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The structure and stability of clusters on surfaces

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Abstract. The structure and the stability of clusters on surfaces are simulated by using the constant-energy molecular-dynamics method. The necessary condition for a cluster to be supportable on a surface is studied. It is found that the lattice mismatch has a strong effect on the stability of clusters on surfaces; the structures obtained are surface dependent. The thermal stability of the supported clusters on surfaces is also investigated.

1. Introduction

In the last few decades, cluster science has been an important field for physicists, chemists and materials scientists. Much research effort has been devoted to studies of the physical and the chemical properties of isolated clusters. Recent studies on the structure and stability of clusters on surfaces are becoming of considerable interest. On one hand, they might be closely related to the applications of clusters, such as in synthesizing cluster-assembled material [1, 2] and surface growth [3–7]. On the other hand, most experiments on the structure and the stability of clusters have been carried out on surfaces. So studies of clusters on surfaces have great physical and technical importance. Some experiments [8, 9] have shown that the surface may play an important role in determining the structure and the stability of clusters. In a recent experiment [10] involving Au and Ag clusters supported on a tungsten tip, the melting point of the clusters was found to be a constant value when the diameter of the clusters was less than 2 nm; some authors [11] have suggested that this may be attributed to the strong interaction between the clusters and the surfaces.

A few phenomenological models have been proposed to account for the properties of clusters on surfaces. In almost all of the studies [12, 13], the role of the surface was considered by modifying the Wulff [14] construction, changing the free energy of the contact plane by adding a component to the free energy of adhesion. The shape of the cluster is obtained by minimizing the free energy. Although this might be correct for large clusters, it is doubtful whether such simple models can give valid results for small clusters with number of atoms $N \leqslant 10^2$.

In fact, it is very useful to obtain a microscopic description of the structure and stability of clusters interacting with surfaces. The molecular-dynamics (MD) method is regarded as the standard tool for the study of the structure of complicated systems. Within the current capability of computers, first-principles molecular dynamics methods, in which the electrons and ions are taken into account simultaneously, are not really applicable to systems containing a few hundred atoms—also in view of the long simulation runs. Consequently, one has to restore an interatomic force model for some complicated systems, such as clusters

on surfaces. Some work along these lines has been presented in the literature. For instance, Antonelli *et al* [11] have studied the thermal stability of Be_{55} on the Be(0001) surface. Luedtke and Landman [15] have investigated the process of collapse of small gold particles on Ni and Au surfaces at elevated temperatures by means of MD simulation, and they have found that the structure collapses via a dislocation-mediated setting mechanism. Blaisten-Barojas *et al* [16] have studied the melting behaviour of a Lennard-Jones (LJ) cluster on a structureless surface; in fact, as shown below, the structure of a surface can play an important role as regards the stability of clusters. Now, in experiments one can put small clusters on surfaces—e.g. Ag_n on a Pt surface [17]. A Si_{10} cluster supported on an Au(001) surface has also been observed, using a scanning tunnelling microscope [18]. In a recent theoretical study of magic clusters on surfaces using the first-principles method [19], it was shown that the stability of a magic Na_8 cluster is strongly dependent on the surface. However, up to now, some questions have remained open—for instance, those of under what conditions a cluster can be stable on a surface, and how the surface changes the structure of the cluster when the cluster lands softly on the surface. These are the points that we are aiming to study in the present paper.

In the rest of this paper, we present the calculation details in section 2, and section 3 gives the main results. Section 4 includes some discussion and a very brief summary.

