Diffusion of Ruthenium in Graphite: The Role of Clustering & Interlayer Stacking.

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The diffusion, penetration and intercalation of metallic atomic dopants is an important question for various graphite applications in engineering and nanotechnology. We have performed systematic first-principles calculations of the behaviour of ruthenium nanoclusters on a graphene monolayer and intercalated into a bilayer. Our computational results show that at a sufficiently high density of single Ru atom interstitials, intercalated atoms can shear the surrounding lattice to an AA stacking configuration, an effect which weakens with increasing cluster size. Moreover, the interlayer stacking configuration, in turn, has a significant effect on cluster diffusion. We therefore find different trends in diffusivity as a function of cluster size and interlayer stacking. For monolayer graphene and an AA graphene bilayer, the formation of small clusters generally lowers diffusion barriers, while the opposite behaviour is found for the preferred AB stacking configuration. These results demonstrate that conditions of local impurity concentration and interlayer disregistry are able to regulate the diffusivity of metallic impurities in graphite.

I. INTRODUCTION

The energetic and dynamical properties of transition metal impurities adsorbed on top of graphene and intercalated between the layers of graphite is a recurring topic of considerable interest in materials science. Foreign elemental impurities are one of the most promising ways to modify the physical properties of pristine graphene [1], and they hold considerable promise in engineering desirable electronic phases [2]. For example, transition-metal doping of monolayer graphene (MLG) and bilayer graphene (BLG) can be exploited to increase the weak intrinsic spin-orbit effects of the native carbon atoms [3–5], allowing the engineering of novel quantum states with advantageous transport properties and prospective applications as topological insulators or in quantum computing [6–8].

Intercalated metallic species are also of interest in their own right, and the layered structure of van der Waals materials, such as graphite, provides an excellent platform to grow quasi-two dimensional sheets of selected transition metals [9–12]. These two-dimensional transition metal sheets have many desirable properties, which are greatly enhanced by their lower-dimensional topology. Due to the higher (2D) bulk to surface ratio and the associated change in coordination, layered metals can completely change electronic properties such as band gaps and transport properties [13–14]. Two-dimensional metallic layers have been grown underneath the top monolayer of highly-oriented pyrolytic graphite (HOPG) [11–15], a process which is known to proceed via the diffusion of impurities through lattice defect “entry portals” (monovacancy and multi-vacancy complexes) [12–14], and vacancy sites are also known to promote the intercalation of other elemental species such as Cs and Dy [17–18].

Transition metals are also important from the perspective of graphite applications. Some of the most important nuclear fission products are transition metals [19], and the penetration of these impurities into the bulk and subsequent diffusion through the graphite lattice is a pressing problem in the design of new reactors and in the assessment of safety and decommissioning of retired reactors [20–22]. Nuclear graphite occurs in various distinct grades, which are defined both by anisotropy and porosity, both of which are proportional to the size and density of graphite crystallites [21–24]. It is likely that penetration into and diffusion within these grades proceeds via a similar entry portal mechanism, as there are ample defect sites which can serve as entry sites to aid the diffusion of intercalated species [25].

In this context, ruthenium is a particularly interesting atomic impurity in graphite. In isotropic nuclear graphite grades, diffusivity experiments demonstrate an unusual turnaround, where above a critical temperature of approximately 700°C the diffusivity temporarily decreases, which is counter to the anticipated trend of increasing diffusivity with increasing temperature [26]. The intercalation and embedding of ruthenium into the bulk and top layer of graphite also displays a sharp temperature dependence [13]. Here, there are distinct morphologies
depending on the annealing temperature. At lower temperatures, atoms are evenly distributed above the capping layer, while above a critical temperature, which is again around 700°C, isolated ruthenium atoms penetrate and agglomerate into more extensive, large and immobile clusters. These encapsulated clusters range in diameter and height and form an identical Moiré pattern to graphene deposited on the Ru (100) surface system [15].

Central to understanding these phenomena is the clustering of Ru atoms on graphene and graphite, and the subsequent effect this has on diffusion. While there have been a variety of studies of the energetics of single adsorbed and intercalated elemental species, the effect of clustering on the dynamics of transition metal diffusion has not been considered in any significant depth to the authors knowledge. However, these factors are liable to play a very significant role in realistic diffusion processes, and properly accounting for dynamics is essential in assessing actual physical behaviour. Furthermore, systematic studies of small metallic clusters can provide insight into the early stages of agglomeration and clustering in graphite.

