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Energetics and many-particle mechanisms of two-dimensional cluster diffusion on Cu(100) surfaces

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We study the energetics and stability of small Cu clusters on Cu(100) surfaces using molecular statics combined with systematic saddle-point search methods. We find several previously overlooked concerted many-particle processes that play an important role in cluster energetics. In particular, for smaller clusters there is an internal atom row shear mechanism that in some cases determines the rate-limiting step for center-of-mass motion. Our results suggest specific reaction paths for experimentally observed cluster diffusion events.

Adatom and island diffusion are important in understanding crystal growth and thin-film formation.¹ They have been intensively studied both theoretically and experimentally. Experimental methods, such as field ion microscopy² and scanning tunneling microscopy,³ can provide direct microscopic information. However, usually these methods do not give any conclusive information on the microscopic mechanisms of diffusion processes and thus theoretical studies are needed.

Single adatom diffusion mechanisms on metal surfaces are mostly well understood. However, island or 2D cluster diffusion mechanisms even on low-index fcc metal surfaces have turned out to be nontrivial.⁴ Recent studies have shown that in metal-on-metal systems even large clusters can have significant mobility at moderate temperatures.⁵ This is due to such mechanisms as evaporation-adsorption, terrace (or vacancy) diffusion, and single-atom diffusion along the periphery.^{4,6} Smaller clusters can diffuse with more complicated mechanisms, however.^{7,8} For example, on fcc(111) surfaces small clusters have been found to move with a snake-like diffusion mechanism which involves the successive shear translations of adjacent subcluster regions.⁹ On fcc(110) missing-row reconstructed (1×2) surfaces, 1D chainlike clusters have been found to move according to the so-called leapfrog mechanism.¹⁰

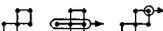
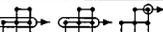
For fcc(100) surfaces, experiments suggest that the diffusion of small Rh clusters on Rh(100) surfaces takes place by the sequential displacements of edge atoms rather than by the glide of the entire cluster as a unit across the surface.¹¹ Some of such moves lead to localized cluster dynamics with no center-of-mass motion. In addition, for compact geometric structures the diffusion has a higher activation energy than that for structures with an extra atom at the periphery.^{6,11} These findings have been confirmed in recent embedded-atom-model (EAM) calculations by Shi *et al.*¹² for Ag, Cu, and Ni. They found a new mechanism for cluster diffusion through concerted dimer shearing which gives better agreement between experiments and calculations for the oscillatory behavior of diffusion as a function of cluster size. The idea of dimer shearing is based on bond-counting arguments which work in many cases for fcc(100) metal surfaces.^{6,12,13}

The dimer shear mechanism suggests that other concerted diffusion processes could play a role on fcc(100) surfaces for small clusters. However, in general it is very difficult to find such mechanisms due to the possibility of many different transition paths. Recently, systematic methods for finding transition paths (saddle points) for many-particle systems have been developed.^{8,14}

In this work, we apply such methods to study the energetics and stability of small Cu clusters on the Cu(100) surface using the EAM (Ref. 15) of Ref. 12 (Ref. 16). We indeed show that there exist competing many-particle mechanisms which have been overlooked. We show that the dimer-shear mechanism is just a special case of a more general row-shear mechanism that controls the energetics of some smaller clusters. In particular, this row shearing may occur *inside the cluster* with an activation barrier E_a lower than at the periphery. We report the lowest barriers in detail up to $n = 10$ atom clusters, and discuss mechanisms that determine their stability. Our results for the oscillatory behavior of diffusion barriers for different cluster sizes are in good qualitative agreement with previous studies.^{6,12}

Given the interatomic potential, the standard method of finding lowest energy transition paths is the drag method, which was used to find the cluster energetics in Ref. 12. The most serious drawback in this method is that one must guess the transition path in advance. In case only the initial and final states are known, the nudged elastic band (NEB) (Ref. 17) method is a much better choice.¹⁴ For a more systematic search of possible saddle points, there exist new methods¹⁸⁻²¹ where the idea is to follow along the lowest eigenvector of the Hessian matrix. This is particularly easy to implement in cases such as the EAM potential where the elements of the Hessian matrix can be calculated analytically. After that, one can use a modified eigenvector-following (EF) approach²¹ with which one can find the lowest eigenvalue without diagonalizing the Hessian. In our calculations we have used both the NEB and EF methods combined with minimization done by quenched dynamics. In our system, the substrate comprises a slab with 10 atomic layers and 128 atoms in each layer. The positions of the two bottom layers of the substrate remain fixed. Periodic bound-

TABLE I. Equilibrium shapes of small Cu clusters up to ten atoms, with the corresponding RLS's with activation energies E_a for CM motion (boldfaced) and dissociation listed. In every case the RLS involves only one saddle point. We also show the corresponding values from Ref. 12 when available.

