Stacking domains and dislocation networks in marginally twisted bilayers of transition metal dichalcogenides

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We apply a multiscale modeling approach to study lattice reconstruction in marginally twisted bilayers of transition metal dichalcogenides (TMD). For this, we develop DFT-parametrized interpolation formulae for interlayer adhesion energies of MoSe2, WSe2, MoS2, WS2, combine those with elasticity theory, and analyze the bilayer lattice relaxation into mesoscale domain structures. Paying particular attention to the inversion asymmetry of TMD monolayers, we show that 3R and 2H stacking domains and a network of dislocations develop for twist angles $\theta^o < \theta^o_A \sim 1^o$ and $\theta^o < \theta^o_P \sim 2.5^o$ for, respectively, bilayers with parallel (P) and antiparallel (AP) orientation of the TMD unit cells and suggest how the 3R domain structure would manifest itself in tunneling characteristics of marginally twisted P-bilayers.

Layer-by-layer assembly of van der Waals (vdW) heterostructures of two-dimensional crystals (H2DCs) became a popular method of creating new hybrid materials [1]. The underlying physics of optoelectronic properties of such systems includes the interlayer hybridization of electronic states of the layers and the superlattice effects, produced by the periodic moiré patterns characteristic to pairs of mutually twisted or slightly incompatible lattices. Such effects have been extensively investigated in graphene-hBN heterostructures [2–6] and twisted graphene bilayers [7–9], and these studies have identified two distinct structural forms of H2DCs. One corresponds to larger twist angles, $\theta$, and a stronger lattice mismatch, $\delta$, for which the periodic variation of local stacking of the atoms (moiré pattern with period $\ell = a/\sqrt{\delta^2 + \theta^2}$) is due to the superposition of rigid crystalline lattices of the two layers [2,9]. The other, "marginally twisted bilayers" [10] regime is peculiar to a very small misalignment in graphene bilayers which reconstruct into large-area Bernal stacking domains, separated by networks of domain walls [11–18].

Beyond graphene and hBN, moiré superlattice effects have been observed in MX$_2$/MX’$_2$ heterostructures of transition metal dichalcogenides (TMD) [19–25], and it has been suggested theoretically [26–28] that twisted bilayers of TMD can undergo lattice reconstruction. Here, we determine parametric conditions for the formation of and the types of domain structures in twisted TMD homo- and heterobilayers, enriched by the lack of inversion symmetry of the individual 2D crystals. Different domain wall networks form for parallel- (P-bilayers) and antiparallel- (AP-bilayers) orientations of unit cells in the two layers, and we find crossover angles, $\theta^o_{AP} \sim 1.0^o$ and $\theta^o_P \sim 2.5^o$, for the marginality of the twist and, then, dis-

FIG. 1. (a) Sketch of lattice relaxation across moiré supercell of marginally twisted AP-bilayers ($\theta < \theta_{AP}$). Insets show local stacking configurations in 2H domain and MM’ seed. X(X’) and M(M’) label chalcogen and metal atoms, respectively, in the bottom (top) layer; (b) the left/right panel reveals side-view of 3R/2H-stacked TMD bilayers with the size of dots reflecting the layer-asymmetry of the electronic states at the conduction band edge. Central panel: the first reciprocal lattice star and the first Brillouin zone of the TMD bilayers with marked conduction (CBQ, CBK) and valence band (VBF, VBK) extrema.
cuss how the resulting domain structures can be observed in scanning tunneling experiments.

In this study, we employ the multiscale modeling: a combination of density functional theory (DFT) leading to interpolation formulae for adhesion energy, $W_{P/AP}(r_0, d)$, between the layers at a distance $d$ from each other and lateral offset $r_0$, and elasticity theory for the lattice relaxation [27]. We perform this analysis for small misalignment angles, $\theta \ll 1$ (i.e., $\theta^0 \ll 5^\circ$), and lattice mismatch $\delta \ll 1$. In this case, energetics of local stacking can be described in terms of a lateral offset, $r_0(r) = \theta \hat{z} \times r + \delta r + \mathbf{u}^{(i)} - \mathbf{u}^{(b)}$, between two aligned commensurate lattices, which vary across the moiré supercell and includes the effect of local deformations, $\mathbf{u}^{(i)}(r)$, in the bottom/top layers. This multiscale approach enables us to overcome the system-size limitations of molecular dynamics ions [20–28].