In this work, we present a systematic study of the interaction of Ru atom nanoclusters (n = 1, 2, 3, 4, 5, 7) on MLG, BLG and bulk graphite, using accurate first-principles calculations to systematically investigate the effect that clustering and local carbon environment have on Ru diffusion in graphite. Ruthenium is chosen both as a representative element and in order to provide new insight into the relevant microstructural processes underlying transition metal diffusion on the graphite basal (0001) surface, and the penetration and diffusion into the bulk of more complex graphite grades.

II. COMPUTATIONAL METHODS

All DFT calculations have been performed using the Quantum ESPRESSO ab-initio package [27–29]. The generalized gradient approximation (GGA) was used to approximate the exchange-correlation functional, as parameterized by Perdew, Burke, and Ernzerhof (PBE), and Vanderbilt ultrasoft pseudopotentials are employed to approximate the effect of core electrons [30]. The wavefunction basis was expanded as a series of plane-waves with maximum cut-off of $E_{\text{cut}} = 40$ Ry (544 eV), and a charge density cut-off of $E_{\rho} = 500$ Ry (6803 eV), which are found to be in close agreement to the more highly-converged calculations. A non-zero electron temperature of $kT_e = 0.02$ eV is applied to aid convergence, using a Fermi-Dirac smearing function, and the Brillouin zone is sampled using a Monkhorst-Pack $5 \times 5 \times 1$ k-point grid. More highly converged parameters, using a denser $13 \times 13 \times 1$ k-point grid and an energy cutoff of $E_{\text{cut}} = 60$ Ry have been applied for density of states calculations.

The Grimme DFT-D2 method has been employed to model the interlayer van der Waals interaction [31]. In monolayer and bilayer calculations, a vacuum thickness of 20 Å along the z-direction is found to avoid any spurious self-interactions between periodically repeated images. Structural optimisations were performed until the residual force on each atom is less than 0.01 eV/Å and the energy difference between subsequent iterations is less than 0.01 eV.

The adsorption energy per atom (chemical potential) has been calculated as

$$\mu(n) = \frac{E_{\text{tot}} - E_{\text{Gr}}} {n} - E_{\text{Ru,FCC}},$$  \hspace{1cm} (1)

where $E_{\text{Gr}}$ is the energy of the respective perfect graphitic material (monolayer and AB stacked bilayer graphene), $E_{\text{Ru,FCC}}$ is the energy of bulk fcc Ru lattice, taken from a well-converged bulk calculation sampled with a $21 \times 21 \times 21$ k-point grid, $E_{\text{tot}}$ is the total energy of the fully-optimised combined Ru nanocluster/graphite system, and $n$ is the number of adsorbed or intercalated Ru atoms [15]. To facilitate the comparison of energies between different bilayer stacking configurations, we have calculated all intercalation energies relative to the AB-stacked minimum. This expression gives the relative energy per Ru adatom of different ruthenium-carbon configurations. It is defined such that energetically-preferred structures have lower formation energy, and configurations with $\mu < 0$ are preferred over bulk Ru. In this way, we can gain full insight into the relative preference for adsorption, intercalation and clustering both on the monolayer graphene surface and intercalated into the bilayer or bulk lattice.

III. RESULTS

A. Energy & Structures

In order to understand the interaction of ruthenium nanoclusters with graphite, we will initially focus on the adsorption (on a graphene monolayer), and intercalation (within a bilayer) of small (n \leq 7) clusters. By evaluating the dependence of structure and diffusivity on nanocluster size, we can extract many of the essential physical factors moderating the behaviour of ruthenium in graphite at low concentrations.

Monolayer — We first compare the adsorption and intercalation of single-atom, dimer and trimer ruthenium (n = 1, 2, 3) nanoclusters. Our initial calculations are performed in a $6 \times 6$ graphene supercell, on monolayer as well as bilayers with AA stacking (AA BLG) and AB stacking (AB BLG). In the bilayer case, carbon atoms are restricted to relax out of plane so as to maintain the initial stacking configuration. Relaxations were performed for a number of different initial configurations, which are detailed in Fig. 1. The formation energy of all fully relaxed structures was then evaluated according to Eq. 1, and the lowest-energy configurations are taken to be the most thermodynamically stable. Tables of the
FIG. 1. High symmetry Ru atom and dimer positions on graphene. (a) Top (T), bond (B) and hollow (H) sites of an adatom adsorbed on graphene. (b)-(d) Various combinations of the single atom positions are used to fully investigate the morphology of adsorbed Ru dimers.

formation energy corresponding to each initial condition are provided in the supplementary information.

