Composite super-moiré lattices in double aligned graphene heterostructures

Zihao Wang¹†, Yi Bo Wang¹†, J. Yin¹,², E. Tóvári¹, Y. Yang¹,², L. Lin³, M. Holwill³, J. Birkbeck³, D. J. Perello¹,³, Shuigang Xu¹,³, J. Zultak³, R. V. Gorbachev¹,³,⁴, A. V. Kretinin³,⁵, T. Taniguchi⁶, K. Watanabe⁶, S. V. Morozov⁷, M. Andelković⁸, S. P. Milovanović⁸, L. Covaci⁹, F.M. Peeters⁸, A. Mishchenko¹,³, A. K. Geim¹,³, K. S. Novoselov¹,³,⁹,¹⁰, Vladimir I. Fal'ko¹,³,⁴, Angelika Knothe³*, C. R. Woods¹,³*

† These authors contributed equally.
* Corresponding Author (CRW: colin.woods@manchester.ac.uk, AK: angelika.knothe@manchester.ac.uk)

Affiliations:

¹School of Physics and Astronomy, University of Manchester, Oxford Road, Manchester, M13 9PL, UK
²Institute of Nano Science, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China
³National Graphene Institute, University of Manchester, Oxford Road, Manchester, M13 9PL, UK
⁴Henry Royce Institute for Advanced Materials, Oxford Road, Manchester, M13 9PL, UK
⁵School of Materials, University of Manchester, Oxford Road, Manchester, M13 9PL, UK
⁶National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Japan
⁷Institute of Microelectronics Technology RAS, Chernogolovka 142432, Russia
⁸Department of Physics, University of Antwerp, Groenenborgerlaan 171, Antwerp, Belgium
⁹Centre for Advanced 2D Materials, National University of Singapore, 117546 Singapore
¹⁰Chongqing 2D Materials Institute, Liangjiang New Area, Chongqing, 400714, China
Abstract: When two-dimensional atomic crystals are brought into close proximity to form a van der Waals heterostructure, neighbouring crystals can start influencing each other’s electronic properties. Of particular interest is the situation when the periodicity of the two crystals closely match and a moiré pattern forms, which results in specific electron scattering, reconstruction of electronic and excitonic spectra, crystal reconstruction, and many other effects. Thus, formation of moiré patterns is a viable tool of controlling the electronic properties of 2D materials. At the same time, the difference in the interatomic distances for the two crystals combined, determines the range in which the electronic spectrum is reconstructed, and thus is a barrier to the low energy regime. Here we present a way which allows spectrum reconstruction at all energies. By using graphene which is aligned simultaneously to two hexagonal boron nitride layers, one can make electrons scatter in the differential moiré pattern, which can have arbitrarily small wavevector and, thus results in spectrum reconstruction at arbitrarily low energies. We demonstrate that the strength of such a potential relies crucially on the atomic reconstruction of graphene within the differential moiré super-cell. Such structures offer further opportunity in tuning the electronic spectra of two-dimensional materials.

Introduction: Van der Waals heterostructures allow combining different two-dimensional (2D) materials into functional stacks(1, 2), which has already produced a range of interesting electronic(3, 4) and optoelectronic(5-8) devices and resulted in observation of exciting physical phenomena. The large variety of the heterostructures is mainly due to the large selection of 2D materials. However, the assembly of van der Waals heterostructures allow one extra degree of freedom: apart from the selection of the sequence of the 2D crystals – the individual crystals can be differently oriented with respect to each other. Previously such control over the rotational alignment between crystals resulted in the observation of the resonant tunnelling(9-11), renormalisation of exciton binding energy(12) insulating(13) and superconducting(4) states.

Probably one of the most spectacular results of the rotational alignment between different 2D crystals is the observation of the band-reconstruction due to electron scattering on the moiré pattern in graphene aligned with hexagonal boron nitride (hBN). Because the lattice constants of graphene and hBN are relatively close to each other, the alignment between the two crystals leads to the formation of a moiré pattern(14, 15) with relatively small wavevector, which results in the appearance of the secondary Dirac points(16-18) in the electronic spectrum. Furthermore, the strong van der Waals interaction also leads to the atomic reconstruction of the graphene lattice(19-22). Unfortunately the characteristic energies at which the electronic spectrum can be reconstructed are given by the difference between the lattice constants of graphene and hBN, which doesn’t allow changes to be made to the low energy part of the spectrum.

Here, we demonstrate how we can gain further control over the band reconstruction of graphene by utilising the differential between two moiré patterns (super-moiré) created by top and bottom hBN in hBN/graphene/hBN heterostructures. Such super-moiré patterns are not related to the difference in the lattice constants between the two crystals and thus can be of any arbitrary wavenumber, which makes it possible to arrange the spectrum reconstruction at arbitrary low energies.

Results: To this end we created encapsulated graphene devices where the graphene layer was aligned to both bottom and top hBN layers (alignment angles $\theta^a$ and $\theta^b$). The fabrication and transfer procedures have been previously described in (23) with the exception that not only the bottom but also the top hBN is now crystallographically aligned to the graphene. In brief, we started by identifying the top-hBN layer on SiO$_2$. We then use a thin film of PPC on PDMS to lift the hBN from its substrate. This film then facilitates bringing the top-hBN into contact with a graphene crystal, Fig. 1a,b. We use very long and straight edges of the crystals to identify crystallographic axes and align them using a
commercially available transfer rig (24). The graphene can then be lifted away from its substrate, Fig. 1b. At this point, we perform atomic force microscopy (14, 15, 19) and Raman spectroscopy (25) experiments on the hBN/graphene bilayer to confirm the alignment. One such AFM image is presented in Fig. 1e, clearly showing the characteristic hexagonal pattern (the Fourier transformation is shown in Fig. 1h). The crystals are then aligned and brought into contact with a second thin hBN-layer (typically less than 1.5 nm or 5 atomic layers thick), Fig. 1b. This layer is also lifted away from its substrate leaving a triple layer on the thin polymer film, Fig. 1c. We then perform AFM and Raman characterisation again. Fig. 1f and Fig. 1i are an example of one of our double-aligned moiré AFM images and its Fourier transformation for the case of the second hBN layer being 1 atomic layer thick, which allows one to see both moiré patterns simultaneously. Although not immediately clear in the real-space image, the Fourier transformation clearly shows two sets of peaks corresponding to two hexagonal patterns (red and green dashed hexagons), as also schematically shown on Fig. 1d. The triple layer is then misaligned (~15°) and placed on top of a thick substrate-hBN (Fig. 1c). Finally, we use standard lithographic techniques to create the Hall-bar geometry.
The longitudinal resistance ($R_{xx}$) as a function of carrier concentration is presented on Fig. 2a. Here, apart from the resistance peak associated with the main Dirac point (26), several additional peaks can be seen. Most of such peaks correspond to the change of sign of the transversal (Hall) resistance ($R_{xy}$) measured in non-quantised magnetic field, Fig. 2b. Typically, if graphene is aligned with only one hBN, a single moiré pattern is produced, and only one secondary Dirac point for electrons and one for holes can be seen at concentrations which correspond to the wavevector determined by the periodicity of the moiré pattern (14-18). Aligning graphene to both the top and the bottom hBN will produce two moiré
patterns (if $\theta^\alpha$ and $\theta^\beta$ are not equivalent), which should result in two secondary Dirac points for electrons and two for holes. However, if electrons can feel potential from both moiré patterns simultaneously, then second order processes can be allowed, which would result in the reconstruction of the electronic spectrum at many other wavevectors.

In quantized magnetic fields, Landau fans can be seen to originate from these peaks, Fig. 2c. The Landau fans for most peaks exhibit both positive and negative indexes (positive and negative slopes in Fig. 2c), which suggests that those are indeed originating from the additional Dirac points and not from the higher order zone edges (27).

To interpret these additional peaks we recall that the perfectly aligned graphene on hBN should produce moiré pattern with approximately 14nm periodicity, which corresponds to carrier concentration $n \approx 2.3 \times 10^{12}$ cm$^{-2}$. Thus, for our double-aligned graphene we interpret the most pronounced peaks at $\pm 1.98 \times 10^{12}$ cm$^{-2}$ and $\pm 2.34 \times 10^{12}$ cm$^{-2}$ as coming from the moiré patterns from the top and bottom hBN layers.

