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Rapid Diffusion of Magic-Size Islands by Combined Glide and Vacancy Mechanism

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Using molecular dynamics, nudged elastic band, and embedded atom methods, we show that certain 2D Ag islands undergo extremely rapid one-dimensional diffusion on Cu(001) surfaces. Indeed, below 300K, hopping rates for "magic-size" islands are orders of magnitude faster than hopping rates for single Ag adatoms. This rapid diffusion requires both the *c*(10x2) hexagonally-packed superstructure typical of Ag on Cu(001) and appropriate "magic-sizes" for the islands. The novel highly-cooperative diffusion mechanism presented here couples vacancy diffusion with simultaneous core glide.

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Surface diffusion is a fundamental physical phenomenon critical to the description of surface phase formation, epitaxial film growth, heterogeneous catalysis, and other processes on surfaces. A variety of mechanisms for surface diffusion have been described in the literature, which can be separated into two general classes: single-atom jumping, and cooperative processes involving the simultaneous motion of two or more atoms. Historically, single-atom hopping dominated discussions of surface diffusion, thus surface diffusion of islands was thought to occur by adatom hopping via mechanisms such as edge running,[1] terrace diffusion,[2] and evaporation-condensation.[2] Our understanding of surface diffusion was changed dramatically by the discovery of cooperative diffusion in field ion microscopy (FIM) experiments.[3,4,5] Subsequently, a number of processes have been observed which allow whole islands to diffuse over a surface with multiple island atoms moving collectively. These have included a simultaneous motion of all island atoms typically termed an island glide[6] and dislocation mechanisms,[7,8] during which a portion of the island switches from fcc to hcp sites due to the nucleation and motion of misfit dislocations. Likewise, in both dimer shear[9] and reptation[10] mechanisms, compact clusters undergo concerted shear motions as a means of translation. In this letter, we describe a novel collective diffusion mechanism involving vacancy diffusion on the perimeter coupled to simultaneous glide of the island core.

Here, we consider the system Ag on Cu(001). Previous theoretical work on this system[11] and the related Ag on Ni(001) system[12] has shown substantial sliding of entire Ag overlayers but no diffusion of 40-atom islands or single chains of Ag atoms. In this letter, we reexamine finite island diffusion for the Ag-Cu system using the embedded atom method[13] with potentials developed by Mishin *et. al.* [14,15] We confine our attention to hexagonally-packed islands having pseudohexagonal *c*(10x2) superstructures typical of Ag monolayers on Cu(001) substrates.[16,17,18] By virtue of the lattice mismatch ($[a_{Ag} - a_{Cu}]/a_{Ag} = 11.7\%$), the monolayer of silver is row-aligned with the substrate with 9 Ag atoms for every 10 Cu atoms. We focused on the set of hexagonal silver islands that have 3, 4, 5, 6, 7, 8, and 9 atoms along each hexagon edge. These islands exhibit a "magic-size" effect[8] in that the activation energy for diffusion varies dramatically with size. In particular the 169-atom islands and the 217-atoms (with 8 and 9 atoms along the edge) diffuse much faster than the other island sizes and much faster than a single Ag atom.

We have used three complementary techniques, molecular dynamics (MD), parallel replica dynamics (ParRep)[19] and nudged elastic band (NEB),[20] to investigate this system. MD was used to provide a detailed atomistic view of every aspect of the diffusion process, allowing us to discover unexpected mechanisms for diffusion and to quantify hopping rates for the islands. ParRep dynamics was used to extend MD simulations to longer times and lower temperatures in order to find lowest-barrier pathways for island hopping. NEB is a complementary technique which directly calculates activation energies_given detailed initial and final configurations.[20] _We used NEB to calculate activation barriers for processes discovered in MD and ParRep runs.

Our starting configurations consisted of a hexagonally-packed c(10x2) Ag island placed atop four to five atomic layers of Cu(001) substrate with periodic boundary conditions in the in-plane directions. The bottom two layers of the Cu(001) substrate were frozen in place in all simulations. A large number of quenched MD runs revealed that the stable ground state configurations for the 127-atom,169-atom, and 217-atom islands are hexagonally packed and include vacancies in the two edges oriented along the {110} direction. These vacancies are stable, accommodating the large size mismatch by separating the line of edge atoms into two shorter lines.

