Atomically sharp non-classical ripples in graphene

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Abstract: A fundamental property of a material is the measure of its deformation under applied stress. After studying the mechanical properties of bulk materials for the past several centuries, with the discovery of graphene and other two-dimensional materials, we are now poised to study the mechanical properties of single atom thick materials at the nanoscale. Despite a large number of theoretical investigations of the mechanical properties and rippling of single layer graphene, direct controlled experimental measurements of the same have been limited, due in part to the difficulty of engineering reproducible ripples such that relevant physical parameters like wavelength, amplitude, sheet length and curvature can be systematically varied. Here we report extreme (>10%) strain engineering of monolayer graphene by a novel technique of draping it over large Cu step edges. Nanoscale periodic ripples are formed as graphene is pinned and pulled by substrate contact forces. We use a scanning tunneling microscope to study these ripples to find that classical scaling laws fail to explain their shape. Unlike a classical fabric that forms sinusoidal ripples in the transverse direction when stressed in the longitudinal direction, graphene forms triangular ripples, where bending is limited to a narrow region on the order of unit cell dimensions at the apex of each ripple. This non-classical bending profile results in graphene behaving like a bizarre fabric, which regardless of how it is pulled, always buckles at the same angle. Using a phenomenological model, we argue that our observations can be accounted for by assuming that unlike a thin classical fabric, graphene undergoes significant stretching when bent. Our results provide insights into the atomic-scale bending mechanisms of 2D materials under traditionally inaccessible strain magnitudes and demonstrate a path forward for their strain engineering.

Main text:

Being only a single atom thick, 2D materials are the ultimate limit of thin fabrics. From a fundamental viewpoint, it is important to understand how mechanical properties and rippling of 2D materials differ from those of classical fabrics. The potential of developing flexible electronics using 2D materials makes these studies also relevant from a practical and engineering viewpoint. One of the earliest studies of graphene’s mechanical properties was done by Lee et al.1, by making indentations with an atomic force microscope. They found that graphene has a Young’s modulus of 1TPa (five time that of most steels) and an intrinsic strength of 130 GPa (fifty to a hundred times of most steels) – the highest for any material ever measured. Moreover, their discovery of a non-linear stress-strain relationship spurred theoretical studies to explain the origin of the non-linearity2–4. Efforts were also made to go beyond numerically expensive first principle calculations towards equivalent continuum models that can explain the mechanics of larger graphene sheets as a fabric5–7. Finding an equivalent description of 2D materials analogous to classical fabrics is challenging for two main reasons. First, the inability to properly define the plate thickness of a single atomic layer results in wide variations in bending and Young’s moduli among different studies, known as Yakobson’s paradox8,9. Secondly, an equivalent description of a discrete lattice is challenging when the length scale of strain variation becomes comparable to the lattice constant. Indeed, Tapaszto et al.10 found nanometer length scale graphene ripples have shapes that cannot be described by a continuum mechanics approach valid for a classical fabric11. Interestingly, Bai et al.12 found this discrepancy persists for ripples measuring up to 100 nm, length scales which are much larger than the lattice constant, whereas micron sized ripples were well described by continuum mechanics13.
Figure 1: Rippling in Classical Fabrics: (a) Applying tensile stress to a fabric in the longitudinal direction (x) results in a Poisson compression in the transverse direction (y), creating ripples. The shape of ripples in a classical fabric is determined by the balance of energy contribution from two deformations: the stretching in the longitudinal direction (with corresponding energy cost $U_{st}$) and bending in the transverse direction (with corresponding energy cost $U_b$). (b) Plastic wrap spread over two concentric cylinders, with taller inner cylinder, also yields such tension ripples. As strain $\gamma$ is kept constant, ripple wavelength $\lambda$ and sheet length $L$ follow a scaling law $L \sim \lambda^2$, as derived in Equation 5 of the text. In the figure, ripples on the right have smaller wavelength (red) and amplitude than those on the left. But to stabilize the larger ripples, the left ripples must run diagonally, increasing the effective sheet length $L$ (blue).

Ripples in graphene are observed quite commonly and are also necessary for the stability of 2D materials. However, development of a thorough formalism of 2D material deformation at the nanoscale, equivalent to that for classical fabrics, has been hindered due to the difficulty of creating reproducible nanoscale ripples such that physically relevant parameters like wavelength, amplitude, sheet length and curvature can be systematically varied and measured over a large parameter space. Instead, experimental studies have typically relied on the good fortune of finding wrinkles in 2D materials. Though it is possible to induce controlled strain by patterning substrates, this approach tends to create wrinkles with deformation length scales much larger than the lattice spacing. Though measurable strains exceeding 2% in 2D materials have been achieved recently in large samples by macroscopic mechanical engineering, atomic scale distortions have not been imaged in these systems. Here we investigate the nature of nanoscale ripples in graphene by scanning tunneling microscopy (STM) to test the applicability of classical theories in the discrete atomic limit and understand how it falls inadequate. Our observations can be explained well if unlike a thin classical fabric, graphene undergoes significant stretching when bent creating non-classical ripple shapes.

The deformation of a thin sheet was described by Lord Rayleigh in his book *Theory of Sound*. There are two ways a uniform isotropic thin sheet can deform: by out of plane bending and by in-plane stretching. When a sheet of thickness $t$ bends with a radius of curvature $R$, then the strain varies through its thickness as $\gamma_b \sim z/R$ where $z$ is the axis normal to the sheet surface. Hence the energy density due to bending $U_b \sim \int \gamma_b^2 \, dz \sim t^3$. Similarly, the energy density due to a uniform stretch is $U_{st} \sim \int \gamma_{st}^2 \, dz \sim t$. Then the total energy $U$ due to deformation is
\[ U \sim t^3 \text{(Bending)} + t \text{(Stretching)} \]  
(1)

As the deformation should be such that the energy cost is minimized, Rayleigh remarked that ‘when the thickness is diminished without limit, the actual displacement will be one of pure bending’\textsuperscript{28}. The scaling laws relating the wavelength, sheet length and strain magnitude for a classical rippled sheet were deduced by Cerda and Mahadevan\textsuperscript{11}. As a sheet under tension in the longitudinal direction ripples in the transverse direction, the shape of ripples is determined by balancing the energy contributions from these two deformations (Fig. 1a). If we consider a sheet of thickness \( t \), length \( L \) and Young’s modulus \( E \) rippling under applied tension per unit length \( T \), it results in a longitudinal strain \( \gamma = \frac{T}{Et} \). The energy due to this longitudinal extension integrated over a wavelength \( \lambda \) of the ripples is
\[ U_{st} \sim \int T \left( \frac{dx}{dx} \right)^2 dxdy, \]
which leads to an energy associated with longitudinal stretching
\[ U_{st} \sim E\gamma \left( \frac{A}{L} \right)^2 L \cdot \lambda = \frac{EtyA^2}{L} \]
(2)

where \( A \) is the ripple amplitude. On the other hand, the bending energy of a ripple is
\[ U_b \sim t^3 \int E(\text{curvature})^2 dxdy. \]

