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Adsorption of graphene to metal (111) surfaces using the exchange-hole dipole moment model

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ABSTRACT

Graphene has a unique electronic structure and excellent tribological properties. A promising method for graphene production involves depositing vaporized carbon on metal substrates, which can also be used to modify graphene's electronic structure through charge transfer. In this work, graphene adsorption on the (111) surface of seven metals (Al, Cu, Ag, Au, Ni, Pd, and Pt) is investigated computationally using density-functional theory with the exchange-hole dipole moment (XDM) dispersion correction. Two distinct graphene-metal orientations, corresponding to 0° and 30° relative rotation of the graphene layer, are considered to investigate how lattice mismatch affects adsorption. Our results reproduce reference data from the random-phase approximation more closely than other dispersion-corrected density functionals, confirming that XDM is an excellent method for surface chemistry. The rotational orientation of graphene is found to strongly affect its interaction with the substrate. There is an energetic drive for graphene to align with the metal lattice, particularly for Pd and Pt, which causes the formation of multiple Moiré patterns, in agreement with experimental observations.

1. Introduction

Graphene is a material that holds the potential to revolutionize the semiconductor industry. Various applications have been proposed that utilize graphene's unique two-dimensional electronic structure [1–14]. Graphene has also been shown to be an excellent solid lubricant [14–16] that can reduce friction and wear in mechanical devices either through direct surface deposition or as an additive to petroleum-based lubricants [11,17]. While the original scotch-tape method for graphene isolation [1] easily produces laboratory samples, it is not scalable for mass production. Lack of a suitable mass-production method has hindered commercialization of graphene-based technologies [6,18], but several methods have showed promising results. One such method is chemical vapor deposition (CVD) [19–22], where a carbon feedstock is vaporized to produce pure carbon that is deposited on to a metal surface. Additionally, charge transfer from the underlying metal substrate [22] provides a mechanism to tune graphene's electronic structure through the alteration of its valence band [23].

Graphene-metal systems have been extensively investigated experimentally [18,24–38] to understand electronic and tribological properties as well as monolayer growth mechanisms. These investigations have shown that graphene can either chemisorb, physisorb, or form a carbide phase on the surface [18,24]. Metals on which graphene chemisorbs or physisorbs are of the most practical interest because the adsorbed graphene will retain its unique electronic structure.

The most promising substrates for graphene mass production are Cu and Ni. Not only are these metals inexpensive, but their surface lattice constant is close to that of graphene. This excellent lattice match results in a limited number of observed Moiré patterns and reliable formation of large continuous graphene monolayers on the surface [39–43]. In particular, a CVD method using Cu has shown promising results for graphene mass production [44]. Metals such as Pd [28–30], Pt [27,31–36] and Au [26,35,37,38] have also been investigated for graphene synthesis, but their lattice mismatch results in multiple Moiré patterns on single surface samples. Indeed, experiments suggest that there exist an infinite number of Moiré patterns for Pt and Pd [28,30–33]. In the early stages of graphene patterning on Pd and Pt, local graphene domains will bind strongly to the surface, but as the monolayer size increases, the overall surface-substrate interaction weakens because of the lattice mismatch. Light emitting electron diffraction (LEED)

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experiments have shown that strong surface-substrate interactions occur on Pd and Pt, but depend on the rotational alignment [29,36], which has resulted in conflicting reports as to the nature of graphene-Pd/Pt interactions.

Many previous publications have used density-functional theory (DFT) to investigate graphene adsorption on metal surfaces [42,45–49]. Most studies employed the local density approximation (LDA) because it predicts reasonable chemisorption geometries [29,32,50–54]. However, the LDA is known to over-estimate chemisorption energies and under-estimate physisorption because it does not include the physics of London dispersion. This results in narrow potential energy surfaces (PES) at chemisorption distances, with only shallow binding at typical physisorption distances, in disagreement with higher levels of theory, such as the random-phase approximation (RPA) [48].

Functionals of the generalized-gradient-approximation (GGA) type combined with a dispersion correction are quite accurate for van der Waals complexes [55–60]. However, the majority of these dispersion corrections are less reliable for metal surfaces due to the empirical nature of the dispersion coefficients [61–66] and it has been argued that many-body effects may be important for accurate modeling of surface adsorption [67]. Non-local van der Waals density functionals (vdW-DF) [68–71] are typically more reliable for molecular physisorption on metal surfaces [66,72]. Several groups [46,47,49] have studied adsorption of graphene on multiple metals using vdW-DF functionals; however, there are massive differences between the results depending on the base GGA functional used. For example, vdW-DF2 [71] (which uses revPBE [73]) predicts weak physisorption on Cu and Ni, while vdW-DF2-C09 [74] predicts stronger chemisorption [47]. The best available theoretical reference data for graphene adsorption is a study using the random phase approximation (RPA) by Olsen and Thygesen [48]. Though the RPA agrees with most experimental observations, the scope of this investigation was limited to a single Moiré pattern on each studied metal that minimized lattice strain [48], which precludes prediction of the orientation dependence [52].

