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Coalescence of heteroclusters Au_{767} and Ag_{767}: a molecular-dynamics study*

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This paper studies the coalescence of heteroclusters Au_{767} and Ag_{767} by using molecular dynamics with the embedded atom method, where layer atomic energy is employed to describe the potential energy variation of per atom in different layers along radial direction. The results show that the coalescence is driven by releasing the atomic energy of the coalesced zone. The deformation, which is induced by substitutional and vacancy diffusion during the coalescence, makes the coalesced cluster disorder. If the summation of the thermal energy and the released atomic energy is large enough to keep the disorder state, the clusters form a metastable liquid droplet; otherwise, the clusters coalesce into a solid cluster when the coalesced cluster reaches the equilibrium state, and the coalesced cluster experiences liquid to solid ordering changes during the coalescence of a solid Au_{767} with a liquid Ag_{767} and a liquid Au_{767} with a liquid Ag_{767}. The centre of figure of the cluster system is shifted during the coalescence process, and higher coalescence temperature causes larger shift degree.

Keywords: molecular dynamics, embedded atom method, heterocluster, coalescence
PACC: 3640J, 6146

1. Introduction

Film technology is applied extensively in recent years. From a fundamental point of view, the behaviour of cluster in atomic scale during the formation of film can affect the structure, morphology and properties. However, it is very difficult to observe the cluster dynamic process directly through experiments. Computer simulation methods, in particular molecular dynamics, have become a popular tool to discover early-stage film growth mechanism and predict the distribution of cluster sizes.[1] With the development of film technology, the alloy films are found to have more applications because of their specific physical and chemical properties. Since the coalescence of clusters occurs prior to the formation of a continuous film, it is important in understanding the growth morphology of alloy film. At the same time, the research into the interaction of the heteroclusters during the formation of film can reveal the growing mechanism of alloy film.

Recently, the studies on the thermal dynamics of bimetallic clusters have already exhibited some new findings which distinguished from those of pure metals.[2−5] The interactions of heteroclusters have been mostly focused on the collision under constant energy condition. For example, there was a solid–liquid transition region during the collision of two clusters of Ag and Pd;[6] both clusters of Ni and Al were fused at low colliding energies, and the complex was fragmented at high colliding energies;[7] the structures of the complexes were different with different collision conditions.[8] The coalescences of clusters under constant temperature condition were limited to the homoclusters. For example, Lewis *et al*[9] examined the coalescence of gold clusters, and reported that the macro sinter theory was unable to describe the coalescence of two small clusters. Ding *et al*[10] found that the coalescence of iron clusters occurred at the temperatures lower than the cluster melting point, and the difference between coalescence and melting temperatures increased with the decrease of cluster size. Yu and Duxbury[11] studied the kinetics of nonequilibrium shape change in gold clusters and concluded

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that at most temperature conditions large solid clusters coalesced smoothly by surface diffusion, while the coalescence of smaller solid clusters occurred abruptly at a certain temperature which was sufficiently close to the melting temperature.

In the current study, a molecular dynamics with the embedded atom method (EAM) is developed to investigate the heteroclusters coalescence under constant temperature condition. Gold and silver are selected as the investigated objects on account of the following considerations: 1) gold and silver have similar lattice parameters and atomic size, which make them have the similar cutoff distance for the EAM potential. This can ensure the EAM potential yield accurate results; 2) solid state phase transformations and structure changes disappear during the coalescence since gold and silver have FCC structure, and can form complete solid solution, it is helpful to reveal the coalescence mechanism; 3) gold and silver are applied broadly. The coalescences of identical size clusters Au_{767} with Ag_{767} are investigated by using molecular dynamics with the EAM. The cluster size is selected randomly. The coalescence processes of the different states of heteroclusters Au_{767} and Ag_{767} are mainly discussed.

This paper is arranged as follows. Section 2 contains the system and simulation method. The results and discussion are described in Section 3. In Section 4, the main conclusions are summarized.

2. Simulation method

In order to simulate the coalescence processes of heteroclusters, the semiempirical analytic EAM is used as the interatomic potential and the analytical methods of the homoclusters coalescence are extended to those of the heteroclusters. The molecular dynamics calculations employ the predictor–corrector algorithm[12] to integrate the equations of Newton in this work.