The curvature of the sheet as it ripples is approximately \( \frac{A}{\lambda^2} \), making the bending energy integrated over a ripple wavelength to be
\[ U_b \sim Et^3 \left( \frac{A}{\lambda^2} \right)^2 L\lambda = \frac{Et^3A^2L}{\lambda^3} \]
(3)

Equations 2 & 3 imply that \( U_{st} \) tries to reduce the wavelength \( \lambda \) while \( U_b \) tries to increase it. The ultimate shape of the ripples results from a balance between these two energies,
\[ \frac{d(U_b+U_{st})}{d\lambda} = 0 \Rightarrow \frac{d}{d\lambda} \left( \frac{Et^3A^2L}{\lambda^3} + \frac{EtyA^2}{L} \right) = 0 \]
(4)

which gives us a scaling law relating the wavelength, strain, sheet length and thickness:
\[ L \sim \frac{\sqrt{EtA^2}}{t} \]
(5)

as also derived by Cerda and Mahadevan\textsuperscript{11}. The scaling law implies that for a sheet under constant strain, the sheet length \( L \) varies as \( \lambda^2 \). An example of this is illustrated in Fig. 1b, where the ripples on the left have a larger wavelength and amplitude than those on the right, but to accommodate the larger ripples, the sheet must drape down diagonally, effectively increasing the sheet length.

For most STM studies of graphene an atomically flat substrate is desired in order to facilitate the growth of large grains and to ease scanning. However, to encourage the rippling of graphene in our study, graphene is grown via low pressure chemical vapor deposition at high temperature (1020°C) on an electropolished Cu substrate (See Supplement Sec. 1). Under these growth conditions, several studies have investigated the process of step bunching whereby the growth of graphene promotes the migration of smaller Cu steps to bunch together to form large step heights\textsuperscript{32,33}. Step bunching leads to the formation of large steps up to 35 nm tall (Fig. 2a). It is these sites, where graphene is draped over large step heights, that we use to investigate rippling in graphene. The monolayer nature of the graphene in these systems
Figure 2: Engineering Nanoscale Ripples in Graphene: (a) STM image of graphene grown on copper with large (up to ~35 nm high) step edges (current setpoint $I_{\text{set}} = 70$ pA, sample bias $V_s = 0.1$ V; all displayed data is obtained at temperature $T = 80$ K and unfiltered, unless otherwise noted). The graphene drapes over step edges. (b) A closer look at a step edge ($I_{\text{set}} = 80$ pA, $V_s = 0.1$ V) reveals ridges, highly commensurate above and below the step. The draped region is adorned with ripples. (c) Atomic resolution imaging of a ridged terrace, with darker regions in contact with and lighter regions elevated above the substrate ($I_{\text{set}} = 120$ pA, $V_s = 0.15$ V, Fourier filtered to enhance atomic contrast). (d) FFT of atomic resolution topography from an unstrained graphene lattice. Peaks (marked by white dashed circles for clarity) are equidistant from the center (as grey dotted circle). (e) Topographic FFT from the draped region (grey box in (b)) shows superlattice components (blue circles) and lattice distortion due to strain. Measuring deviation from the unstrained positions (grey circle) yields strains of 1) 10.3%, 2) 6.8% and 3) -3.3%. Scalebars here and in (d) are 5 nm$^{-1}$. (f) Analogous to corners of a draped tablecloth, high curvature regions are associated with higher ripple density (and smaller ripple wavelength) as highlighted in topographic profile (g), extracted along the blue line ($I_{\text{set}} = 170$ pA, $V_s = 0.12$ V).

is shown by Raman spectroscopy (Supplement Sec. 1) and further confirmed by the fact that no Moiré pattern was ever observed by STM.

In Fig. 2b two distinct types of deformations are observed: one is found at the Cu steps, which will be referred to as ripples; the other type is found on the flat Cu regions, which will be referred to as ridges. As the system is cooled from 1020°C, graphene expands due to its negative coefficient of thermal expansion, and Cu shrinks. This creates strain in the system and causes buckling of the graphene on flat Cu regions while also stretching the draped graphene over a step, analogous to an elastic sheet getting stretched and forming ripples. Figure 2c images one of the graphene ridges. The ridges are found to be commensurate above and below a step and to terminate at the crests and troughs of a ripple indicating an interaction between the two. The ridges may act as nucleation sites for the buckling of graphene, initiating the formation ripples over the step.
We estimate strain in our system by comparing Fourier transforms of atomic resolution images taken on the draped and flat regions (Fig. 2e, d). The graphene lattice on an unstrained flat region (Fig. 2d) is characterized by a hexagonal pattern with peaks marked by white dashed circles, equidistant from the center, indicating an unstrained system. Graphene imaged on the draped region (Fig. 2e) yields a distorted hexagonal lattice, in addition to superlattice peaks (marked in blue). The ratio of lattice constants from these two regions (both imaged with the same tip to eliminate systematic differences due to calibration) suggests a strain of over 10%. We also note that such superlattice periodicities (marked by blue circles in Fig. 2e) in strained graphene were also observed by Ziatdinov et al.34.

When analyzing ripples in the draped regions we observe (Fig. 2f, g) that they occur preferentially in regions of higher step edge curvature. This is analogous to the classical case of ripples forming at the corners of a tablecloth, a result of having more expendable material at that location. In Fig. 3 we present measurements of their wavelength, amplitude, and sheet length. The wide variation of parameters from more than two hundred independent measurements across multiple steps, enables us to explore a large parameter space. This, in turn, allows us to avoid the necessity of estimating experimentally unmeasured quantities like the effective thickness of the graphene sheet and its Poisson’s ratio at the nanoscale10,12, and instead look for scaling relationships to directly test classical laws.

Fig. 3c shows that contrary to a sinusoidal profile of ripples observed in a classical fabric, ripples in graphene observed on the draped regions have a triangular shape. More interestingly, all ripples have the same bending angle at the vertex, regardless of their wavelength (Fig. 3d), step height or curvature. The measured angle of 163° (±3°) is consistent not only across order of magnitude variations in wavelength, amplitude, and step height for which we have measured, but also in studies from different groups on different graphene systems. For example, Tapaszto et al.10 and Bai et al.12 created nanoscale ripples in graphene on Cu substrates, and from their reported data we calculate a bending angle consistent with ours. A detailed comparison of our observations with other published results is provided in Supplementary section 4.