2. Calculation details

By means of a constant-energy MD simulation, we have studied two clusters with different symmetries on surfaces. The first one has icosahedral structure, and contains 13 atoms (an I_h cluster). The second one has the same number of atoms, but has octahedral symmetry (an O_h cluster). Since we are interested in general results for clusters on surfaces, rather than the properties of any specific material, the LJ potential is adopted to describe the interatomic interaction. Extensive comparisons with physically better justified many-body potentials have demonstrated that this simple potential represents face-centred-cubic metals remarkably well [20]. In our present simulation, the LJ potential ϕ reads

$$\phi_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right]. \tag{1}$$

Here α and β donate the atom A in the clusters and the atom B in the surfaces, respectively. Reduced units are used in this calculation, namely σ for length, ε for energy, $\tau = (m\sigma^2/\varepsilon)^{1/2}$ for time, and $T^\star = KT/\varepsilon$ for temperature, where K is the Boltzmann constant and m is the mass of the atoms. In all of the calculations, we assume $\sigma_{BB} = 1.0$, $\sigma_{AB} = \frac{1}{2}(\sigma_{AA} + \sigma_{BB})$ and $\varepsilon_{AA} = \varepsilon_{BB} = 1.0$. The interaction cuts off at $r_c = 2.5\sigma_{\alpha\beta}$. The surface consists of five layers of atoms, and each layer contains 100 atoms and 88 atoms for the fcc(100) surface and the fcc(110) surface, respectively; the atoms in the top two layers are allowed to move, while the rest are kept rigid to simulate the semi-infinite solid. Furthermore, periodic boundary conditions are imposed in the directions parallel to the surface. The temperature is controlled by scaling the velocity of the atoms in the second layer. The structure and stability of clusters on surfaces are studied for different values of ε_{AB} and σ_{AA}. To quantitatively characterize the structural changes, we have calculated the deformation energy of a cluster, E_d, which is defined by

$$E_d = E_{13}^d - E_{13}^0$$

where E_{13}^0 is the total energy of a free I_h cluster, and E_{13}^d denotes the total energy of a cluster when it is on a surface. The energy of the interaction between the clusters and

surfaces, E_i, is also calculated, from

$$E_i = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \phi_{AB}(r_{ij}).$$

We use E_d^c and E_i^c to denote the deformation energy and interaction energy when the cluster collapses. The initial configurations are constructed by placing a cluster above a surface at a large distance. Using the steepest-descent method, we can obtain the structures for clusters on surfaces. The structures obtained may not be energetically favoured structures at finite temperatures. After determining the structures at $T = 0$ K, we also studied the thermal behaviour of clusters on surfaces.

3. Results

First, we have studied the stability of free I_h and O_h clusters. The I_h cluster is the stable magic cluster for the LJ potential, whose cohesive energy is 43.05. It is also thermodynamically stable; it becomes unstable upon heating up to $T = 0.27$ [21]. The O_h cluster has the smaller cohesive energy 39.60, and we find that, at very low temperature, it will become icosahedral-like. But the O_h cluster cannot be transformed into an I_h cluster at 0 K by the steepest-descent method, which indicates that there is an energy barrier between the I_h cluster and the O_h cluster, although it should be very small.
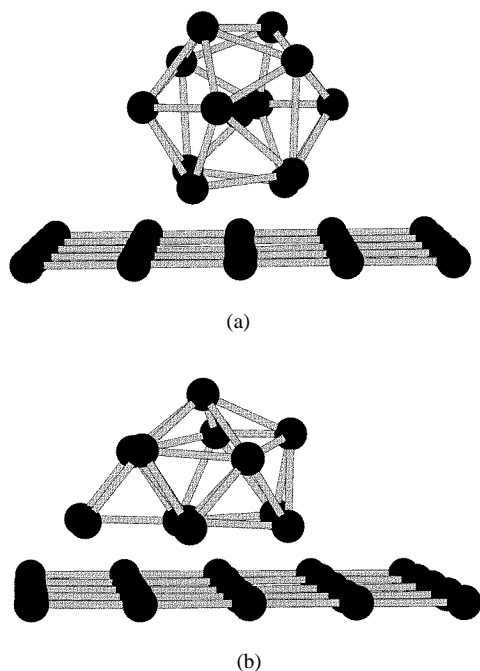

(a)

(b)

Figure 1. Equilibrium structures of the I_h cluster on an fcc(100) surface with $\varepsilon_{AB} = 0.5$ (a) and 1.0 (b).

