Rotation misorientated graphene moire superlattices on Cu(111): classical molecular dynamics simulations and scanning tunneling microscopy studies

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Graphene on copper is a system of high technological relevance, as Cu is one of the most widely used substrates for the CVD growth of graphene. However, very little is known about the details of their interaction. One approach to gain such information is studying the superlattices emerging due to the mismatch of the two crystal lattices. However, graphene on copper is a low-corrugated system making both their experimental and theoretical study highly challenging. Here, we report the observation of a new rotational Moire superlattice of CVD graphene on Cu (111), characterized by a periodicity of \( 1.5 \pm 0.05 \) nm and corrugation of \( 0.15 \pm 0.05 \) Å, as measured by Scanning Tunneling Microscopy. To understand the observed superlattice we have developed a newly parameterized Tersoff-potential for the graphene/Cu (111) interface fitted to nonlocal van der Waals density functional theory (DFT) calculations. The interfacial force field with time-lapsed CMD provides superlattices in good quantitative agreement with the experimental results, for a misorientation angle of \( 10.4 \pm 0.5,^\circ \) without any further parameter adjustment. Furthermore, the CMD simulations predict the existence of two non-equivalent high-symmetry directions of the Moiré pattern that could also be identified in the experimental STM images.

**keywords**: atomistic and nanoscale simulations, molecular dynamics simulations, corrugation of graphene, moire superstructures, graphene on Cu(111)

**INTRODUCTION**

Chemical vapor deposition (CVD) on transition metal surfaces represents a promising and scalable approach to achieve reasonably uniform high-quality monolayer graphene for device application [1–3]. Polycrystalline copper foil thin films have widely been used for chemical vapor deposition (CVD) growth of graphene [3, 4]. On the other hand the Cu(111) facet of the single crystal has been proposed to be the ideal surface to produce large-scale uniform high-quality monolayer graphene [10].

The characterisation and verification of various graphene (gr) superstructures, such as the moire supercells [5, 6] and the corresponding nanotopography requires sophisticated experimental and theoretical studies [7–9]. Recent studies show that weakly adhered graphene on various substrates exhibits multiple oriented rotated moire regions with different misorientation angles [10–21].

In systems with stronger adhesion (e.g. gr/Ru(0001)) the appearance of rotated moire superstructures is still under debate [9, 16, 22–23]. In a most recent study it has been shown that the moire hills (called moirons) are nonequivalent and therefore the large coincident supercell is the unit cell of moire patterning in gr/Ru(0001) [9] in accordance with other experimental works [22].

It has also been shown that few types of rotated moire patterns could coexist, as in gr/Pt(111) and gr/Ir(111). In gr/Cu(111) the occurrence of rotated gr grains is much less studied [10] than on other substrates (e.g. Ir(111), Pt(111), Ni(111)) which could be due to the imaging difficulties in this important low-corrugated system with large repeat distance [10, 12]. The possible number of periodic graphene superstructures existing on Cu(111) is still largely unknown. Until now, two types of rotated domains have been identified: one with nearly vanishing rotation angle \( \Theta \) with large moire supercells (the cell size is around 6 nm) and another one with \( \Theta \approx 7^\circ \) (R7) with a much smaller periodicity of \( \sim 2 \) nm [10,12]. The bump-to-hump corrugation is \( \xi \approx 0.035 \) nm for the aligned gr/Cu(111) [11], however, for rotation misorriented samples no data is available yet.

