Self-learning kinetic Monte Carlo simulations of self-diffusion of small Ag islands on the Ag(111) surface

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Abstract

We studied self-diffusion of small two-dimensional Ag islands, containing up to ten atoms, on the Ag(111) surface using self-learning kinetic Monte Carlo (SLKMC) simulations. Activation barriers are calculated using the semi-empirical embedded atom method (EAM) potential. We find that two- to seven-atom islands primarily diffuse via concerted translation processes with small contributions from multi-atom and single-atom processes, while eight- to ten-atom islands diffuse via single-atom processes, especially edge diffusion, corner rounding and kink detachment, along with a minimal contribution from concerted processes. For each island size, we give a detailed description of the important processes, and their activation barriers, responsible for its diffusion.

Keywords: self-learning kinetic Monte Carlo, Ag island diffusion, self-diffusion

(Some figures may appear in colour only in the online journal)

1. Introduction

Diffusion of atoms, either individually or collectively, plays a key role in the kinetics of various phenomena such as heterogeneous catalysis, epitaxial growth, surface reconstruction, phase transition, segregation, sintering and other topics in surface science [1, 2], and also in microstructural evolution in bulk materials [3]. Therefore, a great deal of effort has been devoted to understanding diffusion of atoms on metal surfaces both theoretically and experimentally, as well as to finding the activation barriers and prefactors for adatom diffusion processes [4, and references therein], so much so that providing an exhaustive list of references is nearly impossible. Modeling diffusion related phenomenon is particularly challenging because it involves interplay of multiple diffusion processes simultaneously. Importantly, their activation barriers depend on the local atomic arrangement of atoms and will be different even for similar looking diffusion processes (e.g. edge diffusion along A and B step edges on the fcc (111) surface.) Adding to the complexity, during an island diffusion, its morphology (or shape) determines which processes are activated or deactivated and is never stationary during its diffusion. Accordingly, in our previous article [5] in addition to identifying various processes which occur during the self-diffusion of small Ni islands on the Ni(111) surface. In this article in addition to the identification of diffusion processes for self-diffusion of small Ag islands on the Ag(111) surface, we provide an in-depth discussion of how various processes contribute to and affect the effective energy barrier and prefactor of an island’s diffusion. Since the self-learning kinetic Monte Carlo (SLKMC) method [6] is well suited for these kinds of study, we have used the on-lattice SLKMC method using the extended pattern recognition scheme [5] to study diffusion of small Ag islands.

This paper is organized as follows. In section 2 we only discuss important simulation details that are particular to this study. In section 3 we present general details on single-atom,
multi-atom and concerted diffusion processes, which are common to all island sizes, followed by a detailed discussion of island diffusion. In section 4 we provide quantitative analysis and discussion of diffusion coefficients, and effective energy barriers and prefactors. Section 5 is devoted to conclusions.

2. Simulation details

To study self-diffusion of Ag islands on the fcc Ag(111) surface, we have carried out SLKMC simulations using an extended pattern recognition scheme [5], which uses atoms located at both fcc and hcp sites to identify the local neighborhood around an atom. Additional details such as simulation cell size, calculation of energy barriers for various diffusion processes etc can be found elsewhere [5]. In all our calculations, we use the same pre-exponential factor of $10^{12}$ s$^{-1}$ for all types of diffusion process and at all temperatures studied in our KMC simulations, and this was proven to be a good assumption for systems such as the present one [7, 8]. We carried out KMC simulations for $10^7$ steps for each island at 300, 400, 500, 600 and 700 K, and collected the center of mass (CM) location of an island at regular intervals of time.

3. Results

3.1. General details

On the fcc (111) surface, to uniquely identify whether an adatom is on an fcc or an hcp site requires knowledge of its position relative to atoms in the top layer of the substrate and the layer below. In order to make visualization simpler, we adopt the convention that the center of an upward-pointing triangle formed by the substrate atoms is considered as an fcc site, while the center of a downward-pointing triangle is considered as an hcp site. Atoms of an island are either located only at fcc or hcp sites or a combination of both fcc and hcp sites and are called fcc, hcp and fcc–hcp islands, respectively (also referred to, as the type of an island). In addition, an island is considered compact if it has no kink (a periphery site with at most three broken bonds); otherwise, it is called a non-compact island. On the Ag(111) surface, an fcc island always has lower energy than an hcp island unless otherwise stated. Note that the relative stability of two islands is equal to the difference in the activation barriers for the processes which transform the island from one into the other.

