On a relationship between the collective migration of surface atoms in microclusters and the saddle points on the potential energy surface

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(Dated: Nov 24, 2002)

Plenty of saddles on a multidimensional potential energy surface (PES) of two-dimensional microclusters, where atoms are interacting via Morse potential, are numerically located. The reaction paths emanating from the two types of the local minima, which represent the compact and the non-compact shape of Morse clusters, to their neighboring saddles on PES are elucidated. By associating the reaction path crossing these saddles with the atomic rearrangements, we evaluate the barrier height corresponding to various characteristic atomic motion accompanied by the floaters (i.e. surface atoms popped out of the cluster surface). Our findings are summarized as: (i) The saddle points implying the gliding motion of a single floater over the cluster surface yields extremely small values of the energy barriers regardless of the shapes of clusters. In particular, the gliding motion of a train composed of a few surface atoms also appears as the low-lying saddles. As a result, the barrier height corresponding to the simultaneous gliding motion, which is a manifestation of the reaction path crossing the higher-index saddles on PES, is significantly low. (ii) A surface rearrangement, where floaters are created or annihilated, implies relatively high barrier energy which is still accessible below melting point. (iii) On the other hand, the atomic motion, where atoms located deep inside of the clusters are rearranged as well as surface atoms, yields extremely high barrier energies. Some relations between these results and the recent experimental study of the surface cluster diffusion are also pointed out.

PACS numbers: 36.40.-c, 36.40.Mr, 36.40.Sx

One of the most remarkable dynamical features of microclusters which are experimentally and theoretically observed is that their motion is dominated by large fluctuation\[1, 2\]. The floppy motion of microclusters can be attributed to a wandering motion among many local minima which are partitioned by substantially low saddles on the multidimensional potential energy surface (PES)\[3, 4\]. In fact a PES of atomic clusters is populated by many saddles and minima even if a cluster contains at most order of $10^1$ atoms. A number of minima and saddles of microclusters are enumerated by brute force of the current computational power, while a variety of schemes to search for the saddle point is proposed. Provided that the size of cluster is enough small, it is possible to obtain nearly complete distributions of minima and saddles. An accumulation of such numerical research has been shed light into the global feature of potential landscape whose topography is considered to be a origin of the complicated and exotic nature of the glass forming material, microclusters, peptides and proteins\[5\]. If we restrict ourselves to microclusters, there exists a wide variety of characteristic atomic motion in it as well as that on a bulk surface. A representative example is motion of a floater which continues to wander among stable sites on the cluster surface. According to Cheng and Berry, the floaters are surface atoms which are popped out of the surface and keep migrating above or outside the outer layer of the cluster as shown in Fig.1\[6\]. Since the majority of constituent atoms of a cluster are located on surface, many floaters are expected to be created and annihilated throughout dynamics. Most of the previous works related to the atomic diffusion on a surface put their focus on the motion of a single surface atom. However, these floaters may interact with each other and move collectively. A collective migrating motion of floaters are expected to play an important role in the mass-transport such like an alloying behavior of the nano-sized metal clusters and an island migration on a bulk surface\[7, 8, 9\]. Indeed, the migration of atoms along the edge of a surface Ar and Ir cluster was experimentaly observed\[10, 11\]. Moreover, it was nu-
merically verified that the active surface atoms move freely and cooperatively along the cluster surface and diffuse into the inside of a cluster due to an accumulation of rearrangements of surface atoms well below the melting point[12]. On the other hand, a detailed analysis of the collective motion of surface atoms is still left untouched. The most straightforward way probing a complicated motion of surface atoms is to clarify the relationship between the characteristic motion of surface atoms in a cluster and the corresponding reaction path on a multidimensional PES[9]. The purpose of this Letter is to give a brief sketch of a relationship between characteristic motion of surface atoms in a configurational space and that on a multidimensional PES. The numerical results as mentioned below. Another reason why we select a 2D system is that the present model is a concise model of the atomic rearrangements in an island on bulk surface, if one neglects the interaction between a cluster and substrate. As the temporal motion of atoms in 2D cluster was recently observed by the field ion microscope(FIM) [13] [14], a close analysis of the present 2D model is expected to bring some insights into these experimental results as mentioned below. Another reason is that it is an illustrative and transparent example which demonstrates how cluster atoms move individually and collectively in a microcluster at a glance. In addition, most of the results obtained in the present 2D model are expected to remain unaltered in the realistic 3D model as far as the following topics are concerned. A numerical search for the saddle points which are reachable from the given local minimum is carried out in terms of the so-called eigenvector-following method[15]. The saddle points are explored by starting the searching procedure from a given local minimum on PES. More precisely, a random fluctuation is added to the atomic configurations at a local minima in order to reach every saddle point which may be randomly distributed about the given local minima. The reachable saddle points are enumerated for 10000 initial points. The intensity of random fluctuation is about 7% of the local minima. The size of the cluster is chosen to give enough number of the saddle points to extract a significant statistical trend from data. In particular, two kinds of the clusters different in shape are examined. One is a compact cluster i.e., a geometrically packed structure, which is located at a deep minimum on PES. Another is a non-compact cluster which is possessed by 4 floaters capable to move almost freely, as shown in Fig.3 and 4[16]. The presence of many floppy floaters is an indication of the fact that unpacked configurations of a cluster is located at a shallow minimum on PES. The resulting number of the numerically found 1st and 2nd order saddles of the non-compact $M_{67}$ are 89 and 656, respectively. Those for the compact $M_{67}$ are 185 and 1020, respectively.