The periodicity of a moiré pattern, $L$, can be related to the carrier concentration required to reach edge of its first Brillouin zone by, $n_{SDP} = \frac{8}{\sqrt{3} L^2}$. Utilising this, we get periodicities of 15.3nm and 14.0 nm respectively for the two most prominent features. The moiré periodicities are dependent upon both the lattice constant mismatch and the alignment angle, as given by $b^{\alpha \beta} = |b_n^{\alpha \beta}| = \frac{4\pi}{\sqrt{3}a} \sqrt{\delta^2 + g^{\alpha \beta \gamma}^2}$, where $b_n^{\alpha \beta} = G_n - g_n^{\alpha \beta}(n = 1,..,6)$ are the moiré reciprocal lattice vector between the $\alpha$ or $\beta$ hBN layer (with reciprocal lattice vectors $g_n^{\alpha \beta}$) and graphene (with reciprocal lattice vectors $G_n$), $\delta$ is graphene-hBN lattice constant mismatch, $\theta^{\alpha \beta}$ is the misalignment angle for $\alpha$ or $\beta$, and $\alpha$ is graphene’s lattice constant. Interestingly, one of the observed periods is larger than that could be expected for graphene aligned with hBN ($\approx 15.3$nm, see(14-19)). We attribute this slightly larger moiré period to stretching of graphene as it interacts more strongly with the two aligned hBN layers. Since the angle is zero, or sufficiently close to zero ($\delta \gg \theta$), we may calculate a new $\delta$. In this case, the lattice mismatch to achieve the periodicity of 15.3nm...
Fig. 3: Super-moiré geometry. a Reciprocal-space image of the area around graphene’s K-point. \(b_m^α\) (green) and \(b_m^β\) (red) for \(m = 1, 2…6\) are the graphene-hBN moiré reciprocal lattice vectors. \(b_k^α - b_k^β\) (blue) are the six super-moiré reciprocal lattice vectors. The blue hexagonal area indicates the \(b_1^α - b_1^β\) first Brillouin zone. b Carrier concentration of the first Brillouin zone edge for the two moiré and four lowest-energy super-moiré features as a function of \(θ^β/δ = 1.64%, θ^α = 0°\). c \(R_{xx}\) peak positions in carrier concentration. Dashed lines connect values of carrier concentration for \(θ^β = 0.4°\) in b to the position in c. Each line matches a peak. d carrier concentration of the \(b_1^α - b_1^β\) super-moiré feature vs |θ^α - θ^β | for four of ours samples (blue circles) and by calculation (red line).

should be ~1.64%. This corresponds to ~ 0.16% strain in the graphene crystal.

Then we would like to notice the small peaks at ±0.35×10^{12} \text{cm}^{-2} which corresponds to the largest differential moiré pattern. From the carrier concentration we can infer a periodicity of 35 nm. Further still, there is a pronounced peak at approximately ±0.90×10^{12} \text{cm}^{-2}, which would yield a period of 22.7 nm. These features represent previously impossible periodicities for the graphene/hBN moiré pattern.

In Fig. 3a, we schematically describe the geometric origin of the super-moiré features. \(b_m^α\) and \(b_m^β\) (red and green vectors, \(m = 1, 2…6, k = 1, 2…6\)) are the α and β moiré patterns. Their combination produces six new super-moiré patterns by the combinations of the vectors. In Fig. 3a we highlight the \(b_k^α - b_k^β\) vectors (blue). In Fig. 3b we present the position of the moiré and super-moiré zone edges in carrier concentration as a function of the angle between the second hBN layer (\(θ^β\)) and graphene for the case when the first hBN layer is held at zero angle mismatch (\(θ^α = 0\)), and \(δ = 1.64\%), as calculated. For \(θ^β = 0.4°\), the features correspond exactly to the observed peaks in \(R_{xx}\) (as shown by the dotted lines connecting Fig. 3b and Fig. 3c), and sign reversal of \(R_{xy}\), thus revealing the presence of new secondary Dirac points in the low energy electronic spectrum. Such low energy peaks originate from the differential super-moirés, \(b_1^α - b_1^β, b_1^α - b_6^β\), and \(b_2^α - b_2^β\). Further, in Fig. 3d, we show the position of the \(R_{xx}\) peak in carrier concentration for the \(b_1^α - b_1^β\) super-moiré, against the calculated angle between the two hBNs (|θ^α - θ^β |). This peak is unique because its period is independent of the graphene sheet as it is geometrically identical to moiré pattern between the two hBN layers. As expected, Fig. 3d shows the peak position for four of our samples (blue circles) follows exactly expectation (red line).

To check that all these peaks indeed originate from the spectrum reconstruction because of scattering on the additional periodic potential we measured the Brown-Zak oscillations at elevated temperatures (\(T\)) where cyclotron oscillations are suppressed, Fig. 4. At \(T > 70K\) oscillations independent of the carrier concentration can be clearly seen. At low fields \(B < 2.5T\) (Fig. 4b) the oscillations are clearly
Fig. 4: Brown-Zak oscillations in one of our doubly-aligned hBN/graphene/hBN devices. a Map of $\sigma_\alpha(n, B)$, scale of blue to red is $0.5e^2/h$ to $70e^2/h$. b Zoom in into the low field part of the map, marked by yellow rectangle in (a), scale of black to white is $7e^2/h$ to $37e^2/h$. The Brown-Zak oscillations correspond to a moiré structure with periodicity of 22.7nm and the fundamental field is 9.3T. c Zoom in into the high field part of the map, marked by white rectangle in (a), scale of blue to red is $7e^2/h$ to $37e^2/h$. The Brown-Zak oscillations correspond to a moiré structure of different periodicities are marked by dashed lines of different colours. Black - 15.3nm ($B_F=20.5T$), green 14.0nm ($B_F=24.2T$) and brown – 11.2nm ($B_F=38T$). All measurements are done at $T=70K$.

periodic in $1/B$ with the fundamental field $B_F=9.3T$. Assuming a hexagonal unit cell, such fundamental field can be calculated to correspond to moiré periodicity of 22.7nm, which corresponds to the peak in $R_{xx}$ at $n=\pm 0.90 \times 10^{12}\text{ cm}^{-2}$, Fig. 2a.

The behaviour at high fields is more complex, as several Brown-Zak oscillations which originate from different periodicities overlap. However, by taking the periodicities which correspond to the most prominent peaks in $R_{xx}$ at $B=0$ (15.3nm, 14nm and 11.2nm, see Fig. 2a) we could identify most oscillations in terms of fractions of the flux quantum per the corresponding plaquette, labelled in Fig. 4c. Thus, the graphene-hBN moiré periods (14.0 and 15.3 nm) and super-moiré periods (11.2 nm, 22.7 nm, and 36.3 nm) each give features attributable to secondary Dirac points at well understood values of carrier concentration. Also they produce clear Brown-Zak oscillations for unitary flux through moiré unit cells for the 11.2 nm, 14.0 nm, 15.3 nm, and 22.7 nm periods.

Further to our previous observations, we would like to note that there are several unexplained features in $R_{xx}$ (Fig. 2a) and $R_{xy}$ (Fig. 2b), most pronounced at $n_c \approx \pm 3.2 \times 10^{12}\text{ cm}^{-2}$ and $n_s \approx \pm 4.1 \times 10^{12}\text{ cm}^{-2}$. One possible explanation for these features is higher order moiré periodicities, that is, moiré patterns between further zone edges ($2^{\text{nd}}, 3^{\text{rd}}, \ldots$ Brillouin zone edges of the graphene/hBN moiré) or a more exotic superlattice phenomenon.

**Discussion:** Theoretically (28), moiré effects on graphene can be described in terms of a periodic superlattice (SL) potential applied to Dirac electrons produced by incommensurable lattices of two (top and bottom) hBN flakes,

$$\hat{\mathbf{H}} = v \mathbf{p} \cdot \mathbf{\sigma} + \sum_{j=\pm} \sum_{n=0,5} \left[ U^j_0 + (-1)^n (iU^j_3 \sigma_3 + U^j_4 \frac{a_n \sigma}{a}) \right] e^{i(G_n^j + r^j_0) \mathbf{\sigma}} e^{iG_n^j \mathbf{u}(r, B)}.$$  \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} \hspace{1cm} (1)

Here, $\sigma_3$ and $\mathbf{\sigma} = (\sigma_1, \sigma_2)$ are Pauli matrices acting in the sublattice space of graphene’s Bloch states; $j=\pm$ identifies layers $\alpha$ (+) and $\beta$ (-); $U^j_0, U^j_1,$ and $U^j_4$ parameterise a smoothly varying moiré potential, the asymmetric sublattice on-site energies, and hopping between A and B sublattices, respectively
(based on the earlier studies(29-31), \( U_j^0 \approx 8.5 \text{ meV}, U_j^1 \approx -17 \text{ meV}, U_j^2 \approx -15 \text{ meV} \) for \( \theta \ll \delta \)). Vector \( R \) describes the phase shift between moiré produced by hBN flakes \( \alpha \) and \( \beta \).

