Surface Normal Deviation in Graphene and n-Layer Graphene- A Molecular Dynamics Study

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BACKGROUND

Experimental Observations

- Graphene is a monolayer of sp^2 bonded carbon packed in a honey comb lattice. It exhibits many novel properties such as unusual electronic, including high electronic mobility, large tunable band gap, high thermal conductivity, high mechanical strength and many others.
- Experimental observation of 2-dimentionality of graphene was made using transmission electron microscope, where suspended graphene and bilayer graphene were found to be stable at room temperature because of variable amount of rippling in the out of plane direction[1].
- Our study is preceded by experimental observation of deviation of surface normal by a few degrees in n-layered graphene with the deviations becoming weaker with increasing number of graphene layers.

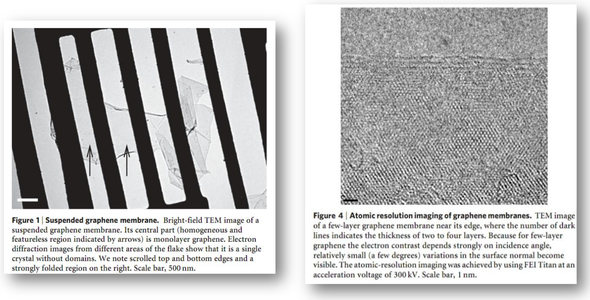


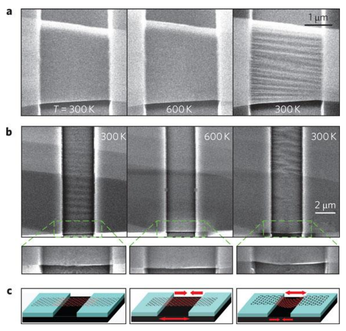
Figure 1 | Suspended graphene membrane. Bright-field TEM image of a suspended graphene membrane. Its central part (homogeneous and featureless region indicated by arrows) is monolayer graphene. Electron diffraction images from different areas of the flake show that it is a single crystal without domains. We note scrolled top and bottom edges and a strongly folded region on the right. Scale bar, 500 nm.

Figure 4 | Atomic resolution imaging of graphene membranes. TEM image of a few-layer graphene membrane near its edge, where the number of dark lines indicates the thickness of two to four layers. Because for few-layer graphene the electron contrast depends strongly on incidence angle, relatively small (a few degrees) variations in the surface normal become visible. The atomic-resolution imaging was achieved by using FEI Titan at an acceleration voltage of 300 kV. Scale bar, 1 nm.

1. Meyer et al., *Nature,* **446**, 60 (2007)

Motivation

- Electronic mobility of graphene is seen to be affected by the amount of rippling in graphene which gives another degree of freedom in device engineering[2].
- These ripples can also be used to advantage in steering and manipulation of electrons due to the intrinsic magnetic field produced by curvature in graphene and bilayer graphene sheet.
- Recently reversible hydrogen storage has been proposed by making use of the curvature in graphene sheet[3].
- Recently thermal manipulation of ripples in graphene was made possible thus being of advantage in controlled fabrication of nanoscale devices and electronics[4].

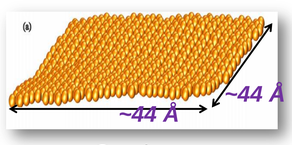


a,**b**, *In situ* SEM images of two devices taken before, during and after annealing. The bottom panels of **b** are higher magnification images of the edge of the graphene membrane, which sags into the trench after annealing. **c**, Schematic of buckling of a graphene membrane due to thermal contraction. From left to right, the panels depict the membrane in its original state, during heating and during cooling, respectively. The arrows indicate the contraction/expansion of the substrate and graphene.

