Twist boundary in graphene: energetics and electric field effect

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Abstract
The energetics of the translational and rotational degrees of freedom of graphene layers are investigated using density functional theory. It is found that the sliding (translation) energy of a bilayer depends dramatically on whether such layers are mutually rotated or not. While for unrotated layers the sliding energy is large, with the AB stacked bilayer lowest in energy, for mutually rotated layers the sliding energy is zero. Turning to the rotational degree of freedom, we find that dependence of energy on the relative rotation between layers is considerable, and that the lowest energy structure is that generated by $30° \pm 2.208°$. The impact of a perpendicular electric field on mutually rotated graphene layers is explored. The electronic decoupling of such layers ensures that the Dirac cones simply shift relative to each other to accommodate the charge transfer between the layers. Interestingly, this shift is approximately the same in magnitude as that of the field induced gap opened when an electric field is applied to an AB stacked bilayer.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The recent experimental realization of graphene [1], a honeycomb lattice of carbon, has presented the solid state physics community with a fascinating new material which, moreover, holds out the promise of great technological impact. The band structure of a pristine graphene sheet is, for energies close to the Fermi level, well described as a set of circular conical manifolds whose vertices intersect the Fermi level at high symmetry (K, K') points in the Brillouin zone, the so-called Dirac points. Graphene is, therefore, a zero gap semiconductor. Furthermore, the equivalence of the two basis atoms in the graphene honeycomb lattice ensures a charge conjugation relation between the electron and hole excitations; low energy excitations in graphene are therefore governed by an effective massless Dirac equation. A host of novel electronic properties follows from this fact. Amongst the most striking are the $\sqrt{B}$ dependence of Landau level energies, an anomalous phase in a room temperature Quantum Hall effect, and quasi-ballistic transport with high electron mobilities [2]. It is these last two that, combined with graphene's rather favourable structural properties, lead to the promise of coherent carbon-based nanoelectronics.

While graphene was initially isolated by a mechanical exfoliation technique that resulted in single or bilayer graphene flakes deposited on an insulating SiO_2 substrate [1], it has also since been epitaxially grown by sublimation of Si from the hexagonal faces of 4H- and 6H-SiC [3–9], and more recently by surface segregation of C on Ru [10]. This technique of epitaxial growth, however, produces not single layer graphene (SLG) but multiple graphene layers, so-called graphene stacks [5]. As two layers of graphene in the lowest energy configuration (AB stacking) already possess a dramatically different low energy band structure from SLG—a quadratic dispersion near the Dirac point instead of linear [11–14]—the SLG behaviour of such graphene stacks is surprising. A sustained research effort has therefore focused on understanding how these complex graphene-based systems may result in SLG physics [15–20].

The nature of the epitaxial growth on the (0001), i.e. Si-face, and the $(000\bar{1})$, i.e. C-face of SiC are quite different [5]. Growth on the C-face is rapid and does not self-limit; up to

≈100 graphene layers may result in the graphene stack. On the other hand, the growth of graphene layers on the Si-face is slow and self-limits to a few layers of graphene at 1300 °C. In this latter case, density functional theory calculations [15–17] have shown that the first graphene layer is strongly and covalently bound to the SiC substrate, and that this layer is insulating in nature. This is true whether a simple model [15, 16] is used to describe the interface or the more complex $6\sqrt{3} \times 6\sqrt{3}$ structure seen in LEED experiments [17]. The second graphene layer then binds weakly (van der Waals type bonding) to this first layer and, since the Dirac point is located in the insulating gap, the Dirac cone is preserved. It is, however, shifted from the Fermi level due to the presence of dangling bond states at the Si-face.

An understanding of the situation for the C-face has recently been provided by the observation of Hass *et al* that graphene stacks grown on this face display a high degree of rotational disorder [18]. Furthermore, for the particular rotation angle seen in experiment (30° ± 2.204°), it was found that two layers with the same relative rotation exhibited a remarkable electronic decoupling; *ab initio* calculations of the mutually rotated layers showed that *both* displayed the linear dispersion characteristic of SLG [18]. An important question raised by this result is whether arbitrary rotations cause decoupling, or only a 'magic subset' of angles. This is particularly relevant as the occurrence of rotation angles different from those found by Hass *et al* have been reported [21]. Recently, it has been shown that all rotation angles do result in an approximate (but for nearly all cases effectively perfect) decoupling, and that this is true whether one considers a mutual rotation between two layers or, more realistically, the rotation of a single layer in an arbitrary graphene stack [22]. The essential mechanism was shown to be a destructive interference of quantum states between rotated layers, which in turn leads to a vanishing of interlayer overlap matrix elements and hence SLG dispersion in both layers.