The final, energetically-preferred structures for \( n = 1, 2, 3 \) are shown in Fig. 2. For \( n = 1 \) adsorption, Fig. 2 (a)-(c), we find that a single Ru atom prefers to adsorb on the H-site of the graphene sheet. The interaction between the Ru and C atoms is predominantly covalent, and a single ruthenium adatom is best able to hybridise valence electrons at the most highly-coordinated, symmetrical hollow site [32].

With increasing Ru cluster size, Fig 2 (b) and (c), the constituent ruthenium atoms show significant energetic preference for the formation of metallic bonds with each other, and there is a progressive decrease in the adsorption energy per adatom from 4.82 eV to 4.25 eV, to 3.46 eV for \( n = 1, 2, 3 \) respectively. This preference is exemplified by the difference between the dimer and trimer structures. As a result of reduced Ru-C hybridization, a pair of Ru adatoms will move away from the hollow site and adopt positions above the C-C bonds, on opposite sides of a graphene hexagon - essentially configuration BB1 in Fig. 1, with a slight reduction in Ru-Ru bond length after relaxation. This is similar to the behaviour of an Ir dimer adsorbed on graphene [33], which adsorbs in the BB2 configuration, due to the relatively shorter Ir dimer bond length.

This tendency continues for the trimer, where we find that the additional Ru atom is lifted entirely out of the plane, with two Ru adatoms which "carry" the remaining one. They thus effectively form a pair of conjoined dimers, which maximise preferred Ru-Ru interactions while reducing the contact area of the cluster with the graphene sheet.

**AA/AB Bilayer** — We now examine the corresponding behaviour of small clusters intercalated within bilayer graphene, and the effect that the stacking (lateral offset between the graphene sheets) has on intercalation energy. The tendency to prefer the higher coordination hollow site is again observed for an Ru atom intercalated between two graphene layers. For an AB bilayer, it sits at a TH-site (see Supplementary Information), which lies above a H-site of one layer and a T-site in the opposite layer, with an intercalation energy of 3.86 eV. For AA BLG, a single Ru atom adopts the site between the two H-sites on both layers, with an intercalation energy of 3.44 eV, a value which is notably lower than the AB BLG value. Our results indicate that at the chosen, relatively high Ru density of one atom per 72 carbon basal plane atoms, an intercalated Ru atom can shear adjacent sheets and reverse the preferred stacking orientation of perfect graphite, behaviour which is qualitatively similar to a graphite intercalation compound [34].

Dimer adsorption is relatively similar to the monolayer case, with the Ru-Ru bond lying parallel to the BLG basal plane in both stacking orientations. For AA stacking each dimer atom sits on adjacent H-sites, and there is
FIG. 2. Plan and front views of (a) $n = 1$, (b) $n = 2$, (c) $n = 3$ Ru clusters adsorbed on monolayer graphene, (d) $n = 1$, (e) $n = 2$, (f) $n = 3$ clusters intercalated into AA BLG, and (g) $n = 1$, (h) $n = 2$, (i) $n = 3$ clusters intercalated into AB BLG,
FIG. 3. Adsorption (intercalation) energy per Ru atom of Ru nanoclusters adsorbed (intercalated) on graphene (AA/AB graphite) as a function of Ru nanocluster size.

FIG. 4. Partial density of states of Ru clusters on ML graphene, for (a) \( n = 1 \), (b) \( n = 4 \) and (c) \( n = 7 \).
FIG. 5. Energy difference, $E_{sf} = E_{AA} - E_{AB}$ and critical radius to create a stacking fault, $r_c$, vs ruthenium density for equally-spaced Ru atoms in bilayer graphene.

the interlayer stacking fault energy, which favours Bernal, AB stacking, and the preference of intercalated atoms for the hollow site. At small Ru cluster sizes $n = 1, 2$, the Ru-C interaction both weakens the overlap between the graphene sheets, and permits the intercalated cluster to overcome the stacking fault energy and pull the surrounding graphene sheets to the preferred hollow site. For larger cluster sizes $n \geq 3$, this ability is significantly reduced due to the reduction of the Ru-C interaction, and because the hollow site becomes relatively less favoured.

