

Rolling: A fast diffusion mechanism for small clusters on a solid surface

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We have performed molecular-dynamics simulations to analyze diffusion of small clusters on a solid surface, and found a new diffusion mechanism in which a spherical-like cluster can move rapidly with a rolling motion. When applied to Ni_n ($n=1-14$) clusters on the $\text{Au}(110)-(1\times 2)$ surface, our model predicted a cluster-size dependence in diffusion, with the most spherical-like Ni_4 and Ni_{13} having the largest diffusion constants. Our model also confirmed that diffusion of Ni across the $[1\bar{1}0]$ troughs is slower than diffusion along the troughs. For the transverse diffusion, rolling of Ni_4 is, once again, an effective mode of cluster motion. [S0163-1829(99)03139-2]

Understanding how small clusters move on a solid surface has drawn an increasing research interest in surface science and materials research. The incentive for this is not only its relevance to the development of new thin-film structures,¹ and one-dimensional and two-dimensional nanostructures,²⁻⁴ but also the evidence that advances in experimental atomic imaging of surface dynamics and theoretical tools for simulating such surface dynamics have led to the discovery of fascinating modes of cluster motion. Most importantly, there have been quite a few independent reports of fast cluster diffusion, which ensures the possibility of cluster diffusion being a determining factor in the overall surface dynamics. For example, Kellogg and Voter⁵ demonstrated experimentally by field-ion microscopy that for Pt diffusion on $\text{Pt}(001)$ at 175 K, a Pt dimer migrates over 50 times faster than a single atom, and a trimer is as mobile as a single atom. More recently, Shi *et al.*⁶ predicted, with the embedded-atom method,⁷ a similar behavior for $\text{Cu}/\text{Cu}(100)$ and $\text{Ni}/\text{Ni}(100)$.

Diffusion of clusters larger than a trimer has also been observed experimentally. Wang and co-workers⁹⁻¹² have reported a series of reports on rather intriguing modes of motion for Ir_n ($n=1-19$). For even larger clusters, Bardotti *et al.*⁸ observed a surprisingly high preexponent diffusion constant of $1.6\times 10^4 \text{ cm}^2 \text{ s}^{-1}$ and a relatively small activation energy of 0.7 eV for Sb_n on graphite with spherical-shape clusters and an average cluster size of 2300 atoms.

A number of cluster diffusion mechanisms have been shown in the literature, most of which deal with one-dimensional and two-dimensional clusters. Among them, the evaporation and recondensation model¹³⁻¹⁵ is similar to the dynamics in the formation and dissolution of nuclei. The periphery diffusion model,^{11,12,16,17,13,18} on the other hand, deals with a cluster displacement arising from diffusion of atoms at the periphery of the cluster. The diffusion mechanism of Ir_{18} , a two-dimensional cluster of Ir, on $\text{Ir}(111)$ re-

ported by Wang and co-workers,^{11,12} gives an elegant example of periphery diffusion. The cluster has a relatively low symmetry, and its periphery diffusion is accompanied by a shape change which can be detected experimentally by field-ion microscopy (FIM). Another intriguing example of periphery diffusion was observed very recently¹⁹ for a one-dimensional Pt cluster on $\text{Pt}(110)-(1\times 2)$ by scanning tunneling microscopy, the motion of which involves the climbing of an atom at the end of the cluster chain to the top of the chain terrace, its travel along the chain, and its descent as the new head of the chain.

In addition to these models which involve sequential atom diffusion, several collective diffusion modes have also been proposed recently. For example, Wang *et al.*^{11,12} showed experimentally that diffusion of symmetrical Ir_7 and Ir_{19} occurs without any changes in shape. They inferred from this that these two clusters both move by collective gliding of all atoms. In a different example, Shi *et al.*⁶ predicted that a cluster can move effectively by a shearing motion which obviously involves two or more neighboring atoms of the cluster. More recently, a Brownian motion induced by the internal vibration of a cluster and/or vibrations of the substrate has been proposed²⁰ to explain for fast diffusion of relatively large clusters, such as the experimental results of $\text{Sb}_{2300}/\text{graphite}$.⁸

In this paper we report on an extension of the quest of knowledge regarding cluster diffusion to the examination of three-dimensional metal clusters on a metal surface. With molecular-dynamics simulations, we predict that rolling can be an effective mode of motion of spherical-like metal clusters on a metal surface.