A conserved bending angle at the vertex of a triangular ripple implies that the ripple’s wavelength is proportional to its amplitude. If we consider the classical theory of rippling, such a situation can arise for ripples with uniform strain. As an unstretched sheet of width λ gets stretched to a width λ’ in forming a ripple with amplitude (z-distance from ripples’s crest to base) A, then, as \((\frac{\Delta \lambda}{\lambda})^2 = (\frac{1}{2})^2 + A^2\), we get \(\Delta \lambda = \lambda’ - \lambda \approx \frac{2A^2}{\lambda}\) for \(\Delta \lambda \ll \lambda\). Thus, the strain \(\gamma = \frac{\Delta \lambda}{\lambda} = \frac{2A^2}{\lambda^2}\). A more rigorous proof of \(A \sim \sqrt{\gamma} \lambda\) was also provided by Cerda and Mahadevan11. However, if the \(A \sim \lambda\) triangular ripples we observe are uniformly strained classical ripples, then theory predicts a scaling relation between sheet length \(L\) and wavelength \(\lambda\) of \(L \propto \lambda^2\), as derived in Equation 5. We test this prediction directly by measuring sheet length \(L\) and wavelength \(\lambda\) of ripples. Fig. 3a displays two regions on the same step where measurements were taken. For these two regions, the local ripple wavelengths, shown in Fig. 3c along the ripple direction \(A_1\) and \(B_2\), differ by a factor of 2 (\(A_2 \approx 2A_1\)) while the sheet lengths (Fig. 3b) are nearly identical, \(L_B \approx L_A\) in strong contrast with the classical prediction of \(L_B \approx 4L_A\) (from Equation 5). In Fig. 3e we compare the sheet
Figure 3: The Shape of Graphene: (a) Topography of ripples on draped graphene ($I_{\text{set}} = 30\text{pA}, V_s = 0.1 \text{V}$) from whence profiles in (b) and (c) are extracted. (b) Profiles down the sheet ($A_1/B_1$) reveal sheet length $L$ of the tautly pulled sheet. (c) Profiles along the sheet ($A_2/B_2$) highlight local wavelength and apex angle ($163^\circ$) of these triangular ripples. The profiles in (b) and (c) are offset for clarity, and have different scales for the horizontal and vertical axes. (d) The rippling angle (from (c)) is conserved at $163^\circ (\pm 3^\circ)$, and is independent of step height and curvature, and ripple wavelength and amplitude. We only show the independence with respect to wavelength here for brevity. (e) Measurement of sheet length and wavelength of ripples on three separate step edges show the violation of classical scaling, which predicts $L \propto \lambda^2$.

Length $L$ and wavelength $\lambda$ of several ripples observed on three different step edges, to demonstrate the lack of any clear correlation between the two variables. The disagreement between classical theories of rippling and the measured quantities ($\lambda$ and $L$) presented here imply that classical theories are not valid for nanoscale ripples in graphene.
To explain the origin of the non-classical shape of the ripples, we restate our three main observations: (i) ripples in graphene are triangular in shape, as opposed to sinusoidal as observed in a classical sheet (Fig. 3c), (ii) all ripples are observed to have the same vertex angle (measuring 163°(±3°)), implying that graphene always bends the same way, irrespective of boundary conditions (Fig. 3d), and (iii) there is no apparent relation between wavelength $\lambda$ and sheet length $L$ (Fig. 3e). The derivation of the classical theory of rippling of thin sheets neglects any transverse in-plane stretching as the sheet bends, following Rayleigh’s statement. However, if graphene stretches significantly when bent (Fig. 4a), then the energy considerations we presented earlier for the classical fabric must be modified. In particular, the bending energy will be accompanied by an extra “stretching due to bending” energy contribution $U_{sb}$:

$$U_b = t^3 \int E(curvature)^2 \, dx \, dy = t^3 \int E(curvature)^2 \, dx \, dy + t \int E \gamma_{sb}^2 \, dx \, dy = U_b + U_{sb}$$

This new energy contribution ($U_{sb}$) results in a transverse stretching strain $\gamma_{sb}$ over the bent region. If graphene bends with a radius of curvature $R$ at the crests and troughs (Fig. 4b), with the bent region (colored yellow in Fig. 4b) subtending an angle $\varphi$ at the center of the circle, then the bending energy is $U_b \sim Et^3 \int \left(\frac{1}{R^2}\right) \, dx \, dy \sim \frac{Et^3 \varphi}{R}$, as the bending region has an arclength of $R \varphi$. The resultant stretching energy coming from this bending is $U_{sb} \sim Et \gamma_{sb}^2(R \varphi)L$, where for simplicity we have assumed $\gamma_{sb}$ to be spatially uniform in the stretched region. The energy cost due to bending $U_b$ tries to increase the radius of curvature, but the associated stretching term $U_{sb}$ penalizes bending with large radii of curvatures. The final radius of curvature is then determined by the balance of these two competing energy scales.

$$\frac{d(U_b+U_{sb})}{dR} = 0 \Rightarrow R = \frac{t}{\gamma_{sb}}$$

(Equation 6)

This simple phenomenological model can well explain our three key observations we made earlier for the ripples. First, having an optimal bending radius means graphene should always bend the same way, irrespective of the boundary conditions, as we have observed. While equation 6 implies the existence of an optimal bending radius, an accurate value of $R$ is difficult to calculate from it as it involves the effective thickness $t$ of the graphene sheet, estimation of which varies widely in literature. Instead, we measure the bending radius directly (in Supplementary sec. 5) to be $R = 0.8$ nm. To minimize the total energy, we choose the arclength of the bent region to be the smallest length scale over which graphene can deform (0.25 nm, graphene lattice constant), to get $\varphi = \frac{0.25 \text{ nm}}{0.8 \text{ nm}} = 0.3 \text{ rad} = 17^\circ$. The calculated rippling angle $\theta = 180^\circ - \varphi = 163^\circ$ is consistent with our observed $163^\circ(±3^\circ)$ (in Fig. 3d). Second, this consistency suggests that the bending and transverse stretching of graphene is limited to a very small region - of the order of graphene unit cell dimensions - instead being distributed as a smaller stretch across all bonds, as happens while bending a thick classical plate. Thus we expect triangular ripples, as observed. Finally, from equation 6, the bending radius $R$ is also independent of the sheet length $L$, which explains why, contrary to the classical prediction (equation 5) there is no relation between wavelength $\lambda$ and $L$. Neither the wavelength (which depends only on the local step edge curvature (Fig. 2f, g) and hence can vary independently), nor the fixed bending radius $R$ affect the effective sheet length $L$. 
Figure 4: A phenomenological model for graphene bending: (a) Analogous to a classical fabric under tension in the longitudinal direction, graphene ripples in the transverse direction. However, unlike a classical fabric which does not stretch significantly in the transverse direction when bending (discussed in Fig. 1a), graphene undergoes significant stretching when bent, resulting in triangular ripples where the bending is confined to a narrow region of the order of the unit cell dimensions. The crests and troughs of the ripples (yellow, where the graphene bends) undergo significant stretching in the transverse direction compared to the unbent regions (turquoise). As observed in Fig. 3d and explained in the text using a phenomenological model, balance of the transverse bending and stretching energies ($U_b$ and $U_{sb}$ respectively) cause graphene to always bend with the same angle ($\theta$ in (b), and measured in the experiment in Fig. 3d). The effect of the longitudinal stretching energy $U_{st}$ over the narrow bending region is negligible, as explained in the text. (b) Schematic side view of (a) showing graphene bending with a radius of curvature $R$. Features are not to scale. The bending region (yellow) is exaggerated for clarity resulting in a rippling angle $\theta$ at the vertex that is much smaller than our observed $163^\circ$.