2.1. Embedded atom method

EAM, which is based on density functional theory, was proposed by Daw and Baskes.[13,14] Afterwards, a simplified analytical EAM, developed by Johnson,[15] has been fairly successful in a wide range of applications. Present study uses the simple analytical EAM model including a long range force which was extended by Cai and Ye.[16] Simulations based on this potential are expected to give valid data for the cluster dynamics. It has been used to study the nucleation of bulk Cu–Ni,[17] and it is also extended to research into the bimetallic clusters of Au–Pd,[18,19] Au–Cu,[20] and Ag–Ni.[21] The total energy is given as

$$E_{\rm tot} = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{i,j}\phi_{ij}(r_{ij}), \qquad (1)$$

where $\phi_{ij}(r_{ij})$ is a two-body potential between atoms i and j with the separation distance r_{ij}, $F_i(\rho_i)$ is the embedding function of atom i with the electron density ρ_i due to all its neighbours. For a binary alloy system with type-a atoms and type-b atoms, there exist seven functions $f_{\rm a}(r)$, $f_{\rm b}(r)$, $\phi_{\rm a}(r)$, $\phi_{\rm b}(r)$, $\phi_{\rm ab}(r)$, $F_{\rm a}(\rho)$, $F_{\rm b}(\rho)$. The six functions $f_{\rm a}(r)$, $f_{\rm b}(r)$, $\phi_{\rm a}(r)$, $\phi_{\rm b}(r)$, $F_{\rm a}(\rho)$, $F_{\rm b}(\rho)$ are obtained from the monoatomic systems to alloy systems. $\phi_{\rm ab}(r)$, which obtained by Johnson,[22] is shown as

$$\phi_{\rm ab}(r) = \frac{1}{2}\left[\frac{f_{\rm b}(r)}{f_{\rm a}(r)}\phi_{\rm aa}(r) + \frac{f_{\rm a}(r)}{f_{\rm b}(r)}\phi_{\rm bb}(r)\right]. \qquad (2)$$

In order to identify the validity of this potential on the cluster, the thermodynamic process is simulated in this study. The clusters are subjected to a heat-and-cool cycle. The process is that the cluster is heated to 1200 K from 300 K and followed by cooling to 300 K. The temperature is changed in the steps of either 10 K or 100 K. The relaxation time is 0.16 ns at each temperature.

The time evolution of the potential energy in the heating process at different temperature is shown in Fig.1. The potential energy reaches equilibrium before 0.16 ns. The potential energies, which are used to identify the melting point, are obtained by averaging their equilibrium values.

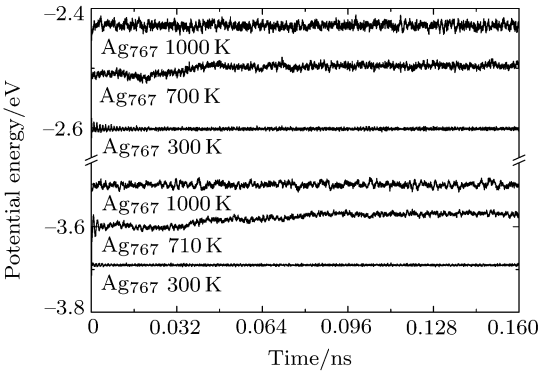


Fig.1. Potential energy of clusters versus time in the heating process at different temperature.

The melting point is identified by examining the variation of potential energy with temperature. As a result, the melting point of Au_{767} is 710K, and that

of Ag_{767} is 700 K. The corresponding thermal curves are plotted in Fig.2, the hysteresis in the annealing process is in good agreement with the results of Lewis *et al.*[9] On the other hand, the relationship between the cluster melting point and the cluster size is given by[5,23]

$$T_{\mathrm{m}}^{\mathrm{b}} - T_{\mathrm{m}}^{\mathrm{c}}(N) = aN^{(-1/3)}, \tag{3}$$

where N is the atomic number involved in the cluster, $T_{\mathrm{m}}^{\mathrm{b}}$ is the bulk melting point, $T_{\mathrm{m}}^{\mathrm{c}}(N)$ is the cluster melting point, and a is a constant. For Au_{767} in the present study, $T_{\mathrm{m}}^{\mathrm{c}}(N)$, N, a are 710 K, 767, and 5880.5 K, respectively. Therefore, the calculated melting point of bulk gold is 1352K, which agrees with the experimental data 1337 K very well. Hence, the validity of this model is identified, and this simulation method can provide a qualitatively correct description of cluster.