In this paper we would like to show that an another rotated phase could exist on Cu(111) with a larger rotation angle (R10). Experimental (STM) and theoretical classical molecular dynamics (CMD) methods have been used to characterize the possible new rotated phase. A new CMD force field is developed for gr/Cu(111) to analyse the moire superstructures in atomic detail and the height variation is measured by STM along different symmetry directions for the low-angle rotated gr/Cu(111) system. It has been shown recently that the development of a new angular dependent interfacial force field provides the adequate description of the prototypical gr/Ru(0001)
TABLE I: The fitted Tersoff parameters for the graphene/Cu(111) interface.

| Parameter | Value |
|-----------|-------|
| A (eV)    | 977.7958178888248 |
| B (eV)    | 320.779450004024  |
| λ₁        | 3.13081741577273   |
| λ₂        | 2.0455964256718    |
| γ         | 0.08831675141470   |
| c         | 0.95287532769728   |
| h         | 0.90505284108358   |
| R₀ (Å)    | 4.197860487827     |
| D₀ (Å)    | 0.479447718668     |
| β (Å⁻¹)   | 1.0               |
| λ₃        | 1.552786576027     |
| n,m       | 1                 |

*(pw: present work, The parameters have been fitted to small flat gr/Cu(111) systems. Notations are the same as used in ref. [24] (supplementary material) and on the web page of lammps [29]. λ₃ is denoted as μ and h = cosΘ₀ in the supplementary material of ref. [24].)*

System [24]. First principles calculations (such as DFT) have widely been used in the last few years to understand corrugation of nanoscale gr sheets on various substrates [7, 8, 27, 28], the modelling of larger systems above 1000 Carbon atoms remains, however challenging, especially if at least geometry optimization is included. The minimal supercell of the gr/Cu(111) system includes few thousands of Carbon atoms which definitely exceeds the size limit of accurate DFT geometry optimizations and/or ab initio DFT molecular dynamics. We would like to show that using a new DFT adaptively parameterized interfacial Tersoff-potential [32] one can account for the observed surface reconstructions of gr (moire superstructures).

METHODOLOGY

Simulation rules

Classical molecular dynamics has been used as implemented in the LAMMPS code (Large-scale Atomic/Molecular Massively Parallel Simulator) [29]. The graphene layer has been placed nearly commensurately on the substrate since the lattice mismatch is small in gr/Cu(111). However, even this tiny misfit is sufficient to form an incommensurate overlayer by occupying partly registered positions (alternating hexagonal hollow and ontop sites) which leads to a moiré superstructure.

Periodic triclinic simulations cells have been constructed with 85 × 85 and 255 × 255 gr-unit cells. We find these structures are suitable for simulations which lead to nearly commensurate superstructures. The systems are carefully matched at the system edges in order to results in lateral periodic superstructures. Arbitrary system sizes lead to non perfect match at the edges. Moreover, nonperiodic cells lead to unstable moire patterns due to the undercoordinated atoms at the system border which can not be handeled by the present force field with CMD. Nonperiodic structures can be, however, optimized by simple minimalizers which also provide moire pattern. This pattern is sometimes is not sufficiently developed and becomes unstable during nonperiodic CMD due to the improper treatment of the undercoordinated border atoms. Further refinement of the pattern can be obtained by time-lapsed CMD. The moire pattern is extremely sensitive to weak effects during CMD such as e.g. the improperly treated edge atoms and/or the arising tensile stress or strain at the simulation cell border.

Isobaric-isothermal (NPT ensemble) simulations (with Nose-Hoover thermostat and a prestostat) were carried out at 300 K, vacuum regions were inserted between the slab of the gr-substrate system to ensure the periodic conditions not only in lateral directions (x,y) but also in perpendicular direction to the gr sheet (z). The variable time step algorithm has been exploited. The code OVITO [33] has been utilized for displaying atomic and nanoscale structures [24, 34].

The molecular dynamics simulations allow the optimal lateral positioning of the gr layer in order to reach nearly epitaxial displacement and the minimization of lattice misfit. The relaxation of the systems have been reached in 3 steps: first conjugate gradient geometry optimization (cg-min) with a subsequent simulation box relaxation (boxrel) of the rhomboid simulation cell has been carried out. Finally variable time step CMD simulations have been utilized in few tens of a thousand simulation steps to allow the further reorganization of the system under thermal and pressure control (NPT, Nose-Hoover thermostat, prestostat). Therefore we use in general the combined cg-min/CMD simulations. Time-lapsed CMD (TL-CMD) has been used at 300 K in order to average the morphology over longer timescale and also to consider the effect of temperature. We find that 10000 steps is sufficient for the occurrence of stable moire pattern. The pattern remains stable for time averages with much longer simulations. Shorter simulations give unfocused pattern.