We have performed calculations for $\varepsilon_{AB} = 0.4$–1.25, with $\sigma_{AA} = 1.0$. We find that the final structures for I_h and O_h clusters on surfaces are similar for small ε_{AB}. In figures 1 and 2, we show the structures for I_h and O_h clusters on surfaces with $\varepsilon_{AB} = 0.5$ and 1.0. Comparing

Table 1. The structures of clusters on surfaces for different values of ε_{AB} ($\sigma_{AA} = \sigma_{BB} = 1.0$). The distorted I_h structure (d-I_h) is shown in figure 1(a), and the distorted I_h^* structure (d-I_h^*) is shown in figure 10—see later.

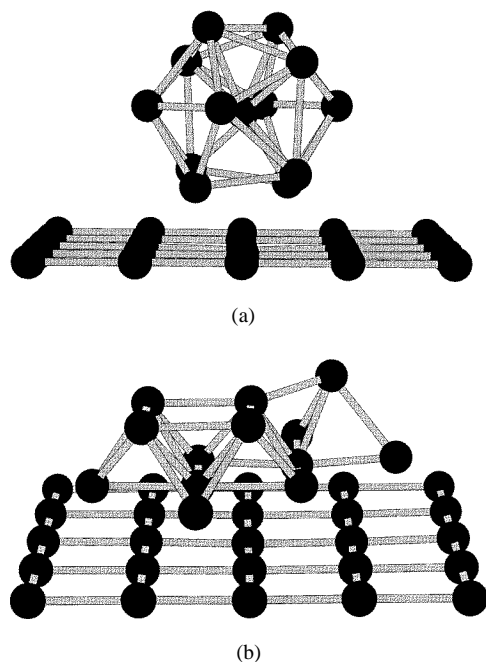| The fcc(100) surface				
$\varepsilon_{AB} =$	0.5	0.8	1.0	1.2
I_h cluster	d-I_h	d-I_h	Collapse	Collapse
O_h cluster	d-I_h	d-I_h	Collapse	Collapse
The fcc(110) surface				
$\varepsilon_{AB} =$	0.5	0.8	1.0	1.2
I_h cluster	d-I_h^*	Collapse	Collapse	Collapse
O_h cluster	d-I_h	Collapse	Collapse	Collapse

(a)

(b)

Figure 2. Equilibrium structures of the O_h cluster on an fcc(100) surface with $\varepsilon_{AB} = 0.5$ (a) and 1.0 (b).

figure 1(a) with figure 2(a), for which $\varepsilon_{AB} = 0.5$, we can see that the two structures are similar, where both of the supported clusters have distorted icosahedral symmetry. Detailed calculations verify that the two structures obtained are the same. This indicates that the O_h cluster has been transformed into the more stable I_h cluster on interaction with the surface. Since the O_h cluster has the same symmetry as the fcc crystal, it is expected that the O_h cluster will be more stable on an fcc(100) surface than the I_h cluster. The change in the symmetry may be attributed to the low stability of the O_h cluster, whose structure can be easily changed by interaction between the cluster and the surface. In addition, to see whether the supported structures are dependent on initial configurations or not, we have chosen several initial configurations with different orientations of the cluster to the surface; the structures obtained are found to be the same. Therefore the dependence of the structure