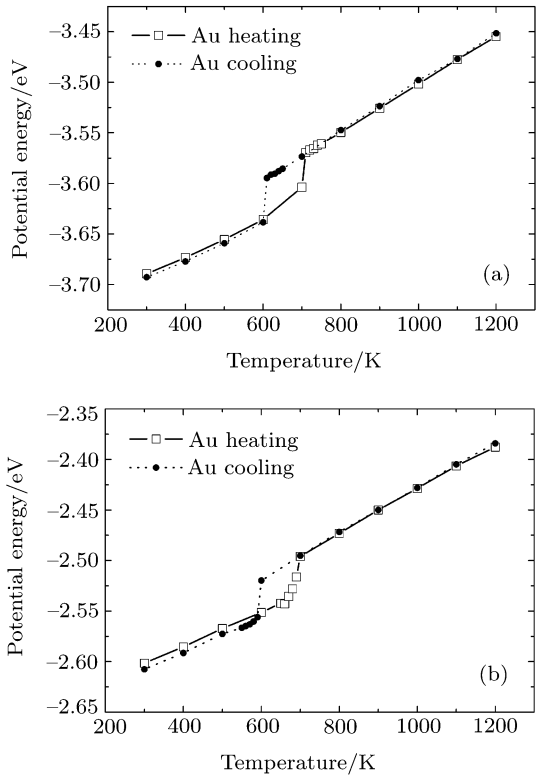


Fig.2. Potential energy as a function of temperature in heating and cooling process. (a) Au and (b) Ag.

2.2. Analysis and calculation formulas

The pair distribution function $g_{\mathrm{L}}(r)$ gives the probability of finding a pair of atoms with a distance r in the layer L and can be used to describe the change of systemic structure

$$g_L(r) = \frac{V}{N}\left\langle \sum_{i\in L}\sum_{j\neq i\in L}\delta(r - r_{ij})\right\rangle, \tag{4}$$

where the term in angular brackets represents time average, V is the volume of the simulated cell, and N is the atomic numbers of system.[24]

Aligning the clusters along the x axis, this study defines the aspect ratio to be $2R_x/(R_y + R_z)$, where R_α is the radius of gyration along axis $\alpha = x, y, z$.

2.3. Setup of clusters

The initial spherical clusters are carved out from a large FCC bulk, the radii of cluster gold and cluster silver are 1.47 nm, and 1.472 nm, respectively. There are 767 atoms involved in each cluster. In this work, Au_{767}, Ag_{767} are used to express the cluster gold with 767 atoms, and the cluster silver with 767 atoms, respectively. Then the initial clusters Au_{767} and Ag_{767}, which are on the nonequilibrium state, are put together to form a cluster system. The centre of figure of Au_{767} and Ag_{767} is initially placed 3.3 nm apart on the x axis of the coordinate system. This cluster system is used as the research object. Rotation will occur during the coalescence process because of the difference of the initial angular momenta. Because this phenomenon is beyond the scope of the present study, the initial angular momentum vanishes in this procedure. The relaxation time at each coalescence temperature is 3.2ns, which can make the system close to equilibrium. The time step is taken to be 1.6×10^{-15} s.

3. Results and discussion

3.1. Energy distributions

The difference of atomic energy during the coalescence process will influence the structure of cluster. Layer atomic energy E_{a} is employed to describe the potential energy per atom in different layers along radial direction, and the thickness is 0.1 nm for each layer. This is similar to the method in Ref.[25]. In this study, the E_{a} is regarded as a function of the atomic distance from the centre of figure R_{cf}. Layer atomic energy of the isolated Au_{767} at different temperatures is plotted in Fig.3. As one can see clearly, the E_{a} of the interior atoms is invariable with the increase of R_{cf} at the same temperature, but it enhances with the increase of R_{cf} due to atoms gradually change from interior to surface. The E_{a} enhances with the increase of the temperature. Furthermore, it is observed that the increased atomic energy of the interior atoms is higher than that of the surface atoms with the increase

of temperature. The variation of E_a with temperature and R_{cf} will contribute a lot to the coalescence of clusters.

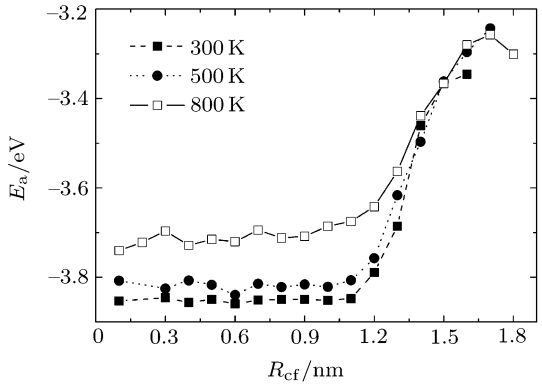


Fig.3. Layer atomic energy of the isolated cluster Au_{767}, whose relaxation time is 0.8 ns at different temperatures.