From this, the super-moiré periods for the individual moiré SLs (\( \alpha, \beta \)) in graphene originate in two ways. One is due to the quantum mechanical interference, which appears in the second order perturbation theory. In this case, Eq. (1) allows for the electron scattering from the combined \( j = \pm \) superlattices with the Bragg vectors \( b_m^a - b_k^A \). These comprise of different moiré SL reciprocal vectors, leading effectively to the SLs with Fourier components described in Fig. 1g and 3a. The second possibility is the reconstruction of graphene, which leads to a displacement field, \( u(r, R) \), generating mixing of the moiré SL’s reciprocal vectors. When this is considered, the longest period super-moiré SL \( (m = 1, k = 1) \) that determines the low-energy part of graphene spectrum can be described by following SL potential,

\[
\mathbf{R}_{1,1}^P \approx -12U_3\omega_{as}\sigma_3 - \sum_m \left[ 2U_3\omega_{as}\sigma_3 + 4U_j^1 \frac{v_{ib}}{v_{ub}} + i\frac{2U_j^{2}}{v_{ub}} b_m^a \right] e^{ib_m^a R} e^{i(b_m^a - b_m^b) \cdot R}
\]

\[
\mathbf{R}_{1,1}^{AP} \approx \sum_m \left[ i(-1)^m 2U_3\omega_{as} - 4U_j^1 \frac{v_{ib}}{v_{ub}} + i\frac{2U_j^{2}}{v_{ub}} b_m^a \right] e^{ib_m^a R} e^{i(b_m^a - b_m^b) \cdot R}
\]  

This expression was derived for \( \theta \ll \delta \) for both parallel (P) and antiparallel (AP) mutual orientations of the two hBN crystals (hence, approximately, \( b_m^a - b_k^A \perp b_m^{A,a} \)), and, here, \( \omega_{as} \) parameterises the amplitude of inversion asymmetric component of strain.

Vital to this description is the understanding that the displacement field \( u(r, R) \) develops due to the competition between stacking-dependent van der Waals adhesion, of graphene and hBN, and elasticity of graphene. Previous work(19, 20) has identified that the crystals form a 2D fixed-density commensurate state when graphene and hBN are close to perfect alignment. The effect relies upon strain, and thus \( u(r, R) \), modulating with a period matching that of the moiré pattern to minimise adhesive and elastic energy. The commensurate state is characterised by hexagonal domains with increasingly sharp domain walls near \( \theta = 0 \), observed in PeakForce atomic force microscopy(32), and broadening of the 2D-peak in the Raman spectrum(19, 25).

To evaluate the degree of strain within our super-moiré samples we have employed Raman spectroscopy. In Fig. 5a we show the 2D-peak and its full-width half-maximum (FWHM) for a typical unaligned sample (black circles), a sample aligned to one hBN (blue triangles), and one of our doubly aligned samples (red squares). In the case that the two hBN layers may be treated entirely independently, the signature in the Raman spectrum would remain unchanged from the singly-aligned case (FWHM (2D) \( \approx 36 \text{ cm}^{-1} \)). However, it is clear that when a second aligned hBN layer is added, the width of the 2D-peak increases by a factor of \( \approx 2 \), Fig 5a. We attribute this to restructuring of strain within the super-moiré unit cells. This observation supports the

**Fig. 5:** Strain distribution in the aligned graphene-hBN heterostructures. Raman spectra (2D-peak region) for an unaligned sample (grey), single-aligned sample (blue), and double-aligned sample (red). (a) Experimental results. (b) Molecular dynamics relaxation simulations.
proposed model of the two moiré patterns mixing through strain fields. Therefore, \( \mathbf{u}(r, R) \) should have periodicities described by \( b^a_m \) (\( \alpha \)-moiré), \( b^B_k \) (\( \beta \)-moiré), and \( b^a_m - b^B_k \) (super-moirés). This is also supported by molecular dynamics simulations of the relaxation in the doubly aligned systems, as shown in Fig. 5b, where the Raman spectra of simulated relaxed configurations is presented (see Supplementary Materials).

**Conclusion:** To conclude, graphene’s electronic spectrum is significantly altered by scattering from super-moiré structures described by the pre-existing moiré between graphene and its substrate and encapsulating hBN layers. These alterations may be considered in two ways; as double scattering events from both graphene-hBN moiré patterns, or as single scattering events from a reconstructed graphene layer. Such super-moiré potential can be of arbitrarily small wavevector (unlike moiré potential from single hBN aligned with graphene), which allows modification of the graphene band structure at arbitrarily low energies.

**Materials and Methods:**

**Fabrication:** Further to the sample preparation described previously. The general process is as follows. We use Polypropylene carbonate (PPC), or sometimes polymethyl methacrylate (PMMA), spun on a thick polydimethylpolysioxane (PDMS) membrane to facilitate moving and orientating the crystals. This membrane is used to pick up the first hBN layer. The crystal may then be positioned and aligned to graphene before the two are brought into contact. Removing the membrane quickly, then lifts the graphene off from its substrate. At this point we can invert the membrane and perform various characterisation techniques on the half-assembled heterostructure. We then pick up a further thin-hBN crystal, before repeating our characterisation. These previous steps may be repeated multiple times to produce increasingly complex heterostructures with a variety of crystals (although here we limit ourselves to graphene and hBN). Finally, the stack of crystals is positioned and brought into contact with a final ‘substrate’ hBN. The membrane is removed slowly and all the crystals are left on a SiO\(_2\) wafer.

**Atomic Force Microscopy:** Superlattice-resolution AFM images of the moiré patterns are taken in PeakForce-Quantitative Nanomechanical Mapping (PF-QNM) mode on a Bruker Icon AFM. PF-QNM allows the capture of individual tip-sample force curves for each pixel in the image. These force curves are used to extract additional elastic information about the sample as well as topographic information. We use ‘scansyst fluid+’ probes whose resolution is regularly better than 2nm.

**Raman Spectroscopy:** Raman spectroscopy measurements were performed on a Horiba Xplora Plus Raman spectrometer. The laser wavelength was 532nm with a power of 0.5mW through a x100 objective.

**Moiré Fourier Analysis:** The analysis of moiré patterns in double aligned heterostructures was done following an approach described in Ref. (33). The methodology is based on the Fourier analysis of moiré patterns appearing when two hexagonal lattices are combined.

**Molecular Dynamics Simulations:** Molecular dynamics simulations are performed for the singly-aligned hBN/graphene and the double-aligned hBN/graphene/hBN by allowing the relaxations of both hBN and graphene layers. We used the bond-order Brenner potentials for the graphene layer, Tersoff potentials for the B-N interaction in the hBN layers and the Morse potential developed in Ref. (34) for the inter-layer interactions. The simulations are performed within the “large-scale atomic/molecular massively parallel simulator” (LAMMPS) (35, 36) by considering a disk of radius 120nm. We fix the
atoms in a boundary region of 2nm but allow the relaxation of all other atoms. The total energy is minimized until the forces are below $10^{-6}$ eV/Å.