An island on an fcc (111) surface can perform concerted translations in three directions, and we follow the number convention for directions as shown in figure 1 throughout this article to tabulate activation barriers for various concerted diffusion processes. It is important to note that, although the numbering scheme is the same, hop directions for an fcc or an hcp island are opposite to each other. In addition, we frequently use the symbols ‘$\rightarrow$’ and ‘$\rightarrow'$ to represent a bidirectional and a unidirectional transformation of an island, respectively. Concerted diffusion processes always transform an fcc island into an hcp island and vice versa, which in shorthand notation is given as $\text{fcc} \Rightarrow \text{hcp}$ transformation. It is either a translation in one of the three directions as shown in figure 1 or a rotation around the axis through the CM of the island perpendicular to the substrate surface in both directions (clockwise and anti-clockwise). Concerted translation processes always produce the largest displacement of the CM of an island, which is equal to the distance between an fcc and an hcp site ($= a_0/\sqrt{6}$, where $a_0$ is the lattice constant of Ag). While concerted translation processes are observed for all island sizes, concerted rotation processes are observed only for a dimer and a trimer. Except for highly symmetric geometries or shapes, activation barriers for the concerted translation processes along the three directions are different and depend on both the type and shape of an island.

Multi-atom diffusion processes, particularly shearing and reptation processes, were found to occur for island sizes from four to ten atoms. In a shearing process, part of an fcc (hcp) island moves from fcc to fcc sites (hcp to hcp sites). On the other hand, a reptation process [9] is a two-step shearing process that moves the cluster from all-fcc $\Rightarrow$ all-hcp sites. In the first step, part of the island moves from fcc to hcp sites (hcp to fcc), creating a dislocation and transforming the island into an fcc–hcp island. In the second step, the rest of the island moves from fcc to hcp (hcp to fcc). Shearing processes start to occur from island size 4 and usually along an A step edge (the activation barrier along a B step edge is large). Activation barriers for multi-atom processes depend on the type of the island as well as the type of step edge along which the process occurs. Note that every island on the fcc (111) surface has two other symmetric orientations, separated by 120° clockwise and anti-clockwise rotations. Either individually or via a combination, both single- and multi-atom processes transform an island from one symmetric orientation into the other. The number of multi- and single-atom processes increases with island size, but multi-atom and concerted processes are discussed for each island size while single-atom processes are discussed separately in section 3.2.10.

3.2. Key diffusion processes

In this section we present a detailed discussion of key diffusion processes and their activation barriers, which are responsible for the diffusion of an island of size from two to ten atoms. In addition, we discuss how those key diffusion processes contribute to the island diffusion.
3.2.1. Dimer. A dimer can have three possible arrangements of atoms: two with both atoms either on hcp sites (called an hh dimer) or on fcc sites (called ff dimer) shown in figure 2, and a mixed dimer with one atom on an fcc and the other on an hcp site (called an fh dimer) shown in figure 3(a).

Figure 2 shows a concerted translation and a clockwise concerted rotation process. Activation barriers for the rotation in both clockwise and anti-clockwise directions are the same due to symmetry while for the translations directions 2 and 3 are symmetric. Table 1 shows the activation barrier for concerted translations in all three directions. Although concerted rotation is a frequent process, its contribution to the dimer diffusion is minimal. Note that an individual concerted rotation produces a small shift in the CM of a dimer, but by enumerating a sequence of unidirectional concerted rotations one can easily see that the CM of the dimer rotates around a top site nearest to it. The primary role of concerted rotations is to rotate the dimer axis, in other words to change its orientation by 120°. A dimer diffuses predominantly via concerted translation processes.

Figures 3(a)–(d) show single-atom processes transforming ff (hh) dimer ⇌ fh dimer. These processes are like reptation processes observed during the diffusion of larger islands and are called dimer-reptation processes. In the case of the dimer it only involves a single atom and is treated as a single-atom process. These processes not only change the orientation of the dimer axis, but also change its type (fcc ⇌ hcp). They also produce a small shift, like concerted rotations, in the dimer’s CM and will only make a small contribution to the dimer diffusion. Figures 3(e) and (f) show single-atom long hop processes in which an atom moves from the fcc (hcp) to next fcc (hcp) site as well as detachment processes, and corresponding activation barriers are given in table 2.