For adhesion energy, we use the form, $W_{P/AP}(r_0, d) = \sum_n f_n^{(P/AP)}(d)e^{G_n r_0}$, where $G_n$ are the reciprocal lattice vectors of TMD. We truncate this sum at the first star of reciprocal lattice vectors, $\pm G_{1,2,3}$, $(|G_{1,2,3}| = G$, Fig. 1) and set $r_0 = 0$ at the XX' stacking for both P- and AP-bilayers. This choice—along with the $D_{3h}$ lattice symmetry of TMD monolayers—suggests $W_P = f(d) + \sum_{n=1}^3 \tilde{f}_1(d) \cos (G_n r_0) + \tilde{g}_1(d) \sin (G_n r_0)$. Then, we inspect the adhesion energies for various H2DCs, computed using vdW-DFT with the optB88 functional [30] implemented in Quantum Espresso [31] for stacking configurations shown in Fig. 2. For bilayers, the most energetically favorable are configurations MX$'$ ($r_0 = (0, -\sqrt{3}/\sqrt{3})$) and XM$'$ ($r_0 = (0, \sqrt{3}/\sqrt{3})$), which have equal energies [32] and correspond to twins of a 3R bulk phase of a TMD. For AP-bilayers, 2H-stacking ($r_0 = (0, -\sqrt{3}/\sqrt{3})$) has the lowest energy in agreement with the 2H bulk phase of these TMDs, rather than MM$'$-stacking (configuration 5, $r_0 = (0, \sqrt{3}/\sqrt{3})$) suggested in Ref. [27]. Configurations 6, $r_0 = -\sqrt{3}(1, 1, \sqrt{3})$ and $r_0 = -\sqrt{3}(1, 0, 0)$, are such that $W_P = f$ and $W_{AP} = \tilde{f}$. The remaining two (2 and 4) are identical to the configuration 2, and $\tilde{g}_1(r_0)$, and plot them in Fig. S2. By inspection, we find that $f \approx \tilde{f}$ and $f_1 \approx \tilde{f}_1 + \tilde{g}_1$, over the broad interval of interlayer distances that covers the minima of $W_{P/AP}(r_0, d)$, and, then, consider the following factors to make an informed choice of functions, $\tilde{f}$, $\tilde{f}_1$, and $\tilde{g}_1$: (i) Coulomb potential of a lattice of $zq$ ions, whose potential decays exponentially, $\sum_\alpha \alpha e^{-G_n d_{\alpha \mathbf{G}_n} r_0}$, with $n$ from their plane ($\alpha_0 = 0$ is due to the electron neutrality of each layer). This suggests a choice of $\tilde{g}_1 = A_2 e^{-G_0 d}$ for the first star of reciprocal lattice vectors $\pm G_{1,2,3}$. (ii) The overlap of atomic orbitals, strongest for chalcogen atoms in the outer (top/bottom) sublattices in each layer is determined by the exponential decay of atomic wave functions away from the plane, $|\psi(z)|^2 \propto e^{-\varepsilon z}$. Also, tunneling between the layers is suppressed for electrons with a larger in-plane wave number $23$, $\sum_n \beta_n e^{-\sqrt{G_n^2 + \rho^2}} \cos (G_n r_0)$, so that we choose $\tilde{f}_1 = A_1 e^{-d\sqrt{G_0^2 + \rho^2}}$. (iii) Finally, following the earlier studies [34] of vdW interaction of H2DCs, which has a long-distance asymptotic, $\propto C/d^3$, we combine the short range repulsion and long-range vdW attraction into $\tilde{f} = -\sum_n C_n / d^n$. Then, we use

$$W_{P/AP}(r_0, d) = \sum_{n=1}^3 \left[ -\frac{C_n}{d^{4n}} + A_1 e^{-d\sqrt{G_0^2 + \rho^2}} \cos (G_n r_0) + A_2 e^{-G_0 d} \sin (G_n r_0 + \varphi_{P/AP}) \right] ,$$

with $\varphi_{P} = \pi/2$, $\varphi_{AP} = 0$, and fit the values of parameters $C_{1,2,3}$, $A_1, A_2$, $\rho$ to the DFT data listed in Table S1 in SI [30].

Lattice reconstruction in H2DCs happens when energy gain from the formation of favourable stacking overcomes elastic energy cost of strain produced by the local mutual adjustment of the two lattices, $U = \sum_{\alpha \beta = 1} \left[ \lambda \mu \left( u^{(i)}_{\alpha \beta} \right)^2 + \mu \left( u^{(l)}_{\alpha \beta} \right)^2 \right]$, where $\lambda_{i/b}$, $\mu_{i/b}$ and $u^{(i)}_{i/b}$, $u^{(l)}_{i/b}$ are the first Lamé coefficient, shear modulus, and strain tensors related to the local in-plane displacements in top/bottom layer. We neglect the energy cost of flexural deformations allowing for
the out-of-plane bending of the layers towards the optimal interlayer distance, \(d_{P/AP}(r_0)\), for each offset \(r_0\). We describe the latter by expanding \(W_{P/AP}\) into Taylor series about the minimum point, \(d_0\), of the zeroth Fourier harmonic term, \(f(d) \approx f(d_0) + \varepsilon (d - d_0)^2\) (Table S1 in SI [23]), and, then, find \(u_{\ell/b}(r)\) that minimize energy,