**Raman Spectrum Simulation:** Using the relaxed structures, we calculate the shift of the 2D peak and the entire Raman spectrum of the graphene layer. Calculations are performed using the prescriptions given in Ref. (37-39).
1. A. K. Geim, I. V. Grigorieva, Van der Waals heterostructures. *Nature* **499**, 419-425 (2013).
2. K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. Castro Neto, 2D materials and van der Waals heterostructures. *Science* **353**, aac9439-aac9439 (2016).
3. L. Britnell *et al*., Field-effect tunneling transistor based on vertical graphene heterostructures. *Science* **335**, 947-950 (2012).
4. Y. Cao *et al*., Unconventional superconductivity in magic-angle graphene superlattices. *Nature* **556**, 43 (2018).
5. L. Britnell *et al*., Strong light-matter interactions in heterostructures of atomically thin films. *Science* **340**, 1311-1314 (2013).
6. F. Withers *et al*., Light-emitting diodes by band-structure engineering in van der Waals heterostructures. *Nat. Mater.* **14**, 301-306 (2015).
7. F. Withers *et al*., WSe2 light-emitting tunneling transistors with enhanced brightness at room temperature. *Nano Lett.* **15**, 8223-8228 (2015).
8. T. Low *et al*., Polaritons in layered two-dimensional materials. *Nature Materials* **16**, 182 (2016).
9. T. L. M. Lane, J. R. Wallbank, V. I. Fal'ko, Twist-controlled resonant tunnelling between monolayer and bilayer graphene. *Appl. Phys. Lett.* **107**, 203506 (2015).
10. J. R. Wallbank *et al*., Tuning the valley and chiral quantum state of Dirac electrons in van der Waals heterostructures. *Science* **353**, 575-579 (2016).
11. A. Mishchenko *et al*., Twist-controlled resonant tunnelling in graphene/boron nitride/graphene heterostructures. *Nature Nanotechnology* **9**, 808 (2014).
12. E. M. Alexeev *et al*., Resonantly hybridized excitons in moire superlattices in van der Waals heterostructures. *Nature* **567**, 81-86 (2019).
13. Y. Cao *et al*., Correlated insulator behaviour at half-filling in magic-angle graphene superlattices. *Nature* **556**, 80-84 (2018).
14. J. M. Xue *et al*., Scanning tunnelling microscopy and spectroscopy of ultra-flat graphene on hexagonal boron nitride. *Nat. Mater.* **10**, 282-285 (2011).
15. M. Yankowitz *et al*., Emergence of superlattice Dirac points in graphene on hexagonal boron nitride. *Nat. Phys.* **8**, 382-386 (2012).
16. L. A. Ponomarenko *et al*., Cloning of Dirac fermions in graphene superlattices. *Nature* **497**, 594-597 (2013).
17. C. R. Dean *et al*., Hofstadter's butterfly and the fractal quantum Hall effect in moire superlattices. *Nature* **497**, 598-602 (2013).
18. B. Hunt *et al*., Massive Dirac fermions and Hofstadter butterfly in a van der Waals heterostructure. *Science* **340**, 1427-1430 (2013).
19. C. R. Woods *et al*., Commensurate-incommensurate transition in graphene on hexagonal boron nitride. *Nat. Phys.* **10**, 451-456 (2014).
20. C. R. Woods *et al*., Macroscopic self-reorientation of interacting two-dimensional crystals. *Nat. Commun.* **7**, 10800 (2016).
21. M. Yankowitz, K. Watanabe, T. Taniguchi, P. San-Jose, B. J. LeRoy, Pressure-induced commensurate stacking of graphene on boron nitride. *Nature Communications* **7**, 13168 (2016).
22. M. Yankowitz *et al*., Dynamic band-structure tuning of graphene moiré superlattices with pressure. *Nature* **557**, 404-408 (2018).
23. T. Uwanno, Y. Hattori, T. Taniguchi, K. Watanabe, K. Nagashio, Fully dry PMMA transfer of graphene on h-BN using a heating/cooling system. *2D Materials* **2**, 041002 (2015).
24. Y. Cao *et al*., Quality heterostructures from two-dimensional crystals unstable in air by their assembly in inert atmosphere. *Nano Lett.* **15**, 4914-4921 (2015).
25. A. Eckmann *et al*., Raman fingerprint of aligned graphene/h-BN superlattices. *Nano Lett.* **13**, 5242-5246 (2013).
26. K. S. Novoselov *et al*., Electric field effect in atomically thin carbon films. *Science* **306**, 666-669 (2004).
27. R. K. Kumar *et al*., High-temperature quantum oscillations caused by recurring Bloch states in graphene superlattices. *Science* **357**, 181-184 (2017).
28. J. R. Wallbank, A. A. Patel, M. Mucha-Kruczynski, A. K. Geim, V. I. Falko, Generic miniband structure of graphene on a hexagonal substrate. Phys. Rev. B 87, 245408 (2013).
29. M. Lee et al., Ballistic miniband conduction in a graphene superlattice. Science 353, 1526-1529 (2016).
30. R. K. Kumar et al., High-order fractal states in graphene superlattices. Proc. Natl. Acad. Sci. U. S. A. 115, 5135-5139 (2018).
31. J. R. Wallbank et al., Excess resistivity in graphene superlattices caused by umklapp electron-electron scattering. Nat. Phys. 15, 32-36 (2019).
32. B. B. Pittenger, N. Erina, C. Su, in Application Note #128. (2012).
33. P. Zeller, S. Günther, What are the possible moiré patterns of graphene on hexagonally packed surfaces? Universal solution for hexagonal coincidence lattices, derived by a geometric construction. New Journal of Physics 16, 083028 (2014).
34. G. Argentero et al., Unraveling the 3D Atomic Structure of a Suspended Graphene/hBN van der Waals Heterostructure. Nano Letters 17, 1409-1416 (2017).
35. S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics. Journal of Computational Physics 117, 1-19 (1995).
36. S. J. Plimpton, A. P. Thompson, Computational aspects of many-body potentials. MRS Bulletin 37, 513-521 (2012).
37. S. Reich, J. Maultzsch, C. Thomsen, P. Ordejón, Tight-binding description of graphene. Physical Review B 66, 035412 (2002).
38. T. Vincent et al., Probing the nanoscale origin of strain and doping in graphene-hBN heterostructures. 2D Materials 6, 015022 (2018).
39. T. M. G. Mohiuddin et al., Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Gruneisen parameters, and sample orientation. Physical Review B 79, 205433 (2009).
40. D. A. Cosma, J. R. Wallbank, V. Cheianov, V. I. Fal'ko, Moiré pattern as a magnifying glass for strain and dislocations in van der Waals heterostructures. Faraday Discussions 173, 137-143 (2014).
41. M. Mucha-Kruczyński, J. R. Wallbank, V. I. Fal'ko, Heterostructures of bilayer graphene and $\text{h}$-BN: Interplay between misalignment, interlayer asymmetry, and trigonal warping. Physical Review B 88, 205418 (2013).
42. X. Chen et al., Dirac edges of fractal magnetic minibands in graphene with hexagonal moiré superlattices. Physical Review B 89, 075401 (2014).
43. R. Krishna Kumar et al., High-temperature quantum oscillations caused by recurring Bloch states in graphene superlattices. Science 357, 181 (2017).
44. R. Krishna Kumar et al., High-order fractal states in graphene superlattices. Proceedings of the National Academy of Sciences 115, 5135 (2018).
Acknowledgements: The authors acknowledge support from EU Graphene Flagship Project (contract CNECTICT-604391), European Research Council Synergy Grant Hetero2D, the Royal Society, EPSRC grants; EP/S019367/1, EP/S030719/1 and EP/N010345/1, US Army Research Office (W911NF-16-1-0279), FLAG-ERA project TRANS2DTMD. S.V.M. was supported by RFBR (17-02-01129a). J.Y. and A.M. acknowledge the support of EPSRC Early Career Fellowship EP/N007131/1. S.P.M. is supported by the Flemish Science Foundation (FWO). ET acknowledges the support of the Marie Skłodowska-Curie Grant Agreement No 751883.

Author contributions: Concept of the experiment was developed by KSN and CRW. HBN was created by TT and KW. Device fabrication performed by YBW, YY, LL, MH, JB, DJP, SX, JZ, and CRW. Raman spectroscopy and AFM measurements were made by YBW, YY, LL, MH, and CRW. Transport measurements performed by ZW, JY, ET, and SVM. Experimental analysis was done by ZW, KSN, and CRW. Results were interpreted by ZW, KSN, VF, AK, and CRW with help from RVG, AVK, AM, and AKG. Theoretical calculations were done by MA, SM, LC, FMP, VF and AK. Molecular dynamics simulations were performed by MA, SM, LC, and FMP. Manuscript and S.I. were written by ZW, KSN, VF, AK, and CRW with additional contributions from all authors.

Competing interests: All authors declare that they have no competing interests.

Data and material Availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.
Composite super-moiré lattices in double aligned graphene heterostructures

Authors: Zihao Wang\textsuperscript{1†}, Yi Bo Wang\textsuperscript{1†}, J. Yin\textsuperscript{1,2}, E. Továri\textsuperscript{3}, Y. Yang\textsuperscript{1,3}, L. Lin\textsuperscript{3}, M. Holwill\textsuperscript{3}, J. Birkbeck\textsuperscript{3}, D. J. Perello\textsuperscript{1,3}, Shuigang Xu\textsuperscript{1,3}, J. Zultak\textsuperscript{3}, R. V. Gorbachev\textsuperscript{1,3,4}, A. V. Kretinin\textsuperscript{3,5}, T. Taniguchi\textsuperscript{6}, K. Watanabe\textsuperscript{6}, S. V. Morozov\textsuperscript{7}, M. Andelkovic\textsuperscript{8}, S.P. Milovanovic\textsuperscript{8}, L. Covaci\textsuperscript{8}, F.M. Peeters\textsuperscript{8}, A. Mishchenko\textsuperscript{1,3}, A. K. Geim\textsuperscript{1,3}, K. S. Novoselov\textsuperscript{1,3,9,10}, Vladimir I. Fal’ko\textsuperscript{1,3,4}, Angelika Knothe\textsuperscript{3∗}, C. R. Woods\textsuperscript{1,3∗}

† Correspondence to: CRW ‘colin.woods@manchester.ac.uk’, AK ‘angelika.knothe@manchester.ac.uk’

Supplementary Information

Contents:

Details of the super-moiré superlattice perturbation theory

Details of the super-moiré superlattice perturbation theory

We study the long-range periodic "super"-moire pattern which appears due to beatings between the two moires at the top and bottom interfaces. The six reciprocal lattice vectors of the top (bottom) moire pattern are given by $b_\alpha m = G_m - g_\alpha m$ ($b_\beta k = G_m - g_\beta m$) for $m = 0, \ldots, 5$, where $G_m$ denote the reciprocal lattice vectors of graphene, and $g_\alpha m$ ($g_\beta m$) are the reciprocal lattice vectors of the top (bottom) hBN. From these, we construct the combinations $d_{m,k} = b_\alpha m - b_\beta k$. For twist different angles $\theta_\alpha$ ($\theta_\beta$) of the top (bottom) hBN layer, these become very small or vanish completely and hence constitute the shortest reciprocal lattice vectors of the "super"-moire pattern. These cases are studied below.