The effective activation barrier for dimer diffusion is 0.096 eV and is very close to the average of forward and backward concerted translations perpendicular to the dimer axis (figure 2(b)), which is 0.0975 eV. The extra decrease of 1.5 meV in the effective activation barrier is due to the small displacement of CM due to concerted rotation and dimer-reptation processes, which have lower activation barriers than concerted translation processes. Therefore, we conclude that the dimer diffuses primarily via concerted translation processes perpendicular to its axis and the reorientation of its axis due to concerted rotation and dimer-reptation processes.

3.2.2. Trimer. A triangular trimer has two possible arrangements of atoms, one centered around an hcp site, called the F3H trimer (figure 4(a)), and the other around a top site, called the F3T trimer (figure 4(e)). Similarly, hcp trimers are called the H3F and H3T trimers, respectively. In contrast to Ni [5],

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**Table 1. Activation barriers (eV) for concerted translations for the dimer shown in figure 2(a).**

| Directions | fcc → hcp | hcp → fcc |
|------------|-----------|-----------|
| 1          | 0.098     | 0.097     |
| 2          | 0.116     | 0.115     |
| 3          | 0.116     | 0.115     |

**Table 2. Activation barriers (eV) for long hops in different directions shown in figures 3(e) and (f).**

| Directions | Figure 3(e) | Figure 3(f) |
|------------|-------------|-------------|
| 1          | 0.055       | 0.124       |
| 2          | 0.366       | 0.369       |
| 3          | 0.383       | 0.383       |
| 4          | 0.369       | 0.366       |
| 5          | 0.123       | 0.055       |
the F3H trimer is energetically 5.0 meV more favorable than the F3T trimer.

Figure 4 shows concerted translation and rotation processes observed during the trimer diffusion. The concerted rotation process transforms an H3T ⇌ F3T trimer, while the concerted translation processes transform an F3T (H3T) ⇌ H3F (F3H) trimer. Note that concerted rotation of the F3H or H3F trimer was not observed during trimer diffusion. Due to symmetry, activation barriers for both concerted translation and rotation processes in all directions are the same. Our results for the activation energies of various concerted processes for trimers agree very well with those obtained from effective medium theory (EMT) potential as reported in [10].

Concerted rotations do not lead to trimer diffusion as they do not produce a displacement of its CM. The main role of rotations is to act as a low energy pathway between the combination of F3H ⇌ H3T (figure 4(a)) and F3T ⇌ H3F (figure 4(b)) translations (F3H ⇌ H3T ⇌ F3T ⇌ H3F). In the absence of trimer rotation, the effective energy barrier for trimer diffusion will be the average of forward and backward moves for either F3H ⇌ H3T translations or F3T ⇌ H3F translations. In both cases the average activation barrier is 0.176 eV, which is 3.0 meV smaller than the effective energy barrier (0.179 eV) for trimer diffusion. Therefore, the trimer diffuses predominantly via concerted translations. Due to concerted rotation, F3T → H3F and H3T → F3H are the rate-limiting steps for the long-range diffusion of the trimer, and the average of their activation barriers is 0.1795 eV, which is much closer than the effective energy barrier for trimer diffusion.

Figure 5 shows single-atom processes (long hops) for a trimer. Directions 1 and 4 correspond to edge/corner diffusion hops, which will transform a trimer into a chain of three atoms, while directions 2 and 3 correspond to detachment processes. The activation barriers along different directions are shown in figure 5, the different types of trimers are given in table 3. Due to high activation barriers they occur very rarely during the trimer diffusion.

### Table 4. Activation barriers (eV) of concerted processes for fcc and hcp tetramers shown in figure 6(a).

| Directions | fcc → hcp | hcp → fcc |
|------------|-----------|-----------|
| 1          | 0.193     | 0.191     |
| 2          | 0.193     | 0.191     |
| 3          | 0.245     | 0.244     |

3.2.3. Tetramer. A diamond shape is the only possible compact shape for a tetramer, as shown in figure 6. Figure 6(a) shows concerted translation in direction 2 (off-long-diagonal move) and is symmetric to direction 1, while the non-symmetric move (not shown) in direction 3 displaces the tetramer along its long diagonal. Table 4 shows activation energies for concerted processes in all three directions.