In Fig.2 the number of the 1st and 2nd order saddles with respect to the value of the barrier height is displayed for the compact and the non-compact $M_{67}$. One can immediately notice that the non-compact cluster has more saddles lying in the low energy region both for the 1st and 2nd order index saddles. If one takes into account the presence of many floppy floaters, it is not a surprising result to appear more low-lying barriers near the local minimum representing the non-compact $M_{67}$. Indeed, as exhibited in Fig.3(a), the reaction paths crossing the extremely low-lying barrier, whose height is about 0.3\(\epsilon\), are attributed to the hopping motion of a single floater. Similarly, the bounded train of a few surface atoms is easy to glide over the cluster surface as shown in Fig.3(b) and Fig.4(g), and the barrier heights for such motion are considerably low (about 0.6\(\epsilon\) and 0.9\(\epsilon\), respectively). Since a hopping of a floater costs about 0.3\(\epsilon\), the barrier height for the gliding motion shown in Fig.3(b) and Fig.4(g) are roughly estimated as 0.6\(\epsilon\)(0.3\(\epsilon\times 2\)) and 0.9\(\epsilon\)(0.3\(\epsilon\times 3\)), respectively. The migrating motion of a bounded train composed of the surface atoms running along the edge is experimentally observed in the 2D cluster of Ir_{18} and Ir_{36}, and is a possible elementary process of the periphery diffusion, which is one of the driving factors for the motion of a 2D Ir cluster on Ir(111)[13] [14]. On the other hand, it should be noted that there appear significantly many low-lying 2nd order saddles on the PES for the non-compact $M_{67}$. In Fig.5 the atomic configurations of the typical low-lying higher-index saddle points are depicted. Those low-lying saddles reveal the simultaneous gliding motion oc-

\[ \text{Number of Saddle} \]

\[ \text{Barrier Height [eV]} \]

FIG. 2: Histograms for the number of the saddle points with respect to the value of the barrier height. The barrier energy is normalized by the depth of the pair potential \(\epsilon\). (a)The data of the 1st and 2nd order index saddles for the non-compact $M_{67}$ are shown by thick and thin line, respectively. (b)The data of the 1st and 2nd order index saddles for the compact $M_{67}$ are also shown by thick and thin line.
The barrier height is also inserted in the figure. Each atom is colored by black or gray randomly just to identify its location before and after the displacement. As demonstrated in these examples, there exits a wide variety of collective motion accompanied with surface atoms and floaters. Such collective behaviors are experimentally of interest. Considering the present Morse cluster as a model of an island on a bulk surface, the introduction of the substrate may bring the significant effect upon the values of the barrier height. However, it is pausible to expect that the hierarchy in the barrier height of the saddle points is not much altered. If so, by improving the time resolution of the experiment, the complicated simultaneous rearrangement of surface atoms illustrated above should be experimentally observed. However, the isomerization process, where atoms located deep inside of the clusters are rearranged as well as surface atoms, yields the apparently high energies barrier of saddle points as depicted in Fig.3(f) and Fig.4(l). These motions induced by a running crack are infrequent event and are expected to be hard to occur, when the temperature of the system is well below the melting point.

In summary, plenty of saddles on a multidimensional PES of the 2D Morse clusters, are numerically located in order to
clarify the relation between the characteristic motion of surface atoms with the reaction path. We evaluate the barrier height corresponding to various characteristic atomic motion for compact and non-compact $M_{67}$. Our findings are: (i) The 1st order saddles implying the lowest barrier energy is an indication of a gliding motion of a floater. In particular, a collective gliding motion of a train composed of a few surface atoms also appears as low-lying saddles on PES. As the combination of these two types of the low-lying 1st order saddles, there appear many low-lying higher-order saddles, which represent the simultaneous gliding motion of floaters especially in the non-compact cluster. Note that the usual higher order saddles do not necessarily correspond to the simultaneous gliding motions which are spatially separated on the cluster surface. (ii) Another characteristic atomic motion which implies sufficiently low barrier energy is associated with the collective behavior of surface atoms, where floaters are created or annihilated. The saddle point for such a motion lies relatively high, but is still reachable at substantially low temperature below the melting point. (iii) On the other hand, atomic displacements, where atoms located deep inside of the clusters are rearranged as well as surface atoms, yield the high-lying saddle points which are scarcely reachable below the melting temperature. From these observations, we emphasize that the motion illustrated in (i) and (ii) are expected to be observed in rearrangements of a surface cluster, provided that the time resolution of the the experimental technique is improved. The above-mentioned ingredients on the PES of a non-compact and a compact clusters lead us to the following overview about how the isomerization of a generic cluster proceeds in its dynamics substantially below the melting point: When the cluster shape becomes non-compact, floaters and the train of surface atoms actively migrate to form a resultant stable compact shape. The quiescent state of the compact cluster will last for relatively longer period until the atomic rearrangement eventually generates new floaters by climbing over the saddles which are exemplified in Fig.4(h) and (i). If there appear floaters and train of surface atoms in this way, an active surface motion again continues to alter the cluster shape to be compact. A cluster keeps changing its shape from compact to non-compact intermittently by activating and suppressing motion of the surface atoms.

Authors acknowledge Dr. T. Kobayashi and Prof. H. Yasuda for their helpful comments. One of authors (Y.S) thanks Prof. K. Hirao for his encouragement and the financial support from NEDO fellowship. The present work was partly supported by the fellowship of Kwansei Gakuin University.

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