# Multiscale simulations of the early stages of the growth of graphene on copper

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## ABSTRACT

We have performed multiscale simulations of the growth of graphene on defect-free copper (111) in order to model the nucleation and growth of graphene flakes during chemical vapour deposition and potentially guide future experimental work. Basic activation energies for atomic surface diffusion were determined by *ab initio* calculations. Larger scale growth was obtained within a kinetic Monte Carlo approach (KMC) with parameters based on the *ab initio* results. The KMC approach counts the first and second neighbours to determine the probability of surface diffusion. We report qualitative results on the size and shape of the graphene islands as a function of deposition flux. The dominance of graphene zigzag edges for low deposition flux, also observed experimentally, is explained by its larger dynamical stability that the present model fully reproduced.

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## 1. Introduction

Graphene is a material that has recently attracted considerable attention due to its exceptional mechanical, electrical or optical properties [1–3] and its status as a model 2D system. Graphene flake synthesis can be achieved by multiple methods such as mechanical exfoliation [4] and chemical vapour deposition (CVD). In this article we consider the synthesis of graphene through CVD on copper (111) substrates, though CVD can be achieved on many other substrates such as Ni or Pt [5]. CVD on copper substrates is advantageous as it can produce large area thin (monolayer) flakes of graphene [6] (this can also be achieved on other substrates [7,8]). However, implementation of graphene devices requires effective control of the quality of the film. Understanding the growth mechanisms is therefore important for the improvement of the quality of the grown layer. For example, a large amount of nucleation tends to create grain boundaries that can deteriorate the electrical conductivity [9]. This problem has been extensively studied experimentally [10,11], but no complete atomic model of the growth has yet been proposed (see below).

CVD of graphene on copper is a relatively high temperature process (usually 1273 K, with copper melting at 1357 K) that uses a combination of gases (*i.e.*, methane and hydrogen) in a chamber [6,12]. At an atomic level, CVD growth of graphene on Cu is initiated with the adsorption and dissociation of methane on the surface. The C adatoms then diffuse on

the surface and form small nuclei that, eventually, grow into larger islands [13]. Experimental articles have pointed out the influence of hydrogen partial pressure [14], chamber pressure [15], state and orientation of the substrate [16] and temperature [17] on the size and shape of graphene domains. Many different shapes have been observed, such as hexagons [9,18,19], multiple-lobed islands [20,21], snowflake-like graphene [13] or hexagons with dendritic edges [20].

Various approaches have been reported to model or simulate the growth of graphene. For the specific case of CVD growth, at the macroscopic level, thermodynamic calculations of gas phase equilibrium in the CVD chamber [22] have been proposed to correlate to gas phase species with the graphene film growth. The decomposition of hydrocarbon on copper and the growth of small islands has been studied by first-principle thermodynamics [23]. Models of nucleation and growth during CVD (including qualitative models, such as [11]), explained the role of hydrogen [24] and can include calculations of the density of nuclei [17]. Monte Carlo studies have covered the evolution of defects [25], or growth mechanisms of graphene [26]. At the atomic level, stability and diffusion of carbon atoms and dimers have been evaluated by DFT *ab-initio* calculations for perfect [27] and stepped [28] copper surfaces. Surface adsorption has been found to be favourable on a Cu (111) surface for isolated atoms but surface orientation is less important for small clusters of carbon atoms [29]. *Ab-initio* methods have also demonstrated the stability of zig-zag edges based on static calculations for small carbon clusters on a perfect Cu (111) surface [18] or related to the presence of "free" Cu atoms on the surface [30].

Beside these macroscopic or *ab-initio* calculations, Kinetic Monte Carlo (KMC) simulations provide a large-scale atomistic view with an insight into the dynamics of the growth process going from atomic

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diffusion to cluster formation. KMC has been used to model the growth of numerous nanomaterials [31–33] but, to the best of our knowledge, not for graphene. Exceptions are pattern formation during growth, based on the *a priori* presence of carbon island and on the attachment of small clusters [13] and the study of vacancy migration [34].

In this article, we focus on the specific case of the simulations of the early stages of the growth of graphene on Cu (111) by CVD. We first present *ab initio* calculations for the surface diffusion activation energies for a few typical cases. Secondly, we present our KMC modelling scheme and compare results obtained when atomic diffusion depends on first neighbours only and when it also depends on second neighbours. Our KMC algorithm takes into account the effect of detachment from carbon clusters and atomic diffusion, and does not require seeds or steps to obtain graphene flakes. Our project is therefore to implement multiscale simulations with the first scale being *ab initio* and the second scale the KMC simulations. Our main results are on the qualitative effect of the deposition rates on the graphene island shape that can be compared to experimental results. We also note that, at low deposition flux, our flake edges are mainly zigzag, with armchair edges being relatively rare. This result is in agreement with experimental data and other models [14,18,35].

## 2. *Ab initio* calculations

Plane wave supercell calculations were carried out to determine activation energies of diffusion events of carbon atoms on Cu (111) substrate by using the VASP5.3 code [36,37] with the projector augmented wave method [38] (PAW). We applied the standard C and Cu PAW-potentials [38] from the VASP5.2 database. Cu $3d$ electrons were treated as valence electrons. The valence wave functions were expanded by plane waves with a kinetic energy cut-off $E_{cut} = 420$ eV. We used the generalized gradient approximation (GGA) in the parametrization of Perdew–Burke–Ernzerhof [39]. We considered graphene on top of a free Cu (111) surface. The substrate consists of a 9 monolayer thick Cu (111) substrate (see Fig. 1). We used the Cu bulk equilibrium GGA lattice constant of 3.63 Å. Free Cu (111) substrate coordinates were fully relaxed and then fixed throughout the study.