**Varying concentration** — All of our results so far have focused on nanoclusters in MLG and BLG systems with the same lateral dimensions. However, both the stacking fault energy for poor stacking between the graphene sheets, and the ability of interstitial Ru atoms to weaken the interlayer carbon bonds and shift adjacent graphene layers are naturally extensive properties, i.e., they will vary with graphene lateral cell dimensions. We have therefore performed additional calculations of the intercalation energy of a single Ru adatom in AA and AB BLG, with different graphene supercell sizes. We thus vary both the distance between intercalated Ru atoms and, equivalently, the density of Ru in the graphene sheet. These results are shown in Fig. 5, which plots the energy difference $E_{sf} = E_{AA} - E_{AB}$, (i.e., the effective stacking fault energy in the presence of intercalated single Ru atoms), as a function of Ru atom density.

The energy difference $E_{sf}$ is a positive quantity when AA stacking is preferred, and negative for AB. We then see that with decreasing Ru content isolated interstitial ruthenium atoms are not able to surmount the stacking fault penalty, as would broadly be expected. However, above a critical concentration of $\rho \approx 0.005 \text{Å}^{-2}$, the increasing density of interstitial atoms and decreasing overlap of interlayer carbon pi-bonds, Ru atoms are able to shear the adjacent graphene sheets in order to sit at the preferred H position and reverse the typical Bernal (AB) stacking preference of multilayer graphite, resulting in AA stacked configurations.

This behaviour suggests that intercalated Ru atoms will preferentially migrate towards basal (interlayer) dislocations and stacking faults. In addition, it should also result in a stacking fault in ruthenium rich regions, which will return to perfect stacking through the passage of a basal dislocation. The typical energy of such a dislocation is around $E_b = 7 \text{meV/Å}$ [35]. Taking the Ru-induced stacking fault energy as a function of density to be $E_{sf}(\rho)$, a circular region of intercalated ruthenium atoms will shear the adjacent layers under the condition that $2\pi r E_b < \pi r^2 E_{sf}(\rho)$. To illustrate this, in Fig. 5 we also show the critical loop radius above which a stacking shift is initiated, where we see that at Ru concentrations above approximately 0.01 atoms/Å² (one Ru atom per 72 carbon, i.e. a $6 \times 6$ cell), stacking will easily shift, while at lower densities this tendency rapidly decreases. Notably, this loop radius is significantly smaller than the graphite basal dislocation width [35] [36], and so the actual minimum radius is likely to be higher to facilitate the formation of well-defined dislocation cores.

**Validity of results in bulk** — We have largely performed calculations in isolated monolayer and bilayer cells. However, we are also interested in the behaviour of Ru nanoclusters in bulk. We now briefly compare our bilayer calculations to structural relaxation of Ru nanoclusters in bulk graphite. Cells are constructed similarly to the bilayer cells, with small clusters of $n = 1, 2, 3$ Ru atoms inserted at symmetric initial positions between two layers within the bulk of graphite. A $6 \times 6 \times 4$ graphite bulk supercell is used, and both AA and AB stacked configurations are examined through considering two different supercell stacking configurations, one perfect Bernal (ABAB) and one with a rhombohedral stacking fault relative to two Bernal layers (AABC). We find broadly similar behaviour to the bilayer calculations, with small differences in the intercalation energy, and structural distortions of the adjacent graphene layers being reduced by a small amount (see Supplementary Information), overall justifying their use as an approximation of the bulk lattice.

**B. Diffusion**

Thus far we have focused on the structure and energetics of elemental Ru as a function of nanocluster size. However, the penetration of small clusters into the graphite lattice will be determined by dynamical processes which can be understood through calculation of transition states and diffusion barriers. We now examine the diffusivity of the previously discussed clusters, again considering MLG, AA and AB bilayers, and paying particular attention to the effect that interlayer stacking has on diffusive properties. Calculations of diffusion
FIG. 6. Diffusion paths for ruthenium atoms in (a) monolayer graphene (H-site to H-site), (b) AA bilayer graphene (HH-site to HH-site) and (c) AB bilayer graphene (TH-site to TH-site).