In our phenomenological model we argued that the transverse in-plane stretching energy ($U_{sb}$) restricts the graphene from bending over a wider region while the discrete nature of the lattice stops it from bending over a narrower region. The actual size of the bending region is determined by the balance of these two competing energy scales. Note that the actual bending region can be larger than the graphene unit cell dimensions. In our model above we assume the bending shape to be a perfect circle with no bending/transverse stretching outside this region and uniform strain $\gamma_{sb}$ inside it. Furthermore, bending should be the result of individual atoms changing positions in the graphene lattice, and not bending of the unit cell in a circular shape. Also, in deriving equation 6, we have treated graphene as an effective thin uniform isotropic sheet and assumed the form of bending and stretching energies to remain unchanged from what we discussed in equation 1 for classical fabrics. In particular, the bending energy expression discussed in equation 1 requires the sheet to have a finite thickness, which is difficult to define for graphene. While our phenomenological model can provide good order of magnitude estimates, strain distribution profiles in an atomically thin discrete lattice should be different from that of a thin continuous classical sheet and more detailed theoretical calculations will be required to supplement it.
In our phenomenological model, we have neglected the contribution of the longitudinal stretching energy $U_{st}$. Next, we justify this approximation that the contribution of the longitudinal stretching energy over the narrow bending region is negligible compared to the bending and transverse stretching energies. In particular, we argue $U_{st} \ll \langle U_b + U_{sb} \rangle_R = t/\gamma_{sb}$, which implies that longitudinal stretching plays a minor role in determining the ultimate shape of bent graphene. A small out of plane deformation $\Delta$, in addition to the in-plane stretching in the transverse direction, will result in small deviations of the graphene sheet from the ideal circular shape derived earlier. Analogous to the classical case derived earlier (equation 2), the contribution of the longitudinal stretching energy integrated over the bent region is

$$U_{st} = \int T \left( \frac{d\gamma}{dx} \right)^2 dx \, dy = E t y \left( \frac{L}{L} \right)^2 L(R \phi).$$

The ratio $\frac{U_{st}}{U_b + U_{sb}} = \frac{E t y \Delta^2 R / L}{2 E t^2 L_0 / R} = \frac{\gamma \Delta^2 R^2}{2 t^2 L^2}$. We can make an order of magnitude estimation of this ratio from our experiment with $\gamma \approx 0.1$ (measured in Fig. 2c), $R \approx 0.8$ nm (measured directly in Supplementary sec. 5) and $L \approx 20$ nm (from Fig. 3e). Estimates of the thickness $t$ varies widely in literature. Assuming the thickness to be the interlayer spacing of graphite would make $t = 0.335$ nm. On the other hand, ab-initio bond-orbital models estimate the effective thickness to be as low as 0.08 nm. The out of plane buckling $\Delta$ as graphene is stretched is also difficult to estimate, but, as the shape at the ripple crests deviate very little from a perfect circle (supplementary sec. 5), $\Delta < R$. Even considering the smaller thickness $t = 0.08$ nm and $\Delta \approx R$ as an upper bound, $\frac{U_{st}}{U_b + U_{sb}} = \frac{\gamma \Delta^2 R^2}{2 t^2 L^2} = 0.008 \ll 1$, proving that the energy contribution from longitudinal stretching $U_{st}$ is indeed negligible over the narrow region over which graphene bends. Notably, Tapaszto et al. observed a similar rippling angle as ours (supplementary sec. 4) even though their longitudinal strain magnitude (2%) was much smaller than ours ($>10\%$), implying very different longitudinal stretching energy $U_{st}$ for the two studies. This adds further credence to our above analysis that the longitudinal stretching energy $U_{st}$ plays a minor role in determining the ultimate shape of the ripples.

The local strain $\gamma_{sb}$ at the ripples’ crests and troughs is difficult to measure directly by atomic imaging as done in Fig. 2d, e. While the atomic lattice can be imaged at the crests and troughs, imaging a stretched region of the length of the order of the unit cell dimensions and inferring accurate strain magnitudes from it is difficult. Instead, we use a phenomenological model to explain the other observations we make about the ripples, viz. non-classical relation between wavelength and sheet length, conserved rippling angle and triangular ripples. These other properties, like wavelength, sheet length and rippling angle can be measured much more accurately than the local strain $\gamma_{sb}$, and hence lets us do a more thorough analysis of how graphene bends.

Our results and model can also contribute to our understanding of other observations and predictions in the literature. As mentioned earlier, we extract similar rippling angles from published results by Tapaszto et al. and Bai et al. (see Supplementary sec 4). In addition, Zhang et al. recently wrinkled graphene by growing it on a close packed lattice of SiO$_2$ nanospheres of different diameters (20-200 nm). From AFM images they observed that the wavelength of the wrinkles (and hence how graphene bends) in different graphene sheets is independent of the nanosphere diameter, consistent with our observations that graphene has a preferential bending configuration, and that the wavelength is independent of the sheet length. We also observed the conserved rippling angle over a multitude of step edges some of which curved significantly (as in Fig. 2f), meaning that the rippling angle does not depend
strongly on the orientation of the graphene sheet with respect to the strain direction. This supports the predictions by Min and Aluru\textsuperscript{36} and Zhou et al.\textsuperscript{37} that the elasticity and Poisson’s ratio of graphene do not depend strongly on the chirality direction. Although we do not have a good understanding of why, contrary to classical fabrics, graphene is susceptible to stretching while bending, we note that in-plane stretching was also required to explain electronic measurements of the same system\textsuperscript{38}.