Processes	E_a (eV)	E_a (eV) in Ref. 12
	0.488	0.503
	0.484, 0.820	0.494, -
	0.548, 0.621	0.552, -
	0.686 , 0.818	0.688, 0.815
	0.528 , 0.547	- , 0.551
	0.701 , 0.714, 0.834	- , 0.713, 0.835
	0.454, 0.499 , 0.836	0.45, - , -
	0.634 , 0.757, 0.838	- , 0.758, 0.838
	0.810 , 0.821, 0.947	- , 0.857, 0.975
	0.667 , 0.682, 0.846	- , - , -

ary conditions are applied in the plane parallel to the surface.

To find the transition paths, we first determine the equilibrium shape of each small Cu cluster on the Cu(100) surface. We then employ the EF method to map all the possible processes that we can find with 50 attempts, with randomly chosen Gaussian displacements of 0.1 Å for the cluster atoms.²² After this we study each single process in detail with the NEB using a linear interpolation between the initial and final states. A typical interpolation path contains 30–40 images and requires a few hundred iterations to converge. The E_a 's calculated with the two methods are within 0.008 eV in all the processes studied, which is the maximal error in our results.

Our main results using the NEB method for clusters of ten atoms or less are shown in Table I. In each case we show the equilibrium shape(s) and the rate-limiting steps (RLS) for center-of-mass (CM) motion, and dissociation. Bond-counting arguments work well for determining the equilibrium configuration for each cluster size. Breaking a nearest-neighbor (NN) and next-nearest-neighbor (NNN) bond costs 0.32(2) eV and 0.03(2) eV, respectively, where the differences shown in parentheses correspond to a different shape of the cluster with the same number of NN and NNN bonds. However, as will be shown below, such arguments do not in general determine the RLS.

Our results for the cases $n = 1$ and 2 are in agreement with Ref. 12, except that the easiest pathway for the whole dimer to move is perpendicular to its bond direction (Table I). The same result has been obtained recently for an Al dimer on the Al(100) surface in Ref. 23. Also, for the dimer case we find that its orientation can change by concerted motion of the two atoms. In this process there are two saddle points separated by a shallow minimum even though the bond length grows less than about 13% during the process. This process is energetically very close to dissociation and may lead to CM motion at finite temperatures.

For $n = 3$ dissociation is favored, but dimer motion can be activated with a slightly higher E_a as shown in Table I. For $n = 4$, we confirm the dimer shearing discovered by Shi *et al.*¹² with $E_a = 0.686$ eV. For larger clusters, dimer shearing has even larger energy. However, a dimer at the edge can break up with a barrier of only 0.54 eV, followed by adatom detachment (0.55 eV). Thus, dimer shearing will *not* be the RLS for larger clusters as will be shown below.

For $n = 5$, Shi *et al.* find that adatom detachment is favorable. However, as seen in Table I, there is a lower energy process in which a dimer shears *within the cluster* with $E_a = 0.528$ eV. It is thus the RLS leading to CM motion, as shown in detail in Fig. 1. Similarly, for $n = 6$ and 7 we find that CM motion is activated with the motion of two and three atoms within the cluster, respectively. We call this process *internal row shearing*. For $n = 7$, Shi *et al.*¹² did not consider the three-atom internal row shearing that is in fact the RLS (the second configuration in Table I). This configuration has the same number of NN and NNN bonds as the leftmost one and is only 0.02 eV higher in energy from the EAM potential. For $n = 8$, the same process is the RLS from the equilibrium configuration instead of dimer shearing suggested in Ref. 12. For $n = 9$, CM motion is also activated by three-atom internal row shearing.

For the case $n = 10$, there are two different shapes that have the same energy within the accuracy of the EAM potential. The CM motion is activated by internal three-atom row shearing in both cases with almost the same E_a .

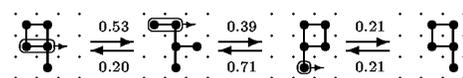


FIG. 1. Series of processes leading to CM motion for a five-atom cluster. Black circles represent cluster atoms and small dots atoms in the surface layer of the substrate. The activation energies for reverse processes are also presented. Energies are in eV.

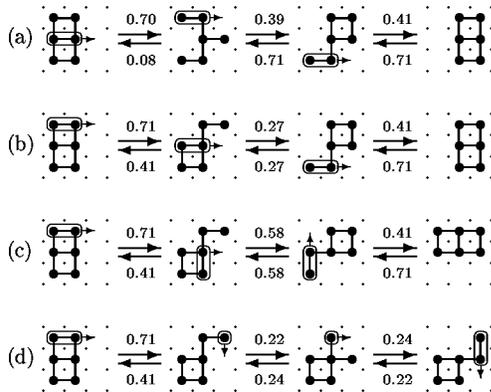


FIG. 2. Series of processes for the CM motion of a six-atom cluster, with translation in (a) and (b), and rotation in (c) and (d). Note that in (d) the last configuration has not been drawn. See text for details.