In our molecular-dynamics simulations, we used the Johnson alloy potentials,²¹ which was deduced from the embedded-atom method,^{22,7} to describe the atomic interaction for Ni and Au. With this potential, we found that the

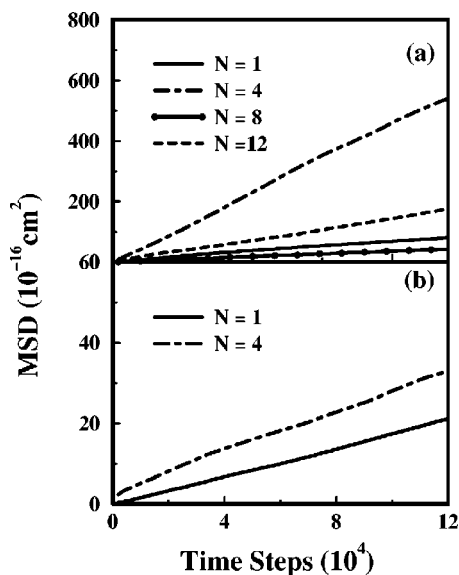


FIG. 1. The time dependence of mean-square displacement (\AA^2) for some selected clusters: (a) for diffusion along the troughs and (b) across the troughs. The presence of a linear behavior in these plots gives a valid means for the determination of a diffusion constant for each plot.

Au(110)-(1 \times 2) surface is stable until 600 K, which is in agreement with the relevant experimental results.²³ We also found that Ni clusters on Au(110)-(1 \times 2) are three dimensional at 400 K, while a one-dimensional Ni chain in the trough can be stable below 200 K. The stable phase at the lower temperature was indeed observed experimentally recently.^{24,25}

To further confirm the validity of our methodology, we have also calculated the structures of isolated Ni_n clusters with the Johnson potential. The resultant ground-state structures are very close to the results predicted by the Finnis-Sinclair (FS) potential^{26,27} and *ab initio* method.²⁸ As such, we are confident that the Johnson potential can properly describe the behaviors of Ni clusters on the Au(110)-(1 \times 2) surface.

Our simulation cell consisted of 11 atom layers of Au atoms. Each layer contained 320 atoms, except the surface layer which contained only 160 atoms due to the presence of the missing row. The atoms in the two bottom layers of the cell were kept as static to mimic the bulk of the Au crystal. Periodic boundary conditions were imposed in the lateral direction to mimic an infinite surface. The simulation temperature, which was controlled by scaling the atom velocities of the two layers immediately above the static layers,²⁹ was set to 400 K. The model temperature was thus well below the temperature of the surface roughening transition (650–700 K).²³ This temperature setting ensured that the surface structure remained stable during the simulations. Our simulations consisted of 3.6×10^6 steps (~ 40 ns) for every cluster on the surface.

For the determination of diffusion constants, mean-squared displacements (MSD's) were calculated as a function of time for each cluster. The slope of each "MSD vs time" curve gives one diffusion constant measurement. Some examples of such MSD plots are shown in Fig. 1. The results indicate that the time duration of 40 ns chosen for the

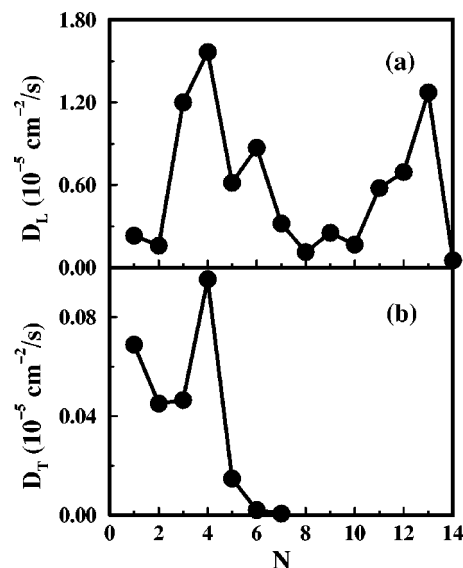


FIG. 2. Size dependence of diffusion constants for Ni clusters on the Au(110)-(1 \times 2) surface determined from the mean-square displacement plots: (a) diffusion along the missing row (upper panel) and (b) diffusion across the missing row (lower panel).

simulations was indeed long enough to ensure an acceptable statistics in the analysis of cluster diffusion.