Figure 6(b) shows the dimer-shearing process, which is a frequent multi-atom process, along one of the A step edges of an fcc tetramer. The activation barriers for dimer shearing for an fcc and an hcp tetramer are 0.285 eV and 0.283 eV, respectively. Activation barriers for dimer-shearing processes along the B step for both fcc and hcp tetramers are very high and hence...
3.2.4. Pentamer. Figure 7 shows the only possible compact shape of a pentamer, but it can have two different arrangements of atoms; one has three A step edges (A-type pentamer shown in figure 7(b)) and the other has three B step edges (B-type fcc pentamer shown in figure 7(a)). Moreover, an A-type fcc pentamer has lower energy due to the longer A step edges compared to the B-type fcc pentamer.

Figure 8 shows concerted translation processes which transform an A-type fcc (hcp) to B-type fcc (hcp) pentamer and back. Table 5 shows the activation barriers in all three directions for all the configurations of a compact pentamer. Single- and multi-atom processes are essential to transform an A-type into a B-type fcc pentamer or to transform from one symmetric orientation into the other. Figure 9 shows a single-atom corner-rounding process for an fcc pentamer which converts an A-type fcc (hcp) into B-type fcc (hcp) pentamer. Pentamers diffuse mostly via concerted diffusion processes. The average of all the activation barriers for concerted forward and backward translations is 0.285 eV, and is very close to the effective activation barrier, which is 0.287 eV. Single- and multi-atom processes contribute to the remaining difference in the activation barrier.

3.2.5. Hexamer. Figures 10 and 11(a)–(d) show the only two possible compact shapes for a hexamer: one with a parallelogram shape with equal lengths of A and B step edges, and the other with a triangular shape. While there is only one possible arrangement of atoms for a parallelogram-shaped hexamer, a triangular hexamer has two possible arrangements of atoms; one with all A step edges and the other with all B step edges as shown in figures 11(a)–(d). In the case of the hexamer, an A-type hcp pentamer (figure 11(d)) is energetically more favorable than a B-type hcp pentamer (figure 11(c)) by 10 meV, which is a breakaway from general behavior observed for island sizes discussed up to now.

Figure 10 shows concerted translation processes for a parallelogram-shaped hexamer along direction 1 and table 6 gives activation barriers in all three directions. Note that the activation barriers are not the same in all three directions. Figure 11 shows concerted translations for triangular hexamers along direction 1 and for a non-compact hexamer. For a triangular hexamer, activation barriers in all three directions are the same due to symmetry. Concerted translations for a triangular hexamer transform an A-type fcc (hcp) to a B-type hcp (fcc) triangular hexamer and back.

It is also obvious from figures 10 and 11 that edge/corner atoms are present in all the shapes of a hexamer. For triangular hexamers, there are three edge/corner atoms and the activation barriers for edge-diffusion and corner-rounding processes are similar to those for concerted translations, and therefore are quite frequent when the hexamer is in the triangular shape. These edge-diffusion and corner-rounding processes transform a triangular hexamer into a non-compact hexamer (figures 11(e) and (f)). Although not shown here, dimer shearing along an A step (similar to the one shown for a tetramer in figure 6) is a frequent process when the hexamer has non-compact shape, and has an activation barrier.
of 0.266 eV. Dimer-shearing processes transform a non-compact hexamer into a parallelogram-shaped hexamer. Note that concerted processes for a parallelogram hexamer have lower activation barriers than edge-diffusion and corner-rounding processes and hence contribute the most to the hexamer diffusion among all concerted translation processes. Importantly, for a parallelogram-shaped hexamer the average of activation barriers for concerted processes is 0.299 eV, which is very close to the effective diffusion barrier of 0.298 eV for the hexamer diffusion. Note that the average of the activation barrier for all concerted processes is 0.321 eV, which is noticeably higher than the effective diffusion barrier. This actually shows that the difference between the effective energy barrier and the average of the concerted processes is an indicator implying the contribution of non-concerted processes, but not an exact one.

3.2.6. Heptamer. A heptamer has a compact closed-shell structure with all periphery atoms having at least three nearest-neighbor bonds, as shown in figure 12. It diffuses primarily via concerted translations, as shown in figure 12. Activation barriers for single- and multi-atom processes which break up the compact shape are very high and do not occur during its diffusion at any temperature studied. Accordingly, the effective activation barrier of the heptamer is close to the average of the activation barrier for concerted translations.