While the electronic structure consequences of introducing twist boundary faults into graphene stacks have been well explored, the energetics of such stacking faults has not enjoyed the same attention. In this paper we therefore investigate the dependence of stacking fault energy upon the various degrees of freedom of the twist boundary. Furthermore, in order to gain additional insight into the nature of mutually rotated graphene layers we consider the effect of a perpendicular electric field on the electronic structure of the twist boundary.

The remainder of this paper is as follows. In section 2 we review the commensuration conditions between graphene layers developed in [19, 22], and discuss the Móire pattern periodicity in this context. Numerical details pertaining to subsequent sections are presented in section 3. Section 4 then describes the energetics of twist boundaries, and section 5 the consequence of a perpendicular electric field upon them, after which we conclude.

2. Commensurate twist structures and the Móire periodicity

Rotational disorder between *honeycomb* crystal layers leads to a large scale *hexagonal* interference pattern known as a

Móire. This may be observed with the aid of scanning tunnelling microscopy (STM) and is one of the signatures of such rotational disorder, found in both the C-face growth of graphene on SiC [21] and the surface layer of graphite under certain circumstances [23]. In this section we shall derive the relation between the relative rotation of the two layers and the periodicity of the emergent Móire pattern. Although this formula is well known, it does not appear to have been related to analytic results for finite commensuration before [23].

The commensuration conditions for mutually rotated graphene layers were recently derived in [22], for ease of exposition we shall briefly review the relevant results obtained in that work.

The basic condition to arrive at a commensurate crystal structure upon rotating two graphene layers is that the cosine of the rotation angle be rational valued [22, 24]. All commensurations must thus be labelled by two integers (as two integers are needed to specify an arbitrary rational), which we term p and q. For a coprime (p, q) with $q > p$ one finds an unique commensuration with the angle of rotation of the two lattices given by [22]

$$\theta = \cos^{-1}\left(\frac{3q^2 - p^2}{3q^2 + p^2}\right) \tag{1}$$

and with the number of primitive vectors in the commensuration cell given as

$$N = \frac{3}{\delta}\frac{1}{\gamma^2}(3q^2 + p^2), \tag{2}$$

where $\delta = 3/\gcd(p, 3)$ and $\gamma = \gcd(p + 3q, p - 3q)$. Commensurations with $N < 2000$ are plotted in the lower panel of figure 1 against the corresponding rotation angle. One should note that although this plot has a clear symmetry about $\theta = 30°$, this is not a symmetry with respect to crystal structures, as is vividly brought out by comparing pairs (1, 2), with the relevant points in the lower panel circled for easy identification.

Following the structures 3, 4, and 5 (again indicated by red circles in the lower panel) one notices that, as the rotation angle tends to zero, the areas in approximate AA stacking (red/white areas) and AB stacking (red/black areas) are increasing. This pattern of AA/AB stacking is the emergent Móire, which may be observed by local probes such as STM. It is worth noting, however, that structures (1, 2)—which correspond to the stacking faults observed by Hass *et al* [18]—could not be observed in this way; there is no separation into such AA and AB stacked areas. Thus only a subset of possible twist faults may be observed by local techniques such as STM.

A relation between rotation angle and the periodicity of the Móire may be derived by first, from equations (1) and (2), noting the following relation