obtained on the initial orientation should be very weak. The structures for $\varepsilon_{AB} \leqslant 0.95$ are similar to those for $\varepsilon_{AB} = 0.5$, and the change from O_h to I_h symmetry is also observed. The supported structures for $\varepsilon_{AB} \leqslant 0.95$ and the structures for $\varepsilon_{AB} \geqslant 1.0$ are quite different— the initial structures no longer exist. Figure 1(b) shows the structure for an I_h cluster on a surface with $\varepsilon_{AB} = 1.0$; the initial icosahedral symmetry has been completely destroyed, and only a pentagon can be observed. Also, if one starts from an O_h cluster, the collapsed structure is very like a fragment of fcc solid (figure 2(b)). These collapsed structures depend on the initial configurations; that is, different initial configurations will lead to different final structures. However, the collapsed structures are similar in the interface; the interfacial layer (layer 1 of the cluster) forms an fcc(100) surface structure for both I_h and O_h clusters on surfaces. The structural changes for a few ε_{AB}-values are summarized in the first part of table 1.
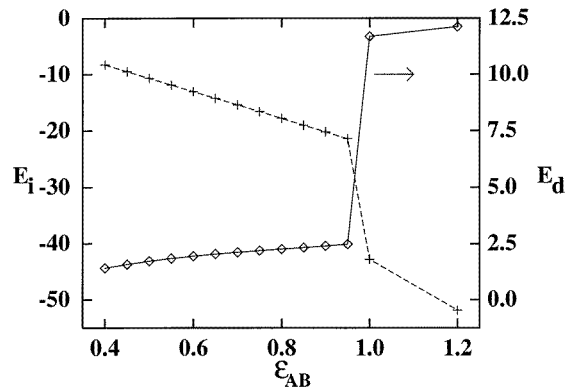

Figure 3. The deformation energy, E_d, and the interaction energy, E_i, as functions of ε_{AB} for an I_h cluster on an fcc(100) surface.

To quantitatively describe the structural changes with ε_{AB}, we have calculated the interaction energy E_i and the deformation energy E_d. The results are shown in figure 3. As ε_{AB} is less than 0.95, the deformation energy of the cluster is small and increases linearly with ε_{AB}. The cluster can be supported on the surface. When ε_{AB} is around 1.0, the deformation energy of the cluster suddenly increases, which indicates that the collapse process is occurring. Similarly, when ε_{AB} is smaller than 0.95, E_i decreases almost linearly with ε_{AB}. Also E_i significantly decreases when the structure collapses. According to the previous definitions of E_i^c and E_d^c, from the figure we can obtain values of E_i^c and E_d^c of 20.0 and 2.5 respectively.

To see the effect of lattice mismatch on the stability of clusters on surfaces, we have also studied the case where $\sigma_{AA} \neq \sigma_{BB}$. It is easy to understand that the smaller σ_{AA}, the larger the energy of interaction between the cluster and the surface, and the lattice mismatch can deform the cluster by driving the lateral displacement of atoms near the interface. So the collapse process may take place with changes of σ_{AA}. For $\varepsilon_{AB} = 0.4$–1.25, we have studied the structural changes with different values of σ_{AA}. In table 2 the results for $\varepsilon_{AB} = 0.8$ are summarized. From the table, we can see that when $\sigma_{AA} = 0.9$ the structures of both O_h and I_h clusters collapse. The clusters become very flat at $\sigma_{AA} = 0.8$, and are octahedral-like. When σ_{AA} is larger than 1.0, the cluster can be supported on the surface. The changes of the cluster structure due to the lattice mismatch are dramatic. For $\sigma_{AA} = 0.8$, the large lattice mismatch makes the I_h cluster unstable, and it is transformed into a flat O_h cluster
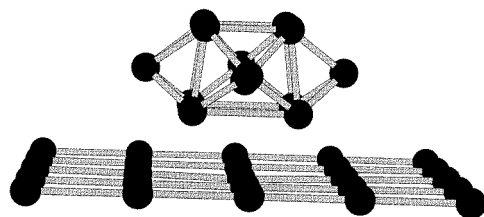
Figure 4. The equilibrium structure of the I_h cluster on an fcc(100) surface with $\sigma_{AA} = 0.8$.

Table 2. The structures of clusters on surfaces for different values of σ_{AA} ($\varepsilon_{AB} = 0.8$). The d-I_h structure is shown in figure 1(a), the d-I_h^* structure is shown in figure 10 (see later), and the d-O_h structure is shown in figure 4.

