Adsorbate-induced curvature and stiffening of graphene

Supporting Information

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1. STM data acquisition and image processing
The STM experiments were conducted with an Agilent Technologies 4500 PicoPlus STM using a PicoScan controller and STM tips were formed from cut PtIr (80:20) wire. A droplet of TTC (Sigma Aldrich, 7098-22-8), dissolved in tetradecane (1.32 mg/mL), was deposited onto each substrate under ambient conditions. A metal clip holding the sample in place provided an electrical contact to the graphene layer. For lateral calibration the atomic structure of graphite (0001) served as a reference. The open source SPM software Gwyddion¹ was used to process the STM images prior to roughness analysis and the calculation of Fast Fourier transforms. The raw data was leveled by a mean plane subtraction and a median line correction. All the STM images which appear in the main text have been compared with their counter-scanned image and corrected for drift assuming a constant linear drift rate.

2. Sample preparation
hBN single crystals, prepared using previously published methodologies¹ ², were exfoliated onto thermally oxidized Si wafers (300 nm SiO₂) using Scotch tape and subsequently annealed in forming gas (5% H₂ in Ar) at 400 °C to drive off tape residue. Ruby muscovite mica (Agar Scientific) was used in our experiments and was cleaved before the graphene was transferred.

To transfer graphene, G/copper (see below) was coated with PMMA and placed on a FeCl₃ etching solution (Transene, CE-100) until the copper was visibly gone and then left for a further 30 minutes. The PMMA/G film was placed into a HCl bath and subsequently into five de-ionised
water baths for rinsing and was transferred onto the substrate. The PMMA was removed in solvent baths (acetone, IPA) and annealed in forming gas (5% H₂ in Ar) at 400 °C.

3. Graphene growth and characterisation

Graphene was grown by low-pressure chemical vapour deposition (LP-CVD) on copper. Copper foils (99.5% purity, 0.025 mm thick, Alfa Aesar product number 46365) were prepared by electropolishing (10 s at 5 V, ≈1.5 A) in an electrolyte solution (100 mL de-ionised water, 50 mL orthophosphoric acid (85 wt % in H₂O), 50 mL ethanol, 10 mL isopropanol, and 1 g urea) followed by rinsing in acetone then isopropanol and drying under a flow of nitrogen.

The foils were heated from room temperature to 1000 °C in a tube furnace within a 1 inch diameter quartz tube under a hydrogen atmosphere at a flow rate of 20 standard cubic centimetres per minute (sccm), at a pressure of 10⁻¹ mbar. This hydrogen flow rate was maintained throughout. The foils were annealed at 1000 °C for 20 mins then methane was introduced at 10 sccm for 10 min, before cooling to room temperature. While cooling to 600 °C, the flow rate of methane was reduced to 2 sccm, but after that the methane flow was stopped.

Figure S1 shows a typical SEM image of the copper foil after graphene growth. The surface is mostly homogeneous, indicative of uniform, predominantly monolayer coverage, with occasional darker regions (often interpreted as bi-layer graphene regions), darker lines (wrinkles in the graphene that occur due to the differential thermal expansion between graphene and copper upon cooling from the growth temperature) and lighter regions (cracks in the graphene). Analysis of the SEM images indicates that the as-grown graphene is >95% monolayer; this is supported by the TEM analysis (see below). AFM topography, (Fig. S1) shows that the copper surface is highly faceted underneath the graphene overlayer. The facets are typically ~ 100 nm across and the graphene on copper is locally flat within these facets, enabling atomic resolution STM.

Graphene TEM grids were fabricated by etching away the copper foil and transferring the resultant graphene film to a TEM support grid. A typical selected area electron diffraction pattern from these films is shown in Figure S2. The hexagonal pattern of diffraction spots, and their spacing, is characteristic of graphene. The rings of intensity are due to the amorphous support. A line profile through the diffraction spots, Figure S3, indicates that the inner, first order, spots are of similar intensity to the outer, second order, ones. This is indicative of monolayer graphene.

Composite darkfield TEM imaging reveals the polycrystalline nature of the graphene film and confirms that the film is predominantly monolayer with a typical graphene
grain size of ~ 3-5 µm under these growth conditions. For some of our experiments we have also used commercially supplied graphene on copper (supplied by Graphene Supermarket; this material was characterised prior to use to confirm that graphene monolayers were present both before and after the transfer to dielectrics.

Figure S2: (left) TEM selected area electron diffraction pattern and (right) intensity profile from the region marked by the dashed box. The diffraction pattern has been inverted for clarity.