\[
E = \int d^2r \left\{ U - \varepsilon Z_{P/AP}^{\ell/b}(r) + \sum_{n=1}^{3} \left[ A_1 e^{-\sqrt{G^2 + p^2}d_0} \cos \left( g_n r + G_n [u^{(\ell)} - u^{(b)}] \right) + A_2 e^{-G d_0} \sin \left( g_n r + G_n [u^{(\ell)} - u^{(b)}] + \varphi_{P/AP} \right) \right] \right\}.
\]

Here, \(g_n = \delta G_n - \theta \hat{z} \times G_n\) are reciprocal lattice vectors of moiré superlattice, which we also use to expand \(u^{(\ell/b)}(r)\) in Fourier harmonics up to the fourteenth reciprocal space star. Then, we minimize \(E\) with respect to those Fourier amplitudes numerically and obtain the displacements in each layer of the reconstructed bilayer. This method enables us to study moiré structure with \(\theta^0 \geq 0.5^\circ\).

Representative examples of lattice reconstructions in P- and AP-bilayers are shown in Fig. 3. For a larger angle, \(\theta = 4^\circ\) (Fig. 3a,b) adhesion-induced displacements are small and the two layers behave as rigid lattices. For \(\theta^0 < 1\(^{\circ}\), twisted bilayers reconstruct into domain structures. For P-bilayers, Fig. 3c, each reconstructed moiré supercell comprises two equal area triangular domains of 3R(XM'/MX') stacking, separated by partial dislocations, with XX' regions squeezed to the nodes on that partial dislocations network, Fig. 3d. For AP-bilayers, Fig. 3e, the reconstructed lattice features a honeycomb array of 2H domains separated by a dislocation network, where one half of the nodes are the seeds of the quasi-equilibrium MM' phase (stacking configuration AP-5). As a quantitative measure for domain formation, we use a lateral distance, \(\delta\), between the closest metal and sulfur atoms in top and bottom layers (for ideal 2H and 3R domains, \(\delta = 0\)) and compute its mean square, \(\langle \delta^2 \rangle / a^2\), over the supercell normalized by the TMD lattice constant, \(a\). For rigidly rotated monolayers, \(\langle \delta_{P}^2\rangle \approx 0.14a^2\) and \(\langle \delta_{P}^2\rangle \approx 0.08a^2\). Upon the formation of 2H/3R domains, main contribution to \(\langle \delta^2 \rangle\) comes from domain boundaries so that the asymptotic behaviour, \(\langle \delta^2 \rangle \propto 1/\ell \propto \theta\), in Fig. 3h signals the formation of a domain structure at \(\theta < \theta_{P} \approx 0.044(2.5^\circ)\) and \(\theta < \theta_{AP} \approx 0.017(1^\circ)\). These quantitative estimates also explain why the molecular dynamics simulations performed in Refs. 20,28 for \(\theta > 3^\circ\) failed to establish the full picture of the lattice reconstruction in H2DCs, having interpreted MM' areas in almost rigid AP-bilayers, Fig. 3a, as fully developed domains. Note that superlattice pattern – perfect domains and the dislocation network – also appear in TMD heterobilayers with the same chalcogens (WS2/MoS2 or WSe2/MoSe2), which have lattice mismatch \(\delta \lesssim 0.3\%,\) whereas bilayers with \(\theta > \theta_{P/AP}\), or MS2/M'Se2 heterostructures with \(\delta \approx 3.8\%\) behave as almost rigid crystals.

The formation of domain structures takes place when the energy gain from the expanded 2H (for AP) or 3R (for P) areas overcomes the energy cost of domain walls. The latter are nothing but dislocations: screw dislocations in

![Figure 3](image-url)
The calculated profiles for various TMDs (shown by different colours) almost coincide. (e) and (f) illustrate the structure of 2H-2H and 3R-3R (which should be observable in the optical Stark shift), such an asymmetry would be main formation in, e.g., a conductive tip microscopy of band edges marked in Fig. 1b. In addition to a substantial electric dipole moment, interesting features resulting from their lack of inversion symmetry. In Table I, we display the atomic decompositions of DFT states, the out-of-plane electric dipole moment $d_z$ in 3R-bilayer $M(Mo,W)X(S,Se)_2$, and ratio between tunneling currents into $X'$ and $XM'$ stacking domains, for band edges labelled in Fig. 4.