The fcc(100) surface					
$\sigma_{AA} =$	0.8	0.9	1.0	1.1	1.2
I_h cluster	d-O_h	Collapse	d-I_h	d-I_h	d-I_h
O_h cluster	d-O_h	Collapse	d-I_h	d-I_h	d-I_h
The fcc(110) surface					
$\sigma_{AA} =$	0.8	0.9	1.0	1.1	1.2
I_h cluster	d-I_h^*	Collapse	Collapse	d-I_h	d-I_h
O_h cluster	Collapse	Collapse	Collapse	Collapse	Collapse

(figure 4), whose interface forms a shrunken fcc(100) structure. For $\sigma_{AA} = 0.9$, the interface becomes complicated; it can be considered as a distorted fcc(100) structure. For large σ_{AA}, the O_h cluster will be transformed into an I_h cluster and supported on the surface. These supported structures are similar to what is shown in figure 1(a), and these structures seem to be weakly dependent on the initial configuration.
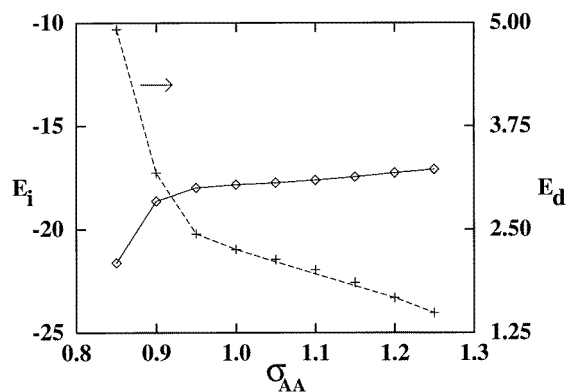

Figure 5. The deformation energy E_d and the interaction energy E_i as functions of σ_{AA} with $\varepsilon_{AB} = 0.8$ for the I_h cluster on an fcc(100) surface.

In figure 5 we present the interaction energy and deformation energy as functions of σ_{AA} with $\varepsilon_{AB} = 0.8$ for the I_h cluster. From this figure, we find that, when σ_{AA} is changed from 1.25 to 0.95, E_d increases by about 1.0. When σ_{AA} reaches about 0.95, E_d exhibits a sudden increase, which indicates structural changes. The energy of interaction E_i between

the cluster and the surface decreases by about 0.9 when σ_{AA} is changed from 1.25 to 0.95. Like E_d, E_i also exhibits a sudden decrease at $\sigma_{AA} = 0.95$. For $\sigma_{AA} = 0.95$–1.25, since the changes of E_i and E_d are almost the same, the total potential energy remains almost unchanged. However, after the structure changes, the decrease of E_i is significantly larger than the increase of E_d. So we can see that for $\varepsilon_{AB} = 0.8$ the smallest value of σ_{AA} (called σ_{AA}^c) for an I_h cluster supported on a surface is 0.95.
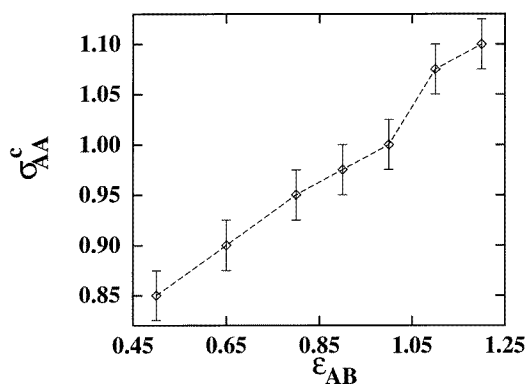

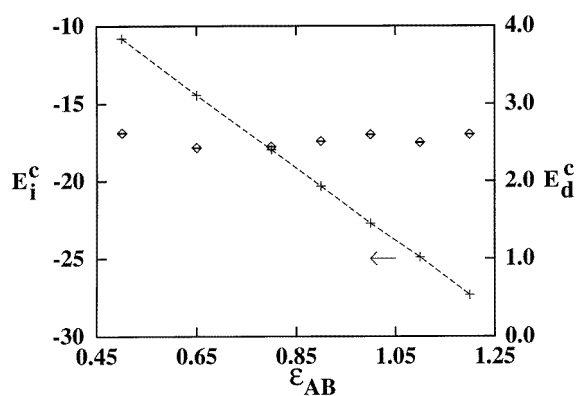**Figure 6.** The critical value σ_{AA}^c for a cluster supported on a surface as a function of ε_{AB}.