Theoretical studies generally treat bending and stretching deformations of graphene independently\textsuperscript{3,7,39–41}. Our study shows such an approach to be erroneous as bending of graphene is associated with significant stretching. Interestingly, the effect of this stretching over a narrow region is significant enough that even ripples significantly larger than unit cell dimensions (up to tens of nanometers, where one might be tempted to use a continuum approximation) differ fundamentally from classical fabrics. This observation should be considered carefully while developing strain enabled and flexible electronics. Also interesting would be the exploration whether such non-classical behavior is unique to graphene or common to other 2D materials. Our technique of terrace engineering by step bunching is expected to work for other systems with different 2D materials and metal substrates\textsuperscript{33}, and such an investigation should be straightforward. The techniques developed in this paper to engineer and study the effects of strain at the nanoscale present a strong foundation for future work in understanding the mechanical properties of 2D materials and realizing the promise of straintronics.

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References

(1) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* 2008, 321 (5887), 385–388.
(2) Cadelano, E.; Palla, P. L.; Giordano, S.; Colombo, L. Nonlinear Elasticity of Monolayer Graphene. *Phys. Rev. Lett.* 2009, 102 (23), 235502. https://doi.org/10.1103/PhysRevLett.102.235502.
(3) Lu, Q.; Huang, R. NONLINEAR MECHANICS OF SINGLE-ATOMIC-LAYER GRAPHENE SHEETS. *Int. J. Appl. Mechanics* 2009, 01 (03), 443–467. https://doi.org/10.1142/S1758825109000228.
(4) Wei, X.; Fragneaud, B.; Marianetti, C. A.; Kysar, J. W. Nonlinear Elastic Behavior of Graphene: *Ab Initio* Calculations to Continuum Description. *Phys. Rev. B* 2009, 80 (20), 205407. https://doi.org/10.1103/PhysRevB.80.205407.
(5) Scarpa, F.; Adhikari, S.; Srikantha Phani, A. Effective Elastic Mechanical Properties of Single Layer Graphene Sheets. *Nanotechnology* 2009, 20 (6), 065709. https://doi.org/10.1088/0957-4484/20/6/065709.
(6) Scarpa, F.; Adhikari, S.; Gil, A. J.; Remillat, C. The Bending of Single Layer Graphene Sheets: The Lattice versus Continuum Approach. *Nanotechnology* 2010, 21 (12), 125702. https://doi.org/10.1088/0957-4484/21/12/125702.
(7) Zhang, D.-B.; Akatyeva, E.; Dumitrică, T. Bending Ultrathin Graphene at the Margins of Continuum Mechanics. *Phys. Rev. Lett.* 2011, 106 (25), 255503. https://doi.org/10.1103/PhysRevLett.106.255503.
(8) Shenderova, O. A.; Zhrinov, V. V.; Brenner, D. W. Carbon Nanostructures. *Critical Reviews in Solid State and Materials Sciences* 2002, 27 (3–4), 227–356. https://doi.org/10.1080/10408430208500497.
(9) Huang, Y.; Wu, J.; Hwang, K. C. Thickness of Graphene and Single-Wall Carbon Nanotubes. *Phys. Rev. B* 2006, 74 (24), 245413. https://doi.org/10.1103/PhysRevB.74.245413.
(10) Tapasztó, L.; Dumitrică, T.; Kim, S. J.; Nemes-Ince, P.; Hwang, C.; Biró, L. P. Breakdown of Continuum Mechanics for Nanometre-Wavelength Rippling of Graphene. *Nature Physics* 2012, 8 (10), 739–742. https://doi.org/10.1038/nphys2389.
(11) Cerda, E.; Mahadevan, L. Geometry and Physics of Wrinkling. *Phys. Rev. Lett.* 2003, 90 (7), 074302. https://doi.org/10.1103/PhysRevLett.90.074302.
(12) Bai, K.-K.; Zhou, Y.; Zheng, H.; Meng, L.; Peng, H.; Liu, Z.; Nie, J.-C.; He, L. Creating One-Dimensional Nanoscale Periodic Ripples in a Continuous Mosaic Graphene Monolayer. *Phys. Rev. Lett.* 2014, 113 (8), 086102. https://doi.org/10.1103/PhysRevLett.113.086102.
(13) Bao, W.; Miao, F.; Chen, Z.; Zhang, H.; Jang, W.; Dames, C.; Lau, C. N. Controlled Ripple Texturing of Suspended Graphene and Ultrathin Graphite Membranes. *Nature Nanotechnology* 2009, 4, 562.
(14) Meng, L.; He, W. Y.; Zheng, H.; Liu, M.; Yan, H.; Yan, W.; Chu, Z. D.; Bai, K.; Dou, R. F.; Zhang, Y.; et al. Strain-Induced One-Dimensional Landau Level Quantization in Corrugated Graphene. *Physical Review B - Condensed Matter and Materials Physics* 2013, 87 (20), 3–8. https://doi.org/10.1103/PhysRevB.87.205405.
(15) Kang, J. H.; Moon, J.; Kim, D. J.; Kim, Y.; Jo, I.; Jeon, C.; Lee, J.; Hong, B. H. Strain Relaxation of Graphene Layers by Cu Surface Roughening. *Nano Letters* 2016, 16 (10), 5993–5998. https://doi.org/10.1021/acs.nanolett.6b01578.
(16) Xu, K.; Cao, P. G.; Heath, J. R. Scanning Tunneling Microscopy Characterization of the Electrical Properties of Wrinkles in Exfoliated Graphene Monolayers. *Nano Letters* 2009, 9 (12), 4446–4451. https://doi.org/10.1021/nl902729p.
(17) Li, S. Y.; Zhou, M.; Qiao, J. Bin; Duan, W.; He, L. Wide-Band-Gap Wrinkled Nanoribbon-like Structures in a Continuous Metallic Graphene Sheet. Physical Review B 2016, 94 (8), 1–6. https://doi.org/10.1103/PhysRevB.94.085419.

(18) Li, S. Y.; Bai, K. K.; Yin, L. J.; Qiao, J. Bin; Wang, W. X.; He, L. Observation of Unconventional Splitting of Landau Levels in Strained Graphene. Physical Review B - Condensed Matter and Materials Physics 2015, 92 (24), 3–8. https://doi.org/10.1103/PhysRevB.92.245302.

(19) Yan, H.; Chu, Z. D.; Yan, W.; Liu, M.; Meng, L.; Yang, M.; Fan, Y.; Wang, J.; Dou, R. F.; Zhang, Y.; et al. Superlattice Dirac Points and Space-Dependent Fermi Velocity in a Corrugated Graphene Monolayer. Physical Review B - Condensed Matter and Materials Physics 2013, 87 (7), 1–6. https://doi.org/10.1103/PhysRevB.87.075405.