For specificity, we will emphasize the 169-atom island in what follows. We found it useful to characterize the states using a notation, n:8-n|m:8-m, where the integers n and m specify the position of the vacancy along the two edges (see figure 1). The two ground states of the 169-atom island are related by mirror symmetry and labeled as 5:3|5:3 and 3:5|3:5. The rapid collective diffusion mechanism we report here is driven by vacancy diffusion along the edges. First, the vacancies diffuse along the two edges, reach the end of the edge, and annihilate. Second, to complete a hop, new vacancies must nucleate at the other end of the edge, and diffuse until the (translated) ground state reforms, denoted as 5:3|5:3 T.[21] The remaining island atoms maintain hexagonal packing, and glide in concert with the vacancy diffusion on the two edges. This diffusion process occurs exclusively along a single {110} type direction along the long side of the c(10x2) reconstruction.

For the 169-atom Ag island, we ran MD simulations at temperatures, $200K \leq T \leq 300K$, and generally observed one or more island hops in the 50 ns MD simulations. We also ran longer ParRep simulations at 175K and 200K. Figure 2 displays an Arrhenius plot of the hopping rates for the 169-atom island as a function of reciprocal temperature. Also shown are hopping rates for the 127-atom and 217-atom islands at 300K and for a single Ag adatom at $350K \leq T \leq 425K$.[22] Upon extrapolating the monomer hopping rates to temperatures at and below room temperature,[23] we conclude that the monomer hopping rates are orders of magnitude lower than those of the 169-atom or the 217-atom island. The reader is directed to reference 22 for the movie of an MD simulation showing the disparity in hopping rates of the monomer and 169-atom island at 250K.

We mention that for temperatures, $T \geq 250\text{K}$, islands would occasionally depart from perfect hexagonal shapes. This "break-up" process involved atoms escaping from edge sites to become adatoms along the edge. Islands which deviated from a perfect hexagon, were trapped, and no longer diffused by the vacancy/glide mechanism. Although such islands would occasionally return to the perfect hexagonal shape and resume diffusion, we included only simulation data prior to any island break-up in our analysis. This procedure was used to measure hopping rates for vacancy/glide mechanism of the perfect hexagonal islands.

We turn now to consider the complex "energy landscape" of the 169-atom island. For all the MD runs, we recorded atomic coordinates at 5ps intervals. All these configurations were quenched using steepest descent energy minimization. The left side of figure 3 displays a scatter plot of the center of mass (c.m.) coordinate (in the diffusion direction) vs. the energy of the quenched states. The energy zero is chosen to be the energy of the stable ground states. We see that this system has a very large number of low-lying metastable states. The island energy exhibits translation symmetry with the 2.56Å periodicity of the substrate. The ground states occur in pairs at $x_{cm} = 2.56p + 0.78(1 \pm 1)\text{Å}$ where p is an integer. We will see that a full hop of the island requires that p increase or decrease by one.

The right portion of figure 3 shows the quenched c.m. coordinate as a function of time for the same MD run. In order to emphasize hops between the stable ground states (and closely associated metastable states), we plot the c.m. coordinate (red square symbol) only for configurations with energies in the range $0 < E_{quenched} < 0.04\text{eV}$. The lines connecting these red points give us a map of the diffusion path between the low-lying states. We notice relatively rapid diffusion between pairs of states with the same value of p (transitions between the states 5:3|5:3 and 3:5|3:5), and much slower diffusion between states with different values of p (corresponding to transitions between 3:5|3:5 and 5:3|5:3 T). The rate limiting transition between states with different values of p must occur to complete a hop. Hopping rates were determined by counting crossings of the horizontal, black lines.

Finally, we consider the activation energy for diffusion of the 169-atom island. It is possible to fit an Arrhenius expression (blue line in figure 2) to the hop rates, however we will show that the inferred activation energy, $E_A = 0.178$ eV, is completely incorrect. In figure 4 the lowest observed energy diffusion pathway (extracted from a 175K ParRep run and refined using NEB) is plotted.[24] The highest transition state in this pathway has $E_A = 0.243$ eV. An examination of the pathway reveals the two governing processes seen in figure 3: a rapid process with considerable glide (5:3|5:3 to 3:5|3:5) and a slower one that primarily consists of vacancy diffusion (3:5|3:5 to 5:3|5:3 T). Our MD runs and NEB calculations are consistent in showing that the rate-limiting process involves the annihilation of vacancies at one edge end and the nucleation of vacancies at the opposite end. It should be noted that two other pathways observed at 175K had overall energy barriers of 0.246 eV and 0.266 eV. Thus, while it is possible that other pathways with slightly lower activation energies may exist, it is clear that the overall diffusion barrier is much larger than the 0.178 eV barrier yielded by the Arrhenius fit.