$$N = \frac{3}{\gamma^2\delta}\frac{p^2}{\sin^2\theta/2}. \tag{3}$$

Now, using the theorem that if $\gcd(x, y) = \gamma$ then $\gcd(x, x + cy) = \alpha\gamma$ with α a factor of c, we find that for any coprime (p, q) if $\gcd(p, 3) = 1$, i.e. that $\delta = 3$, then $\gamma = 2$ if (p, q) are
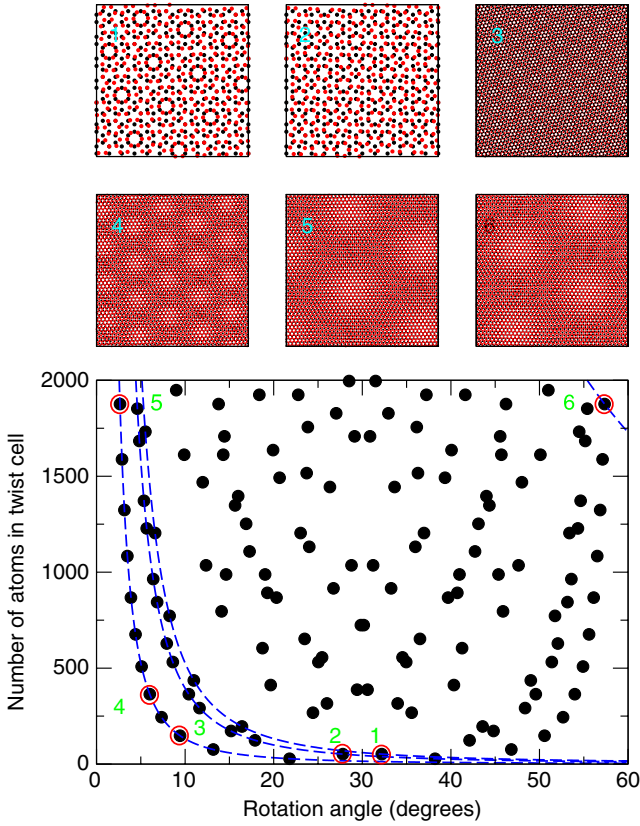
Figure 1. Lower panel: number of C atoms in the twist boundary commensuration cell plotted against the angle of rotation between the two graphene layers. Upper panels: specific twist boundary structures generated by rotating about the two atom high symmetry axis in an initially AB stacked bilayer. Numbering of upper panels corresponds to that in the lower panel.

both odd and $\gamma = 1$ otherwise. The parameters which give the curve of minimal N from equation (3) are thus $p = 1$, $\delta = 3$, and $\gamma = 2$. We therefore find that the structures 3, 4, and 5 must lie on the curve given by

$$N = \frac{1}{4\sin^2\theta/2}. \tag{4}$$

If we then use the fact that N, the number of primitive vectors within the commensuration cell, is clearly $N = D^2/d^2$ where D is the Móire periodicity and d the underlying lattice periodicity then we arrive at

$$D = \frac{d}{2\sin\theta/2} \tag{5}$$

relating the periodicity the Móire to the rotation of the two lattices [23], a formula also sometimes known as the 'Móire hypothesis' [25–27].

3. Computational details

Our calculations have been performed using the local density approximation (LDA) to density functional theory, with the Kohn–Sham equations solved within the projected augmented
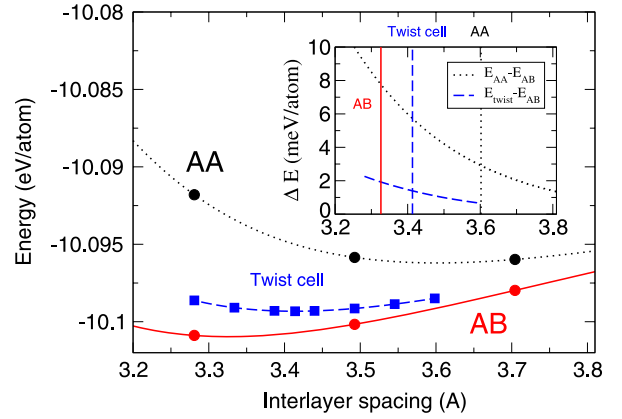

Figure 2. Total energy per C atom of an AA stack bilayer (black dotted line), an AB stacked bilayer (red continuous line), and a 21.79° twist boundary cell (blue dashed line). The twist boundary is generated by a rotation taken about the high symmetry two atom axis in an initially stacked AB bilayer. Displayed in the inset are the energies of the AA and twist structures relative to the AB structure, with vertical lines indicating equilibrium lattice spacings.

wave method [28], as implemented in the electronic structure program VASP [29]. We have used settings corresponding to a so-called 'HIGH PRECISION' calculation in VASP, e.g. $E_{\text{cut}} = 500$ eV. The number of **k**-vectors was found to converge in energy to better than 0.1 meV/atom for **k**-meshes of 30×30, 18×18, 14×14, and 10×10, for twist boundary cells with 4, 28, 52 and 76 atoms respectively. The vacuum separation of our graphene slabs we take to be 12 Å, which is enough to converge the bilayer $E_{\text{AA}} - E_{\text{AB}}$ energy difference to better than 1 meV/atom, sufficient for our purposes. Several of our results have been cross checked with the full potential all electron code EXCITING [30].