(20) Teague, M. L.; Lai, A. P.; Velasco, J.; Hughes, C. R.; Beyer, A. D.; Bockrath, M. W.; Lau, C. N.; Yeh, N.-C. Evidence for Strain-Induced Local Conductance Modulations in Single-Layer Graphene on SiO₂. Nano Letters 2009, 9 (7), 2542–2546. https://doi.org/10.1021/nl9005657.

(21) Klimov, N. N.; Jung, S.; Zhu, S.; Li, T.; Wright, C. A.; Solares, S. D.; Newell, D. B.; Zhitenev, N. B.; Stroscio, J. A. Electromechanical Properties of Graphene Drumheads. Science (New York, N.Y.) 2012, 336 (6088), 1557–1561. https://doi.org/10.1126/science.1220335.

(22) Pacakova, B.; Verhagen, T.; Bousa, M.; Hübner, U.; Vejpravova, J.; Kalbac, M.; Frank, O. Mastering the Wrinkling of Self-Supported Graphene. Scientific Reports 2017, 7 (1), 1–11. https://doi.org/10.1038/s41598-017-10153-z.

(23) Gill, S. T.; Hinnefeld, J. H.; Zhu, S.; Swanson, W. J.; Li, T.; Mason, N. Mechanical Control of Graphene on Engineered Pyramidal Strain Arrays. ACS Nano 2015, 9 (6), 5799–5806. https://doi.org/10.1021/acsnano.5b00335.

(24) Vázquez De Parga, A. L.; Calleja, F.; Borca, B.; Passeggi, M. C. G.; Hinarejos, J. J.; Guinea, F.; Miranda, R. Periodically Rippled Graphene: Growth and Spatially Resolved Electronic Structure. Physical Review Letters 2008, 100 (5), 056807. https://doi.org/10.1103/PhysRevLett.100.056807.

(25) Blees, M. K.; Barnard, A. W.; Rose, P. A.; Roberts, S. P.; McGill, K. L.; Huang, P. Y.; Ruyack, A. R.; Kevek, J. W.; Kobrin, B.; Muller, D. A.; et al. Graphene Kirigami. Nature 2015, 524 (7564), 204–207. https://doi.org/10.1038/nature14588.

(26) Pérez Garza, H. H.; Kievit, E. W.; Schneider, G. F.; Staufer, U. Controlled, Reversible, and Nondestructive Generation of Uniaxial Extreme Strains (>10%) in Graphene. Nano Letters 2014, 14 (7), 4107–4113. https://doi.org/10.1021/nl5016848.

(27) Mos, M.; Lloyd, D.; Liu, X.; Christopher, J. W.; Cantley, L.; Wadehra, A.; Kim, B. L.; Goldberg, B. B.; Swan, A. K.; Bunch, J. S. Band Gap Engineering with Ultralarge Biaxial Strains in Suspended Monolayer MoS₂. 2016, 4–9. https://doi.org/10.1021/acs.nanolett.6b02615.

(28) Strutt, J. The Theory of Sound, Cambridge Library Collection-Physical Sciences.; Cambridge University Press, 2011.

(29) Fasolino, A.; Los, J. H.; Katsnelson, M. I. Intrinsic Ripples in Graphene. Nature Materials 2007, 6 (11), 858–861. https://doi.org/10.1038/nmat2011.

(30) Meyer, J. C.; Geim, A. K.; Katsnelson, M. I.; Novoselov, K. S.; Booth, T. J.; Roth, S. The Structure of Suspended Graphene Sheets. Nature 2007. https://doi.org/10.1038/nature05545.

(31) Mermin, N. D. Crystalline Order in Two Dimensions. Physical Review 1968. https://doi.org/10.1103/PhysRev.176.250.

(32) Hayashi, K.; Sato, S.; Yokoyama, N. Anisotropic Graphene Growth Accompanied by Step Bunching on a Dynamic Copper Surface. Nanotechnology 2013, 24 (2), 025603. https://doi.org/10.1088/0957-4484/24/2/025603.

(33) Yi, D.; Luo, D.; Wang, Z.-J.; Dong, J.; Zhang, X.; Willinger, M.-G.; Ruoff, R. S.; Ding, F. What Drives Metal-Surface Step Bunching in Graphene Chemical Vapor Deposition? Physical Review Letters 2018, 120 (24), 246101. https://doi.org/10.1103/PhysRevLett.120.246101.
(34) Ziatdinov, M.; Fujii, S.; Kiguchi, M.; Enoki, T.; Jesse, S.; Kalinin, S. V. Data Mining Graphene: Correlative Analysis of Structure and Electronic Degrees of Freedom in Graphenic Monolayers with Defects. *Nanotechnology* 2016, 27 (49), 495703. https://doi.org/10.1088/0957-4484/27/49/495703.

(35) Zhang, Y.; Heiranian, M.; Janicek, B.; Budrikis, Z.; Zapperi, S.; Huang, P. Y.; Johnson, H. T.; Aluru, N. R.; Lyding, J. W.; Mason, N. Strain Modulation of Graphene by Nanoscale Substrate Curvatures: A Molecular View. *Nano Lett.* 2018, 18 (3), 2098–2104. https://doi.org/10.1021/acs.nanolett.8b00273.

(36) Min, K.; Aluru, N. R. Mechanical Properties of Graphene under Shear Deformation. *Appl. Phys. Lett.* 2011, 98 (1), 013113. https://doi.org/10.1063/1.3534787.

(37) Zhou, L.; Wang, Y.; Cao, G. Elastic Properties of Monolayer Graphene with Different Chiralities. *J. Phys.: Condens. Matter* 2013, 25 (12), 125302. https://doi.org/10.1088/0953-8984/25/12/125302.

(38) Banerjee; V.-H. Nguyen; T. Granvier-Nakajima; L. Pabbi; A. Lherbier; A.R. Binion; J.-C. Charlier; M. Terrones; E.W. Hudson. Strain Modulated Superlattices in Graphene. arXiv:1903.10468.

(39) Wei, Y.; Wang, B.; Wu, J.; Yang, R.; Dunn, M. L. Bending Rigidity and Gaussian Bending Stiffness of Single-Layered Graphene. *Nano Lett.* 2013, 13 (1), 26–30. https://doi.org/10.1021/nl303168w.

(40) Lu, Q.; Arroyo, M.; Huang, R. Elastic Bending Modulus of Monolayer Graphene. *J. Phys. D: Appl. Phys.* 2009, 42 (10), 102002. https://doi.org/10.1088/0022-3727/42/10/102002.

(41) Wu, Y.; Zhai, D.; Pan, C.; Cheng, B.; Taniguchi, T.; Watanabe, K.; Sandler, N.; Bockrath, M. Quantum Wires and Waveguides Formed in Graphene by Strain. *Nano Lett.* 2018, 18 (1), 64–69. https://doi.org/10.1021/acs.nanolett.7b03167.