Figure 7. The critical interaction energy E_i^c and the critical deformation energy E_d^c as functions of ε_{AB}.

It is interesting to see how ε_{AB} changes the smallest value of σ_{AA}, σ_{AA}^c, for which the I_h cluster can be supported on a surface. In figure 6, we show the ε_{AB}-dependence of σ_{AA}^c. If $\sigma_{AA} > \sigma_{AA}^c$, the I_h cluster can be supported on a surface. If $\sigma_{AA} < \sigma_{AA}^c$, the cluster will become unstable and collapse on the surface. According to the present results, to make a cluster supportable on a surface, we require a value of σ_{AA} larger than σ_{AA}^c for a given ε_{AB}, i.e. any points in the region above the line in figure 6. We can also see that if a cluster of atoms A can be supported on a surface of atoms B, it may be hard to support a cluster of atoms B on a surface of atoms A. In a recent experiment, Bromann *et al* [17] have made an Ag cluster land softly on a Pt surface. The atomic radius of Ag is about 4% larger than

the atomic radius of Pt. According to our results, if we believe that the interaction between the Pt surface and the Ag cluster is not much larger (a few per cent) than the interaction in the Ag cluster, Ag_n can be softly landed on a Pt surface. In figure 7, we show the critical values of E_d and E_i as functions of ε_{AB}. We find that E_d^c hardly changes with ε_{AB}; this is because the collapse of the cluster is mainly dependent on its own stability and its potential energy surface. E_i^c decreases almost linearly with the increase of ε_{AB}, which implies that, at the critical point, the contact faces of the cluster with the surface are very similar for different values of ε_{AB}.
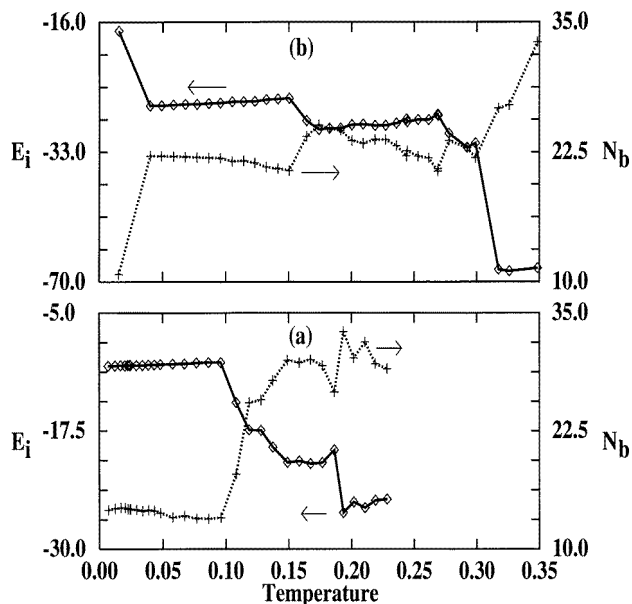

Figure 8. The bond number N_b and the interaction energy E_i as functions of temperature with $\varepsilon_{AB} = 0.5$ (a) and 0.8 (b).
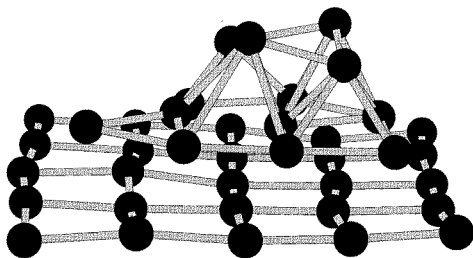

Figure 9. A snapshot of the collapsed structure at $T = 0.15$ for $\varepsilon_{AB} = 0.5$.