Derivation of the Hamiltonians of shortest period

The low-energy contribution (for the shortest effective Bragg vectors $d_{m,k} = b_\alpha m - b_\beta k$) of the superlattice Hamiltonian which originates from interference reads in second order perturbation theory

$$H_{n,m}^{int} = \delta H_{\alpha\beta}^{(2)} + \delta H_{\beta\alpha}^{(2)},$$

14
with

\[
\delta H^{(2)}_{\alpha \beta} = \sum_{m,k} \frac{\nu}{\sqrt{2}} \left( U_0 U_1 (-1)^k \frac{1}{a} b^{\alpha}_k \cdot a_k + U_0 U_1 (-1)^m \frac{1}{a} b^{\beta}_k \cdot a_m \\
+ U_1 U_3 (-1)^{m+k} \frac{1}{a} (\ell_z \times b^{\alpha}_k) \cdot (a_k + a_m) e^i \frac{\theta_0 + \theta_m}{2} e^{i(b^0_k - b^0_m) \cdot r} \right)
\]

while the corresponding contribution due to strain caused by reconstruction is given by (40)

\[
H^{\text{rec}} = \sum_{m,k} \left( i U^\alpha_0 G_m \cdot u_k^\beta - U^\alpha_0 G_m \cdot u_{-k}^\beta \right) + i \sigma_3 \left( (-1)^m i U^\beta_3 G_m \cdot u_k^\alpha + (-1)^k i U^\alpha_1 G_m \cdot u_{-k}^\beta \right) \\
+ \left( (-1)^m i U^\beta_1 a^\alpha_1 a_k u_k^\beta - (-1)^k i U^\alpha_1 a^\alpha_1 a_m u_{-k}^\beta \right) e^{i(b^0_k - b^0_m) \cdot r}.
\]

We consider the terms of the Hamiltonians above with \( m = k \), under the assumption of very small angles (for which \( U^\beta_i \approx U^\alpha_i =: U^\alpha_i \)):

\[
\delta H^{m=m}_{\alpha \beta} = \delta H^{(2)}_{\alpha \beta} = \sum_{m,k} \frac{\nu}{\sqrt{2}} \left( 2 U_0 U_1 (-1)^m \frac{1}{a} (b^0_k - b^0_m) \cdot a_m \\
+ 2 U_1 U_3 (-1)^m \frac{1}{a} (\ell_z \times b^0_m) \cdot a_m + (\ell_z \times b^0_m) \cdot a_m \right) e^{-i \frac{\theta_0 + \theta_m}{2}} e^{i(b^0_k - b^0_m) \cdot r} \\
+ \left[ i U^\beta_1 \frac{1}{a} [(a_m, b^\beta_m) - (a_m, b^\beta_m)] (a_m, \sigma) \\
+ \left[ i a^\alpha_1 (\ell_z \times b^\beta_m) \right] \left[ (a_m, \ell_z) \cdot a_m \right] \right] e^{-i \frac{\theta_0 + \theta_m}{2}} e^{i(b^0_k - b^0_m) \cdot r} \\
+ \left[ U^\alpha_0 (b^0_k - b^0_m) - U^\beta_0 (b^0_m - b^0_m) + 2 U_0 U_3 (-1)^m (\ell_z \times b^0_m) + (\ell_z \times b^0_m) \right] e^{-i \frac{\theta_0 + \theta_m}{2}} e^{i(b^0_k - b^0_m) \cdot r}
\]
For the contribution due to strain, the cases in which the two hBN layers are either parallel, or antiparallel with respect to each other must be distinguished:

Parallel case:

$H_{P}^{m,m} = -U_{0}(w_{s}^{\alpha} + w_{s}^{\beta})f_{1}^{(m,m)}(r) - U_{3}(w_{s}^{\alpha} - w_{s}^{\beta})f_{2}^{(m,m)}(r)\sigma_{3}$

$+ U_{1}(w_{s}^{\alpha} + w_{s}^{\beta})\frac{\sqrt{3}a}{4\pi} \frac{1}{(\theta^{\beta} - \theta^{\alpha})} \nabla f_{2}^{(m,m)}(r)\sigma$

$+ U_{0}(w_{as}^{\alpha} - w_{as}^{\beta})f_{2}^{(m,m)}(r) - U_{3}(w_{as}^{\alpha} + w_{as}^{\beta})f_{1}^{(m,m)}(r)\sigma_{3}$

$+ U_{1}(w_{as}^{\alpha} - w_{as}^{\beta})\frac{\sqrt{3}a}{4\pi} \frac{1}{(\theta^{\beta} - \theta^{\alpha})} \nabla f_{1}^{(m,m)}(r)\sigma$, \hfill (S4)

Antiparallel case:

$H_{AP}^{m,m} = -U_{0}(w_{s}^{\alpha} - w_{s}^{\beta})f_{1}^{(m,m)}(r) - U_{3}(w_{s}^{\alpha} + w_{s}^{\beta})f_{2}^{(m,m)}(r)\sigma_{3}$

$+ U_{1}(w_{s}^{\alpha} - w_{s}^{\beta})\frac{\sqrt{3}a}{4\pi} \frac{1}{(\theta^{\beta} - \theta^{\alpha})} \nabla f_{2}^{(m,m)}(r)\sigma$

$+ U_{0}(w_{as}^{\alpha} + w_{as}^{\beta})f_{2}^{(m,m)}(r) - U_{3}(w_{as}^{\alpha} - w_{as}^{\beta})f_{1}^{(m,m)}(r)\sigma_{3}$

$+ U_{1}(w_{as}^{\alpha} + w_{as}^{\beta})\frac{\sqrt{3}a}{4\pi} \frac{1}{(\theta^{\beta} - \theta^{\alpha})} \nabla f_{1}^{(m,m)}(r)\sigma$, \hfill (S5)

in terms of the functions $f_{1}^{(m,m)}(r) = \sum_{m} e^{i(b_{m}^{\alpha} + b_{m}^{\beta})} \frac{R}{2} e^{i\mathbf{d}_{m,m} \cdot \mathbf{r}}$, $f_{2}^{(m,m)}(r) = i \sum_{m}(-1)^{m} e^{i(b_{m}^{\alpha} + b_{m}^{\beta})} \frac{R}{2} e^{i\mathbf{d}_{m,m} \cdot \mathbf{r}}$ and $\Re[\mathbf{G}_{m} \cdot \mathbf{u}_{b_{m}^{\alpha}}] = \Re[\mathbf{G}_{m} \cdot \mathbf{u}_{-b_{m}^{\alpha}}] = -(-1)^{n} w_{as}^{\alpha}$, $\Im[\mathbf{G}_{m} \cdot \mathbf{u}_{b_{m}^{\alpha}}] = -\Im[\mathbf{G}_{m} \cdot \mathbf{u}_{-b_{m}^{\alpha}}] = w_{as}^{\alpha}$.

Under the assumption that for small and almost equal angles $w_{i}^{\alpha} \approx w_{i}^{\beta} \approx w_{i}$, and keeping in mind that the gradient terms in equations (S3), (S4), (S5) can be removed by a gauge transformation (28) we arrive at the superlattice Hamiltonians $H_{m,m}$ of equation (2) in the main text.