The Au(110)-(1 \times 2) surface was chosen in the present study because the well-known missing row along the $[1\bar{1}0]$ direction leads to the presence of one-dimensional troughs on the surface²³ for us to illustrate the diffusion characteristics of small three-dimensional Ni clusters. Furthermore, Au and Ni are immiscible, which simplifies the reaction variation in the present study and increases the chance of fast diffusion. Indeed, our calculations showed that Ni_n ($n=1-14$) clusters are structurally stable on the gold surface and diffuse fast enough to be modeled with our methodology. In agreement with our expectation, the fastest diffusion modes are those with motion along the troughs. More importantly, the diffusion constants associated with such motion show a rather strong cluster-size dependence. Such a variation, which is summarized in Fig. 2(a), has a peculiar double-maximum pattern, with Ni_4 and Ni_{13} being the most agile clusters. Clearly, the cluster-size dependence is fundamentally different from the diffusion behaviors described by the evaporation-condensation model¹³ and the periphery diffusion models.^{16,17,13} As such, these two common diffusion modes for two-dimensional clusters are inappropriate for our three-dimensional Ni_n ($n=1-14$) clusters.

An examination of the diffusion trajectories simulated for the Ni_n ($n=1-14$) clusters in this study revealed that Ni_4 and Ni_{13} are the most agile clusters because cluster rolling, a cluster motion which has never been reported in the literature, is an effective mode of motion for them, and can be mixed with gliding and other modes of motion to facilitate fast cluster diffusion. In addition, both Ni_4 and Ni_{13} move collectively, with neither any internal cluster rearrangement, cluster dissociation, nor atom-exchange between the cluster and the substrate. Among all clusters studied in this work, Ni_4 and Ni_{13} are the most spherical-like ones, which correlates well with their rolling agility.

To illustrate how cluster rolling participates in the overall

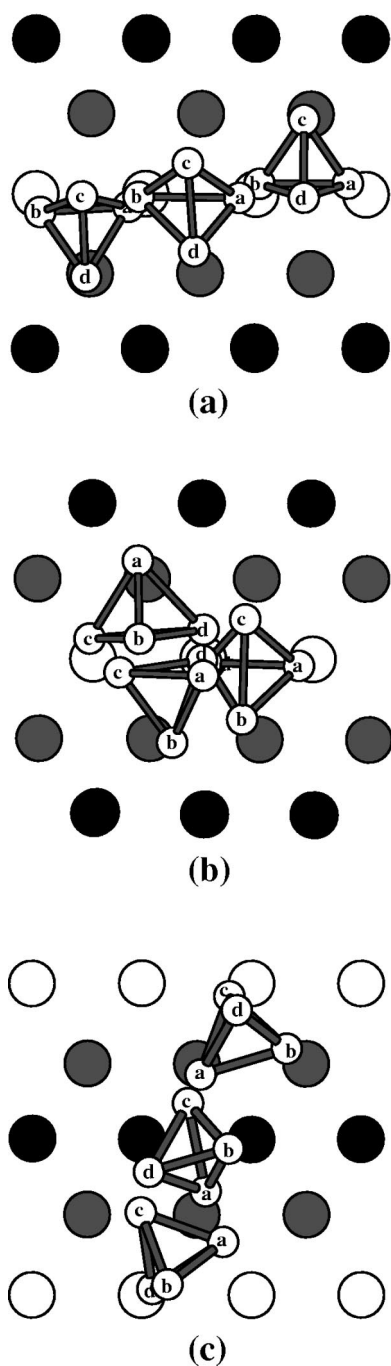


FIG. 3. Representative diffusion trajectories of a Ni_4 cluster on the $\text{Au}(110)-(1 \times 2)$ surface: (a) sliding and tipping motion of Ni_4 , (b) rolling motion of Ni_4 , and (c) diffusion of Ni_4 across the trough direction.