| $|\psi|^2$ [%] | $X$ | $M$ | $X'$ | $M'$ | $X'$ | $d_z$ (eA) | $I_{XM'/1XM'}$ |
|---|---|---|---|---|---|---|---|
| CBQ | 4.2 | 30.6 | 3.3 | 5.5 | 49.6 | 6.8 | 0.73 | 1:1.6 |
| CBK | 0.0 | 0.0 | 0.0 | 2.4 | 95.3 | 2.4 | 3.07 | 0:1 |
| VBΓ | 10.6 | 41.8 | 0.9 | 0.7 | 36.0 | 10.0 | −0.20 | 1:1 |
| VBΓ | 4.7 | 89.9 | 4.7 | 0.0 | 0.5 | 0.1 | −3.04 | 1:0 |
| CBQ | 6.8 | 29.7 | 4.3 | 6.5 | 42.6 | 10.0 | 0.58 | 1:1.6 |
| CBK | 0.1 | 0.0 | 0.0 | 3.8 | 92.2 | 3.8 | 3.22 | 0:1 |
| VBΓ | 14.9 | 36.6 | 1.2 | 1.0 | 31.9 | 14.3 | −0.17 | 1:1 |
| VBΓ | 7.5 | 84.0 | 7.5 | 0.0 | 0.7 | 0.2 | −3.17 | 1:0 |
| CBQ | 4.3 | 28.6 | 4.0 | 6.8 | 48.9 | 7.4 | 0.81 | 1:1.7 |
| CBK | 0.0 | 0.0 | 0.0 | 1.8 | 96.3 | 1.8 | 3.09 | 0:1 |
| VBΓ | 10.3 | 41.5 | 1.6 | 1.3 | 35.5 | 9.9 | −0.21 | 1:1 |
| VBΓ | 6.5 | 86.5 | 6.5 | 0.0 | 0.5 | 0.2 | −3.05 | 1:0 |
| CBQ | 7.0 | 24.4 | 6.2 | 10.3 | 40.6 | 11.5 | 0.80 | 1:1.6 |
| CBK | 0.0 | 0.4 | 0.0 | 3.6 | 92.3 | 3.6 | 3.21 | 0:1 |
| VBΓ | 14.5 | 36.3 | 2.2 | 1.8 | 31.4 | 13.7 | −0.19 | 1:1 |
| VBΓ | 9.8 | 79.0 | 9.9 | 0.7 | 0.1 | 0.4 | −3.16 | 1:0 |
Another feature of marginally twisted bilayers is a concentration of strain at the sites of their dislocation networks, highlighted in Fig. 2e–g. A generic feature of multivalley semiconductors (that is, both at CB and VB) consists in that inhomogeneous strain generates pseudomagnetic fields for electrons \( B_{\text{e}} \) with the alternating signs in time-reversed valleys, \( B_{\text{e}} \propto \pm [2 \partial_{\nu} \langle u_{\nu}^{(b)} \rangle + \partial_{\nu}(u_{\nu}^{(b)} - u_{\nu}^{(g)})] \). For example, using parameters proposed \( (64) \) for electrons in \( \pm K \) valleys of MoS\(_2\), we estimate that \( B_{\text{e}} \) can reach values 20–30 Tesla over a 20 nm\(^2\) area near the intersections of dislocations separating 2H-stacking domains (Fig. 3). These areas may represent interesting types of semiconductor quantum dots in 2D materials.

Finally, we point out that the described domain structures and dislocation networks result from the fabrication-induced twist in a bilayer. As such, they may slowly relax upon annealing, by dislocations escaping through the sample edges, resulting in larger-size domains of perfect 3R (for P) and 2H (for AP) stackings. Such heterostructure assembly may give an alternative (to the growth) method for fabrication of lattice-matched 2H and 3R MX\(_2\)/M\(_X\)\(_2\) heterostructures.