4. Additional STM images
Figure S3 shows further images of the lamellar rows which are referenced in the main text.
Figure S3: TTC on G/mica. Upper: Larger figure of STM image shown in Fig.1e to show more clearly the extended lamellar; middle differentiated image of the upper; lower left undifferentiated image which appears in Fig. 1i of the main paper; lower right zoomed are (undifferentiated) of lamellar rows running across step edges induced by water layers. (-1 V, 0.15 nA).
5. Analysis of Adsorption Energy of Alkanes on Curved Graphene

5.1 Background variation of energy

Consider an atom placed a height $h$ above a surface interacting through potentials of the form $B/r^m$. Assuming that we have a density of $n$ atoms per unit area in the surface/membrane the potential arising from an element $dA$ in the surface is $C/r^m dA$, where $C = nB$. Summing over the potentials arising from different sites on the surface gives for a planar surface (i.e. no curvature),

$$V_{\text{plane}}(h) = C \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \frac{1}{(x^2 + y^2 + h^2)^{m/2}} = \pi C \frac{2}{m-2} \frac{1}{h^{m-2}}$$

For a cylindrically curved surface (cylindrical axis parallel to $y$) we may approximate in the limit of large radius of curvature ($R >> x, h$),

$$r^2 = x^2 + y^2 + (h + R - (R^2 - x^2)^{1/2})^2 \approx x^2 + y^2 + (h + \frac{x^2}{2R})^2 \approx x^2 \left(1 + \frac{h}{R}\right) + y^2 + h^2$$

Accordingly we can re-write the above integral,

$$V_{\text{cylinder}}(h) = C \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \frac{1}{(x^2(1+R/h) + y^2 + h^2)^{m/2}}$$

After a change of variable, $x' = (1+h/R)^{1/2} x$ this reduces to,

$$V_{\text{cylinder}}(h) = C \left(1 + \frac{h}{R}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy \frac{1}{(x'^2 + y^2 + h^2)^{m/2}} \approx \left(1 - \frac{2h}{R}\right) V_{\text{plane}}(h)$$

as in the main text. This is valid to first to order in $(h/R)$ and the retention of the infinite limits of integration is valid in this limit if $m \geq 4$. Thus the result does not depend on $m$ (for $m \geq 4$) or $C$, i.e. applies to both the attractive and repulsive parts of the potential.

5.2 Energy reduction due to sinusoidal variation of angle

The energy due to distortion is given by,

$$E = \int_{-d/2}^{d/2} \left[ \frac{V_o}{a} \cos 2\pi \frac{d\theta}{a} \frac{s}{s} - \frac{h}{a} \theta(s) \right] - E_A \left(1 - \frac{h}{2} \frac{d\theta}{ds}\right) + \frac{\kappa_B}{2} \left(\frac{d\theta}{ds}\right)^2 + \frac{\kappa_A \sqrt{3}}{2} \left(\frac{d\theta}{ds}\right)^2 ds$$

and we consider the overall energy change due to a small perturbation with a period equal to $d$. Writing $\theta(s) = \theta_0 \sin(2\pi s/d)$, expanding the energy functional to second order in $\theta_0$, and neglecting the terms in bending energy gives,
\[ \delta E = - \frac{V_o}{a} \frac{R_m}{\pi} \sin \left( \frac{\pi d}{R_m} \right) \left( 1 + f \frac{R_m d}{R_m - d^2} - f^2 \left[ 1 + \frac{d^2}{4R_m^2 - d^2} \right] \right) = - \frac{V_o}{a} \frac{R_m}{\pi} \sin \left( \frac{\pi d}{R_m} \right) \left( 1 + f \frac{R_m d}{R_m - d^2} - f^2 \frac{R_m^2}{4R_m^2 - d^2} \right) \]

where \( f = 2\pi \theta_o/a \). This is minimised when

\[ \theta_o = \frac{a}{4\pi h} \frac{4R_m^2 - d^2}{R_m^2 - d^2} \]

giving rise to a peak-to-peak amplitude,

\[ A = \frac{\theta_o d}{\pi} = \frac{a}{4\pi h} \frac{4R_m^2 - d^2}{R_m^2 - d^2} \frac{d^2}{R_m} = \frac{ad}{4\pi h} \frac{4 - \gamma^2}{1 - \gamma^2} \gamma \]

where \( \gamma = d/R_m \), as in the main text.

### 5.3 Reduction factor arising from bending terms

Taking into account the bending terms gives an additional contribution,

\[ \delta E = - \frac{V_o}{a} \frac{R_m}{\pi} \sin \left( \frac{\pi d}{R_m} \right) \left( 1 + f \frac{R_m d}{R_m - d^2} - f^2 \frac{R_m^2}{4R_m^2 - d^2} \right) + \frac{\pi^2 \theta_o^2}{d^2} \left( \kappa_h + \kappa a \sqrt{3} \right) \]

which can be rearranged to,

\[ \delta E = - \frac{V_o}{a} \frac{R_m}{\pi} \sin \left( \frac{\pi d}{R_m} \right) \left( 1 + f \frac{R_m d}{R_m - d^2} - f^2 \left[ \frac{R_m^2}{4R_m^2 - d^2} + \frac{\pi a^3}{4h^2 d V_o R_m \sin(\pi d / R_m)} \left( \kappa_h + \kappa a \sqrt{3} \right) \right] \right) \]

Leading to a reduction in amplitude by a factor \( \beta \),

\[ \beta = \left( 1 + \left( \frac{\kappa_h + \kappa a \sqrt{3}}{d} \left( \frac{4V_o R_m \sin(\pi d / R_m) h^2}{\pi a (4 - \gamma^2) a^2} \right) \right) \right)^{-1} \]