A previous GGA study determined that *fcc* and *hcp* positions were the most stable sites for single carbon adsorption even if between sites might play a role [27]. More recently, it was demonstrated that for small graphene islands on Cu (111) carbon atoms preferentially adsorbed on *fcc* and *hcp* sites [40]. We then considered these adsorption sites in the present study.
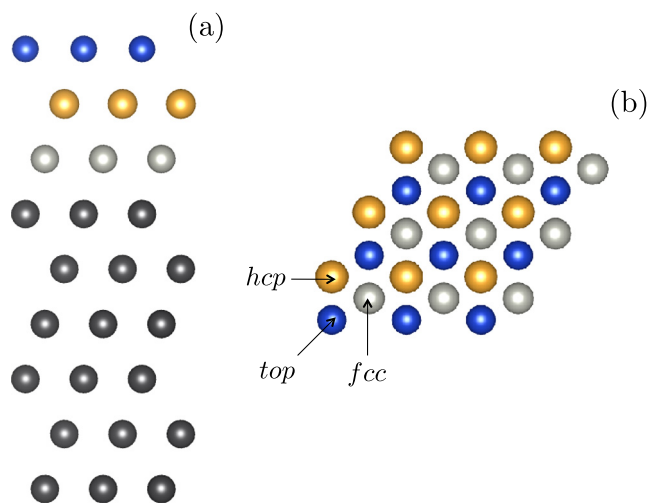


**Fig. 1.** Simulation area for *ab initio* simulations. All dots are copper atoms from the substrate. Figure (a) shows a side view of the substrate, and figure (b) a top view.

We have estimated the diffusion barrier by moving one carbon atom linearly from one configuration to the other. We have considered 5 equidistant images for each calculation. The carbon in-plane coordinates were kept fixed with only the $z$ coordinates allowed to relax. The list of diffusion events that were considered (where the numbers correspond to the event number in Table 1 and Fig. 2) is:

(1) The free carbon diffusion of C atom on the surface. $E_{Diff} = 0.5$ eV, this value is larger than the free diffusion barrier calculated by the nudge elastic band method [27] (0.1 eV). In our KMC model, 0.5 eV will be the lowest diffusion barrier considered.

(2) Formation of a dimer and detachment of an atom from a dimer. For this event, and those that follow, the initial and final energy are different and the diffusion activation barrier is therefore asymmetric. The detachment of a carbon atom from a dimer is very costly (3.2 eV), where the attachment is almost free (0.15 eV).

(3) Attachment (detachment) of a C atoms to (from) an island (one C–C bond). The barrier is, again, not symmetric.

(4) Attachment or detachment of a C atom from a dimer to an island (two C–C bonds). Here again, the barrier is not symmetric since the number of C–C bonds differ for the initial and final positions.

(5) Attachment (detachment) of a C atom to (from) an island (two C–C bonds). Same as before but with higher detachment barrier (3.8 eV) since two C–C bonds have to be broken.

(6) Attachment or detachment of a C atom from a dimer to an island (one C–C bond). We find an almost symmetric energy barrier that is relatively low (1.4 eV).

## 3. Kinetic Monte Carlo model

*Ab initio* simulations are an effective tool for atomistic simulations, yet calculation times become very long when larger systems are considered. To examine these larger systems (up to a few thousand atoms) and to have some insight into the dynamics of the process we used kinetic Monte Carlo simulations based on the results of the previous *ab initio* calculations to obtain a realistic, efficient and fast model.

Our KMC model is based on the NASCAM code [41] and uses a hexagonal lattice that corresponds to the fcc and hcp sites discussed in the previous section (see Fig. 1), and that are the most stable sites. A consequence of this assumption is that the growth of carbon clusters is restricted to hexagonal symmetry so topological defects (such as rings of five or seven atoms) cannot be modelled. We consider that graphene nucleates and grows as carbon is adsorbed and then diffuses on the copper substrate, as seen in the literature [5,15,17], neglecting the possible presence of species other than carbon and copper. The evaporation of carbon atoms and the diffusion of copper atoms are neglected, which makes our simulations closer to atmospheric pressure experiments as the increased pressure suppresses evaporation [15]. We consider a perfect, fixed copper (111) substrate and monolayer graphene only, as many experimental results focus on producing monolayers.

We consider the copper substrate fixed and neglect copper diffusion on the surface, though it is likely that copper adatoms are present on the surface. The presence of Cu adatoms near individual carbon atoms or graphene flakes might change the mobility of these atoms compared to the case of the perfect substrate. The difference between free diffusion and detachment energy barriers is rather high, so we do not expect to observe qualitative differences from this copper diffusion effect.

The deposition flux of atoms is modelled by adding atoms to random sites at a constant rate $F_0$. If the site is already occupied no atom is deposited, which leads to an effective deposition rate that decreases with coverage, this is similar to the model presented in [8]. This gives