The AIREBO (Adaptive Intermolecular Reactive Empirical Bond Order) potential has been used for the graphene sheet [30]. For the Cu substrate, a recent embedded atomic method (EAM) [31] potential is exploited. For the C-Cu interaction we developed a new angular dependent Tersoff-like angular-dependent potential [32]. In the Tersoff potential file the C-C and Cu-Cu interactions are ignored (nulled out). The CCCu and CuCCu out-of-plane bond angles were considered only. The CuCC and CCCu angles (with in-plane bonds) are ignored in the applied model. The consideration of these angles requires the specific optimization of angular parameters.
which leads to the polarization of angles and which does not fit to the original tersoff model.

Parameter fitting

Parameter fitting has been carried out in a similar way as described in ref. [24]. We used typical small gr/Cu(111) configurations (with flat gr) which are the representatives of binding registries of hollow, top-fcc and top-hcp and bridge alignments (see e.g. ref. [24]) and the potential energy curve (PEC) of the rigid gr-Cu(111) separation has been calculated by nonlocal vdW-DFT [25] using the SIESTA code [35]. Then using a code written in our Lab [10] the interfacial Tersoff potential has been fitted to these DFT PECs. We following conditions had to be satisfied by the new parameter set: (i) minimal rhomboid supercell edge size ($d \approx 6.1$ nm) for flat aligned gr (ii) proper topology of the gr-surface: lump-and-bump morphology with a corrugation of $\xi \approx 0.35 \pm 0.05$ Å (iii) interface energy: adsorption or adhesion energy $E_{adh} \approx 0.11 \pm 0.02$ eV/atom (iv) correct interfacial distances: $d_{C-Cu} \approx 3.1 \pm 0.1$ Å Among these requirements we employed directly only conditions (iii) and (iv) under parameter fitting. However, the new parameter set also satisfied automatically conditions (i)-(ii). Conditions (iii)-(iv) seem to be sufficiently strict to restrict the parameter space in order to account for the morphology and structure and energetics of the moire superstructures on gr/Cu(111). The obtained parameter set is shown in Table I.

Ab initio DFT calculations

First principles DFT calculations have also been carried out for calculating the adhesion energy per Carbon atoms vs. the C/Cu distance for a small ideal system with a flat graphene layer. The obtained PECs can be compared with the similar curve of MD calculations. We also calculate the DFT potential energy curves of various binding registries of gr including the hollow and on-top configurations (atop-fcc and hcp) and also the bridge one.

For this purpose we used the SIESTA code [35][36] which utilizes atomic centered numerical basis set. The SIESTA code and the implemented Van der Waals functional (denoted as DF2, LMKLL in the code [36]) have been tested in many articles for gr (see e.g. recent refs. [37][38]). We have used Troullier Martin, norm conserving, relativistic pseudopotentials in fully separable Kleinman and Bylander form for both carbon and Ru. Double-$\zeta$ polarization (DZP) basis set was used. In particular, 16 valence electrons are considered for Cu atoms and 4 for C atoms. Only $\Gamma$ point is used for the k-point grid in the SCF cycle. The real space grid used to calculate the Hartree, exchange and correlation contribution to the total energy and Hamiltonian was 300 Ry (Meshcutoff).