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[1] K. Novoselov, A. Mishchenko, A. Carvalho, and A. C. Neto, Science 353, 949 (2016).
[2] L. A. Ponomarenko, R. V. Gorbachev, G. L. Yu, D. C. Elias, R. Jalil, A. A. Patel, A. Mishchenko, A. S. Mayorov, C. R. Woods, J. R. Wallbank, and et al, Nature (London) 497, 594 (2013).
[3] C. R. Dean, L. Wang, P. Maher, C. Forsythe, F. Ghahari, Y. Gao, J. Katoch, M. Ishigami, P. Moon, M. Koshino, and et al, Nature 497, 598 (2013).
[4] N. Y. Kim, H. Y. Jeong, J. H. Kim, G. Kim, H. S. Shin, and Z. Lee, ACS nano 11, 7084 (2017).
[5] M. Lee, J. R. Wallbank, P. Gallagher, K. Watanabe, T. Taniguchi, V. I. Fal’ko, and D. Goldhaber-Gordon, Science 353, 1526 (2016).
[6] M. Yankowitz, J. Xue, D. Cormode, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero, P. Jacquot, and B. J. LeRoy, Nature Physics 8, 382 (2012).
[7] Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras, and P. Jarillo-Herrero, Nature 556, 43 (2018).
[8] Y. Cao, V. Fatemi, A. Demir, S. Fang, S. L. Tomarken, J. Y. Luo, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, E. Kaxiras, and et al, Nature 556, 80 (2018).
[9] M. Yankowitz, S. Chen, H. Polshyn, Y. Zhang, K. Watanabe, T. Taniguchi, D. Graf, A. F. Young, and C. R. Dean, Science 363, 1050 (2019).
[10] S. G. Xu, A. I. Berdyugin, P. Kumaravadivel, F. Guinea, R. Krishna Kumar, D. A. Bandurin, S. V. Morozov, W. Kuang, B. Tsim, S. Liu, and et al, Nature Communications 10, 4008 (2019).
[11] J. S. Alden, A. W. Tsen, P. Y. Huang, R. Hovden, L. Brown, J. Park, D. A. Muller, and P. L. McEuen, Proceedings of the National Academy of Sciences 110, 11256 (2013).
[12] H. Yoo, R. Engelke, S. Carr, S. Fang, K. Zhang, P. Cazeaux, S. H. Sung, R. Hovden, A. W. Tsen, T. Taniguchi, and et al, Nature materials 18, 448 (2019).
[13] S. Zhou, J. Han, S. Dai, J. Sun, and D. J. Srolovitz, Phys. Rev. B 92, 155438 (2015).
[14] F. Gargiulo and O. V. Yazyev, 2D Materials 5, 015019 (2017).
[15] M. Van Wijk, A. Schuring, M. Katsnelson, and A. Fasolino, 2D Materials 2, 034010 (2015).
[16] S. Dai, Y. Xiang, and D. J. Srolovitz, Nano letters 16, 5923 (2016).
[17] N. N. T. Nam and M. Koshino, Phys. Rev. B 96, 075311 (2017).
[18] A. Kerelsky, C. Rubio-Verd, L. Xian, D. M. Kennes, D. Halbertal, N. Finney, L. Song, S. Turkel, L. Wang, K. Watanabe, and et al, arXiv:1911.00007.
[19] J. Kunstmann, F. Mooshammer, P. Nagler, A. Chaves, F. Stein, N. Paradiso, G. Plechinger, C. Strunk, C. Schüller, G. Seifert, and et al, Nature Physics 14, 801 (2018).
[20] P. Rivera, H. Yu, K. L. Seyler, N. P. Wilson, W. Yao, and X. Xu, Nature nanotechnology 13, 1004 (2018).
[21] P. K. Nayak, Y. Horbatenko, S. Ahn, G. Kim, J.-U. Lee, K. Y. Ma, A.-R. Jang, H. Lim, D. Kim, S. Ryu, and et al, Acna Nano 11, 4041 (2017).
[22] K. L. Seyler, P. Rivera, H. Yu, N. P. Wilson, E. L. Ray, D. G. Mandrus, J. Yan, W. Yao, and X. Xu, Nature 567, 66 (2019).
[23] K. Tran, G. Moody, F. Wu, X. Lu, J. Choi, K. Kim, A. Rai, D. A. Sanchez, J. Quan, A. Singh, and et al, Nature 567, 71 (2019).
[24] C. Jin, E. C. Regan, A. Yan, M. I. B. Utama, D. Wang, S. Zhao, Y. Qin, S. Yang, Z. Zheng, S. Shi, and et al, Nature 567, 76 (2019).
[25] E. M. Alexeev, D. A. Ruiz-Tijerina, M. Danovich, M. J. Hamer, D. J. Terry, P. K. Nayak, S. Ahn, S. Pak, J. Lee, J. I. Sohn, and et al, Nature 567, 81 (2019).
[26] M. H. Naik and M. Jain, Phys. Rev. Lett. 121, 266401 (2018).
[27] S. Carr, D. Massatt, S. B. Torrisi, P. Cazeaux, M. Luskin, and E. Kaxiras, Physical Review B 98, 224102 (2018).
[28] M. H. Naik, I. Maity, P. K. Maiti, and M. Jain, The Journal of Physical Chemistry C 123, 9770 (2019).
[29] This is because aligned P-oriented TMD bilayers with opposite in-plane offsets represent mirror copies of each other resulting in the same interaction value for \( \pm r_{\sigma} \), whereas for AP orientation, the lack of inversion symmetry in each layer allows for both even and odd terms.
[30] Supplemental Material at ... for details of DFT calculations and values of fitted parameters.
[31] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, and et al, Journal of Physics: Condensed Matter 21, 395502 (2009).
[32] For MoSe\(_2\)/WSe\(_2\) (Fig. 2) and MoS\(_2\)/WS\(_2\) (Fig. S1e,f in
heterobilayers energies of twins (MX' and XM') of 3R-stacking configuration are almost the same.