(42) Das, A.; Pisana, S.; Chakraborty, B.; Piscanec, S.; Saha, S. K.; Waghmare, U. V.; Novoselov, K. S.; Krishnamurthy, H. R.; Geim, A. K.; Ferrari, A. C.; et al. Monitoring Dopants by Raman Scattering in an Electrochemically Top-Gated Graphene Transistor. *Nature Nanotechnology* 2008, 3 (4), 210–215. https://doi.org/10.1038/nnano.2008.67.

(43) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; et al. Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.* 2006, 97 (18), 187401. https://doi.org/10.1103/PhysRevLett.97.187401.

(44) Nečas, D.; Klapetek, P. Gwyddion: An Open-Source Software for SPM Data Analysis. *centr.eur.j.phys.* 2012, 10 (1), 181–188. https://doi.org/10.2478/s11534-011-0096-2.

(45) Liu, Y.; Rodrigues, J. N. B.; Luo, Y. Z.; Li, L.; Carvalho, A.; Yang, M.; Laksono, E.; Lu, J.; Bao, Y.; Xu, H.; et al. Tailoring Sample-Wide Pseudo-Magnetic Fields on a Graphene–Black Phosphorus Heterostructure. *Nature Nanotechnology* 2018, 13 (9), 828. https://doi.org/10.1038/s41565-018-0178-z.

(46) Zeljkovic, I.; Walkup, D.; Assaf, B. A.; Scipioni, K. L.; Sankar, R.; Chou, F.; Madhavan, V. Strain Engineering Dirac Surface States in Heteroepitaxial Topological Crystalline Insulator Thin Films. *Nature Nanotechnology* 2015, 10 (10), 849–853. https://doi.org/10.1038/nnano.2015.177.
Supporting Information

Atomically sharp non-classical ripples in graphene

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1. LPCVD growth and Raman characterization of graphene:

In preparation for growth, a copper foil is electropolished to smooth its surface. Growth is performed in a low-pressure quartz tube furnace. A piece of electropolished copper is placed in a quartz tube and positioned in the center of a high temperature furnace and a boat containing ammonia-borane is placed in the tube upstream of the furnace and wrapped with a heating belt. Subsequently the tube is pumped down to $10^{-2}$ Torr and flushed with 37.5 sccm H$_2$ and 212.5 sccm Ar gas for several minutes. Afterwards the gas is left flowing and the furnace temperature is raised to 1020°C at which point the heating belt is set for 50 °C. When the heating belt reaches the set temperature 10 sccm methane is flowed through the furnace for 5 min. Afterwards the methane is shut off and the furnace cooled naturally to room temperature. Some Boron and Nitrogen dopant atoms were seen embedded in the graphene lattice. They show up clearly as bright spots with STM due to their higher density of states. None were seen in regions where the strained graphene was observed. Raman spectroscopy (Fig. S1) shows that the graphene is indeed monolayer with a characteristic 2D peak. No signature of strain was seen in the Raman spectra as the spot size of several microns was much larger than the width of the draped regions (tens of nanometers).

![Raman spectrum showing 2D nature of graphene](image)

**Figure S1** Raman spectrum shows the 2D nature of the graphene sheet$^{42,43}$.

2. Possible artifacts in scanning and imaging a tilted surface

Generally, STM measurements portray a well approximated description of a sample surface down to atomic level corrugations. However, careful consideration of potential scanning artifacts is necessary for cases where the point of contact between the tip and sample can change during a scan, like when imaging regions with high slopes or large corrugations. In such cases, the finite size of the tip can create artifacts that need to be considered for proper interpretation of the data. Such a scenario indeed arises in our case when scanning the draped region, and it is imperative to address if any of our observations are consequences of scanning artifacts instead of actual topographic features.
Fig. S2a shows the imaged height profile of a draped region. Note the rounded upper edge but sharp bottom one. In Fig. S2b, we argue that this feature is an artifact of having a tip of finite size. As the tip scans across a step edge, the point of contact between the tip and surface changes. The rounded top edge results from the tip scanning itself at the top corner. On reaching the bottom terrace, however, the point of contact between the tip and sample is abruptly changed, resulting in a sharp kink. Thus, the actual curvature of the graphene sheet at its top and bottom corners cannot be imaged by a finite sized tip.

Figure S2: (a) Height profile of draped graphene shows a rounded edge at the top and a sharp edge at the bottom. (b) This is an artifact of scanning with a tip of finite size, as the contact point of the tip with the sample changes in the draped region. See text of supplementary sec. 2 for explanations.

When measuring the height profile of an atomically corrugated surface using a scanned probe technique, the sample rarely lies exactly in the XY scan plane. Small tilts are usually removed using plane subtraction. However, when the tilt is large (as in our draped graphene), this typical STM analysis approach of using plane subtraction leads to artificial compression along the draping direction (it is equivalent to projection into a plane parallel to the terraces – see Fig. S3). Thus we instead locally rotate the coordinate system in order to properly extract all distances in the suspended material. In order to do this we begin with the global (\(\vec{u}, \vec{v}, \vec{w}\)) coordinates of every pixel in a field of view. We identify the top and bottom edge of a draped region by looking for a sharp change in slope. At every point on the draped region we are then able to define local unit vectors (\(\vec{x}, \vec{y}, \vec{z}\)) as follows: we define the local x-axis along lines parallel to the edges, allowing a slight tilt to match the steepest slope (that is, the ripple direction), we define the y-axis as perpendicular to this axis, connecting the two edges, and finally we filter out the ripples along the local x-axis (i.e. along one-dimensional lines parallel to the ripple edges), allowing us to define the local z-axis as perpendicular to this ripple-removed sheet, and redefine the x-axis by projecting it into this sheet. Once we have defined local coordinates everywhere in the ripple-removed sheet we assign (x, y, z) coordinate values by moving from pixel to pixel and projecting the displacements onto the local axes. This method of defining local coordinates allows us to “unwrap” the complex draped, curved and rippled sheet into an
essentially rectangular band of z-values without the artificial skewing that would accompany traditional plane subtraction.

Figure S3: Plane-subtraction on a tilted surface: When imaging the height profile of an atomically corrugated surface (atoms represented by grey spheres), the STM tip moving along the z-height and y-direction follows the red curve. Using the standard analysis technique of plane subtraction results in a profile that is artificially skewed (blue curve on the right). To extract the correct surface features we work in a local coordinate system defined on the draped region \((u,v,w)\) instead of the \((x,y,z)\) coordinate system of the tip. The details of transforming to the \((u,v,w)\) coordinate system from the \((x,y,z)\) coordinate system (in which the data is originally collected) is provided in supplementary sec. 2. The tilt and skewing is exaggerated for clarity.