STM setup

Scanning tunneling microscopy (STM) is perhaps the most suitable characterization tool for studying the Moiré superlattices of graphene on various substrates. This is mainly due to its high (atomic) resolution capability and the ability to reliably detect extremely small height variations. STM investigations have been successfully employed to investigate moire-patterns emerging in graphene on Ru (0001) [12], Ir(111) [43], Rh(111) [44] as well as nonmetallic substrates such as 6H-SiC(000-1) [45] and h-BN [46]. An aspect one has to consider in interpreting such STM images is the influence of the electronic structure on the topographic images. In the case of Moiré-patterns the geometric curvature and substrate interactions, in principle, can induce a redistribution of the local electronic density of states, which might influence the image measured by STM [47]. However, this effect is only expected to be of practical significance for highly curved graphene membranes and strong substrate interactions.

Our STM measurements have been performed at low temperature (78 K) and under UHV conditions. The investigated graphene samples were grown on polished Cu (111) single crystal surfaces by Chemical Vapor Deposition at 990 C and 1250 mtorr base pressure, using a methane/hydrogen (20sccm:5sccm) gas mixture as precursor.

The STM images in Fig 2c,d have been acquired at -230 mV and 5 nA. From Fig. 2d the periodicity of the honeycomb lattice has been removed by Fourier filtering, to better visualize the fine structure of the observed moire pattern. Further details can be seen in ref. [26].

RESULTS AND DISCUSSION

The recorded STM images (Fig. 2c and (d)) suggest the occurrence of an unexpected misoriented phase not reported yet. The new phase (R10) has been reproduced and characterized by CMD simulations which required, however, the development of a new interfacial force field. We also identify the R7 phase by cg-min/CMD simulations which required, however, few other rotated phases have also been found, such as R2, R9 and R16 which could not explored yet.

The angular dependent Tersoff potential [32] has been used for the interface which has been fitted to nonlocal vdw-DFT potential energy curves of small model systems with hcp and hollow binding registries in a similar way as has been done in ref. [24]. No explicit information
FIG. 1: The results of (boxrel/cg-min)/TL-CMD simulations on moire superstructures at the rotation angle of \( \Theta = 0.0^\circ \). (a) Color coded topographic image. Minimal (yellow, \( 1 \times 1 \) supercell) and large supercell (red line, \( 2 \times 2 \) supercell) are also shown. In the latter supercell the moire protrusions called moirons are inequivalent within a \( 1 \times 1 \) subunit. (b) Height profiles along the high symmetry directions. The moire superstructure splits into a twofold symmetry pattern. (c)-(d): Height variations (Å) in the large rhomboid unit supercell of the moire pattern including 14500 Carbon atoms. Inset Fig 1(d) depicts the perfect \( \Theta = 0.0^\circ \) alignment of the gr sheet. The misalignment angle (rotation angle) is calculated as the angle between the Cu(111) atomic rows on the surface and between the zig-zag line of the Carbon atoms. The dimension of the \( x \) and \( y \) axes are in Å. Color coding: light colors correspond to protrusions (humps) and dark ones to bulged-in regions (bumps).

has been used in the fitting procedure on corrugation, supercell size or other relevant properties to be accounted for [24]. The new potential together with the AIREBO [30] C-C potential on Cu(111) is capable of reproducing the moire superstructures seen by STM [10, 11] at nearly zero misorientation angle. The obtained periodicity (\( d_{\text{per}} \)) of the small supercell is 6.1 nm in accordance with the experiment [10, 11] (see Figs 1(a)-(d)). The corrugation \( \xi \approx 0.04 \) nm, which is also in agreement with the available STM data [11].