3.2.7. Octamer. Figure 13 shows the only possible compact shape for an octamer, but based on the arrangement of atoms it can have either a longer A step edge (A-type fcc octamer) or a longer B step edge (B-type fcc octamer), and these are shown in figures 13(a) and (b), respectively. In figures 13(a) and (b), hcp octamers with long A- and B-type step edges are also shown. Figure 13 also shows concerted translation processes for A- and B-type octamers. These processes convert an A (B)-type fcc octamer into a B (A)-type hcp octamer and vice versa. Table 7 gives the activation barriers for these processes in all three directions. It can be seen from figure 13(b) that the
activation barrier to change from an A-type hcp octamer to a B-type fcc octamer is 2.0 meV, which shows that the A-type hcp octamer is 2.0 meV energetically more favorable than the B-type fcc octamer.

Although concerted translations contribute to the diffusion of an octamer, both multi-atom (especially shearing and reptation) and single-atom (especially edge-diffusion, kink-attachment/detachment and corner-rounding) processes are also relatively common. The effective energy barrier for octamer diffusion is 0.413 eV, while the average of activation barriers for all concerted translations is 0.431 eV. Also, the prefactor decreases by an order of magnitude when compared to the prefactor for heptamer diffusion (see table 11). This clearly shows that the non-concerted processes also have an effect on octamer diffusion. Therefore, multi-atom processes for this island are discussed here, while single-atom processes, which are also common in other sizes, are discussed later.

Table 7. Activation barriers (eV) for octamer concerted translation processes shown in figure 13.

| Directions | fcc → hcp | hcp → fcc |
|------------|-----------|-----------|
|            | A type    | B type    | A type    | B type    |
| 1          | 0.472     | 0.467     | 0.463     | 0.469     |
| 2          | 0.418     | 0.411     | 0.409     | 0.413     |
| 3          | 0.418     | 0.411     | 0.409     | 0.413     |

Figures 14(a) and (b) show trimer- and dimer-shearing processes for an octamer.

Figures 15 steps in an octamer reptation diffusion mechanism.

Figures 14(a) and (b) show trimer- and dimer-shearing process, respectively, while figure 15 shows a reptation process; these are commonly observed multi-atom processes during an octamer diffusion. Shearing processes transform a compact octamer into a non-compact octamer, while reptation processes rotate the orientation of non-compact octamers by 120°. These processes were also common during Ni octamer diffusion [5]. Moreover, from figures 13 and 15 one can see that both compact and non-compact octamers have an edge.
atom, and the activation barrier for the edge-diffusion and corner-rounding processes is lower than for both concerted and multi-atom processes (table 10). Therefore, edge-diffusion and corner-rounding processes are the most frequent processes. Importantly, the difference between the activation barriers between the edge-diffusion and concerted processes is larger than 0.1 eV, which explains the noticeable difference between the average of activation barriers for concerted processes and the effective energy barrier for octamer diffusion. In addition, the higher frequency of single-atom processes reduces the diffusion prefactor significantly. The same behavior was also observed during the Ni octamer diffusion [5].

3.2.8. Nonamer. The diamond-shaped nonamer shown in figure 16(b) is the only compact shape for a nonamer. The other frequently observed shapes are non-compact and have a kink in either the A- or B-type step edge, as shown in figure 16(a). The most stable configuration of an fcc nonamer is with an A-step kink, and is 2.0 meV lower in energy than the one with a B-step kink, while hcp nonamers with an A-step and a B-step kink are 4.0 and 5.0 meV, respectively, higher in energy than an fcc nonamer with an A-step kink. Least stable configurations are the symmetric diamond-shaped fcc and hcp nonamers by 7.0 and 10 meV, respectively, w.r.t. the fcc nonamer with an A-step kink. Note that diamond-shaped nonamers are less stable than non-compact hcp nonamers.

Figure 16 also shows concerted translation for non-compact and diamond-shaped nonamers, and activation barriers in all three directions are given in table 8. Note that a diamond-shaped nonamer (figure 16(b)) has two edge atoms at the ends of its long diagonal. The activation barriers for edge- and corner-diffusion processes are lower (table 10); as such, these processes will occur more frequently than concerted translations and transform it into a non-compact nonamer as shown in figure 16(a). The non-compact nonamer has no edge-diffusion atom and the activation barrier for kink detachment is about 19.0 meV higher than for concerted translations. Therefore the contribution of concerted translations to the nonamer diffusion occurs when it is in non-compact shape.