cluster diffusion, we plot three representative diffusion trajectories for a Ni_4 cluster on the surface in Fig. 3. In this set of pictures, the white circles are the gold atoms at the bottom of a $[1\bar{1}0]$ trough, gray circles are the atoms constituting the sidewall, and black circles are the atoms at the top. In Fig. 3(a), a diffusion trajectory is depicted by overlaying three snapshots of the motion of a cluster which moves from the left to the right at the bottom of a trough. In the first snapshot, the cluster is seen at the left, with atoms *a* and *b* resting on two gold atoms at the bottom, and atom *d* on a gold atom of the sidewall. The second snapshot records a simple sliding

motion with which all four atoms of the cluster have translated together to the right by one bond distance of gold atoms along the trough. The third snapshot records the result of a combination of cluster translation and cluster tipping motion.

Cluster rolling can be considered as an extension of the above rocking motion, which is illustrated by the diffusion trajectories shown in Fig. 3(b). In this case, three snapshots are overlapped to show the motion of a cluster from the middle right to the upper left corner. The first snapshot captures the configuration in which atoms *a* and *d* rest on two gold atoms at the bottom, and atom *c* takes the apex position. Between the first and second snapshot, the cluster has rolled to the left with atom *c* tipping downward and atom *a* rising to become the new apex. Concidentally, atom *b* has slipped by one-bond length to the left. The third snapshot records another rolling motion step with atom *a* tipping and atom *b* rising. Since a simple sliding motion such as that illustrated by the first to second snapshot in Fig. 3(a) involves the breakage of all three bonds between the substrate and atoms *a*, *b*, and *d*, and a rolling motion such as that illustrated by the second and third snapshot in Fig. 3(b) requires the breakage of only one bond (atom *b*), rolling is a fast component in the overall diffusion of Ni_4 . A quantitative comparison of the potential surfaces for different modes of motion and different cluster sizes is beyond the scope of this Brief Report and will be detailed elsewhere.

The trajectories shown in Figs. 3(a) and 3(b) illustrate that Ni_4 can climb up the sidewall of the trough while diffusing along it. In fact, Ni_4 is capable of climbing over the top of one trough to reach to the adjacent trough. Such a transverse diffusion is illustrated in Fig. 3(c). In this picture, the first snapshot records a Ni_4 cluster at the middle of the bottom of the first trough (the bottom row of white circles). Between the first and second snapshot, the cluster has rolled around atom *a* (the atom with the least movement) and reached the top of the first trough (the row of black circles in the middle of the figure). The third snapshot indicates that the cluster has descended towards the second trough (the top row of white circles) with a combination of rolling and sliding.

Since the transverse diffusion requires the raise of the cluster over the trough top, it is logical that the associated diffusion constants should be smaller than those for cluster motion along the trough. This difference is shown in Fig. 2, with the addition of the cluster-size dependence in transverse diffusion as Fig. 2(b). It is interesting that once again, Ni_4 clusters are the most agile ones among all small clusters in transverse diffusion. It is conceivable that cluster transverse diffusion may play an active role in the transformation of one-dimensional Ni chains to a two-dimensional Ni island on $\text{Au}(110)-(1 \times 2)$.²⁴

The agility of Ni_4 is reached by a combination of factors, including cluster size, mismatch between the Ni and Au lattice, structure of the Au trough, and electronic structures of the constituents in this system. However, the presence of small three-dimensional clusters and their fascinating modes of motion demonstrated in this study can also be important factors in other surface systems.

In summary, we have studied small Ni clusters diffusing on the $\text{Au}(110)-(1 \times 2)$ surface with molecular-dynamics simulations. Our results demonstrated that small three-

dimensional Ni clusters diffuse on the Au surface without dissociation, and the diffusion constants show a strong size dependence. The diffusion results cannot be explained by the conventional diffusion models for two-dimensional cluster diffusion, such as the evaporation-condensation model and the periphery diffusion model. Instead, collective diffusion of a cluster as a whole occurs, with cluster rolling as a fast motion attribute. The most spherical-like clusters, Ni_4 and Ni_{13} have been found to be the most agile clusters, once again, reinforcing the importance of rolling motion in the

diffusion behavior of small three-dimensional clusters on a solid surface.

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