4. Energetics of the twist boundary

It is well known that the LDA with density functional theory fails to describe dispersion forces and that these are important for graphite and, presumably, also for few layer graphene systems. On the other hand the lattice parameter of graphite calculated in the LDA is quite reasonable [31]. The reason for this can be traced back to a delicate error cancellation between the exchange and correlation energies in the LDA functional [32]. Despite this rather uncertain foundation for calculating graphene-based systems in the LDA, it is clear that it is nevertheless a viable functional for treating graphene-based systems [15–18, 22].

We begin by considering the effect of a mutual rotation between graphene layers on the interlayer spacing, this is shown in figure 2 for the case of a $\theta = 21.79°$ rotation about the high symmetry two atom axis in an initially AB stacked bilayer. The increase in lattice parameter is expected as the destructive interference between the graphene sheets that causes electronic decoupling should also weaken bonding; a similar expansion of the average lattice spacing is also seen in turbostratic graphite crystals. We have performed local ionic relaxations for several twist boundary structures, but found the change in atomic positions to be negligible.
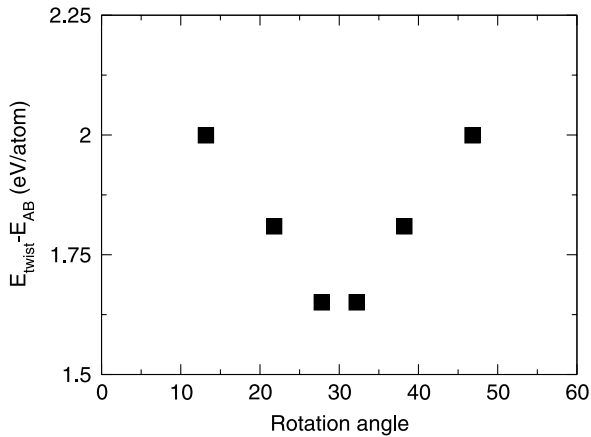
Figure 3. Difference in energy per C atom (eV) between various twist bilayers and the AB stacked bilayer, plotted against the angle of the twist between the two layers.

Figure 4. Sliding energy for the AB bilayer and the twist bilayer with rotation angle $\theta = 38.21°$ (rotation taken about the no atom high symmetry axis in an initially stacked AA bilayer). The sliding vector is given by $\delta \mathbf{a} = \eta(\mathbf{a}_1 + \mathbf{a}_2)$, where $\mathbf{a}_1$, $\mathbf{a}_2$, and $\delta \mathbf{a}$ are indicated in the inset at the top right of the figure.

The energy dependence of the bilayer upon the rotational degree of freedom is shown in figure 3 for rotation angles $\theta = 30° \pm 2.20°$, $30° \pm 8.31°$ and $30° \pm 16.83°$ corresponding to primitive commensuration cells of 28, 32 and 76 atoms respectively. We have again used an initial AB stacking and rotated about the two atom high symmetry point in all cases. For these, and the remaining calculations of the article, we have used a fixed interlayer spacing of 3.34 Å. Clearly, there is a fairly significant dependence of energy on rotation (a spread of nearly 0.5 eV/atom). Interestingly, the lowest energy twist boundary structure, $\theta = 30° \pm 2.20°$ is that found by Hass *et al* in graphene grown on C-face of SiC; this structure is still, however, 1.6 eV/atom less stable than the AB bilayer.

Turning now to the translational degree of freedom, in figure 4 are shown the energies per C atom, relative to the AB stacked bilayer, of translating by $\delta \mathbf{a} = \eta(\mathbf{a}_1 + \mathbf{a}_2)$ two structures: the AA bilayer and a twist boundary. The twist boundary is generated by first rotating 38.21° about the high symmetry zero atom centre in the AA structure, and then translating each atom by $\delta \mathbf{a}$. Remarkably, one can see that in contrast to the rotational degree of freedom, for already mutually oriented graphene bilayers the sliding energy is, (to our numerical accuracy of $\approx 10^{-5}$ eV), zero.