All combinations of short effective moire Bragg vectors

For all the possible shortest effective Bragg vectors $\mathbf{d}_{m,k}$ we list the functions that describe the period and density of the corresponding super-moire
structures.

\[ \star \mathbf{d}_{m,m} = b^\alpha_m - b^\beta_m = \frac{4\pi}{\sqrt{3a(1+\delta)}} \left( \sin \theta^\alpha - \sin \theta^\beta \right) \cos \theta^\beta - \cos \theta^\alpha, \]

\[ A_{m,m} = a(\delta + 1) \frac{1}{\sqrt{2 - 2 \cos(\theta^\alpha - \theta^\beta)}}, \]

\[ n_{m,m} = -\frac{16[\cos(\theta^\alpha - \theta^\beta) - 1]}{\sqrt{3a^2(\delta + 1)^2}}, \]

Divergence of \( A_{m,m} \) and zero \( n_{m,m} \) for all twist angles with \( \theta^\alpha = \theta^\beta \).

\[ \star \mathbf{d}_{m,m+1} = b^\alpha_m - b^\beta_{m+1} = \frac{2\pi}{a(1+\delta)} \left( \frac{3\delta + 2\sqrt{3}\sin \theta^\alpha - \sqrt{3}\sin \theta^\beta - 3\cos \theta^\beta + 3}{\delta - 2\cos \theta^\alpha - \sqrt{3}\sin \theta^\beta + \cos \theta^\beta + 1} \right), \]

\[ A_{m,m+1} \]

\[ = \frac{2\sqrt{3}a(\delta + 1)}{3 \left( \delta - 2 \cos \theta^\alpha - \sqrt{3} \sin \theta^\beta + \cos \theta^\beta + 1 \right)^2 + \left( 3\delta + 2\sqrt{3}\sin \theta^\alpha - \sqrt{3}\sin \theta^\beta - 3\cos \theta^\beta + 3 \right)^2} \]

\[ \approx \frac{\delta^2 + \sqrt{3}\delta(\theta^\alpha - \theta^\beta) + (\theta^\alpha)^2 - \theta^\alpha \theta^\beta + (\theta^\beta)^2}{a(\delta + 1)^2}, \]

\[ n_{m,m+1} \]

\[ = \frac{2 \left( 3 \left( \delta - 2 \cos \theta^\alpha - \sqrt{3} \sin \theta^\beta + \cos \theta^\beta + 1 \right)^2 + \left( 3\delta + 2\sqrt{3}\sin \theta^\alpha - \sqrt{3}\sin \theta^\beta - 3\cos \theta^\beta + 3 \right)^2 \right)}{\sqrt{3a^2(\delta + 1)^2}} \]

\[ \approx \frac{\delta^2 - \sqrt{3}\delta(\theta^\alpha - \theta^\beta) + (\theta^\alpha)^2 - \theta^\alpha \theta^\beta + (\theta^\beta)^2}{\sqrt{3a^2(\delta + 1)^2}}, \]

Angles of the critical points (Divergence of \( A \) and zero \( n \)):
\[ n_{m,m+2} = 2 \left(3(-3\delta + 2\cos\theta^\alpha + \sqrt{3}\sin\theta^\beta + \cos\theta^\beta - 3)^2 + (3\delta + 2\sqrt{3}\sin\theta^\alpha + \sqrt{3}\sin\theta^\beta - 3\cos\theta^\beta + 3)^2\right) \]
\[ \approx \frac{8(3\delta^2 + \sqrt{3}\delta(\theta^\alpha - \theta^\beta) + \theta^\alpha \theta^\beta + (\theta^\beta)^2)}{\sqrt{3}a^2(\delta + 1)^2}, \]

Angles of the critical points (Divergence of \( A \) and zero \( n \)):

\[ \theta^\alpha = -\theta^\beta = \tan^{-1} \left[ \frac{\sqrt{3}\left(-\delta + \sqrt{1 - 3\delta(\delta + 2)} - 1\right)}{3\delta + \sqrt{1 - 3\delta(\delta + 2)} + 3} \right] \approx -\sqrt{3}\delta. \]

\[ \star \mathbf{d}_{m,m+3} = \mathbf{b}_m^\alpha - \mathbf{b}_{m+3}^\beta = \frac{4\pi}{\sqrt{3}a} \left( \frac{\sin\theta^\alpha + \sin\theta^\beta}{1 + 3 \frac{\cos\theta^\alpha + \cos\theta^\beta}{\delta + 1}} \right), \]

\[ A_{m,m+3} = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{-2(\delta + 1)\cos\theta^\alpha - 2(\delta + 1)\cos\theta^\beta + 2\delta(\delta + 2) + \cos(\theta^\alpha - \theta^\beta) + 3}} \]

\[ n_{m,m+3} = -\frac{16(-2(\delta + 1)\cos\theta^\alpha - 2(\delta + 1)\cos\theta^\beta + 2\delta(\delta + 2) + \cos(\theta^\alpha - \theta^\beta) + 3)}{\sqrt{3}a^2(\delta + 1)^2}, \]

with maximum of \( A_{m,m+3} \) and minimum of \( n_{m,m+3} \) at \( \theta^\alpha = \theta^\beta = 0 \).

\[ \star \mathbf{d}_{m,m+4} = \mathbf{b}_m^\alpha - \mathbf{b}_{m+4}^\beta = \frac{2\pi}{a(1+\delta)} \left( \frac{-3\delta + 2\sqrt{3}\sin\theta^\alpha + \sqrt{3}\sin\theta^\beta - 3\cos\theta^\beta - 3\theta^\alpha}{\sqrt{3}a^2(\delta + 1)^2} \right), \]

\[ A_{m,m+4} = \frac{2\sqrt{3}(\delta + 1)a}{\sqrt{3(3\delta - 2\cos\theta^\alpha + \sqrt{3}\sin\theta^\beta - \cos\theta^\beta + 3)^2 + (-3\delta + 2\sqrt{3}\sin\theta^\alpha + \sqrt{3}\sin\theta^\beta + 3\cos\theta^\beta - 3)^2}} \]

\[ \approx \frac{\mathbf{d}_{m,m+4}}{\sqrt{3}\delta(\delta + 1)^2(\theta^\alpha - \theta^\beta) + (\theta^\alpha)^2 + \theta^\alpha \theta^\beta + (\theta^\beta)^2}, \]

\[ n_{m,m+4} = \frac{2\left(3(3\delta - 2\cos\theta^\alpha + \sqrt{3}\sin\theta^\beta - \cos\theta^\beta + 3)^2 + (-3\delta + 2\sqrt{3}\sin\theta^\alpha + \sqrt{3}\sin\theta^\beta + 3\cos\theta^\beta - 3)^2\right)}{3\sqrt{3}a^2(\delta + 1)^2} \]

\[ \approx \frac{8(3\delta^2 + \sqrt{3}\delta(\theta^\alpha - \theta^\beta) + (\theta^\alpha)^2 + \theta^\alpha \theta^\beta + (\theta^\beta)^2)}{\sqrt{3}a^2(\delta + 1)^2}, \]
Angles of the critical points (Divergence of $A$ and zero $n$):

$$\theta^\alpha = -\theta^\beta = \tan^{-1} \left[ \frac{\sqrt{3} \left( \delta - \sqrt{1 - 3\delta (\delta + 2) + 1} \right)}{3\delta + \sqrt{1 - 3\delta (\delta + 2) + 3}} \right] \approx \sqrt{3}\delta.$$
Composite super-moiré lattices in double aligned graphene heterostructures

Zihao Wang1†, Yi Bo Wang1†, J. Yin1,2, E. Tóvári3, Y. Yang1,3, L. Lin3, M. Holwill3, J. Birkbeck3, D. J. Perello1,3, Shuigang Xu1,3, J. Zultak3, R. V. Gorbachev1,3,4, A. V. Kretinin3,5, T. Taniguchi6, K. Watanabe6, S. V. Morozov7, M. Anđelković8, S. P. Milovanović8, L. Covaci8, F. M. Peeters8, A. Mishchenko1,3, A. K. Geim1,3, K. S. Novoselov1,3,9,10, Vladimir I. Fal’ko1,3,4, Angelika Knothe3*, C. R. Woods1,3*

* Correspondence to CRW ‘colin.woods@manchester.ac.uk’, AK: ‘angelika.knothe@manchester.ac.uk’

Supplementary Information

Contents:

Additional experimental materials
Details of super-moiré Analysis
Details of Tight-Binding model used
Details of Raman spectroscopy simulations
More examples of double alignment

Following from our analysis in the main text, we can extend the comparison between the calculated periodicities to the electronic transport characteristics of three more devices. Fig. S1 shows longitudinal resistance $R_{xx}$, hall resistance $R_{xy}$ and their corresponding theoretical fittings of four samples; the device of the main text (Fig. S1a), and three others (Fig. S1b-d). All of these samples are encapsulated graphene heterostructures with perfect alignment in one side graphene-hBN contact surface. From the perfectly aligned moiré period, we can fit $\delta$. The fitted parameters are shown in Supp. Table 1.

We compare $R_{xx}$ and $R_{xy}$ data to confirm the presence of secondary Dirac points, whose signature has both a peak in the $R_{xx}$ data and a reversal of sign in $R_{xy}$. The coexistence of these features rules out other features in the moiré minibands (16).

| Figure label | Lattice mismatch | Second twist angle |
|--------------|------------------|--------------------|
| Sample 1 a   | 1.64%            | 0.4°               |
| Sample 2 b   | 1.66%            | 0.44°              |
| Sample 3 c   | 1.69%            | 1.25°              |
| Sample 4 d   | 1.71%            | 0.25°              |

**Supplementary Table 1: $\delta$ and $\theta_\beta$ for each device.** Lattice mismatch, $\delta$, and angle of the second hBN, $\theta_\beta$, for each device in Fig. S1.

