Cluster on the fcc(111) surface: structure, stability and diffusion

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Abstract

The static and dynamical properties of a highly symmetric cluster on a fcc(111) surface are studied using the molecular-dynamics method. We find that the cluster can only be stable on the surface up to a certain temperature much lower than the melting temperature of the corresponding isolated cluster; the surface can strongly change the thermal properties of the cluster. The fast diffusion of the cluster is attributed to the rolling of cluster as a whole on the surface, and the dependence of diffusion constants on the structural mismatch is also studied. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the past decade, cluster science is one of the important fields for physicists, chemists and material scientists. Much research effort has been devoted to the studies of the physical and chemical properties of isolated clusters. It has been found that clusters can display a variety of so-called finite size effects. Recently, intensive research effort is moved to the design and fabrication of the materials which are assembled from clusters [1–9], because such materials could exhibit many interesting and useful physical properties. For example, the close-packed planar arrays of gold clusters can display the Coulomb charging behavior [1]. The experimental work for the cluster supported on surface stimulates further theoretical study and computer simulation.

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There have been several computer simulations about the structure and stability of clusters supported on surface. Blaisten-Barojas et al. studied the thermal behavior of a Lennard-Jones (LJ) cluster on a continuous surface [10]. The structure and stability of (C_60)_n clusters on surface have also been investigated by using the modified LJ potential [11–14]. However, in those studies where the atomic structure of the surface was treated as a rigid and structureless continuous plane, we have shown that this simplification could be questionable [15]. Using the molecular-dynamics (MD) simulation, several authors studied the structure and stability of a cluster as it approaching to a surface for specific materials [16–21]. Based on first-principle calculations, Hakkinen and Manninen found that the stability of the magic Na_8 cluster is strongly dependent on the surface [22]. All these studies showed that the surface can play an important role in the structure and stability of clusters.
The other important issue concerning cluster-surface system is clusters diffusion on surfaces [23–42]. Most of the recent theoretical studies [26–34] have focused on the two-dimensional cluster epitaxially oriented on the surface, and found very low diffusion coefficients with order $10^{-17}$ cm$^2$ s$^{-1}$. This kind of diffusion is related to the single-atom [26–32] or dislocation mechanisms [33,34]. In contrast, recently Bardotti et al. [35,36] have shown experimentally that large (a hundred to a few thousand atoms) three-dimensional clusters, even a microcrystal, can have a high diffusion coefficient at room temperature. This work is reminiscent of early work [37–41]. Theoretical [42] and experimental [37–41] work suggested that the fast diffusion of the larger three-dimensional cluster may be attributed to the translation motion of the cluster as a whole. It is also found that, during the motion, cluster may rotate as entities on the surface. The translation and rotation as entities for energy, with particular emphasis on the cluster and the surface, behavior for an icosahedral (I).

2. Calculation details

In this paper, we study the structure and thermal behavior for an icosahedral ($I_{13}$) 13-atom cluster on fcc(111) surface, with particular emphasis on the general properties for the cluster being stable on the surface. The calculations are performed on the surface consisting of five layers of atoms, in which each layer contains 100 atoms. The atoms in the bottom two layers are kept fixed to mimic the semi-infinite solid, all the rest are allowed to move. The periodic boundary conditions are imposed in the directions parallel to the surface. Temperature is controlled by scaling the velocity of atoms in the third layer. To see the influence of the system size on the results, we have repeated a few calculations on a larger surface, which consists of six layers of atoms and each layer contains 256 atoms. The calculations show that the system size does not change the results significantly.

The atoms in the cluster and surface interact through LJ type potentials. Empirical potential of this type, originally developed for describing the inert gases, is now commonly used to model the general properties of condensed systems [42]. In the present simulation, the interatomic LJ potential $\phi$ reads:

$$\phi_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{r_{ij}}{\sigma_{ij}}\right)^{12} - \left(\frac{r_{ij}}{\sigma_{ij}}\right)^{6}\right].$$  

where $i$ and $j$ denote the atom $A$ in the cluster and the atom $B$ on the surface, respectively. Reduced units are used in this paper, that is, $\sigma$ for length, $\epsilon$ for energy, $m = (m_A\sigma^2/\epsilon)^{1/2}$ for mass, and $T = k_B T' / \epsilon$ for the temperature, where $k_B$ is the Boltzmann constant and $m$ is the mass of atoms. The reduced unit for the diffusion constants is $\sigma/\sqrt{\epsilon}$. In all of calculations, we assume $\epsilon_{AB} = 1.0$, $\sigma_{AA} = \sigma_{BB} = \sigma_{AB}$, and $\epsilon_{AA} = \epsilon_{BB} = 1.0$. The potential cuts off at $r_c = 2.5 \sigma_{AB}$. Our simulation uses the standard constant-energy MD technique. The equations of motion are integrated using the Verlet method [43].

