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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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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.

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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

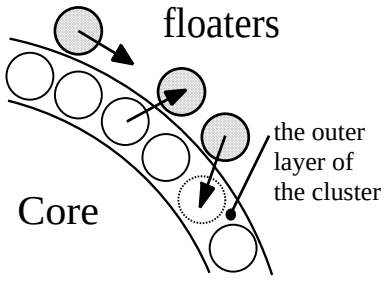

FIG. 1: A schematic picture of creation and annihilation of the floaters in the vicinity of the cluster surface. Surface atoms are denoted by white circles, while floaters are indicated by shaded circles. A vacancy is indicated by a dotted circle.

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 detail analysis of the collective motion of surface atoms are 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 by putting a special emphasis on the reaction paths connecting a local minimum and its neighboring saddles which are climbed over during an isomerization process.

We employ two-dimensional(2D) Morse model given by $U = \sum_{i<j} V(r_{ij})$, where the pair potential function V is given by $V(r) = \epsilon\{e^{-2\beta(r-r^c)} - 2e^{-\beta(r-r^c)}\}$. Note that r is the separation between two atoms. We choose $\beta = 1.3588[A^{-1}]$, $\epsilon = 0.3429[eV]$ and $r^c = 2.866[A]$, those are suitable values for copper[13]. The reasons why we select a 2D system are two folds: One 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)[10, 11], 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 mean separation of the neighboring atoms. Although no one guarantees that all of the saddle points connected to a given local minimum are completely detected by the present method, the authors confirmed that almost all trivial saddles which are noticeable by inspection are successfully found in various size and shape of Morse clusters. The present method is applied to pick up the distinct saddle points of the Morse clusters M_{67}. The size of the cluster is chosen to give enough number of the saddles 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

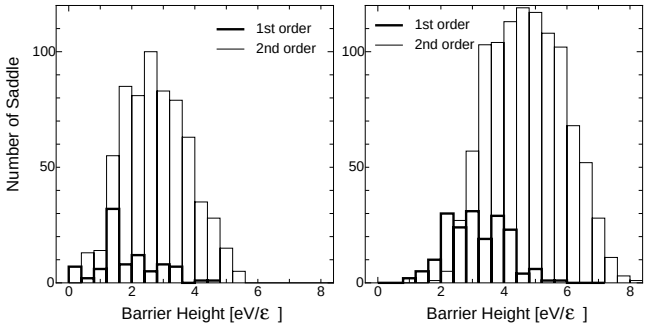

FIG. 2: Histograms for the number of the saddle points with respect to the value of the barrier height. The barrier energy is normalized by the depth of the pair potential ϵ. (a)The data of the 1st and 2nd order index saddles for the non-compact M_{67} are shown by thick and thin line, respectively. (b)The data of the 1st and 2nd order index saddles for the compact M_{67} are also shown by thick and thin line.

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 0.3ϵ, 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 Fig4(g), and the barrier heights for such motion are considerably low (about 0.6ϵ and 0.9ϵ, respectively). Since a hopping of a floater costs about 0.3ϵ, 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 $Ir(111)$[11, 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-

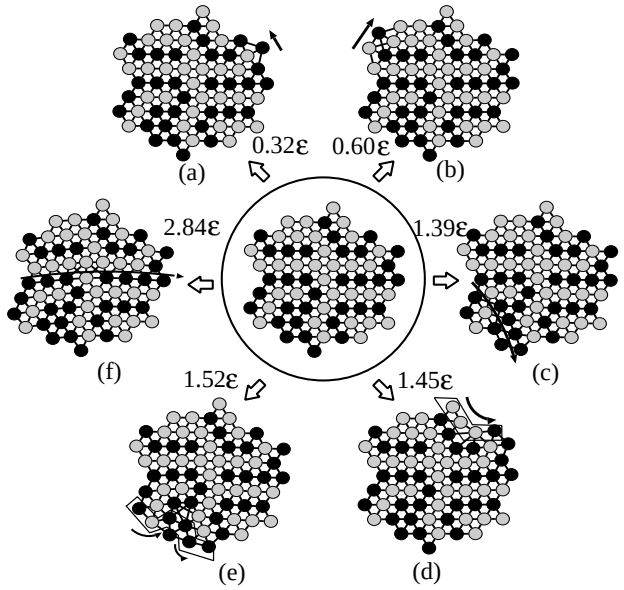

FIG. 3: Representative configurations of the cluster atoms corresponding to the saddle points for the non-compact M_{67} are exhibited by balls and sticks. Sticks are inserted between pair atoms whose separation is shorter than $1.5r^c$. In the center circle, the configuration of the non-compact M_{67} at a local minima is displayed. Typical atomic configurations of the 1st order saddle points are shown in (a)-(f). The direction of the atomic displacement from the initial local minimum to another beyond the saddle point is denoted by arrows. 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.