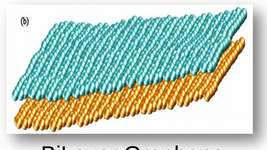
2. Nature Nanotech., **9**, 4446 (2009)
3. J. Phys. Chem. C, **115**, 25523 (2011)
4. Nature Nanotech., **4**, 562 (2009)

METHODS

Computational Methods & Simulation Parameters

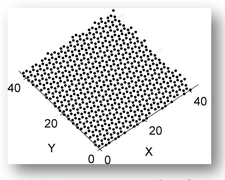


Graphene

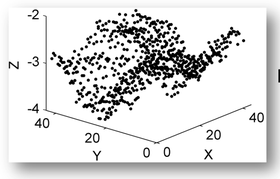


BiLayer Graphene

- LAMMPS Software*; 720-22400 atoms; room temperature; periodic boundary conditions; vacuum spacing-15Å; NPT ensemble with Nose-Hoover thermostat and barostat; adaptive intermolecular reactive bond order (AIREBO) potential as implemented in LAMMPS was modified to be used for the modeling of C-C interactions.
- **Long Time Equilibration**, **equilibrated for 100 ps**, time averages were calculated for 1.6-4.8 ns every 3 ps, time step- 1 fs.

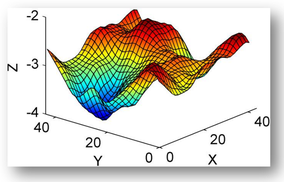


1600 geometrical configurations used from 1.6 ns run.

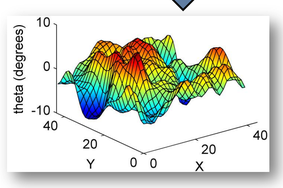


Objective* interpolation, for estimating grid values and smoothing.

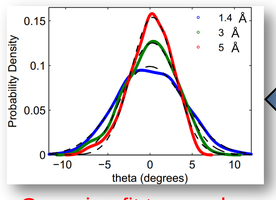
*J. Atmos. Ocean Tech.,11, 1433 (1994)



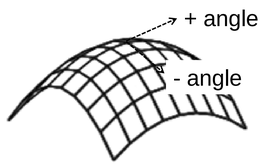
Square grid, grid spacing equal to the bond length of n-layer graphene.



Calculate local angles



Gaussian fit to angular deviations



Notation

- Since the rippling is found to be dynamic the local angles on graphene are computed for several geometrical configurations obtained from the simulation.
- A total of 1600 geometrical configurations were taken from the run of 1.6 ns. This choice ensures that an average deviation of surface normal is computed. We used a square grid of the geometrical configuration with grid spacing equal to the bond length of graphene to calculate the surface normal at each point with respect to the nearest neighboring grid points.
- The grid values were estimated from the original geometrical configuration by an objective interpolation scheme, Barnes interpolation, which also helps in smoothing of the interpolated surface.
- To get a statistical average the probability density of the local angles for all configurations were calculated and fit to a Gaussian.
- The average of 2 sigma deviations from all such fits is an upper limit to the deviation of the surface of the normal and 1 sigma a lower limit.

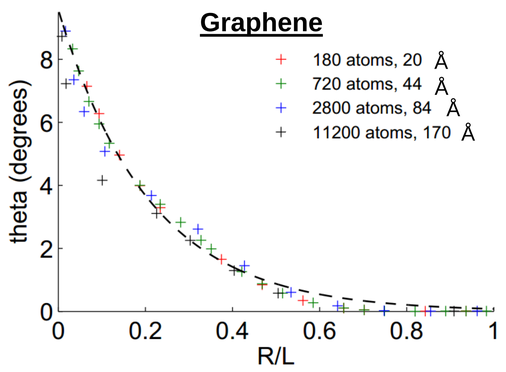
RESULTS

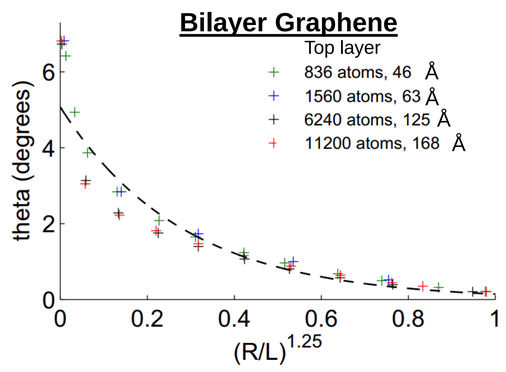
Temperature Effect: Bilayer Graphene

Patch Size, R (Å)	Deviation of Surface Normal (degrees)			
	Temperature			
	300K	400 K	600K	900K
1.4	6.42	6.87	8.62	10.66
3	4.94	4.87	6.40	7.90
5	3.87	3.55	4.88	6.12

Effect of tensile and compressive strain of 1 % is asymmetric.