[33] R. Bistritzer and A. H. MacDonald, Proceedings of the National Academy of Sciences 108, 12233 (2011).

[34] J. F. Dobson, A. White, and A. Rubio, Phys. Rev. Lett. 96, 073201 (2006).

[35] T. Cheiwchanwannij and W. R. L. Lambrecht, Phys. Rev. B 85, 205302 (2012).

[36] L. Debbichi, O. Eriksson, and S. Lebègue, Phys. Rev. B 89, 205311 (2014).

[37] D. A. Ruiz-Tijerina, M. Danovich, C. Yelgel, V. Zólyomi, and V. I. Fal’ko, Phys. Rev. B 98, 035411 (2018).

[38] J. E. Padilha, H. Peelaers, A. Janotti, and C. G. Van de Walle, Phys. Rev. B 90, 205420 (2014).

[39] T.-R. Chang, H. Lin, H.-T. Jeng, and A. Bansil, Scientific reports 4, 6270 (2014).

[40] S. Fang, R. Kuate Deo, S. N. Shirodkar, S. Lieu, G. A. Trittisaris, and E. Kaxiras, Phys. Rev. B 92, 205108 (2015).

[41] Z. Gong, G.-B. Liu, H. Yu, D. Xiao, X. Cui, X. Xu, and W. Yao, Nature communications 4, 2053 (2013).

[42] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105, 136805 (2010).

[43] R. Suzuki, M. Sakano, Y. Zhang, R. Akashi, D. Moriiwasa, A. Harasawa, K. Yaji, K. Kuroda, K. Miyamoto, T. Okuda, and et al, Nature nanotechnology 9, 611 (2014).

[44] A. Chernikov, C. Ruppert, H. M. Hill, A. F. Rigosi, and T. F. Heinz, Nature Photonics 9, 466 (2015).

[45] A. M. Jones, H. Yu, J. S. Ross, P. Klement, N. J. Ghimire, J. Yan, D. G. Mandrus, W. Yao, and X. Xu, Nature Physics 10, 130 (2014).

[46] S. Wu, J. S. Ross, G.-B. Liu, G. Aivazian, A. Jones, Z. Fei, W. Zhu, D. Xiao, W. Yao, D. Cobden, and et al, Nature nanotechnology 9, 149 (2013).

[47] T. Jiang, H. Liu, D. Huang, S. Zhang, Y. Li, X. Gong, Y.-R. Shen, W.-T. Liu, and S. Wu, Nature nanotechnology 9, 825 (2014).

[48] I. G. Lezama, A. Arora, A. Ubaldini, C. Barreteau, E. Giannini, M. Potemski, and A. F. Morpurgo, Nano letters 15, 2336 (2015).

[49] B. Fallahazad, H. C. Movva, K. Kin, S. Larentis, T. Taniguchi, K. Watanabe, S. K. Banerjee, and E. Tutuc, Physical review letters 116, 086601 (2016).

[50] R. Akashi, M. Ochi, S. Bordács, R. Suzuki, Y. Tokura, Y. Iwasa, and R. Arita, Phys. Rev. Applied 4, 014002 (2015).

[51] I. C. Gerber, E. Courtade, S. Shrec, C. Robert, T. Taniguchi, K. Watanabe, A. Balocchi, P. Renucci, D. Lagarde, X. Marie, and et al, Phys. Rev. B 99, 035443 (2019).

[52] R. Pisoni, T. Davatz, K. Watanabe, T. Taniguchi, T. Ihn, and K. Ensslin, Phys. Rev. Lett. 123, 117702 (2019).

[53] A. Arora, M. Koperski, A. Slobodeniuk, K. Nogajewski, R. Schmidt, R. Schneider, M. R. Molas, S. M. de Vasconcellos, R. Bratschitsch, and M. Potemski, 2D Materials 6, 015010 (2018).

[54] A. Kormániros, V. Zólyomi, V. I. Fal’ko, and G. Burkard, Phys. Rev. B 98, 035408 (2018).