FIG. 7. NEB calculated diffusion pathways for \( n = 2, 3 \) clusters on a graphene sheet. (a) BB1 Initial state (b) this can rotate to the BB2 intermediate state and (c) translate to an adjacent BB2 site in a two-step process. (d) Initial and (e) final states of the \( n = 3 \) nanocluster saddle points have been performed between pairs of the lowest-energy sites discussed previously, and the transition path has been optimised according to the CI-NEB method \[37, 38\]. The activation energy for the associated paths can then be used to estimate the thermodynamic likelihood of the associated process.

**Single atom** — We initially consider the diffusion paths taken by \( n = 1, 2, 3 \) Ru nanoclusters. Single Ru diffusion paths are shown in Fig. 6, and involve simple movement between adjacent hollow sites, for the monolayer (Fig. 6 (a)) and AA (Fig. 6 (b)) cases, and from a TH-site to an adjacent HT-site for the AB bilayer (Fig. 6 (c)). There is a notable difference in the diffusion barrier between the three systems. For an Ru atom on single-layer graphene, we find an activation energy of 0.709 eV, which is in very good agreement with our previous results using somewhat different approximations \[32\].

It is notable that the diffusion barriers within the AA and AB bilayers show opposite tendencies with respect to the barriers for graphene. For the AA stacked bilayer, the barrier is more than doubled with respect to the monolayer to 1.88 eV, while for AB stacking the barrier is significantly decreased to 0.152 eV. These differences are readily understood by a calculation of the intercalation energy of the Ru atom as a function of lateral position above a graphene monolayer, or encapsulated within a bilayer. The result is shown in Fig. 8, where we note a very similar energy surface for the monolayer and AA BLG energies.

In both cases, a single Ru atom pays a significant penalty for sitting either directly above a carbon atom or a C-C bond. The energy at a bond site is marginally lower than above a carbon atom, and it is thus the B-site which serves as the transition state for hopping between H-sites. This energy is effectively doubled for AA BLG due to the second graphene layer. In contrast, barrier heights and energy profiles are significantly reduced for AB BLG, see Fig. 6 (c), where we see that carbon atoms at TT-sites (i.e. one carbon atom above another) are now the highest energy positions, while TH-sites serve as energetic minima. In this case, Ru adatoms can now proceed between adjacent TH-sites without crossing a C-C bond and the activation energy is significantly reduced.

**Dimer & Trimer** — Interestingly, the diffusion of \( n = 2, 3 \) Ru clusters on a monolayer is generally faster than the \( n = 1 \) case. The relevant processes are shown in Fig. 7. For \( n = 2 \), diffusion is a two-step process: there is an initial rotation from the BB1 to the BB2 configuration, Fig 7 (a) and (b), with \( E_{\text{rot}} = 0.248 \) eV, following which the barrier for translation between adjacent BB2 sites is \( E_{\text{trans}} = 0.169 \) eV. For the trimer, diffusion takes place through a concerted, simultaneous translation and rotation, Fig 7 (d) and (e), during which the top atom has no contact with the graphene sheet. This process also has a barrier of \( E_b = 0.359 \) eV.

As previously discussed for a single Ru atom, it is largely the increased hybridization at the T and B sites which increases Ru energy at these sites, and the lower barriers of the \( n = 2, 3 \) clusters can then be understood through the observation that the formation of homo-metallic Ru bonds and decreasing contact with the graphene basal plane, decreases the covalent interaction between Ru atoms and graphene.

In the bilayer case, the most important distinction with the monolayer is that the ability to relax out of plane, and thus to reduce the amount of Ru-C interaction, is greatly
inhibited by the surrounding graphene sheets. This has a marked effect on the associated processes. Dimer and trimer diffusion in AA BLG are shown in Fig. 9 (a)-(f), which both proceed via a relatively simple transition state. There is a high degree of contact between the Ru cluster atoms and C atoms at both transition states, yet despite this, the barrier rapidly decreases from $E_b = 0.925$ eV to $E_b = 0.387$ eV. This is highly similar to the behaviour seen in the monolayer, where less covalent interaction with the substrate due to the Ru-Ru cluster bonds aids diffusion.

Conversely, for the diffusion of dimer and trimer clusters in AB BLG, the opposite trend is observed. The transition states in both cases are highly similar to the AA transition states, Fig. 9 (g)-(l), yet the barriers actually increase with increasing cluster size, from $E_b = 0.830$ eV to $E_b = 1.297$ eV. For both clusters, the lowest energy path now requires contact between ruthenium and carbon atoms, which cannot be avoided without paying a significant price for bond stretching and bending, in contrast to single atom diffusion which could entirely avoid these sites.