This paper is the second part of a series [75] investigating graphene-metal adsorption using DFT paired with the exchange-hole dipole moment (XDM) dispersion correction [60,76–79]. The XDM model is a non-empirical dispersion correction that uses the electron density to generate environment-dependent dispersion coefficients. As a result, XDM is uniquely suited to model dispersion interactions across a wide range of chemically diverse systems, such as molecular dimers [78,80], supra-molecular systems [81], organic crystals [82,83], and most closely related to this work, molecular physisorption [66]. The first part of this series was limited to graphene adsorption on nickel, for which XDM was found to provide excellent agreement with both RPA reference calculations and the experimental adsorption energy [75]. However, this is no guarantee that the high accuracy of XDM will be transferable to modeling graphene adsoprtion on other metals.

In the present work, we have broadened our study to include six additional metals: Al, Cu, Ag, Au, Pd, and Pt. The XDM results are found to more closely reproduce RPA interlayer distances and adsorption energies [48] than other, previously applied density functionals. Additionally, this is the first dispersion-corrected DFT study to investigate graphene adsorption in two rotational orientations, corresponding to 0° and 30° Moiré patterns. It is shown that the graphene-substrate interaction strength is highly dependent on rotational orientation. The XDM calculations predict particularly strong graphene-surface interactions in the 0° orientation for Pd and Pt, which explain the experimental observation of multiple Moiré patterns with locally-ordered graphene domains. Finally, our results suggest that larger unit cells (impractical for DFT calculations) are needed to properly model graphene-metal interactions for substrates with large surface-lattice mismatches.

2. Computational methods

The computational methods used here are consistent with our previous work on Ni(111)-graphene [75]. All DFT calculations were performed using periodic boundary conditions with the projector augmented wave (PAW) formalism [84] as implemented in Quantum ESPRESSO [78,85]. The exchange-correlation functional chosen was B86bPBE [86,87], as it provides the best accuracy when paired with the XDM dispersion model [66,82]. An $8 \times 8 \times 1$ Γ-centered **k**-point grid was used, with a plane-wave cutoff of 60 Ry, a density expansion cutoff of 800 Ry, and cold smearing [88] with a smearing parameter of 0.01 Ry.

The XDM dispersion energy is a post-SCF correction to the B86bPBE (base) energy:

$$E = E_{\text{base}} + E_{\text{XDM}} \tag{1}$$

$$E_{\text{XDM}} = -\frac{1}{2} \sum_{n=6,8,10} \sum_{i \neq j} \frac{C_{n,ij} f_n(R_{ij})}{R_{ij}^n} \tag{2}$$

In this equation, i and j run over atoms in the system, R_{ij} is the interatomic distance, f_n is a damping function that attenuates the dispersion correction at short range, and the $C_{n,ij}$ are pairwise atomic dispersion coefficients. Each $C_{n,ij}$ is evaluated using the multipole moments for the interacting atoms arising from a reference electron together with its corresponding exchange-hole distribution, as well as atom-in-molecule polarizabilities [60,79].

In this work, calculations were performed for graphene adsorption on six metal surfaces: aluminum, copper, silver, gold, palladium, and platinum. Additionally, our previous results for nickel [75] are reported again here for comparative purposes. All calculations for the Ni-group metals used an initial spin-polarization, while those for Al and the Cu-group metals did not. All metals considered have a face-centered cubic (fcc) crystal structure and adsorption of graphene on the (111) surface was studied. Two different orientations, or Moiré patterns, were modeled to compare how rotational orientation affects graphene-substrate interactions. These were constructed using the (1×1) surface unit cell for the 0° orientation, where the lattice vectors of graphene's primitive cell align with the (111) metal surface's primitive cell (Fig. 1b and c). The $(\sqrt{3} \times \sqrt{3})$ surface unit cell was obtained by rotating the metal substrate by 30° relative to the graphene sheet (Fig. 1a). Both of these orientations have been established in previous works [45–48], with the (1×1) cell commonly used for Ni and Cu and the $(\sqrt{3} \times \sqrt{3})$ cell used for the remaining metals to minimize lattice strain.

Geometries for graphene adsorbed in the 30° orientation and two of the possible structures (top-fcc and fcc-hcp, using the common nomenclature [42,46–48,75]) for the 0° orientation are illustrated in Fig. 1. Calculations were also performed for the four remaining structures in the 0° orientation (bridge-fcc, bridge-hcp, bridge-top, and top-hcp). The larger $(\sqrt{3} \times \sqrt{3})$ cell for the 30° orientation results in a periodic graphene layer with eight carbon atoms per cell, as the graphene unit cell is 2 times longer in each direction compared to the 0° orientation. The carbon atoms are equally split over void and on-top sites, such that the interactions are degenerate upon $x - y$ translation, and only the structure shown in Fig. 1a need be considered. In the following sections, the geometries for each of these cells will be discussed using the cell lengths represented in Fig. 1. The relations between these quantities are: $a_{1\times1} = r$, $a_{\sqrt{3}\times\sqrt{3}} = r\sqrt{3}$, $a_{cubic} = r\sqrt{2}$, where r is the nearest-