In order to identify the influence of the E_a at the different zones of the cluster during the coalescence process, both Au_{767} and Ag_{767} are divided into A zone and B zone, respectively, as shown in Fig.4. The variation of E_a between the isolated Au_{767} and the coalesced Au_{767} at different zones is investigated in the current study. For the isolated Au_{767}, the E_a of A zone is the same as that of B zone, because the atoms are not affected by coalescence; when $R_{cf} \leq 0.9$ nm, the E_a is invariable with increasing of R_{cf} since the atoms are interior ones; when $R_{cf} > 0.9$ nm, the atoms gradually change from interior to surface, and the E_a enhances with increasing of R_{cf}. For the coalesced Au_{767}, when $R_{cf} \leq 0.9$ nm, both the E_a of A zone and the E_a of B zone are similar to that of the isolated Au_{767}, this is because the atomic sites belong to the inner of the cluster, and the atoms do not take part in the coalescence process; when $R_{cf} > 0.9$ nm, the E_a of A zone is similar to that of the isolated Au_{767} since the atoms of A zone are not affected by coalescence; the E_a of B zone is lower than that of A zone with same R_{cf}, because the atoms of B zone take part in the coalescence; when the outermost atoms of B zone diffuse into the interior of coalesced cluster, the E_a becomes much lower. Finally, the radius of the coalesced Au_{767} is larger than that of the isolated Au_{767} because of the diffusion during the coalescence. Hendy *et al*[26] investigated the coalescence of lead clusters, in which they found that the coalescence of clusters was induced by the release of surface energy. This result is similar to the conclusion of the current study.

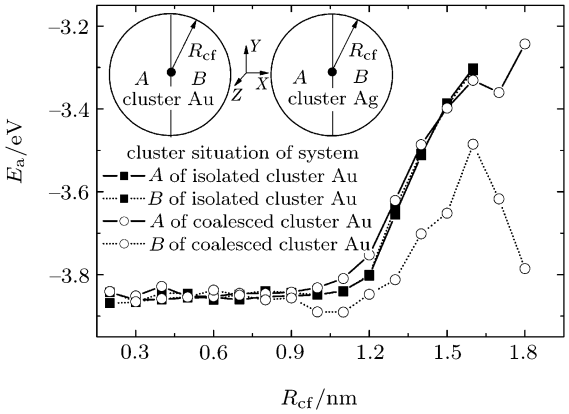


Fig.4. Layer atomic energy of the isolated and the coalesced clusters Au_{767}, whose relaxation time is 0.16 ns at 300 K.

3.2. Coalescence with different time steps

As indicated in Fig.5, the coalescence process at 300 K is discussed in the current study. Firstly, metastable initial clusters contact with each other to form neck region at 7000 steps, and then the neck grows up gradually to form coalesced cluster at 12000 steps. Finally, the coalesced cluster relaxes to the equilibrium state. The coalescence process of heteroclusters is similar to that of homoclusters simulated by Tian and Guo.[27] The coalescence processes at different temperatures are also simulated, which are similar to that of 300 K. During the coalescence process, the higher the temperature is, the shorter the time for the neck formation and growing up is.

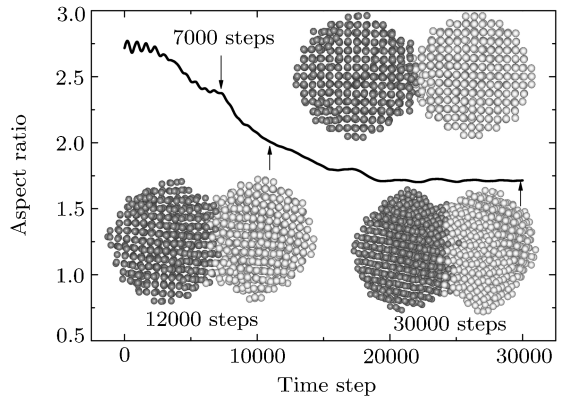


Fig.5. Aspect ratio of clusters at 300K and the snapshots of corresponding time steps (grey ball is Au atoms and black is Ag atoms, the same below).

In this study, the forming process of neck region is researched carefully. It is found that the coalescence is mainly through diffusion of the atoms. Since the radii of gold and silver are almost identical, which make the atomic diameter much larger than that of the interstice; interstitial diffusion is difficult to occur. Therefore, substitutional diffusion and vacancy diffusion play a key role during the coalescence. In addition, as has been reported previously,[28−30] coalescence results from rapid surface diffusion of atoms from unstable high curvature regions to more stable low curvature regions. Fewer neighbouring atoms are at the neck region, thus, the atoms can easily jump to a lattice vacancy to form a neck to induce deformation of the coalesced zone. Furthermore, higher coalescence results in larger distortion: namely, the coalesced cluster becomes disordered gradually during the coalescence process. Therefore, before the coalesced cluster reaches the equilibrium state, the coalescence phenomena will change with relaxation time steps.