For larger rotation we provide both CMD and STM data (see Figs 2(a)-(d)). We find that the larger-angle rotated moire superstructure (\( \Theta \approx 10.4^\circ \)) reproduces the mostly our STM findings (see Figs 2(c)-(d)). Rigidly rotated lattice gives the average angle of \( \Theta \approx 9.7^\circ \) and \( d_{\text{per}} \approx 1.35 \) nm. Until now few works have been reported the rotated phase of \( \Theta \approx 7^\circ \) (R7) with the periodicity of \( d_{\text{per}} \approx 2 - 2.2 \) nm [10, 12]. Our misoriented phase occurs at considerably larger angle and at much smaller repeat distance. Therefore we argue that another misoriented phase could be stable besides the one identified in few recent works [10, 12]. In particular, we find \( d_{\text{per}} \approx 1.5 \pm 0.05 \) nm (STM) and the serious drop of corrugation with respect to \( \Theta \approx 0^\circ \) (\( \xi \approx 0.012 \) nm). We denote this phase as R10. CMD simulations gives a slightly smaller \( d_{\text{per}} \approx 1.4 \pm 0.05 \) nm. We also find by CMD simulations the R7 (\( \Theta \approx 6.7^\circ \)) phase with a somewhat larger repeat distance of \( d_{\text{per}} \approx 2.5 \pm 0.05 \) nm than found by STM in recent publications (2.0 - 2.2 nm, [10, 12]).

In general we report the rapid decrease of the repeat distance, for instance for \( \Theta = 16^\circ \) the value of \( d_{\text{per}} \approx 0.88 \) nm has been found by CMD simulations (see Table II.). We could not identify stable phases with larger rotation angle with CMD. The initially set larger angle rotated...
structures are reorganized by the minimizer (geometry optimization) in such a way that smaller angle phases are found.

In Table II. the various structural and energetical properties of the simulated rotated structures have been summarized. The notable features are the following: Corrugation decreases with $\Theta$ and practically vanishes for $\Theta > 15^\circ$. The lattice constant of the gr sheet show no considerable sensitivity to $\Theta$ and is stabilized at $a_{gr} \approx 2.44$ Å (gr is slightly shrunk).

Contrary to the not negligible lattice misfit of $a_{lm} < 3.56\%$ the aligned gr $\Theta \approx 0^\circ$ is very close in energy to that of the perfectly relaxed flat gr with a vanishingly small energy difference ($\Delta E \approx 0.007$ eV/C) although its corrugation is $\xi \approx 0.45$ Å. Hence it seems that the relatively large lattice misfit and corrugation do not necessarily lead to energetical instability in this particular case. This is due to the strain relief in the large coincidence supercells [9]. We find 0.16 % and 0.04 % mismatch in the minimal and large supercells, respectively. In the case of the misoriented phase with $\Theta = 10.4^\circ$ the misfit of the coincidence supercells are 1.47 % for the minimal supercell and 0.33 % for the $2 \times 2$ supercell.

Concerning the energetical stability with respect to the perfectly flat periodic gr, $\Delta E \approx 0.04$ eV/C (see Table II.) which is somewhat above the magnitude of thermal motion ($\sim 0.026$ eV/K at 300 K). Also the energy difference between the aligned and the rotated case ($\Theta = 10.4^\circ$) is in similar range ($\Delta E \approx 0.033$ eV/C). Interestingly, the large angle rotation ($\Theta > 15^\circ$) also does not require much more energy ($\Delta E \approx 0.04 - 0.05$ eV/C). It suggests that at elevated temperature, however, (few hundred K above room temperature) the complexity of the multiple-oriented rotation domains could
be increased significantly and the weight of the large angle rotated regions could be considerable. Moreover the high temperature conditions (1200 K) of CVD growth of gr could be sufficient for the occurrence of various rotated isomers of supported gr. The pinning of various rotated domains, once formed during CVD growth could also be occurred. Therefore we predict the coexistence of various misaligned gr moire patterns including ultraflat (highly rotated), low-angle rotated and aligned regions (corrugated) which are energetically permitted. It must be noted that the large angle rotated domains ($\Theta > 15^\circ$), if exist, do not show moire pattern due to the vanishing corrugation and repeat distance. Similar findings have been reported for gr/Ir(111) [48] at large angle rotation of 30$^\circ$ at which corrugation was 10 times smaller than for the aligned moire. Considering that the morphology of gr/Cu(111) is rich even without rotation [29] it is hard to characterize certain domains of STM images. Recent studies suggest similar findings for gr/Pt(111) [15] or for gr/Ir(111) [17].