Larger clusters — CI-NEB transition energy barriers for all cluster sizes on a monolayer and in AA and AB BLG are plotted in Fig. 10 (Additional transition states are shown in the supplementary information). Remarkably, we see almost entirely opposite behaviour for the two stacking configurations, which we can ascribe to the changing degree of hybridization for different cluster sizes. At higher concentration this tendency starts to even out to a larger degree, and with increasingly large ruthenium cluster size, we anticipate that these barriers will start to grow linearly in proportion to the contact area between the Ru and graphene, causing the intercalated cluster to become immobile and begin ripening into larger metallic fragments.

IV. DISCUSSION

In this work, we have performed extensive simulations of the adsorption, intercalation, clustering and diffusion of ruthenium nanoparticles in graphite. We find that the clustering of individual Ru atoms has significant impact on the structural, energetic and dynamical properties of ruthenium nanoclusters. Most importantly, we observe that interstitial Ru has the capability of shifting the surrounding graphene layers to an AA stacking configuration. This is a particularly interesting effect as it is accompanied by a substantial increase in the transition barrier, which severely impedes diffusion relative to other cluster sizes and stacking configurations, suggesting an additional mechanism which may impede the diffusion of individual adatoms into graphite near entry portals defects.

In addition, we find that single Ru atoms prefer to intercalate into the bulk of graphite, however, this tendency becomes much weaker with increasing cluster size. We summarise this behaviour in Fig. 11, which shows the segregation energy (difference in adsorption and intercalation energies) vs cluster size extracted from our DFT calculations, which we observe is greatly decreased with increasing cluster size. This happens due to the high preference to form Ru-Ru bonds over the Ru-C bond, hence carbon content in the immediate vicinity of a nanocluster matters less with increasing Ru content, as the inter-metallic bonds begin to dominate. In combination with our observation of higher barriers for single interstitial Ru, this indicates that the high temperature breakup of clusters into single Ru atoms at defect sites will impede overall diffusion through the microstructure.

Notably, it has been found recently that the dynamical process underlying the penetration of metal intercalants into the bulk is mediated by a low energy barrier bond-breaking process of the metal dimer at defect sites \[39\]. This process can effectively filter clustered surface fragments into isolated single atoms, which can intercalate into the bulk. Our observation here provides a comple-
FIG. 9. Diffusion pathways for Ru clusters in BLG. (a) initial state (b) transition state and (c) final state for $n = 2$ Ru cluster in AA BLG. (d) initial state (e) transition state and (f) final state for $n = 3$ Ru cluster in AA BLG. (g) initial state (h) transition state and (i) final state for $n = 2$ Ru cluster in AB BLG. (j) initial state (k) transition state and (l) final state for $n = 3$ Ru cluster in AB BLG.
mentary insight to this result, in that there is a significantly decreasing thermodynamic preference for intercalation with increasing cluster size, necessitating cluster break-up as an active part of the intercalation process.

We find large differences in the activation barrier to motion between adsorbed and intercalated clusters. While in the monolayer case, clustering generally aids diffusion, the bulk behaviour is largely determined by the stacking of graphene sheets. Trends in bulk diffusivity are well explained by considering the hybridization of ruthenium adatoms with the adjacent carbon atom. For AB BLG, the adjacent graphene sheets aid diffusion as the potential barriers between adjacent sites effectively cancel, an effect which reduces with increasing cluster size and number of Ru-Ru bonds. Conversely for AA-stacking energy barriers are approximately doubled in comparison to a monolayer due to an additive contribution from each carbon layer. Here, the adjacent sheets impede diffusion, and decreasing covalent Ru-C interactions can again aid diffusion. Hence, we find that the calculated diffusivity trends are generally inverted between the two stacking configurations as the Ru cluster size increases.

In general, the modelling of the penetration, diffusion and interaction of ruthenium atoms and clusters with graphite is a challenging one which is vital to many applications and prospective uses of graphite. A fuller understanding of these issues requires larger cells and longer timescales than those which are currently feasibly using DFT. While molecular dynamics would be a promising technique to address this problem, there are currently few interatomic potentials available for many of the most interesting metal dopants, and those which are available typically fail to correctly capture both processes of stacking and of clustering. As this is an important and interesting problem, this would be a fruitful and enlightening direction for future research.

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