The apparent discrepancy is resolved as follows: The NEB calculation gives the temperature-independent activation energy between the ground state and the highest-energy transition state along the diffusion pathway. However, the diffusion rate is determined by the (temperature-dependent) Gibbs free energy of activation. At finite temperature, this system has a large number of populated low-lying states (see figure 3). The state population distribution from the MD simulation at 275K is shown as an insert in figure 5. Also plotted is the mean quenched energy, $\bar{E}(T)$, determined from the MD runs at various temperatures. In this temperature range, $\bar{E}(T)$ can be approximated by a linear function, $\bar{E}(T) = -m/kT + b$ with $b = 0.17$ eV and $m = 0.0021$ eV^2. The Gibbs free activation energy is defined as $\Delta G(T') = E_A - \langle \bar{E}(T') \rangle$,[25] and the hopping rate as $H(T') = H_o \exp(-\Delta G(T')/kT')$. The only unknown quantity is the prefactor, H_o, determined by fitting the hopping rate data (shown in figure 2). The resulting curved green line provides a good fit to the hopping rate. The failure of this Arrhenius plot to give the activation energy sends a noteworthy cautionary message to all experimentalists.

In conclusion, we have shown that diffusion of hexagonal islands on a substrate with square symmetry can be remarkably fast. The activation energy of this one-dimensional diffusion process cannot be determined from a standard Arrhenius analysis. We have also proven the existence of magic-sized islands exhibiting fast diffusion at room temperature, contradicting the conclusion reached by Black *et. al.* who reported that Ag islands on Cu(001) do not move in MD simulations at room temperature.[11] We suggest that the islands they studied were not of the "magic-size" required to show collective diffusion. We also note that Monte Carlo models of film growth, which generally allow only single atom hops, would neglect this complex cooperative mechanism for extremely fast diffusion.

Our results suggest a possible modification in the picture of film growth for Ag on Cu(001). The initial stages of film growth would occur via the usual mechanism of deposition and diffusion of single atoms leading to the formation of critical nuclei which are immobile but continue to grow by addition of single adatoms. However, once these islands grow to a "magic-size" they might diffuse rapidly and coalesce forming a network of connected islands. This process should be observable using STM at temperatures slightly below room temperature although it may require very particular deposition conditions to make "magic-size" islands. We hope that these theoretical results will inspire further experimental work to demonstrate this newly discovered diffusion mechanism and determine its effect on film growth in this and similar systems.

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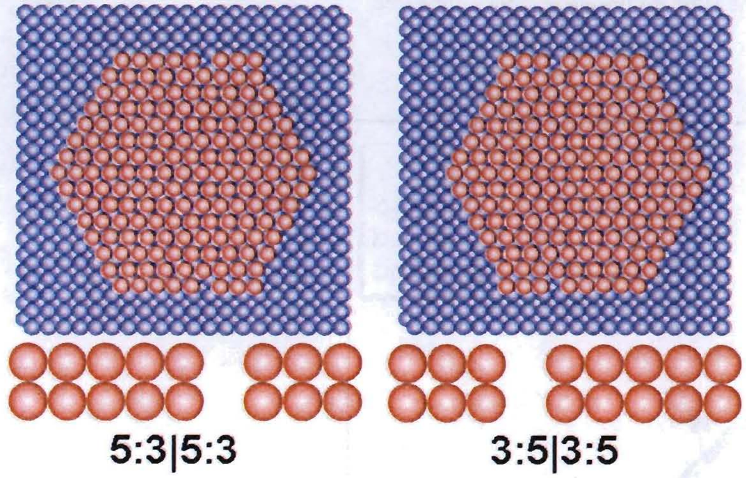
FIG. 1 (color): Two mirror symmetrical ground state configurations of the 169-atom island. We classify island states by the position of vacancies on the horizontal edges. The notation, n:8-n|m:8-m, means that the top edge has n atoms, a vacancy, and then 8-n atoms, with a similar notation for the bottom edge. For configurations with no vacancy, the notation "8" is used.