[55] X. Zhang, W.-Y. Shan, and D. Xiao, Physical review letters 120, 077401 (2018).

[56] J. Yan, J. Xia, X. Wang, L. Liu, J.-L. Kuo, B. K. Tay, S. Chen, W. Zhou, Z. Liu, and Z. X. Shen, Nano letters 15, 8155 (2015).

[57] N. Ubrig, S. Jo, M. Philippi, D. Costanzo, H. Berger, A. B. Kuzmenko, and A. F. Morpurgo, Nano letters 17, 5719 (2017).

[58] Y. Wang, C. Cong, J. Shang, M. Eginligil, Y. Jin, G. Li, Y. Chen, N. Peimyoo, and T. Yu, Nanoscale Horizons 4, 396 (2019).

[59] J. Van Baren, G. Ye, J.-A. Yan, Z. Ye, P. Rezaie, P. Yu, Z. Liu, R. He, and C. H. Lui, 2D Materials 6, 025022 (2019).

[60] J. Shi, P. Yu, F. Liu, P. He, R. Wang, L. Qin, J. Zhou, X. Li, J. Zhou, X. Sui, and et al, Advanced Materials 29, 1701486 (2017).

[61] E. Mishina, N. Shershutyuk, S. Lavrov, A. Sigov, A. Mitiglou, S. Anghel, and L. Kulyuk, Applied Physics Letters 106, 131901 (2015).

[62] M. Zhao, Z. Ye, R. Suzuki, Y. Ye, H. Zhu, J. Xiao, Y. Wang, Y. Iwasa, and X. Zhang, Light: Science & Applications 5, e16131 (2016).

[63] S. Iordanskii and A. Koshelev, Pis‘ma ZhETF 41, 471 (1985).

[64] H. Rostami, R. Roldán, E. Cappelluti, R. Asgari, and F. Guinea, Physical Review B 92, 195402 (2015).

[65] S.-Y. Chen, C. Zheng, M. S. Fuhrer, and J. Yan, Nano letters 15, 2526 (2015).

[66] M.-L. Lin, Q.-H. Tan, J.-B. Wu, X.-S. Chen, J.-H. Wang, Y.-H. Pan, X. Zhang, X. Cong, J. Zhang, W. Ji, and et al, ACS Nano 12, 8770 (2018).

[67] X. Zhang, W. Han, J. Wu, S. Milana, Y. Lu, Q. Li, A. C. Ferrari, and P. Tan, Physical Review B 87, 115413 (2013).

[68] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).

[69] W. Schutte, J. De Boer, and F. Jellinek, Journal of Solid State Chemistry 70, 207 (1987).

[70] K. Bronsema, J. De Boer, and F. Jellinek, Zeitschrift für anorganische und allgemeine Chemie 540, 15 (1986).
Supplemental Material for "Stacking domains and dislocation networks in marginally twisted bilayers of transition metal dichalcogenides"

**DENSITY FUNCTIONAL THEORY (DFT) FOR ADHESION ENERGIES IN TMD BILAYERS AND DATA ANALYSIS**

In van der Waals-DFT (vdW-DFT) calculations of adhesion energies of TMD bilayers we neglected spin-orbit coupling, used a plane-wave cutoff of 816.34 eV (60 Ry), and kept the monolayer structure rigid, varying only interlayer distances and stacking ($r_0$). In modelling of heterobilayers (MoSe$_2$/WSe$_2$ and MoS$_2$/WS$_2$) we fixed the lattice constants to be the same in both layers (to ensure local commensurability), while keeping chalcogen-chalcogen distance in each monolayer equal to their individual monolayer values. For consistency, we performed these calculations using both (i) lattice constant of MoSe$_2$ (MoS$_2$) and (ii) lattice constant WSe$_2$ (WS$_2$) for both layers in MoSe$_2$/WSe$_2$ (MoS$_2$/WS$_2$) heterobilayer, comparing the differences. Such a comparison, Fig. S1e,f for sulphides (Fig. 2e,f of the main text for selenides), shows that these results are hardly distinguishable and their fitting using Eq. (1) produces almost identical parameters (the only noticeable difference is for the value of $A_2$, as shown for lateral lattice constant $a = 0.329/0.328$ nm ($a = 0.316/0.3153$ nm) in Table S1).