To quantitatively characterize structural changes, we calculate the deformation energy of the cluster, $E_{de}$, which is defined by

$$E_{de} = E_{de}^{I_{13}} - E_{de}^{I_{13}} = E_{de}^{I_{13}} - E_{de}^{I_{13}} + E_{de}^{I_{13}} - E_{de}^{I_{13}}.$$

where $E_{de}^{I_{13}}$ is the total energy of the isolated $I_{13}$ cluster, $E_{de}^{I_{13}}$ is the total energy of the cluster when it is on the surface. The interaction energy between the cluster and the surface, $E_{int}$, is also defined by

$$E_{int} = \sum_{i=1}^{N_{cl}} \sum_{j=1}^{N_{surf}} \phi_{AB}(r_{ij}).$$


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The motion of the cluster as a whole has been investigated by calculating the diffusion constant \( D \), which is obtained from the mean-square-displacement of the mass center

\[
\langle R^2(t) \rangle = \langle (t + t_0) - \langle t_0 \rangle \rangle .
\]  

Using the Einstein relation, we can obtain the diffusion constant for the cluster

\[
D = \lim_{t \to \infty} \frac{\langle R^2(t) \rangle}{4t},
\]  

where \( R(t) \) is the coordinate of the mass center of the cluster.

Typically, the length of the simulation time used to calculate thermal properties and diffusion constant are ca. 5 \( \times \) 10\(^6\) and 2 \( \times \) 10\(^5\) MD steps, respectively.

3. Results and discussion

3.1. Structural properties

In contrast to an atom on the surface in which the structure is essentially determined by the position of the adatom, a cluster on the surface may have a complicated structure, since the orientation of the cluster to the surface may play an important role as the cluster approaching to the surface. The importance of structure orientation has been observed in the previous study on clusters [15, 44–46]. To determine the structure of the cluster on surface, we have chosen several initial configurations with different orientations to the surface. By performing the steepest-decent, two different structures, with the cluster slightly deformed, are obtained for \( e_{AB} = 1.0 \) and \( \sigma_{AA} = 1.0 \). In the first obtained structure (labeled as A), one of the 20 triangle faces of the cluster is parallel to the surface, and the three bottom atoms of the cluster are at hcp sites of the surface. In another structure (labeled as B), there are also three atoms at the interface, which occupy three fcc sites of the surface. But the bottom face of the cluster is tilted to the surface, instead of parallel to the surface. The structure B is similar to what obtained for the same cluster on fcc(100) surface [15].

We take structure A as an example to study the influence of different \( e_{AB} \) and \( \sigma_{AA} \) on the cluster. For each \( e_{AB} = 0.5, 0.65, 0.8, 1.0 \) and 1.2, \( \sigma_{AA} \) is changed from 0.6 to 1.4. We find that the cluster can be supported on the surface for all the studied \( e_{AB} \) and \( \sigma_{AA} \) although the deformation can be existed. In Fig. 1, we show the deformation energy \( E_d \) as a function of \( \sigma_{AA} \) for several \( e_{AB} \). It is easy to understand that, the smaller \( e_{AB} \) is, the smaller \( E_d \) is. As \( e_{AB} = 0.5 \), the deformation energy is only ca. 0.2% of the total energy of cluster, but for \( e_{AB} = 1.2 \), \( E_d \) reaches 4% of the total energy of the cluster. The behavior of the deformation energy changing with \( \sigma_{AA} \) is similar for different \( e_{AB} \). For all \( e_{AB} \), \( E_d \) has a minimum ca. \( \sigma_{AA} = 1.0 \), and a maximum at \( \sigma_{AA} = 0.7 \) can clearly observed. For \( \sigma_{AA} \) ca. 1.0, the structure of cluster can well match fcc(111) surface. The bottom triangle face of the cluster can be at the ideal fcc position. So the stress in the interface is very small, which leads to small deformation on the cluster. Whatever \( \sigma_{AA} \) is departing from 1.0, the stress in the interface will increase, which will result in a larger deformation. When \( \sigma_{AA} \) decreases to ca. 0.7, the bottom triangle face of undistorted cluster has difficulty in finding a suitable position. The three bottom atoms of the cluster cannot sit at either the hcp or fcc sites simultaneously. It is not favorable on energy consumption, so the large deformation is expected for
\( \sigma_{AA} = 0.7 \). With \( \sigma_{AA} < 0.7 \), the cluster could match the surface with one bottom atom at the hcp site and other two at the fcc site, so the deformation decreases again. The deformation of the cluster is evidently different on both sides of the commensurate (\( \sigma_{AA} = 1.0 \)). As \( \sigma_{AA} \leq 1.0, E_i \) is larger than that for \( \sigma_{AA} > 1.0 \). For smaller \( \epsilon_{AB} \), \( E_i \) will reach another maximum at \( \sigma_{AA} \) ca. 1.3. These results indicate that the shape of \( E_i \) changing with \( \sigma_{AA} \) is weakly dependent on \( \epsilon_{AB} \).