The structures discussed above are obtained by the steepest-descent method. How stable will the structures be at finite temperatures? We have tried to heat some structures and to study their thermal stability. Three structures obtained for the I_h cluster on the fcc(100) surface with $\varepsilon_{AB} = 0.5$ and 0.8 ($\sigma_{AA} = 1.0$) are studied. According to the results shown in

figure 6, for $\varepsilon_{AB} = 0.5$ and $\sigma_{AA} = 1.0$, which is far above the line, the cluster will be stable at finite temperature. For $\varepsilon_{AB} = 0.8$ and $\sigma_{AA} = 1.0$, which is near to the line, the cluster will be less stable at finite temperature. To quantitatively characterize the structural change of the cluster with increasing temperature, we have calculated the interaction energy (E_i) and the bond number N_b connecting the cluster and the surface (with the cut-off $1.2\sigma_{AB}$). In figures 8(a) and 8(b), we present the interaction energy E_i and the bond number N_b as functions of temperature. The step-like behaviour indicates that the collapse is step by step. For $\varepsilon_{AB} = 0.5$ (figure 8(a)), three steps can be clearly observed. At lower temperature, the cluster does not lose its individual character. It is stable up to $T = 0.10$. Above this temperature, the cluster begins to collapse, and as the cluster is further heated to 0.15, the interface layer builds to nine atoms (figure 9). The collapse process continues and the cluster completely spreads out as the temperature is increased to 0.20. A similar procedure is observed for $\varepsilon_{AB} = 0.8$. But for $\varepsilon_{AB} = 0.8$, the supported cluster collapses quickly at very low temperatures. In an earlier study on the melting of LJ 13-atom clusters on surfaces, Blaisten-Barojas *et al* [16] treated surfaces as structureless planes. They found that the melting point of a cluster on a surface is higher than that of a free cluster. But in our studies, we find that the cluster becomes unstable at temperatures far below the melting points of free clusters. Since the stability of a free LJ 13-atom cluster is very high, the structural change of the supported cluster is mainly due to the interaction between the cluster and the surface.
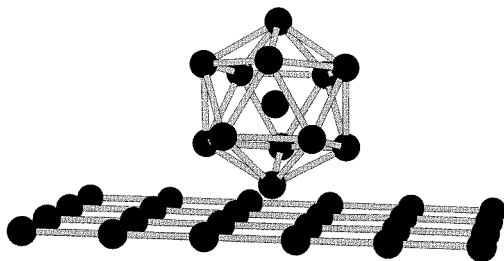

Figure 10. The equilibrium structure of the I_h cluster on an fcc(110) surface with $\varepsilon_{AB} = 0.5$.

To study the surface dependence of the supported cluster structures, we have also studied both O_h and I_h clusters on fcc(110) surfaces. Four values of ε_{AB}, namely 0.5, 0.8, 1.0 and 1.2, are considered, while σ_{AA} and σ_{AB} are kept equal to one. We have summarized the results along with the results for clusters on fcc(100) surfaces in table 1. We find that for $\varepsilon_{AB} = 0.5$, because the interaction strength is very low, both I_h and O_h clusters can be supported on the surface with distorted icosahedral symmetry. But the supported structures are different. Starting from the I_h cluster, we obtain the final structure shown in figure 10, where two pentagons are parallel to the surface. But starting from the O_h cluster, we obtain a structure that is similar to the previous result (figure 1(a)). For $\varepsilon_{AB} = 0.8$, 1.0 and 1.2, both clusters collapse. And these collapsed structures are similar at the interface, where the interface has an fcc(110) surface structure.

We have also studied cluster structures with different values of σ_{AA} by using $\varepsilon_{AB} = 0.8$. We have obtained the structures for $\sigma_{AA} = 0.8$, 0.9, 1.0, 1.1 and 1.2 as given in table 2. For an I_h cluster, when σ_{AA} is equal to 1.0 or 0.9, the cluster collapses. The atomic structure of the cluster at the interface has the distorted fcc(110) structure. Interestingly, when σ_{AA} reaches the value 0.8, the cluster can be supported on the surface again. The supported structures are similar to what is shown in figure 10, which implies that a small σ_{AA} may

be very important as regards determining the structure of a cluster. When σ_{AA} becomes larger than 1.1, the cluster begins to be supported on the surface. Starting from the O_h cluster, the lattice mismatch makes the structure of the collapsed cluster more complicated. The collapsed structures seem to be more compact; the interface can be considered as a distorted fcc(110) surface. Although for $\sigma_{AA} = 1.2$ the I_h cluster can be supported on a surface with distorted icosahedral symmetry, we have not observed the change from the O_h symmetry to the I_h symmetry. This is very different from the case for the fcc(100) surface.