The CM motion of a six-atom cluster is particularly interesting. We show this case in more detail in Fig. 2. Kellogg¹¹ saw in his experiments that six-atom Rh clusters on a Rh(100) surface can move and also change their orientation by 90°. Figure 2(a) shows the two-atom internal row shearing of Table I which is the RLS. However, there is another process that yields almost the same barrier, namely dimer shearing at the periphery [Figs. 2(b)–2(d)].¹² This is an example of a case where bond-counting arguments do not predict the diffusion path since Fig. 2(a) leads to a situation in which there is one NN bond less than in the other cases.

The experimentally observed hexamer rotation can be seen to occur through the sequence of processes in Figs. 2(c) and 2(d). The second process in Fig. 2(c) involves an unusual *internal dimer rotation* which is shown in Fig. 3. It is qualitatively different from the rotation of an isolated dimer because it involves only one saddle point due to the concerted motion of almost all the atoms that are NN to the dimer, as revealed by our NEB calculations.²⁴ During the process, the dimer bond (shown in the figure) remains within 1.5% of its equilibrium value. It is also interesting to note that the second way for hexamer rotation [Fig. 2(d)] involves lower intermediate barriers than the dimer rotation, but requires one more step. We have in fact not seen the sequence of processes of Fig. 2(d) in our calculations.

As might be expected, the internal row shearing of even more than three atoms has a relatively low barrier when it is activated at a kink site. In Fig. 4 we show results of com-

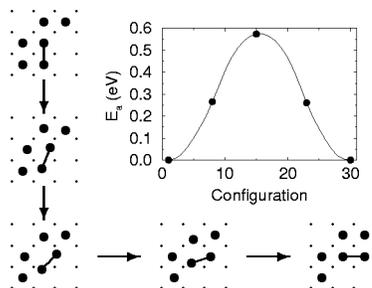


FIG. 3. Some intermediate configurations for internal dimer rotation [second process in Fig. 2(c)]. The potential-energy curve corresponding to the transition has been drawn from 30 intermediate configurations, with dots denoting the five states shown.

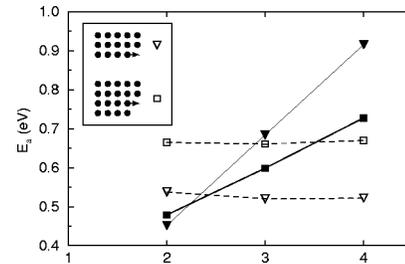


FIG. 4. The activation energy as a function of number of atoms (k) in the row near a kink. In the inset the case $k=4$ is shown. Open symbols correspond to vacancy formation (single-atom hop) and filled symbols to the row shearing.

parisons of edge and internal row shearing as a function of the number of atoms k in the row ($k=2, 3$, and 4). We also show the energy for a vacancy formation (single atom hop at the kink site). These results show that vacancy formation at a kink site is thus favored over row shearing for $k>3$. Recent detailed studies of diffusion of large Cu clusters have shown that vacancy diffusion inside the cluster controls the asymptotic size dependence of the diffusion coefficient.⁶

Next we wish to discuss the stability of the small clusters. As shown in Table I, only the equilibrium shapes for dimers and trimers have barriers that are lowest for single-atom detachment (to a site with one NNN bond left). Analysis of intermediate configurations for $n=4, 5, 6$, and 7 reveals that the barriers corresponding to activated CM motion are lower than for detachment. However, for $n=8$ and 10 the situation is different. The easiest path for detachment of a single atom with only one NN and NNN bond ($E_a=0.55$ eV) can occur only after dimer breakup at the edge ($E_a=0.54$ eV). For $n=9$, this detachment can occur from the nonequilibrium configuration following the three-atom internal trimer shearing. These results indicate that at finite temperatures the dynamics of small clusters is highly non-trivial with many competing processes. Detailed analysis of cluster dynamics and effective diffusion barriers will be presented in future work.²⁵

Finally, we note that our results give oscillatory behavior for the activation energy as a function of the cluster size that is similar to the other calculations^{6,12} and experiments.¹¹

In summary, by combining semiempirical calculations for the energetics of small adatom clusters with efficient saddle-point search methods, we have been able to demonstrate the importance of concerted processes for cluster dynamics. In the case of Cu(100), there are several previously overlooked mechanisms such as internal dimer rotation and internal row shearing that play an important role. This means that CM motion of clusters up to size $n=10$ and even larger can be activated more easily than previously assumed.¹² These results have important implications not only to the mobility of small clusters, but also to metal-on-metal growth. It would be of great interest to perform additional studies to investigate the role of these processes at finite temperatures.²⁶

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