Size Effect and Scaling





40 Å n-layer Graphene Sheet	1050 nm n-layer Graphene Sheet
R of 1.4 Å	R of 35 nm
R of 3 Å	R of 75 nm

- Surface normal deviation
  - follows an exponential scaling

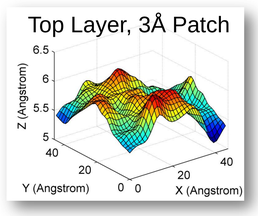
radius of influence

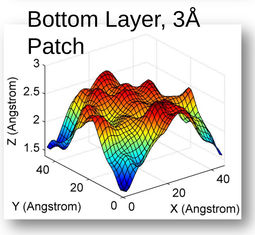
$$\theta(r, L) = \mathbf{a}\exp\left(-\mathbf{b}\left(\frac{R}{L}\right)^{c}\right)$$

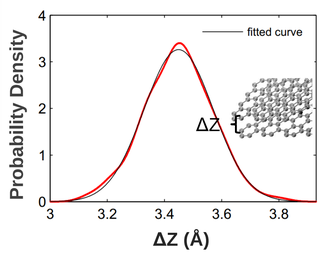
size of n-layer graphene sheet

- Constants a, b and c
  - are dependent on the number of layers in n-layer graphene sheet. The factor c is 1, 5/4 and about 5/3 for graphene, bilayer graphene and trilayer graphene respectively.
- The scaling relation
  - allows a convenient comparison with experimental results where graphene sheet of ~1 μm was used.

Bilayer Graphene: Interlayer Spacing







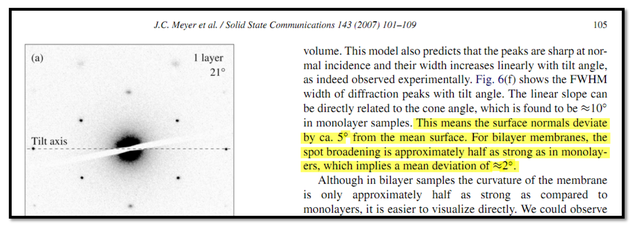
- The top and bottom surfaces do not show same angle profile.
- This is probably because in plane interactions of the layers are much stronger than the out of plane interactions.

CONCLUSIONS

- We find scaling relationships for the average angular deviations as a function of size of the n-layered graphene L and the size of the region over which the angle is averaged R, corresponding to the spot size in TEM.
- For single layer, the average angle scales with R/L, for bilayer it scales as $(R/L)^{5/4}$ and for trilayer it scale as about $(R/L)^{5/3}$. The scaling relations show that, for the same spot size, the measured angular deviations are larger for larger n-layered graphene sheets.
- The angular deviations are in excellent agreement with TEM results and confirm that these ripples can be dynamic in nature.
- Also, angular deviations are found to increase with increasing temperature. Effect of tensile and compressive strain of 1 % are asymmetric.

1050 nm Flake

Patch Size, R (nm)	Deviation of Surface Normal (degrees)		
	Graphene	Bilayer Graphene	Trilayer Graphene
35	8.33	6.42	6.09
75	6.66	4.94	4.54
122	**5.33**	**3.87**	**3.48**



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(a) 1 layer 21° Tilt axis

volume. This model also predicts that the peaks are sharp at normal incidence and their width increases linearly with tilt angle, as indeed observed experimentally. Fig. 6(f) shows the FWHM width of diffraction peaks with tilt angle. The linear slope can be directly related to the cone angle, which is found to be ≈10° in monolayer samples. This means the surface normals deviate by ca. 5° from the mean surface. For bilayer membranes, the spot broadening is approximately half as strong as in monolayers, which implies a mean deviation of ≈2°.

Although in bilayer samples the curvature of the membrane is only approximately half as strong as compared to monolayers, it is easier to visualize directly. We could observe

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