3. Methods

All data was obtained at 80 K in a custom built ultra-high vacuum (UHV) STM system using a SPECS Tyto head with cut Pt-Ir (80%-20%) tips. Part of the analysis was done using the software Gwyddion. Though similar results have been observed with multiple tips on multiple samples, for consistency and calibration, all results presented here are obtained with a single tip on the same sample. Samples were transferred to the UHV environment within 10 minutes of growth to minimize air exposure. The sample was annealed at 300° C for about 1.5 hours in UHV to evaporate any adsorbent that might have settled on the surface during the transfer process. Similar observations have been made even after multiple annealing processes.

4. Comparison of our results with other published results

We observe that nanoscale ripples in graphene are triangular in shape with a conserved vertex angle of 163°. These observations are not only true for the multitude of ripples we have observed with widely varying wavelengths (Fig. 3d), but also for other studies by other groups. We consider below data from
two papers which also grew rippled graphene on Cu and imaged them with STM (Fig. S4). The ripples in both images have a triangular shape (contrary to sinusoidal ripples seen in a classical fabric), and show that the bending of graphene is confined to a very small (sub-nanometer) region at the crests and troughs. This is similar to our results discussed in Fig. 4.

Fig. S4a is a ripple profile observed by Bai et al.\textsuperscript{12}, where they created one-dimensional periodic ripples in graphene grown on a Cu substrate. The ripples have a periodicity \( \lambda \approx 2.8 \text{ nm} \) and a height \( h \approx 0.3 \text{ nm} \), implying a vertex angle of \( \theta = 2 \arctan \left( \frac{2.8}{2 \times 0.3} \right) = 156^\circ \). Fig. S4b is from Tapaszto et al.\textsuperscript{10} where they rippled graphene by growing it over nanotrenches in Cu. The ripples in Fig. S4b have a periodicity of \( \lambda \approx 0.8 \text{ nm} \) and a height of \( h \approx 0.09 \text{ nm} \), implying a vertex angle of \( \theta = 2 \arctan \left( \frac{0.8}{2 \times 0.09} \right) = 155^\circ \).

The fact that different studies on different graphene systems observed remarkably similar rippling shapes and angle as ours adds further credence to our observations. Between the studies of Tapaszto et al.\textsuperscript{10} (Fig. S4b, with sub-nanometer ripples), Bai et al.\textsuperscript{12} (Fig. S4a, with few-nanometer ripples) and us (with ripple wavelengths up to 50 nm), our observations hold for ripples with sizes varying two orders of magnitude. The small systematic difference in the rippling angle (156\(^\circ\) and 155\(^\circ\), compared to 163\(^\circ\) in our case) could be due to small differences in the piezo calibration. The measured height of the ripples depends crucially on the calibration of the Z-piezos, which is much difficult to calibrate than the X and Y piezos (which can be calibrated using an atomic resolution image and knowing the lattice constant).

To observe the triangular shapes and conserved rippling angle, graphene should be sufficiently decoupled form the substrate. The presence of a substrate in very close proximity (within a distance comparable to the Van der Waal radii of the atoms) to graphene can alter the ripple shapes. For example, Liu et al.\textsuperscript{45} grew graphene on black phosphorus to create ripples by forming Moire patterns. The wavelength of the ripples then depends on the relative angle between graphene and the substrate. Lattice mismatch between the sample and substrate can also create strain profiles resulting in ripples with different shapes, as observed by Zelkovic et al.\textsuperscript{46}, by growing thin films of SnTe on cleaved PbSe single crystals. Our observations are possible as we have ripples with amplitude (and hence distance from the substrate) of several nanometers, much larger than the atomic diameter. This is also true for Tapaszto et al.\textsuperscript{10} as they observed rippled graphene on trenches in Cu. The same argument also holds for Zhang et al.\textsuperscript{35} as they grew graphene on close packed nanospheres of SiO\textsubscript{2} where no clear substrate registry is possible. Notably, the ridges we observe on the flat terraces (Fig. 2b and c) do not have triangular shapes nor do they exhibit the conserved rippling angle. This is because the amplitude of the ridges (50-100 pm) prevent them to be sufficiently decoupled from the Van der Waals forces of the Cu substrate.
Figure S4: Graphene ripple profiles observed by (a) Bai et al.\textsuperscript{12} and (b) Tapaszto et al.\textsuperscript{10} also have the same features we observe. The ripples are triangular in shape, with graphene bending over a very narrow region at the crests. By estimating the periodicity (λ) and height (h) of the ripples, we calculate the rippling angle at the crests in Supplementary section 4 to find that they indeed are remarkably close to the angle observed by us in Fig. 3d.

5. Measuring the radius of curvature of graphene at ripple crests

Measuring an accurate value of bending radius of graphene is required to calculate the rippling angle from equation 6. As argued in our phenomenological model, transverse in-plane stretching of graphene results in an optimal bending radius at the crest of each ripple. However, equation 6 could not be used to estimate this radius as it requires estimating the thickness of graphene, value of which vary widely in literature\textsuperscript{9}. Instead, we measure the optimal bending radius directly from our data.

To estimate the bending radius, we take high resolution images of ripples and extract line cut profiles from them (Fig. S5). Note that unlike the previous depiction (Fig. 3c), the horizontal and vertical scales in Fig. S5 are equal. The points at the crests of the ripple is fit to a circle using an optimization routine in scipy package. In particular, we use the optimization routine to fit a circle such that the sum of squared deviations of the fitting circle to the data is minimized. The fitting yields a bending radius of curvature of 0.8 nm. Similar value of radius of curvature was obtained for multiple ripples we studied.

The accurate fitting of a circle to the ripple crest adds further credence to our phenomenological model, where we assumed the ripples to have a circular shape at the crests. The accuracy of our simple model as demonstrated in the main text also suggests that our assumption that the deformation at the crests is dominated by bending and in-plane stretching at the ripple crests is valid. Any significant out of plane deformation (Δ in the discussion about longitudinal stretching energy in the main text) would have resulted in significant deviations from a perfect circle.
6. **Note on measurement of extreme longitudinal strain**

In Fig. 2e we presented the reciprocal space image of the strained graphene lattice and used it to extract the longitudinal strain magnitude. However, our phenomenological model presented later implies that the strain is not uniform everywhere. In particular, the ripple crests and troughs should have larger strain characterized by an additional transverse in-plane stretching. However, due to the triangular shape of ripples, the strain magnitude varies predominantly only around a very narrow region near the crests and troughs. Hence, our estimation of the longitudinal strain in the system (Fig. 2e) is done by by imaging the lattice in a sufficiently small region lying between the ripple crests and troughs.