5:3|5:3

3:5|3:5

FIG. 2 (color): Temperature dependence of island hopping rates. Error bars are based on Poisson statistics with a 95% confidence level. At 300K, the 169- and 217-atom islands diffuse an order of magnitude faster than the monomer or the 127-atom island. On this time scale, we saw no hopping of 37 or 61 atom islands. The standard Arrhenius fit for 169-atom island (blue line) would indicate an activation energy of 0.178eV, but this is in serious disagreement with our NEB calculation (fig 4) of 0.243eV. The curved green line resolves the problem based on a calculation of the temperature-dependent Gibbs free energy of activation described in the text.

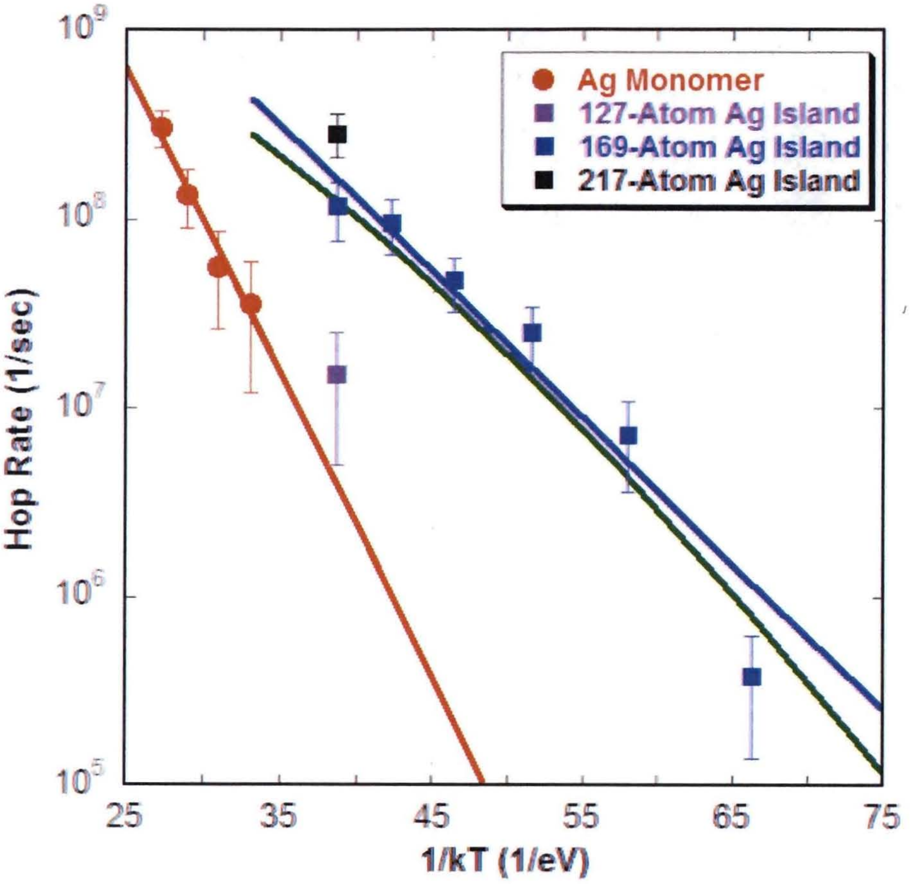


FIG. 3 (color): Center of mass coordinate plots for a 169-atom island MD run at 275K. On the left is a scatter plot of quenched c.m. position vs. potential energy. The system occupies a very large set of metastable states even at low temperatures. On the right is a plot of quenched c.m. coordinate vs. time. The red points show the states in the immediate vicinity of the ground states ($E_{quenched} < 0.04$ eV). Hopping between these red points is of two types. There is a rapid, glide-centric process which repeats frequently between states 5:3|5:3 and 3:5|3:5 but does not allow a complete hop. The rate-limiting vacancy-assisted transitions (3:5|3:5 to 5:3|5:3 T) cross the double black horizontal lines, allow a complete hop of the island, and determine the overall diffusion rate.