Many $R_{xx}$ peaks are observable with good agreement with the calculated periods. The amplitudes of the $R_{xx}$ peaks for super-moiré are typically smaller than those of the moiré Dirac points. This is particularly pronounced on the hole side where the amplitude ratios, shown in Fig S4, result in a big difference between peaks of moiré and super-moiré. The $R_{xx}$ features match with features in $R_{xy}$, indicating the presence of a new Dirac point. Many of the super-moiré features in $R_{xy}$ do not reverse the sign entirely – however, this may be explained as a result of the weakened amplitude of the super-moiré scattering process.
Different fundamental frequencies of Brown-Zak oscillations

Previous literature reported the Brown-Zak oscillations (BZO) as a robust method to study the periodic potential applied on the graphene, for which maxima in $\sigma_{xx}$ occurs following $B = \frac{p}{q}$ where fundamental frequency $B_F = \frac{\phi_0}{S}$, $p, q$ are integers, $S$ is the area of unit cell (43, 44). Here we employ BZO to probe the unit cell resulting from moiré and super-moiré periodicities.

Supplementary Figure 1: Transport properties of doubly-aligned encapsulated graphene devices. a shows the calculated dependence on $\theta^B$ of the moiré and super-moiré periodicities. Dashed lines are a guide for the eye linking intersections with $\theta^B = 0.4$ to the $R_{xx}$ and $R_{xy}$ data. This is a reproduction of Fig. 3b and 3c from the main text. b Same as a for device two, $\theta^B = 0.44$. c Same as a for device three, $\theta^B = 1.25$. d same as a for device 4, $\theta^B = 0.25$. 

a $\theta^B = 1.64$%

b $\theta^B = 1.66$%

c $\theta^B = 1.69$%

d $\theta^B = 1.71$%
The key point is to extract the different frequencies corresponding to different unit cells, and then calculate the periodicity by assuming it corresponds to a hexagonal area.

As reported in (44), with $p, q$ increasing, the amplitude of BZO decays exponentially due to the smaller group velocity and larger super unit cell. Usually $p = 1$ is much more prominent than $p = 2, 3...$ It is experimentally difficult to realise observations of the $p=1, q=1$, oscillations in singly-aligned graphene on hBN since the fundamental frequency is $\sim 24T$. Further, the BZO would be more visible at high carrier densities, high $T$ (up to 150K), and in an electron doped graphene. The increased observation of the BZO at high temperature is due to the smearing of the electronic energy distribution which removes the influence of quantum phenomenon (Landau quantization). The BZO survive because they are transport oscillations, rather than a quantum oscillation.

In our BZO maps (Fig.S2, FigS3), the oscillation corresponding to an aligned graphene-hBN moiré is clearest. It is unobservable at carrier densities around Main Dirac points (MDP). However, other frequencies start to appear around the carrier densities of their corresponding $R_{xx}$ peaks. Also, many BZO may be distinguished more clearly at high densities on electron-doped side of the main Dirac point ($n>4.5e12 \text{ cm}^{-2}$) where the landau fan from the various Dirac point is unobservable. In Fig. S2b, the oscillations of the second largest super-moiré start to appear around its $R_{xx}$ peak $0.9e12 \text{ cm}^{-2}$ (Fig.S1.a). In this range, only one frequency occurs at small magnetic fields, so it can be easily extracted. Then, around $n = 2.0e12 \text{ cm}^{-2}$, shown in Fig.S2.c, the frequency of perfectly aligned graphene-hBN moiré pattern becomes dominant. To distinguish other frequencies, higher $n$ and higher $B$ are both required. In Fig.S2.d, we neglect the two frequencies that have already been extracted in the small $n$. Another two frequencies are observed. In total four distinct periodicities are observable; 2 moirés, and 2 super-moirés.
**Fig. S2 Brown-Zak Oscillations in sample 1.** This sample is the same as the main text. **a**, $\sigma_{xx}$ as a function of carrier concentration and magnetic field (Scale: blue to red $0.5 \text{ e}^2/\text{h}$ to $70 \text{ e}^2/\text{h}$). **b**, **c** and **d** are zoom-in of the region marked by the yellow, white, and grey dashed lines, respectively (scales: blue to red, $7 \text{ e}^2/\text{h}$ to $37 \text{ e}^2/\text{h}$).
Fig.S3 Brown-Zak oscillations for sample 4. a \( \sigma_{xx} \) map of carrier concentration and B-field of sample (scale: blue to red, 4 e\(^2\)/h to 150 e\(^2\)/h). b and c are zoom-in of the a, marked by the yellow and grey rectangles, respectively. (b scale: blue to red, 2.4 e\(^2\)/h to 30 e\(^2\)/h) (c scale: blue to red, 3.5 e\(^2\)/h to 50 e\(^2\)/h). d shows two magnetic field sweepings at carrier densities 6.0e12cm\(^{-2}\) and 8.5e12cm\(^{-2}\) with the same scale as c, dotted lines connecting the peaks of two sweepings to the maxima in the map. The Brown-Zak oscillations correspond to a moiré structures of different periodicities are marked by dotted lines of different colours. Black – 14.6nm (\( B_F \)=22.5T), violet – 14.2nm (\( B_F \)=23.8T), light pink – 8.9nm (\( B_F \)=60.5T), green – 11.9nm (\( B_F \)=33.5T), red – 18.4nm (\( B_F \)=14.1T). The periods are similar with those derived by \( R_{xx} \) and \( R_{xy} \).

All measurements are done at 35K.

Fig.S4 electron-hole symmetry in super-moiré features. a, b and c, scatter plots represent the ratios between hole-side peak amplitudes and their electron-side counterparts with dashed lines connecting their corresponding peaks (red – hole-side, blue – electron-side). Different shapes point to different samples, a (square) – sample 1, b (circle) – sample 2 and c (triangle) – sample 3, same as Main text Fig.4. Different colours point to different moiré vectors and super-moiré vectors, shown clearly in d.
Gap Opening at the main Dirac point

Fig.S5 Gap opening in one of our double aligned samples. a \( R_{xx} \) vs back-gate voltage through the main Dirac point for various temperatures (1.54K-blue to 187.9K-red). b Temperature dependent conductivity at the main Dirac point. Experimental data (black dots) and exponential fit (red line). Fit gives a pseudo-gap of 21meV for data range of T>50K.

Previously, a gap has been observed in the singly-aligned graphene-hBN superlattices of approximately 25 meV\(^{(18, 19)}\). The origin of the gap is in the proximity induced sublattice symmetry breaking in graphene due to the hBN layer. Hunt el Al\(^{(18)}\), showed that the gaps size is correlated with the periodicity of the moiré pattern.

With each sample we have measured the temperature dependent behaviour of the conductivity at the main Dirac point. In Fig.5S5a we present the characteristic plot of \( R_{xx} \) against gate voltage through the main Dirac point, for many temperatures (1.54K – 187.9K). In Fig.5S5b, the \( \sigma_{xx} \) at the Dirac point is plotted against temperature. The gap may then be extracted by fitting the data with to the Arrhenius law. In this case, we observed a 21meV gap. Which is consistent with singly-aligned graphene on hBN.
Atomic force microscopy of other double aligned samples

We have made and measured many doubly-aligned samples. Each sample shows a double moiré pattern in the AFM images (Fig. S6 a-d), principally confirmed by the presence of two sets of independent spots in the Fourier transformation (Fig. S6 e-h). In each case the encapsulation hBN layer is thin (<5 layers). We do not observe the moiré pattern when the hBN is thick (10s of nm). The double alignment is further confirmed by electronic transport data – yielding several moiré and super-moiré features.

Fig.S6. Examples of double aligned samples. a, b, c, and d AFM Young’s Modulus images of super-moiré samples. In some cases, contamination is visible in the image. e, f, g, and h Fourier transformations of the images in a, b, c, and d, respectively. Each image shows two sets of hexagonal spots corresponding to distinct moiré periods.
Uniformity in Heterostructures

**Fig. S7. Uniformity in doubly aligned heterostructures.** *a* Optical image (colour enhanced) of one of our hBN-graphene-hBN doubly aligned heterostructures before lithography. Dark blue highlights the bottom hBN layer, grey highlights overlap of the top hBN layer on the bottom hBN, and darker grey (outlined with dashed red) highlights the graphene region. *a-inset* AFM topography image of the area outlined by green in *a* and *b*. The vertical lines are an AFM artefact due to stray laser interference. Scale black to white is 2nm. *b* Map of the FWHM(2D) in the Raman spectrum. Scale black to white is 15cm⁻¹ to 100cm⁻¹. Each of these characterisation tools builds up an image of where there are distortions and deformations in the heterostructure. The lithography steps are then designed specifically to avoid these imperfections.