In Fig. 2, we present the interaction energy \( E_i \) as a function of \( \sigma_{AA} \). For comparison, \( E_i \) has been renormalized by \( \epsilon_{AB} \). For small \( \epsilon_{AB} \) (~0.5), \( E_i \) almost decreases linearly with the increasing of \( \sigma_{AA} \). For large \( \epsilon_{AB} \) (~0.8, 1.2), the shape of \( E_i \) is similar to that for smaller \( \epsilon_{AB} \) (~0.5) as \( \sigma_{AA} > 0.8 \), but \( E_i \) has significantly decreases ca. \( \sigma_{AA} = 0.7 \) with respect to the linear-like behavior of small \( \epsilon_{AB} \) (~0.5). The different behavior of \( E_i \) for different \( \epsilon_{AB} \) could be attributed to large deformation at \( \sigma_{AA} \) ca. 0.7 for large \( \epsilon_{AB} \) which results in a sudden decrease of \( E_i \).

### 3.2. Thermal stability

To investigate the thermal stability of the cluster on the surface, we choose \( \epsilon_{AB} = 0.5, 0.8 \) and 1.0, and for each \( \epsilon_{AB} , \sigma_{AA} \) is changed from 0.5 to 1.2.

Fig. 3 shows the interaction energy \( E_i \) (right scale) and the distance \( d \) between the mass center of the cluster to the surface (left scale) as a function of temperature. We find that, at the temperature \( T_c = 0.07, E_i \) and \( d \) suddenly change. The significant decreasing of \( E_i \) indicates that the interface between the cluster and surface becomes large, and the sudden decrease of \( d \) indicates the collapse of the cluster. These results imply that the structure of cluster has been changed above \( T_c \). Visual observation demonstrates that, at the temperature lower than \( T_c \), the cluster almost maintains its structural character, at the temperature above \( T_c \), the cluster begins to collapse. Upon heating, the cluster collapses step by step. Fig. 4 shows some snapshots of the cluster on surface during this heating process. Up to \( T = 0.07 \) (Fig. 4a), the cluster exhibits no more than slight deformation with respect to the structure of the cluster on the surface at \( T = 0.08 \), it has collapsed (Fig. 4b) on the surface. Upon heating to \( T = 0.11 \), the cluster collapses further (Fig. 4c). It is necessary to point out that, if we heat the system further, we have not found the liquid-like phase in the cluster before it totally spreads out on the surface. Similar behavior has been observed for all the studied \( \epsilon_{AB} \) and \( \sigma_{AA} \).

We note that the present results are different from the previous results, in which the cluster was found to be stable on the surface up to very high temperature, even higher than the melting temperature of the free 13-atom LJ cluster [10]. Since the energy transfer and the vibrational coupling almost decreases linearly with the increasing of \( \epsilon_{AB} \), and the distance \( d \) between the cluster and surface becomes large, and the sudden decreasing of \( E_i \) and \( d \) indicate that the cluster has collapsed.

Fig. 3. The distance \( d \) of the cluster center to the surface and the interaction energy \( E_i \) as a function of temperature with \( \epsilon_{AB} = 0.8, \sigma_{AA} = 1.0 \). At \( T = 0.07 \), the sudden changes of \( E_i \) and \( d \) indicate that the cluster has collapsed.
Fig. 5. The critical temperature $T_c$ as a function of $s_{AA}$ for several $e_{AB}$. The cluster with smaller $s_{AA}$ tends to be stable on surfaces with higher temperatures.

results in the greater interaction between the cluster and the surface, which is why $T_c$ increases with the decrease of $s_{AA}$ for the same $e_{AB}$. Additionally, the cluster with smaller atoms (small $s_{AA}$) is more hard than that with larger atoms, since the bulk modulus [47] of the cluster is proportional to $1/s_{AA}^3$. This may be another reason for the higher $T_c$ values with larger $s_{AA}$ values.