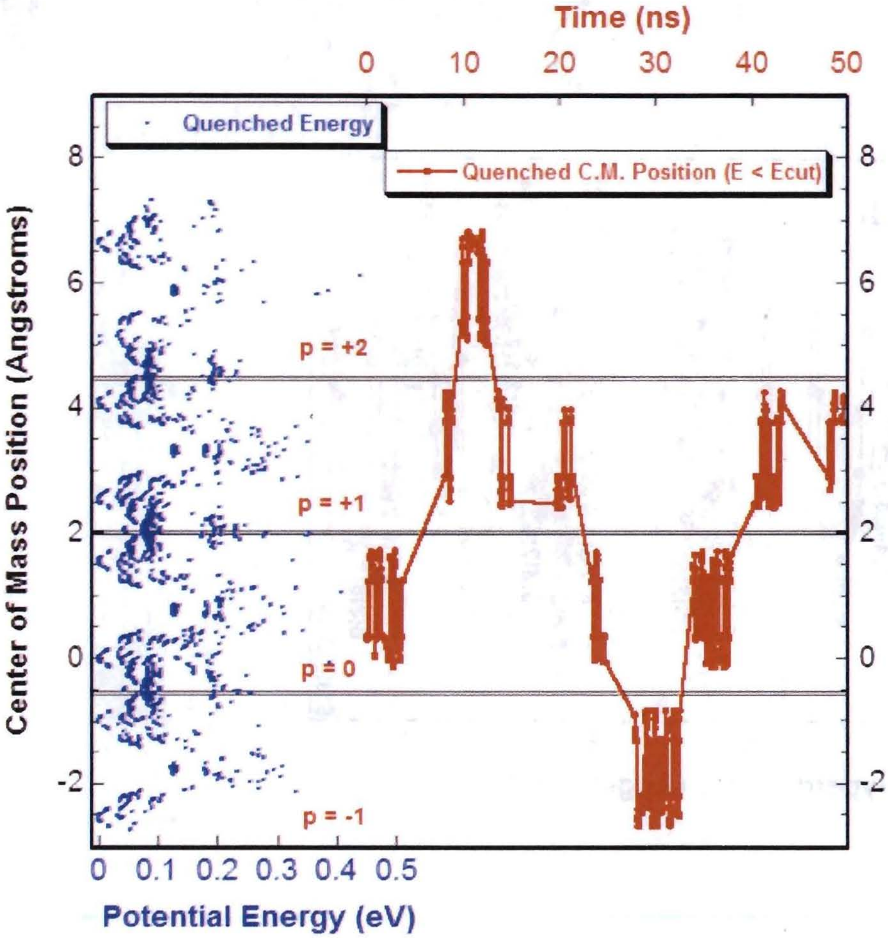


FIG. 4 (color online): Minimum energy path for surface diffusion of a 169-atom Ag hexagonal island based on a ParRep run at 175K and subsequent NEB analysis of transition states. States are labeled as in figure 1. The pathway has an energy barrier of 0.243 eV. The intermediate state (3:5|3:5) is reached via a process that combines extensive core glide with vacancy hops. The rate-limiting process (3:5|3:5 to 5:3|5:3 T) involves vacancy annihilation at one end and vacancy creation at the opposite end of the island edge.