The adhesion energy has also been calculated and is shown for various rotated superlattices in Table II. We find a somewhat larger adsorption energy of $-0.145$ eV/C than by experiment ($-0.11$ eV/C, [11]). In general, the binding energy of gr to Cu(111) is smaller than in other systems, such as gr/Ru(0001) ($0.17 - 0.2$ eV/C, see e.g. ref. [24]) and larger than in the weakest bound systems (e.g. gr/SiO$_2$, $E_{adh} \approx -0.07$ eV/C) [50]. No considerable dependence of $E_{adh}$ has been found on $\Theta$.

The height variation of gr along thin sections can be seen on Figs. 1(b) and 3(a)-3(d). Along the long diagonal of the rhomboid supercells the main peaks are separated by small satellite peaks with $\xi \approx 0.1$ Å. Unfortunately we have no STM images available for $\Theta \approx 0^\circ$. Concerning the larger-angle rotated sample $R10 (\Theta \approx 10.4^\circ$), two main sections are shown along high symmetry directions of the moire pattern. On Figs. 3(a)-(b) the height profiles are seen along the short diagonal of the minimal rhomboid supercell for CMD simulations (3(a)) and for STM (3(b)). Figs. 3(c)-(d) depict the long diagonal height
profiles for CMD simulations (3(c)) and for STM (3(d)). At best of our knowledge it has not yet been reported the split of the height profiles along various directions for gr moire patterns. The corrugation for the rotated pattern remains below 0.015 nm for both profiles. On Figs 3(c)-(d) the appearance of satellite peak can be seen between the moire peaks with a rather low corrugation of ξ ≈ 0.005 nm. The interpeak distances along the shorter diagonal of the rhombic supercell are rather close to each other (Figs 3(a)-(b)). However, we find the 0.2 nm difference for the longer diagonal. STM measures somewhat longer interpeak distance here (Fig 3(d)).

CONCLUSIONS

The rotated moire phases of R0, R7 and R10 have been analysed by STM and by CMD simulations. R10 is a new rotated phase, not reported yet and revealed by STM and reproduced by classical molecular dynamics simulations in the present work.

Another important feature of the present paper is that a new interfacial force field has been developed to describe the moire superstructures in gr/Cu(111). No such interface interaction potential for gr/Cu(111) was available before which adequately describes moire superlattices. Using classical molecular dynamics simulations we have shown that it is possible to provide reasonably accurate structural results for weakly bound extended systems such as gr/Cu(111). A new interface force field has been developed for the weak C-Cu interaction. The new potential properly builds up hollow-protrusions and on-top-bumps and the overall morphology is very similar to that found by scanning tunneling microscopy. The calculated corrugations (ξR0 ≈ 0.45 Å, ξR10 ≈ 0.12 Å) is in agreement with the available experimental measurements.

We find that the repeat distance seen by STM (dper ≈ 1.5 nm) can be accounted for by the rotation angle of Θ = 10.4 ± 0.5° with CMD simulations. Furthermore

TABLE II: The summary of various properties obtained for gr/Cu(111) by classical molecular dynamics simulations using the fitted Tersoff potential for the interface. The main properties of the moire superstructures.