Comparing our previous study about the cluster on the fcc(100) surface [15], we find that $T_c$ for the cluster on fcc(100) surface is much lower than that on the fcc(111) surface. This is understandable since the cluster on the fcc(100) surface has a stronger interaction than that for the cluster on the fcc(111) surface for the same $e_{AB}$.

3.3. Diffusion of the cluster on the surface

To study the diffusive behavior of the cluster on the surface, we choose $e_{AB}=0.5$ and $s_{AA}=0.6-1.4$. The simulations are carried out at $T=0.12$. At $T<T_c$ running after $2 \times 10^5$ steps, the structure of the cluster remains unchanged and does not wet on the surface. Visual observation shows that the diffusion inside the cluster or on the cluster surface is inhibited at this temperature. These results suggest that the cluster diffuses as a whole rather than by a single atom jump or dislocation mechanism.

Fig 6 shows the obtained diffusion constants changing with $s_{AA}$, in which the dashed line indicates the diffusion constant of an adatom on the surface with $e_{AB}=0.5$ at $T=0.12$. From the figure,
we can see that, the diffusion of the cluster is very fast, and is comparable to that of an adatom. The diffusion constant reaches a minimum ca. $\sigma_{AA}=1.0$, and reaches a maxima symmetrically on both sides ca. 1.0, but the diffusion constants are not exactly the same on both sides. Different from previous results [42], the cluster with atoms smaller than the surface atoms tends to move more quickly.

The interface stress between the cluster and surface is the key to understanding the dependence of diffusion constants on $\sigma_{AA}$. As we have discussed in Section 3, wherever $\sigma_{AA}$ deviates from 1.0, the mismatch between the cluster and the surface will increase. As the mismatch occurs there must exist stress between the cluster and surface. The stress will reduce the binding between the cluster and the surface comparing to the well-matched case ($\sigma_{AA}=1.0$) and correspondingly, the diffusion barrier will reduce. From Fig. 1, we can see that the high mismatch case is $\sigma_{AA}$ ca. 0.7 and 1.3 ($\epsilon_{AB}=0.5$ only), and this is why the diffusion constant reaches the maxima ca. $\sigma_{AA}=0.7$ and 1.3, and reaches a minimum ca. $\sigma_{AA}=1.0$.

We find that the motion of the cluster in our case is dominantly due to the rolling of the cluster. We define $\Delta H = z_i - z_0$ as the height of a cluster atom relative to the mass center of the cluster, where $z_i$ and $z_0$ are the coordinates normal to the surface for the cluster atom and mass center of the cluster, respectively. Fig. 7 shows $\Delta H$ changing with time step, the changes of $\Delta H$ from negative to positive suggest the cluster is rolling. If the cluster translates or rotates on the surface, the height should almost remain constant. To further illustrate the rolling process, Fig. 8 shows a snapshot of the rolling processor. The changes of the atom position relative to the surface (see the white atoms, for example) indicates the rolling of the cluster. If the cluster diffuses by translation or rotation, this triangle of white atoms should be parallel to the surface at all times. To our knowledge, this new mechanism presented for
energy of 0.43 and a prefactor $D_0$ of 0.066. The obtained activation energy is only slightly larger than that for adatom ($\sim 0.28$, $e_{AB} = 1.0$ and $s_{AA} = 1.0$).

4. Summary

In this paper, we have studied the structure, thermal stability and diffusion of a highly symmetric cluster on fcc(111) surface. We find that the surface tends to deform the structure of the supported cluster, however, the cluster can easily be stable on the surface without losing its structural characters with different $e_{AB}$ and large structural mismatch. The relationship between the stability of the cluster and the surface properties is obtained. We find that the supported cluster is only stable under a certain temperature $T_c$, which is much lower than the melting point of the free cluster. The dependence of $T_c$ on $s_{AA}$ and $e_{AB}$ is also obtained. Instead of a single atom jump and dislocation mechanism, we find that the cluster can move very fast as a whole on the surface and the fast diffusion is dominantly due to the rolling of the cluster, which has a small activation energy. The close relationship between the diffusion constants and $s_{AA}$ is also obtained.

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