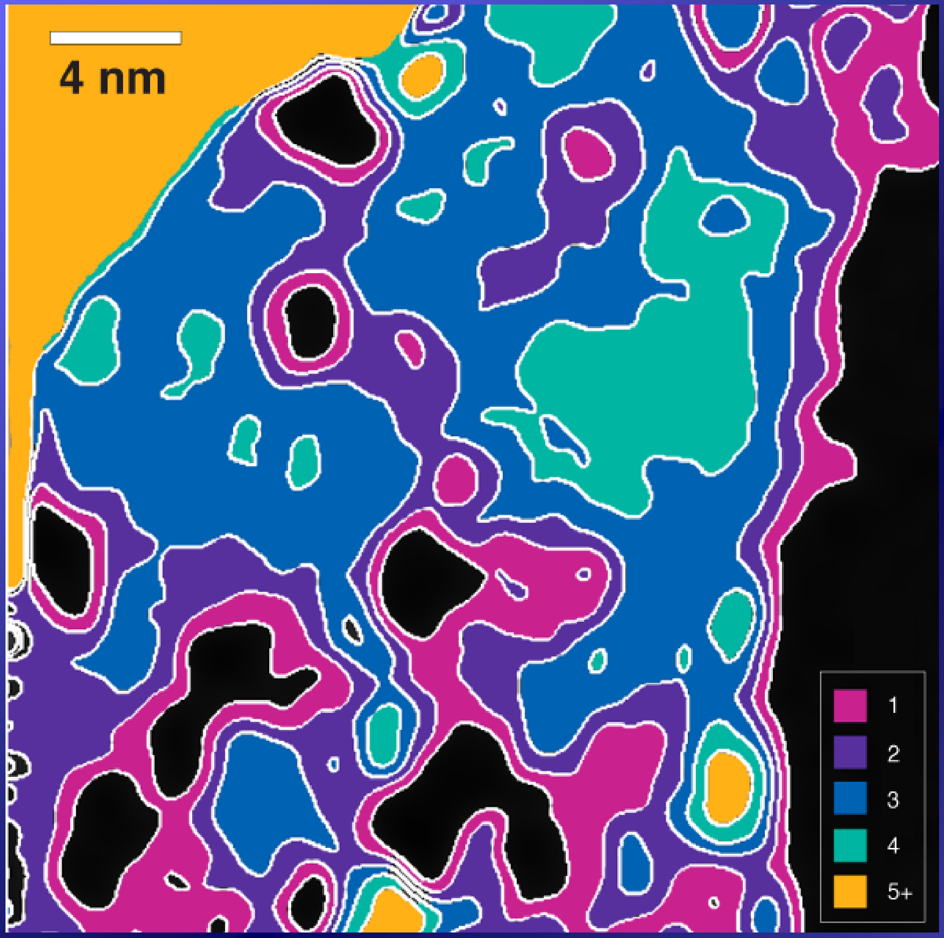
The quality (resolution and sensitivity) of the holographic reconstruction (by FFT) of the phase map depends on the **contrast** and the **interfringe distance** (related to biprism voltage, ...).

Resulting phase map image

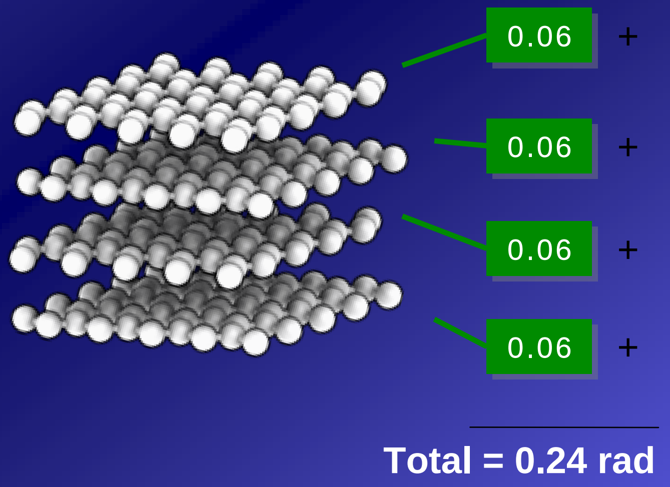


Phase difference profiles: discrete values, multiple of **(0.06±0.01) rad = valeur for single graphene**

Discretisation of the phase image
→ Mapping of local number of stacked graphenes



As a result of the progressive peeling off of the graphenes by the electron beam in the TEM.



For a turbostratic, commensurate FGC

What about other stacking sequences?? Work to come!!

OVERALL CONCLUSION

- Advanced TEM facilities are VERY powerful tools for studies on graphene(s)
- In particular, electron holography (yet formerly devoted to magnetic materials) has revealed being able to provide a new range of information barely accessible by other TEM modes.
- DO NOT neglect the good ol' conventional TEM modes. Dark field imaging, in particular, may tell a lot regarding dimensions and structure of coherent domains in graphene films.