Figure 17 shows a frequently occurring multi-atom process during a nonamer diffusion. This is a dimer-shearing process along an A-type step edge similar to that for the other island sizes discussed before, and rotates or changes the orientation of the nonamer by 120°. Although not shown here, reptation processes also occur during nonamer diffusion, but only when the shape becomes non-compact.

The most frequently observed processes for a nonamer are the single-atom processes such as edge diffusion, corner rounding and kink detachment, as shown in figure 18, where numbers 2, 3, 5 and 11 correspond to the processes shown in figure 21, with corresponding activation barriers given in table 10. Although concerted diffusion processes occur less often, they contribute most to the nonamer diffusion. Nevertheless, single-atom and multi-atom processes do contribute to the island diffusion, owing to the fact that they are the most frequently occurring processes. Accordingly, the effective activation barrier for a nonamer is 0.425 eV, which is less than 0.473 eV, the average activation barrier for all concerted processes (see figure 23) of a nonamer.

3.2.9. Decamer. There is only one compact geometry for a decamer, as shown in figure 19, which also shows the most frequent concerted diffusion process, and the activation barriers for the concerted processes in all three directions are given in table 9. Multi-atom processes such as shearing and reptation occur during decamer diffusion when it changes to a non-compact shape. The previously discussed dimer-shearing process along the A-type step edge is the most frequently observed shearing process. The activation barriers for various single-atom processes, especially corner rounding and corner detachment, and concerted diffusion processes have similar activation barriers, and are also relatively common during...
the decamer diffusion. Figure 20 shows a common reptation process, which as usual occurs only when the island becomes non-compact. When a corner-detachment process occurs, other single-atom low activation energy processes are activated and contribute to the diffusion of the decamer. Accordingly, the effective activation barrier for decamer diffusion is 0.501 eV, which is less than the average activation barrier for concerted diffusion processes as well as kink-detachment processes.

3.2.10. Single-atom processes. Figure 21 shows various types of important single-atom process such as edge diffusion, corner rounding, kink attachment and kink detachment.
and their activation barriers are given in table 10. All single-atom processes involve an atom at an fcc (hcp) site moving to a nearest-neighbor vacant fcc (hcp) site. These single-atom processes are also referred to as long jumps. Note that the activation barriers for single-atom processes depend not only on whether the atom is part of an fcc island or an hcp island but also on the type of step edge (i.e. whether the diffusing atom is on an A-type or a B-type step edge) and its location along the step edge (i.e. corner, kink etc).

To classify single-atom processes in table 10 we have used the same notation as in our previous article [5] and re-described here for convenience, $X_n U \rightarrow Y_m V$, where X or Y is A (for an A-type step edge) or B (for a B-type step edge) or K (for kink) or C (for corner) or M (for monomer), $n_i$ is the number of nearest neighbors of the diffusing atom before the process and $n_f$ is the number of that atom’s nearest neighbors after the process. U or V is A or B (for corner or kink processes) or null (for all other process types).

For example, process 1, $B_2 \rightarrow B_2$, is a single-atom edge-diffusion process along a B-type step edge where the diffusing atom has two nearest neighbors before and after the process. Process 3, $C_1 B \rightarrow B_2$, is a corner-rounding process towards a B step, the diffusing atom starting on the corner of a B step with one nearest neighbor and ending up on the B step with two nearest neighbors. In process 10, $C_2 A \rightarrow C_1 B$, the diffusing atom begins on the corner of an A step having two nearest neighbors and ends up on the corner of a B step with only one nearest neighbor.

4. Diffusion coefficients and effective energy barriers

The Einstein equation [12], $D = \lim_{\Delta t \to \infty} \left( \frac{\langle R_n^2(t) - R_n^2(0) \rangle}{2 \Delta t} \right)$, is used to determine the diffusion coefficient of an island. Here $D$ is the diffusion coefficient, $R_n(t)$ is the location of the CM of an island at time $t$, and $d$ is the dimensionality of the diffusion, which is 2 for two-dimensional island diffusion. Table 11 summarizes the diffusion coefficients and effective energy barriers extracted from Arrhenius plots for the diffusion of islands of sizes 1–10. Figure 22 shows a log-linear plot of diffusion coefficients (shown in table 11) vs. island size for the temperatures studies in this work.