| method | Θ | dper (nm) | ξ (Å) | ξCu (Å) | dave (Å) | aGr (Å) | Gm (%) | Eadh (eV/C) | ΔE | Eg |
|--------|---|-----------|-------|---------|--------|--------|-------|-------------|----|-----|
| CMD   | 0° (R0) | 6.1 | 0.45 | 0.1 | 2.99 | 2.440 | 3.56 | -0.146 | 0.0072 | -7.419 |
|       | 2.2° (R2) | 4.3 | 0.25 | 0.1 | 2.99 | 2.440 | 3.56 | -0.146 | 0.04 | -7.384 |
|       | 6.7 (R7) | 2.5 | 0.14 | 0.06 | 3.02 | 2.445 | 3.44 | -0.145 | 0.035 | -7.391 |
|       | 8.7 (R9) | 1.75 | 0.12 | 0.05 | 3.02 | 2.445 | 3.44 | -0.145 | 0.02 | -7.406 |
|       | 10.4° (R10) | 1.4 | 0.1 | 0.05 | 2.99 | 2.440 | 3.70 | -0.145 | 0.04 | -7.385 |
|       | 16.1° (R16) | 0.88 | 0.03 | 0.02 | 3.02 | 2.444 | 3.56 | -0.145 | 0.04 | -7.385 |
| EXP   | ~0° (R0) | 6.0a | 0.35±0.1a | n/a | n/a | 2.46 | 3.53 | -0.11b | n/a | n/a |
|       | 7° (R7) | 2.0c, 2.2d | n/a | n/a | n/a | n/a | n/a | n/a | n/a | n/a |
|       | 10.4° (R10), pw° | 1.5 | 0.15±0.05 | n/a | n/a | n/a | n/a | n/a | n/a | n/a |
| DFT   | 0° | n/a | n/a | 3.25f, 3.05g | n/a | n/a | -0.062f, -0.198g | n/a | n/a |

[1] pw denotes present work, Θ is the rotation angle in degree (the angle between the line of zig-zag Carbon atoms and the adjacent Cu(111) atoms along the line (110) shown in Inset Fig 2(a).) dper is the periodicity of the minimal moire pattern (the edge length of the rhombus with 4 moire humps, 1 × 1 supercell), ξ and ξCu are the average corrugation for gr and the topmost Cu(111) layer (Å). dave is the average inter-layer (C-Cu) distance (Å) at the interface. aGr, atm are the lattice constant of gr (Å) and the lattice mismatch (%) after simulations (atm = 100(αs − αgr)/αgr). CMD: pw, fitted Tersoff results with cg minimization with CMD at 300 K. EXP: the experimental results: corrugation (ξ): our STM results, DFT results are also given for comparison. All quantities are given per Carbon atom. The adhesion energy Eadh = Etot − Eref, where Eref is the potential energy/C after md simulation. Eref can be calculated using the final geometry of md simulation with heteronuclear interactions switched off. Therefore, Eadh contains only contributions from interfacial interactions. Eadh, the strain energy of the corrugated gr-sheet, ΔE (eV/C) is the energy difference with respect to the perfectly flat periodic gr. ΔE = Egr − Egr,flat, where Egr and Egr,flat = −7.426 eV/C are the cohesive energy of C atoms in the corrugated and in the relaxed periodic flat (reference) gr sheet as obtained by the AIREBO C-potential. The main properties of the moire superstructures. No such interface interaction potential for gr/Cu(111) was available before which adequately describes moire superlattices. Using classical molecular dynamics simulations we have shown that it is possible to provide reasonably accurate structural results for weakly bound extended systems such as gr/Cu(111). A new interface force field has been developed for the weak C-Cu interaction. The new potential properly builds up hollow-protrusions and on-top-bumps and the overall morphology is very similar to that found by scanning tunneling microscopy. The calculated corrugations (ξR0 ≈ 0.45 Å, ξR10 ≈ 0.12 Å) is in agreement with the available experimental measurements.

We find that the repeat distance seen by STM (dper ≈ 1.5 nm) can be accounted for by the rotation angle of Θ = 10.4 ± 0.5° with CMD simulations. Furthermore
the misalignment flatens the gr sheet effectively when \( \Theta > 15^\circ \).

Energetically the various rotated phases show a small difference with respect to the completely flat periodic graphene (CFPG). In particular, the aligned corrugated periodic gr (R0) is as stable as CFPG as estimated by CMD simulations. The rotated corrugated systems are less stable by 0.02-0.04 eV/C. The adhesion energy of the CMD simulations. The rotated corrugated systems are periodic gr (R0) is as stable as CFPG as estimated by

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