5. Electric field effect

Shown in figure 5 is the bilayer band structure corresponding to a mutual rotation of 38.21° about the two atom high symmetry point of an initial AB stacking. Also shown is the same structure but in a perpendicular electric field, the strength of which varies from 0.05 to 0.15 V Å^{-1} as indicated by the line style (colour) of the band lines. As may be seen in figure 5, the applied field results in a relative shift of the Dirac cones from each layer. This results from a flow of charge from one layer to the other under the applied field and hence there is a symmetric shift of the Dirac cones as one layer becomes n type doped and the other p type doped.

It is interesting that the magnitude of this relative shift of the Dirac cones is very close to the corresponding opening of a
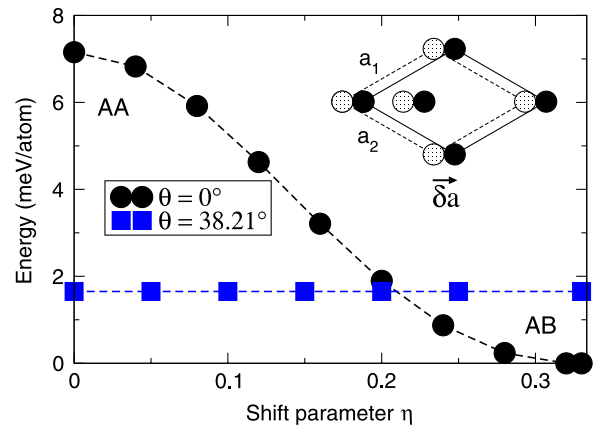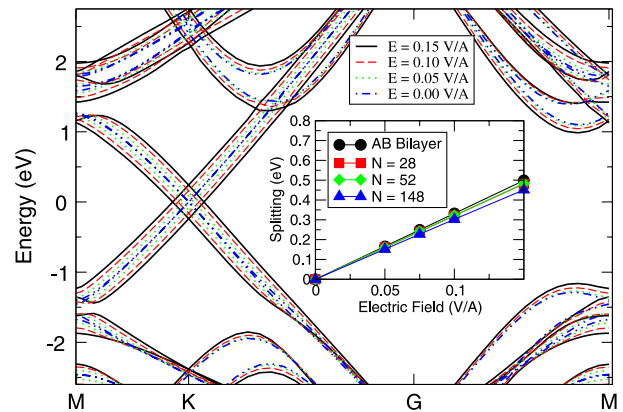

Figure 5. Band structure of the 28 atom twist boundary cell generated by rotating two AB stacked graphene layers 38.21° about the two atom symmetry centre. Different line styles indicate the application of different perpendicular electric fields to the layers. Inset shows the dependence of the cone shift on the applied field, also shown is corresponding data for the magnitude of the gap in the AB bilayer.

gap in the AB stacked bilayer [33] under the same applied field (see inset in figure 5). In a recent paper it was shown how this feature of the bilayer, i.e. the variation in band structure with the charge distribution between the two layers, causes a strong suppression of low frequency $1/f$ noise in the AB bilayer as compared to single layer (and nanotube) devices [34]. The fact that mutually rotated bilayers behave in a very similar way to the AB bilayer thus suggests that such systems will share this strong suppression of noise and, therefore, may be very promising candidates for nanoscale device fabrication.

6. Conclusions

The energetics of mutually rotated graphene layers show a dramatic difference between the sliding energy, which is zero, (at least in the direction $(\mathbf{a}_1 + \mathbf{a}_2)$ see figure 4), and

the rotational degree of freedom which always costs energy. Further calculations are needed to ascertain if this unusual feature of the sliding energy is true for all translation directions. Of the twist boundaries studied in this work, that formed by rotating $\theta = 30° \pm 2.20°$ was found to have the lowest energy. This particular twist boundary was observed in C-face graphene stacks studied by Hass *et al* [18].

Under the application of an external (perpendicular) electric field the Dirac cones from each of two mutually rotated graphene layers shift relative to one another, simply to accommodate a charge redistribution between the layers. This feature may, by analogy with the AB stacked bilayer, lead to a strong suppression of $1/f$ noise in nanodevices.

Acknowledgments

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