Since \( \kappa_m = \frac{1}{3} V_o \frac{\pi^2 h^2 d^2}{a^3} \) we can re-write \( \beta \),

\[ \beta = \left( 1 + \left( \frac{\kappa_h + \kappa a \sqrt{3}}{\kappa_m} \frac{\pi^2 \gamma (4 - \gamma^2)}{12 \sin \pi \gamma} \right) \right)^{-1} = \left( 1 + \frac{\alpha \left( \frac{\kappa_h + \kappa a \sqrt{3}}{\kappa_m} \right)}{\kappa_m} \right)^{-1} \]

where \( \alpha = \frac{\pi^2 \gamma (4 - \gamma^2)}{12 \sin \pi \gamma} \).
6. Numerical and Computational Details

6.1 Code and potential
Simulations of ordered alkane chains physisorbed on graphene were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) classical molecular dynamics code\(^6\). For the carbon-carbon, carbon-hydrogen and hydrogen-hydrogen interactions the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential\(^7\) has been used which was developed to describe hydrocarbon systems. The AIREBO potential is an improved version of Brenner’s well-known second generation Reactive Empirical Bond Order Potential\(^8\) (REBO) but includes a Lennard-Jones (LJ) potential form to describe van der Waals long-range interactions and a torsional term for σ-bond torsions. The LJ cutoffs were set to 10.2 Å, 9.08 Å, and 7.95 Å for C-C, C-H and H-H pairs, respectively. All the structures were optimised via the minimize feature with the conjugate gradient (CG) algorithm and tight convergence criteria (10\(^-10\) eV/Å for forces).

6.2 Structural Models
Model \(\text{C}_{44}\text{H}_{90}\) and \(\text{C}_{8}\text{H}_{18}\) alkane chains are used to study the effect of lattice incommensurability (mismatch) between carbon nanostructures (CNNs) and the chains. In order to investigate the influence of CNNs curvature on the adsorption energy of alkane chain, a set of zigzag carbon nanotubes (CNTs) was built with increasing value of radius ranging from 19.26 Å (a (50,0) CNT) to 1540.19 Å (a (2000,0) CNT). A simulation box contains 6 replicas of the primitive unit cell of a CNT translated along the principal axis, which allows avoiding self-interactions of the alkane chains. For the case of planar graphene, a periodic sheet with dimensions of (99.2 × 92.2) Å was built. An alkane chain is placed along the preferential zigzag direction outside (positive curvature) or inside (negative curvature) the CNT sidewall. The resulting alkane-CNT (or graphene) complex was optimized as described in section 6.1, although in order to separate the contributions from positive and negative curvature the atomic positions of CNTs (graphene) were kept frozen while the structures of alkane chains were fully relaxed.

6.3 Calculations of the Adsorption, Strain and Interaction Energies
The combined adsorption and strain energy \(E_{\text{tot}}\) of alkane chains on CNTs was evaluated as \(E_{\text{tot}} = E(\text{Alk@CNT}) - E(\text{CNT}) - E(\text{Alk})\), where \(E(\text{Alk@CNT})\), \(E(\text{CNT})\) and \(E(\text{Alk})\) are the total electronic energies of the alkane-CNT complex, CNT and alkane chain, respectively. The strain energy \(E_{\text{str}}\) for the alkane chain is evaluated as \(E_{\text{str}} = E(\text{Alk@CNT}) - E(\text{Alk})\), where \(E(\text{Alk@CNT})\) is the total electronic energy of the chain in the geometry of the complex; the strain energy is plotted in Figure 3 of the main text; it has been found to have an approximate parabolic dependence on the inverse radius of curvature. The adsorption energy \(E_{\text{ads}}\) is given by \(E_{\text{ads}} = E_{\text{tot}} - E_{\text{str}}\), and is plotted as blue dots in Figure 3 of the main text.

A scan of the potential energy surface (PES) of CNNs, using both short and long alkane chains as probes, has been performed. In the case of planar graphene the chains were optimized in a vacuum, then positioned at the equilibrium height on the hexagonal lattice and translated step by step (step size of 0.05 Å) along and across the zigzag direction; the total electronic energy was evaluated at each point. In the case of CNTs, the chains were optimized in the geometry of
the complex and then moved around the principal axis of a CNT; the rotation angle was selected in a way to ensure that the segment of each CNT has the same length.

7. Error analysis
7.1 Separation of rows and molecules
The periodicity of the lamellar rows and the intermolecular spacing within the rows which is quoted in the paper is determined from the Fourier transforms of images such as shown in Figure 1. The errors, where quoted, are derived from the widths of the spots in the FT of the image.

7.2 Error estimation for the peak-to-peak amplitude and derived quantities
The quoted error of the peak-to-peak amplitude, \( A \), in the main text is derived from an average over thirty separate profiles extracted from Fig. 1e. The ratio \( \gamma \) is determined from \( A \) using the formulae quoted in the paper and derived above. The error in \( \gamma \) is determined using the same formulae to numerically evaluate the variation of \( \gamma \) with \( A \), followed by conversion of the error in \( A \).

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