curring at spatially distant places on a cluster surface, whilst the generic motions yielding higher-order index saddles are not necessarily decomposed into such a *almost independent* gliding motion. In contrast, in a usual molecular reaction, the barrier of the higher-index saddles are so high that the reaction paths crossing them are neglected. As is evident from the barrier energy indicated in Fig.5, these higher-index saddles are easily accessible even if the temperature of the system is well below the melting point[17]. The presense of many low-lying higher-index saddles is a remarkable ingredient of a medium-sized cluster. If the given cluster shape located at a local minimum on PES is connected with k saddles of the low-lying 1st order index, the number of the low-lying l-th order index saddle which is decomposable into the 1st order saddle is about ${}_kC_l$, the binomial coefficient for l items selected from k. Although microclusters tend to have such low-lying higher-index saddles irrespective of the cluster shapes as shown in Fig.5, the discrepancy in Fig.2 implies that the presence of many floaters significantly reduces the barrier height implying these higher-index saddles. Moreover, it is important to note that the surface atoms other than *floaters* also play an crucial role in a surface rearrangement, where a *floater* is newly created or annihilated as demonstrated in Fig.3(c)-(e) and Fig.4(h)-(k). The barrier energies for these motions are slightly larger than those for a simple gliding motion of *floaters* or surface atoms forming a train. In the crudest approximation, the resultant barrier height is determined by the number of atoms involved by the displacement. The cost for a displacement which undergoes a single bond breaking is about 1.0ϵ, while a hopping of a floater costs about 0.3ϵ. Thus, we can estimate that the displacements in Fig.3(c), (d), and (e) cost about $1.2\epsilon(0.3\epsilon \times 4)$, $1.2\epsilon(0.3\epsilon \times 4)$ and $1.8\epsilon(0.3\epsilon \times 6)$, respectively. Similarly, the displacements given in Fig.4(h), (i),(j), and (k) demand about $2.0\epsilon(1.0\epsilon \times 2)$, $2.0\epsilon(1.0\epsilon \times 2)$, $2.8\epsilon(0.3\epsilon \times 6 + 1.0\epsilon)$, and $2.2\epsilon(0.3\epsilon \times 4 + 1.0\epsilon)$, respectively. 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[18]. If so, by improving the time resolution of the experiment, the complicated simultaneous rearrangement of surface atoms illustrated above should be experimentally observed. However,

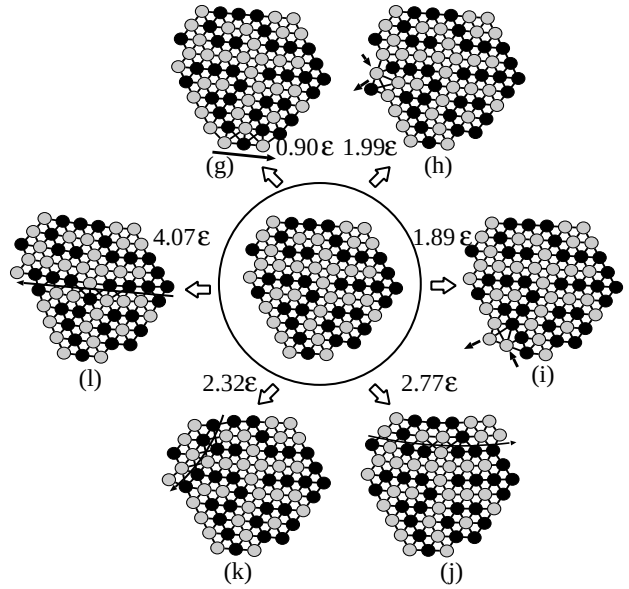

FIG. 4: Representative configurations of the cluster atoms corresponding to the 1st order saddle points for the compact M_{67} are exhibited by balls and sticks in (g)-(l).

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

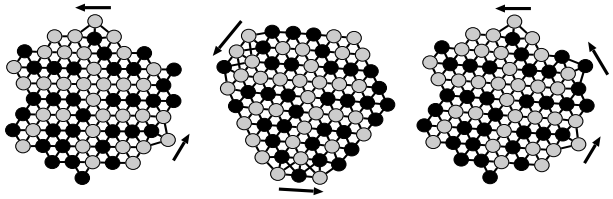

FIG. 5: Representative configurations of atoms corresponding to the higher-index saddle points for the non-compact and the compact M_{67} are exhibited by balls and sticks. (m) and (o) reveal the 2nd and 3rd order saddles of the non-compact M_{67}, respectively. (n)is a manifestation of the 2nd order saddle of the compact M_{67}.

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 highder order saddles do not neccessarily 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.

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[16] In the present 2D model, we employ the term *'floater'* in a rather restrictive sense for clarity. That is, a *floater* is defined as a surface atom which has less than 3 neighbors. Thus, the atoms attached two sticks in figures are floaters.
[17] The melting point of M_{67} is about 670K(0.168ϵ), which is numerically determined by locating an abrupt jump in the caloric curve.
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