**TABLE S1. Fitting parameters for adhesion energy density for TMD bilayers.**

|          | $C_1$, eV·nm$^{-2}$ | $C_2$, eV·nm$^{-6}$ | $C_3$, eV·nm$^{-10}$ | $A_1$, eV·nm$^{-2}$ | $A_2$, eV·nm$^{-2}$ | $\rho$, nm | $d_0$, nm | $\varepsilon$, eV/nm$^4$ |
|----------|---------------------|---------------------|----------------------|---------------------|---------------------|------------|-----------|----------------------|
| WS$_2$/WS$_2$ | 0.137976            | 0.159961            | -0.020753            | 84571600            | 70214               | 0.0495     | 0.65      | 213                  |
| MoS$_2$/MoS$_2$ | 0.134661            | 0.161589            | -0.0209218           | 71928800            | 56411               | 0.0496     | 0.65      | 214                  |
| WS$_2$/WS$_2$ | 0.148820            | 0.247806            | -0.039458            | 121287200           | 110873              | 0.0497     | 0.69      | 190                  |
| MoSe$_2$/MoSe$_2$ | 0.151965            | 0.233975            | -0.0366911           | 96047400            | 81488               | 0.0506     | 0.68      | 189                  |
| MoS$_2$/WS$_2$ | 0.135693            | 0.162478            | -0.0211387           | 79160000            | 6427/65461          | 0.0492     | 0.65      | 214                  |
| MoSe$_2$/WS$_2$ | 0.154394            | 0.236366            | -0.0373244           | 77621500            | 84739/88450         | 0.0520     | 0.69      | 189                  |

We use $W_{P/AP}$ (Eq. (1) in the main text) and DFT results for 2H-stacking to compute the frequencies of layer-breathing modes (LBM) for 2H and 3R TMD bilayers, and compare in Table S2 with those measured in Raman spectroscopy.

**DFT BAND STRUCTURE ANALYSIS FOR 3R AND 2H BILAYERS**

The DFT calculations of 2H and 3R bilayer band structures were carried out in the local density approximation (LDA), as implemented in the VASP code [68], with spin-orbit coupling taken into account using projector augmented wave pseudopotentials. The cutoff energy for the plane-waves was set to 600eV, and the Brillouin zone sampled by a 12x12x1 grid. The bilayers are placed in a periodic three-dimensional box with a separation of 20Å between repeated images to ensure no interaction between them. The structural parameters were taken from experimental measurements of bulk TMDC crystals [69, 70].
TABLE S2. Phonon frequencies of layer-breathing modes (LBM), calculated using Eq.(1) of the main text, 2H vdW-DFT data, and compared to values measured using Raman spectroscopy. We used parameter $\varepsilon$ in configurations-averaged adhesion energy, $f(d)$, to estimate frequency of LBMs, $\omega_{LBM}$, in twisted bilayers.

|       | $\omega_{LBM}^{WS_2/WS_2}$ | $\omega_{LBM}^{MoS_2/MoS_2}$ | $\omega_{LBM}^{MoSe_2/MoSe_2}$ | $\omega_{LBM}^{WSe_2/WSe_2}$ | $\omega_{LBM}^{MoS_2/WS_2}$ | $\omega_{LBM}^{MoSe_2/WSe_2}$ |
|-------|-----------------------------|-----------------------------|-------------------------------|-----------------------------|-----------------------------|-------------------------------|
|       | cm$^{-1}$ exp.              | cm$^{-1}$ 2H DFT            | cm$^{-1}$ from Eq.(1)          | cm$^{-1}$ exp.              | cm$^{-1}$ from Eq.(1)          | cm$^{-1}$ from Eq.(1)          |
| WS$_2$/WS$_2$ | 33.8$^{[65]}$ | 30.1 | 29.6 | 29.4 | 28.3 |
| MoS$_2$/MoS$_2$ | 41.6$^{[56]}$ | 41 | 37.7 | 37.2 | 36.9 | 35.3 |
| MoSe$_2$/MoSe$_2$ | 34.3$^{[65]}$ | 29.4 | 28.8 | 28.5 | 27.5 |
| WSe$_2$/WSe$_2$ | 29.1$^{[65]}$ | 25.4 | 24.7 | 24.4 | 23.6 |
| MoS$_2$/WS$_2$ | 34.1 | 33.6 | 33.3 | 32 |
| MoSe$_2$/WSe$_2$ | 27.6 | 25.9 | 25.6 | 24.6 |
FIG. S1. Fitting of vDW-DFT data to $W_{AP/AP}$ in Eq. (1) in the main text for AP/P-MoS$_2$/MoS$_2$, AP/P-WS$_2$/WS$_2$, and AP/P-MoS$_2$/WS$_2$ bilayers.
FIG. S2. Data-points for $f$, $\tilde{f}$, $f_1$, $\tilde{f}_1$ and $\tilde{g}_1$ extracted from vdW-DFT data (Fig. S1 and Fig. 2 in the main text) showing that $f = \tilde{f}$ and $f_1 = \tilde{f}_1 + \tilde{g}_1$. 