Typical heterostructures produced from mechanically exfoliated flakes (method described in the next section) contain imperfections (creases, folds, contamination blisters, tears, etc.). However, to confirm the uniformity of our doubly-aligned samples we utilise optical images, AFM, and Raman spectroscopy mapping, to characterise the nature of our fully assembled heterostructures (Fig.S7) and design the devices to avoid such inhomogeneities. Fig.S7a shows the optical images of one of our doubly aligned samples. Clearly evident is a crack in the top-hBN layer induced during the fabrication process. Likewise, the crack is visible in the FWHM(2D) map (Fig.S7b). Further, in Fig.S7a-inset we can see
examples of blisters and folds, which are most likely in the graphene layer. However, by only using the area of the heterostructures which is removed from these distortions we can guarantee uniform and homogenenous devices.

**Analysis of super-moiré peaks**

The analysis of moiré patterns in hBN-GR-hBN was done following an approach described in Ref. (33). The methodology is based on the Fourier analysis of moiré patterns appearing when two hexagonal lattices are combined. A hexagonal lattice can be described using the function

\[
f(\vec{r}) = \frac{1}{9} + \frac{8}{9} \cos \left( \frac{1}{2} \vec{k}_1 \cdot \vec{r} \right) \cos \left( \frac{1}{2} \vec{k}_2 \cdot \vec{r} \right) \cos \left( \frac{1}{2} \vec{k}_3 \cdot \vec{r} \right)
\]

(25)

where \( \vec{k}_1 = k [1,0] \), \( \vec{k}_2 = k [-1,1] \), \( \vec{k}_3 = k [0,-1] \), with \( k = 4 \frac{4\pi}{a \sqrt{3}} \) and \( a \) is the lattice constant. This function contains spatial frequencies at 0 (zero order), and \( \vec{k}_1 \), \( \vec{k}_2 \), \( \vec{k}_3 \) (first order). Higher order frequencies can be obtained when considering functions \( f^2 \) (second order) and \( f^3 \) (third order), or even \( f^n \) (n-th order). It is important to note that a perfect lattice would contain harmonics of infinite order with an amplitude in the Fourier transform that's inversely proportional to the order of the harmonic. Using the description of a lattice from Eq. (25), the moiré pattern defined by combining two of such lattices can be expressed as a product between functions \( f_1 \) and \( f_2 \). The Fourier transform of this product would reveal which spatial frequencies appear, and subsequently which are the possible moiré patterns.

We approach the problem of the trilayer heterostructures by considering two moiré patterns (one made by graphene and top hBN and the second one made by graphene and the bottom hBN) as the two lattices and following the approach explained above. Let’s define the moiré reciprocal vectors, \( \vec{m}_{1,2} \) and \( \vec{n}_{1,2} \) corresponding to graphene and hBN layers rotated by an angle \( \theta_1 \) and \( \theta_2 \), respectively,

\[
\vec{m}_i = \hat{g}_i \begin{bmatrix} \cos \theta_1 & -\sin \theta_1 \\ \sin \theta_1 & \cos \theta_1 \end{bmatrix} \hat{g}_i \frac{1}{(1 + \delta_1)}
\]

(26)
and

\[ \tilde{n}_i = \tilde{g}_i \begin{bmatrix} \cos \theta_2 & -\sin \theta_2 \\ \sin \theta_2 & \cos \theta_2 \end{bmatrix} \frac{\tilde{g}_i}{(1 + \delta_2)}, \]

(27)

where \( i = 1,2, \) \( \tilde{g}_i \) are the reciprocal vectors of the graphene lattice, and \( \delta_i \) are the relative ratios of unit cell lengths between graphene and the two hBN lattices. The super-moiré reciprocal vectors that correspond to different spatial periodicities can be defined as a difference between harmonics of different order (any two combinations of the underlying moiré vectors \( \vec{m}_i \) and \( \vec{n}_i \)). Unlike the moiré pattern between graphene and hBN, the three layer problem (hBN-GR-hBN) (within a certain range of small rotation angles) results in higher order beating frequencies in the low frequency range, suggesting the emergence of structures with larger periodicity than the main pattern defined by the difference \( \vec{m}_1 - \vec{n}_1 \) (or \( \vec{m}_2 - \vec{n}_2 \)). Fig.S9 shows an example of frequency spectra obtained for \( \theta_1 = 0^0 \) and \( \theta_2 = 0.8^0 \).
Fig.S9. Frequency analysis of different harmonics of hBN-gr-hBN structure. The reciprocal vectors of moiré patterns are marked with \( m_{1,2} \) using \( \theta_1 = 0^\circ \) (diamonds) and \( n_{1,2} \) using \( \theta_2 = 0.8^\circ \) (stars) while the super-moiré harmonics are labelled as a difference between relative coordinates \( \{p, q\} - \{r, s\} \).

Dominant super-moiré harmonics that fit the experimentally observed features are labelled in Fig.S10. They emerge as the difference between the moiré harmonics of different orders, as shown in the previous plot. Here, we show the super-moiré periods calculated using the following relation

\[
\lambda = \frac{4\pi}{\sqrt{3}|k_i|},
\]  

(4)

where \( \vec{k}_i = (p\vec{m}_1 + q\vec{m}_2) - (r\vec{n}_1 + s\vec{n}_2) \), where \( p, q, r, s \) are integers.
Fig.S10. Super-moiré periods corresponding to different harmonics. Curves obtained using different combination of \([p, q]−[r, s]\) shown in the inset.
Tight-binding model

Tight-binding calculations are performed using standard tight-binding Hamiltonian given by

\[ H = - \sum_{i,j} t(\vec{r}_i, \vec{r}_j) c_i^\dagger c_j, \]

(28)

with

\[ t(\vec{r}_i, \vec{r}_j) = V_\pi \left[ 1 - \left( \frac{\vec{d}_{\vec{e}z}}{d} \right)^2 \right] + V_\sigma \left( \frac{\vec{d}_{\vec{e}z}}{d} \right)^2, \]

(29)

using

\[ V_\pi = V_{\pi 0} e^{-\frac{d-\delta}{\delta}}, \]

\[ V_\sigma = V_{\sigma 0} e^{-\frac{d-d_0}{\delta}}, \]

where \( V_{\pi 0} = -2.7 \text{ eV}, V_{\sigma 0} = 0.48 \text{ eV} \) are the intralayer and interlayer hopping integrals, respectively. \( \vec{a} \) is the bond vector between sites \( i,j \), \( a_0 \) is the equilibrium bond length of each material, and \( \delta = 0.3187a_0 \) is chosen to fit the next-nearest intralayer hopping value. Onsite terms of boron and nitrogen species are set to \( V_B = 3.34 \text{ eV} \) and \( V_N = -1.40 \text{ eV} \) respectively. Hoppings within the layer are considered up to the second nearest neighbour while the interlayer hoppings are considered within the radius of \( 1.5d_0 \), where \( d_0 \) is the equilibrium interlayer distance. This radius is chosen due to the fact that hoppings outside this radius contribute only to a small energy shifts of the spectra, without modifying it significantly. However, neglecting the above mentioned hoppings results in a considerable gain in calculation time due to a reduced number of non-zero elements in the Hamiltonian.
Molecular dynamics simulations and Raman shift calculations

Molecular dynamics simulations are performed for the singly-aligned hBN/graphene and the double-aligned hBN/graphene/hBN by allowing the relaxations of both hBN and graphene layers. We used the bond-order Brenner potentials for the graphene layer, Tersoff potentials for the B-N interaction in the hBN layers and the Morse potential developed in Ref. (34) for the inter-layer interactions. The simulations are performed within the “large-scale atomic/molecular massively parallel simulator” (LAMMPS) (35, 36) by considering a disk of radius 120nm. We fix the atoms in a boundary region of 2nm but allow the relaxation of all other atoms. The total energy is minimized until the forces are below $10^{-6}$ eV/Å. Results of simulations are shown in Fig.S11 where we plotted bond lengths of the relaxed graphene layer in the case of single and double aligned system.

![Fig.S11. Bond lengths in (a) single ($\theta = 0.4^\circ$) and (b) double ($\theta_1 = 0$ and $\theta_2 = 0.4^\circ$) aligned hBN/graphene/hBN system.](image)

Using the relaxed structures, we calculate the shift of the 2D peak. Calculations are performed using the prescriptions given in Ref. (37-39). First, we obtain the strain tensor $\varepsilon(r)$ which is employed to extract the shift of the 2D peak as

$$\Delta \omega_{2D} = -\omega_{2D}^0 Y_{2D} \varepsilon_{r}$$

(30)
where $\omega_{2D}^0$ is the 2D frequency of the unstrained graphene, $\gamma_{2D} = 3.55$ [5], and $\varepsilon_h = \varepsilon_{xx} + \varepsilon_{yy}$ is the hydrostatic component of the strain tensor. This method has been applied to three different systems: graphene aligned with both hBN layers, graphene aligned with top hBN layer, and non-aligned system (Fig. 5b red, blue, and black curve, respectively, in the main text). A histogram of the shifts has been produced and the Lorentzian fitting to the obtained data was performed.