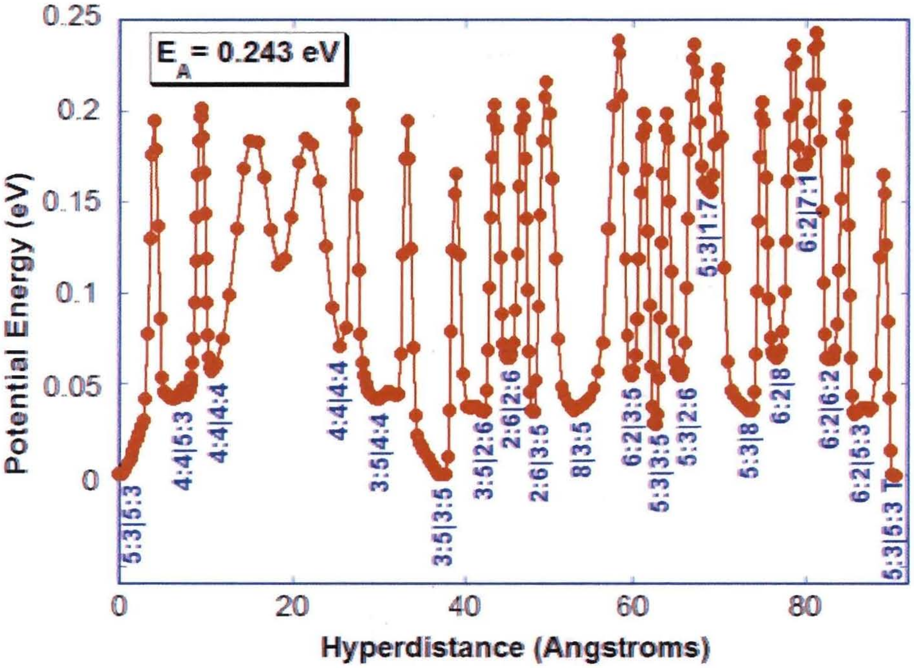
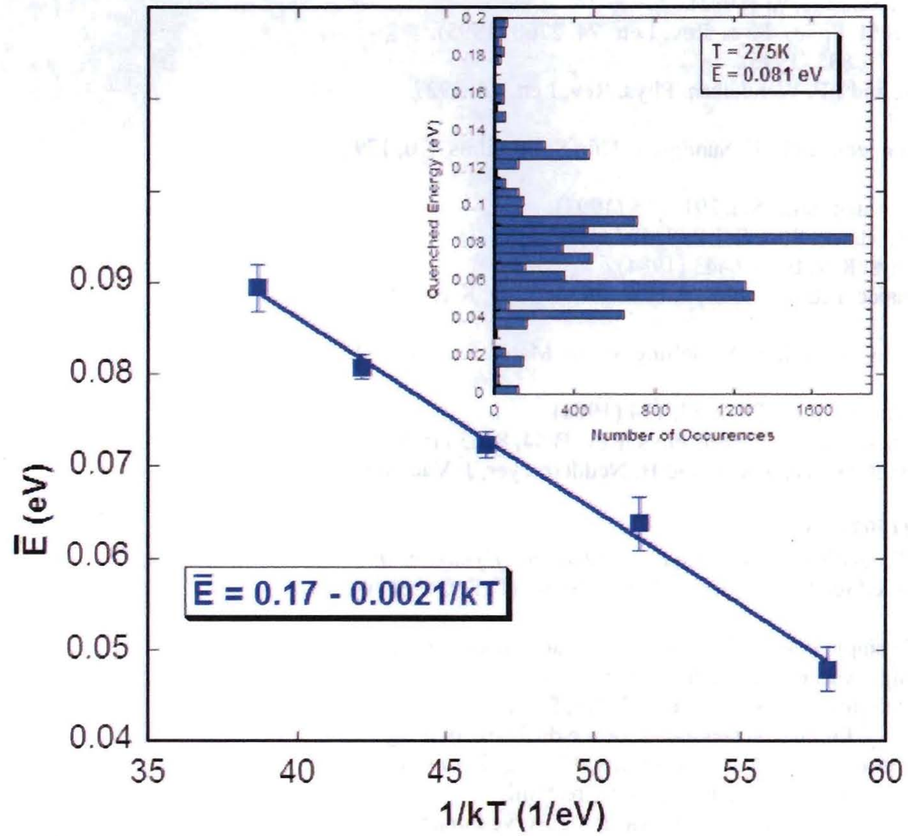


FIG. 5 (color online): The histogram insert shows the energy distribution of 169-atom island states quenched from a 275K MD run. The mean energy, $\overline{E}(T)$, of the quenched states is 0.081eV. The plot shows $\overline{E}(T)$ vs. 1/kT. The curved green line in the Arrhenius plot of figure 2 was fit using the Gibbs free energy of activation, $\Delta G(T') = E_A - \langle \overline{E}(T') \rangle$, with E_A= 0.243eV from the NEB pathway in figure 4.



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[21] An analogy with diffusion of a single line of eight atoms illustrates this point. To translate a line of atoms by single vacancy hops, the line must pass through a sequence of configurations as follows: **5:3**, 6:2, 7:1, 8, 1:7, 2:6, **3:5**, 4:4, **5:3 T**.

[22] See EPAPS Document No. _____ for an MD simulation of the diffusion of a Ag monomer and a 169-atom Ag island on the Cu(001) surface at 250K. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

[23] For the Ag monomer on Cu(001), exchange diffusion was not observed in any of our MD runs, consistent with our NEB calculation of a 1.08 eV barrier for exchange diffusion. This is much higher than the 0.40 eV barrier for adatom hop on the surface.

[24] See EPAPS Document No. _____ for an NEB movie of the lowest energy pathway for diffusion (see figure 4) of a 169-atom Ag island on a Cu(001) surface. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

[25] Note that $\langle \overline{\mathrm{E}}(\mathrm{T}') \rangle$ is the average of $\overline{\mathrm{E}}(\mathrm{T})$ over the temperatures ranging from 0 to β'; thus, $\langle \overline{\mathrm{E}}(\mathrm{T}') \rangle = (1/\beta')\int_0^{\beta'} \overline{\mathrm{E}}(\mathrm{T})\ \partial\beta$ where $\beta' = 1/\mathrm{kT}'$.