4. Discussion and summary

In this paper, we have studied the structure and stability of clusters on fcc(100) surfaces; for comparison, a limited study of the fcc(110) surface is also presented. For clusters on the fcc(100) surface, we find that, for $\sigma_{AA} = \sigma_{BB}$, the I_h cluster can be supported on a surface as long as ε_{AB} is less than 1.0, and the supported clusters are weakly dependent on the initial orientation of the clusters. The O_h cluster can be changed to an icosahedral-like one due to its own instability. Comparing the structure of the clusters on an fcc(110) surface with the clusters on an fcc(100) surface, we find that the structures of the clusters on an fcc(110) surface are more dependent on initial configurations and more complicated, which suggests that the structure and the stability of the supported clusters are strongly surface dependent. For $\varepsilon_{AB} = 0.5$, both I_h and O_h clusters can be supported on (110) surfaces; however, they have different shapes. For larger values of ε_{AB}, neither an I_h cluster nor an O_h cluster can be supported on a (110) surface. It is also interesting to discover that the lattice mismatch can play a very important role as regards the structure and stability of supported clusters. For a (100) surface, when σ_{AA} is very small, both I_h and O_h clusters can be supported on a surface with octahedral symmetry. A small value of σ_{AA} can change the structure from a magic I_h cluster to a low-stability O_h cluster, although the cohesive energy of an O_h cluster is much smaller than that of an I_h cluster in the gas phase. In the transition region, $\sigma_{AA} \leqslant \sigma_{BB}$, the clusters collapse. So we can see how important the lattice mismatch is. From table 2 and figure 6, we can see that in order to have a cluster supported on a surface, we should seek a substrate with a small lattice constant and a cluster with a large atomic distance, and of course a small degree of interaction between the cluster and the substrate. The larger σ_{AA} is, the higher the stability of the supported cluster can be.

From the results presented above, clusters on fcc(100) and fcc(110) surfaces show very different behaviour; this may be because of the difference in binding energy and diffusion activation energy of the adatom on the surface. Because an fcc(110) surface has a larger binding energy, ~4.8, and has higher diffusion activation energies for an adatom: ~2.5 (along the [001] direction) and ~1.7 (along the [1$\bar{1}$0] direction) [22], the atoms of the cluster at the interface are strongly *embedded* in the surface. The embedding mechanism prevents the atoms from moving in the interface. This will result in a strong orientation dependence and hinder the change of the symmetry, and will also tend to make the collapsed structures more compact. An adatom on an fcc(100) surface has a smaller binding energy, ~3.9, and a lower diffusion activation energy, ~1.3 [22], than one on an fcc(110) surface. At the same interaction strength, the atoms in the cluster can have more freedom to move around. This is why an O_h cluster on an fcc(100) surface can be easily changed into an I_h cluster, and show less orientation dependence, which is unlikely to be the case for an O_h cluster on an fcc(110) surface.

In conclusion, we find that the structure and stability of clusters on surfaces are strongly

dependent on the interaction between the cluster and the surface, and also that the lattice mismatch can play a very important role. In the LJ system, the necessary conditions for a cluster to be supportable on a (100) surface are quantitatively described. The quite different behaviours for (100) and (110) surfaces indicate that the stability of a cluster is strongly dependent on its environment. To make a cluster supportable on a surface, we should seek a small interaction strength and a large value of σ_{AA}.

Acknowledgments

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[22] The binding energy and the diffusion activation energy of an adatom are obtained by placing the adatom at a number of positions on a surface, starting with the adatom 2.5 above the surface; the total energies are minimized by moving the adatom close to the surface.