| Island size | 300 K | 400 K | 500 K | 600 K | 700 K | $E_{\text{eff}} (\text{eV})$ | $D_0 (\text{Å}^2 \cdot \text{s}^{-1})$ |
|------------|-------|-------|-------|-------|-------|----------------|----------------|
| 1          | $2.11 \times 10^{11}$ | $3.74 \times 10^{11}$ | $6.62 \times 10^{11}$ | $5.00 \times 10^{11}$ | $7.79 \times 10^{11}$ | 0.059 | $2.08 \times 10^{12}$ |
| 2          | $6.33 \times 10^{10}$ | $1.68 \times 10^{11}$ | $2.76 \times 10^{11}$ | $4.13 \times 10^{11}$ | $5.29 \times 10^{11}$ | 0.096 | $1.63 \times 10^{12}$ |
| 3          | $2.94 \times 10^{10}$ | $1.62 \times 10^{10}$ | $4.72 \times 10^{10}$ | $9.51 \times 10^{10}$ | $1.49 \times 10^{11}$ | 0.179 | $2.95 \times 10^{12}$ |
| 4          | $2.20 \times 10^{09}$ | $1.57 \times 10^{10}$ | $4.48 \times 10^{10}$ | $1.14 \times 10^{11}$ | $1.86 \times 10^{11}$ | 0.202 | $5.40 \times 10^{12}$ |
| 5          | $1.08 \times 10^{08}$ | $1.72 \times 10^{09}$ | $8.73 \times 10^{09}$ | $2.83 \times 10^{10}$ | $6.01 \times 10^{10}$ | 0.287 | $6.97 \times 10^{12}$ |
| 6          | $4.50 \times 10^{07}$ | $7.87 \times 10^{08}$ | $4.36 \times 10^{09}$ | $1.45 \times 10^{10}$ | $3.29 \times 10^{10}$ | 0.298 | $4.58 \times 10^{12}$ |
| 7          | $1.14 \times 10^{06}$ | $6.14 \times 10^{07}$ | $6.90 \times 10^{08}$ | $3.07 \times 10^{09}$ | $1.01 \times 10^{10}$ | 0.410 | $9.02 \times 10^{12}$ |
| 8          | $9.55 \times 10^{04}$ | $4.99 \times 10^{06}$ | $5.64 \times 10^{07}$ | $2.81 \times 10^{08}$ | $1.00 \times 10^{09}$ | 0.413 | $9.31 \times 10^{11}$ |
| 9          | $6.62 \times 10^{04}$ | $3.36 \times 10^{06}$ | $3.67 \times 10^{07}$ | $1.95 \times 10^{08}$ | $6.43 \times 10^{08}$ | 0.425 | $5.91 \times 10^{11}$ |
| 10         | $6.73 \times 10^{02}$ | $8.10 \times 10^{05}$ | $1.53 \times 10^{07}$ | $1.07 \times 10^{08}$ | $4.34 \times 10^{08}$ | 0.501 | $1.73 \times 10^{11}$ |

Figure 22 shows a comparison of effective energy barriers and the average activation barrier for concerted processes. The average activation barrier for concerted processes increases linearly as a function of island size with a slope of 0.055 eV/atom. It can be seen from figure 23 that the effective energy barrier and the average energy barrier for concerted processes increase linearly up to size 7, which demonstrates that islands diffuse predominantly via concerted diffusion processes. The effective energy barriers start to deviate from the average for the activation barrier concerted process with increasing frequency of occurrence of multi- and single-atom processes. Starting from the octamer, the effective energy barrier consistently deviates from the average activation barrier for concerted processes due to the increasing contribution from non-concerted processes. Figure 24 shows the normalized distribution of types of diffusion process accumulated during SLKMC simulations as a function of island size. Although there are exceptions, in general, the fraction of concerted processes decreases with island size. In the case of single-atom processes, their fraction consistently increases beyond size 4, while the fraction of multi-atom processes peaks at sizes 5 and 6, and decreases with island size for large island sizes.

Figure 23 shows a comparison of effective energy barriers and the average activation barrier for concerted processes. The average activation barrier for concerted processes increases linearly as a function of island size with a slope of 0.055 eV/atom. It can be seen from figure 23 that the effective energy barrier and the average energy barrier for concerted processes increase linearly up to size 7, which demonstrates that islands diffuse predominantly via concerted diffusion processes. The effective energy barriers start to deviate from the average for the activation barrier concerted process with increasing frequency of occurrence of multi- and single-atom processes. Starting from the octamer, the effective energy barrier consistently deviates from the average activation barrier for concerted processes due to the increasing contribution from non-concerted processes. Figure 24 shows the normalized distribution of types of diffusion process accumulated during SLKMC simulations as a function of island size. Although there are exceptions, in general, the fraction of concerted processes decreases with island size. In the case of single-atom processes, their fraction consistently increases beyond size 4, while the fraction of multi-atom processes peaks at sizes 5 and 6, and decreases with island size for large island sizes.
Note that there are two parameters for every activated diffusion process, the prefactor and the activation barrier. The frequency of occurrence of a diffusion process and the net displacement of CM it produces during an island diffusion affects not only the effective energy barrier but also the effective diffusion prefactor. Glancing through table 11, one can see that the effective energy barrier increases with island size, but there is no trend of how the effective diffusion prefactor varies with increasing island size. Nevertheless, the change in the diffusion prefactor from one island size to another can be explained based on the frequency of occurrence of the processes that do not contribute to the net displacement of CM of an island. For example, the diffusion prefactor for size 6 is lower than for both sizes 5 and 7. This can be explained based on the fact that an edge atom is present in all the frequently observed shapes during hexamer diffusion, and since their activation barriers are similar to those of the concerted processes they occur frequently, but they produce no net displacement of the CM of the hexamer. The same reasoning also applies to an order of magnitude drop in the diffusion prefactor from size 7 to size 8. A process which produces a net displacement of CM of an island will affect its effective activation barrier, but the frequency with which it produces this displacement affects the prefactor. Therefore, for large islands the prefactor decreases as $N^{−α}$ [13], while the activation barrier remains constant with increasing island size.

5. Conclusions

To summarize, we have performed a systematic study of the diffusion of small Ag islands (one- to ten-atom) on the Ag(111) surface, using SLKMC simulations. We find that island sizes of two to seven atoms diffuse primarily through concerted translations, with minor contributions from multi-atom and single-atom processes. The major contribution of multi-atom and single-atom processes is to the shape change and the rotation of the island’s axis, either clockwise or anti-clockwise. Although their effect on the effective activation barrier is minimal, depending on how quickly these shape changes and reorientations of islands occur, they can have a significant effect on the effective prefactor. For island sizes of eight to ten atoms, single-atom processes such as corner breaking followed by edge diffusion, kink attachment/ detachment, and corner rounding contribute to the diffusion of these islands because of lower activation energies rather than concerted processes. Therefore, one can argue that the crossover of island diffusion [14] from concerted processes driven to single-atom processes starts from the octamer. As a side note, the types of process and the behavior of effective activation barriers and prefactors is similar for Ni-island diffusion [5], and therefore we conclude that the kinetics of small island diffusion in Ni and Ag are also similar.

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References

[1] Zangwill A 1988 Physics at Surfaces (Cambridge: Cambridge University Press)
[2] Kaxiras E 1996 Comput. Mater. Sci. 6 158
[3] Mehrer H 2007 Diffusion in Solids (Berlin: Springer)
[4] Antczak G and Ehrlich G 2010 Surface Diffusion: Metals, Metal Atoms and Clusters (Cambridge: Cambridge University Press)
[5] Shah S I, Nandipati G, Kara A and Rahman T S 2012 J. Phys.: Condens. Matter 24 354004
[6] Trushin O, Karim A, Kara A and Rahman T S 2005 Phys. Rev. B 72 115401
[7] Yildirim H, Kara A and Rahman T S 2007 Phys. Rev. B 76 165421–10
[8] Yildirim H, Kara A, Durukanoglu S and Rahman T S 2005 Surf. Sci. 600 484–92
[9] Chirita V, Munger E P, Greene J and Sundgren J E 2012 Surf. Sci. 436 L641
[10] Boris A and Alberto C 2006 REVCIUNI 10 42–5

[11] Ferron J, Miranda R and de Miguel J J 2014 Phys. Rev. B 90 125437
[12] Einstein A 1956 Investigations on the Theory of the Brownian Movement (New York: Dover)
[13] Voter A F 1986 Phys. Rev. B 34 6819
[14] Karim A, Kara A, Trushin O and Rahman T S 2011 J. Phys.: Condens. Matter 23 462201