The coalescence of Au_{767} with Ag_{767} at 700 K is considered at different time steps. The pair distribution function profiles at different times and temperatures are given in Fig.6. It shows that the coalesced cluster has specific peaks of FCC structure at 700 K for being relaxed for 2.4 ns, which is similar to that of 500 K at 2.4 ns: namely, the coalesced cluster at 700 K also has ordered structure. However, the specific peaks of FCC structure disappear at 700 K for being relaxed for 0.48 ns, it means the coalesced cluster is in a disordered state. Hence, the coalesced cluster experiences from disordered state to ordered state changes during the coalescence process at 700 K. At first, the coalescence temperature can make Ag_{767} melt completely, and premelt the surface of Au_{767}. Thus, the atoms of Ag_{767} and the premelted atoms of Au_{767} can diffuse freely at 700 K, the induced distortion is so large that it can make the cluster system disorder completely at the beginning of the coalescence. The alloy system will exhibit a tendency to order when $U_{\mathrm{Au-Ag}} > (U_{\mathrm{Au-Au}} + U_{\mathrm{Ag-Ag}})/2$, where $U_{\mathrm{Au-Au}}$, $U_{\mathrm{Ag-Ag}}$, and $U_{\mathrm{Au-Ag}}$ are defined to be the interaction energies between neighbouring Au–Au, Ag–Ag, and Au–Ag atoms, respectively.[31] With the progress of the coalescence, the formation of new chemical bonds between the atoms decreases the thermal energy and the released atomic energy. This makes the energy impossible to keep the disorder state. At the same time, the enhancement of $U_{\mathrm{Au-Ag}}$ with the increase of the coalescence leads to $U_{\mathrm{Au-Ag}} > (U_{\mathrm{Au-Au}} + U_{\mathrm{Ag-Ag}})/2$, the atoms reach the ordered equilibrium state with the increase of the relaxation time step. The result is similar to the collision result of Ag–Pd cluster.[6] Kim *et al*[6] found a solid–liquid transition region of the complex by using constant energy molecular dynamics simulation. The difference between them is that the solid–liquid transition is time evolution during the coalescence of Au_{767} with Ag_{767} at 700 K.

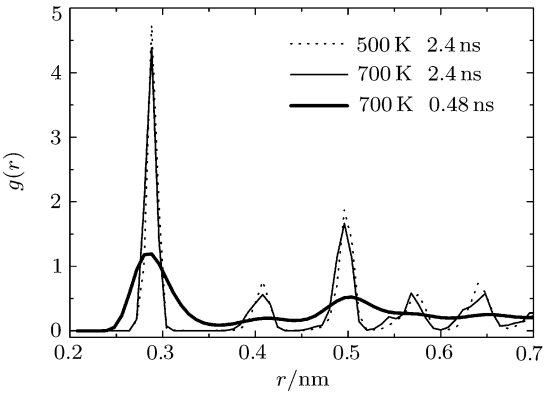


Fig.6. The pair functions profiles with different times and temperatures.

3.3. The coalescence at different temperatures

In this study, three different coalescence cases are considered: a solid Au_{767} with a solid Ag_{767}, a solid Au_{767} with a liquid Ag_{767}, and a liquid Au_{767} with a liquid Ag_{767}. As shown in Fig.7, a solid Au_{767} with a solid Ag_{767} coalesces to a solid dumbbell shape cluster at 300 K while a solid Au_{767} with a solid Ag_{767} coalesces to a solid elongated cluster at 500 K. The morphology of coalesced cluster is similar to that of homoclusters.[9,10] A solid Au_{767} with a liquid Ag_{767} coalesces to a solid spherical shape at 700 K and a liquid Au_{767} with a liquid Ag_{767} also coalesces to a solid spherical shape at 715 K while a liquid Au_{767} with a liquid Ag_{767} coalesces a liquid ovoidal shape at 800 K. The coalescence processes of Au_{767} with Ag_{767} at other temperatures are also simulated. The results show that if the summation of the thermal energy and the released atomic energy is large enough to make the atoms keep disordered state, a metastable liquid ovoidal shape is obtained; otherwise, a solid cluster forms. This is different from the coalescence of cluster lead which was simulated by Hendy *et al*,[25] they found that a metastable molten droplet formed when the temperature lied between the melting points of two clusters. This coalesced structure plays a key role in determining the morphology of the film, and it is necessary to study the coalescence process in detail.

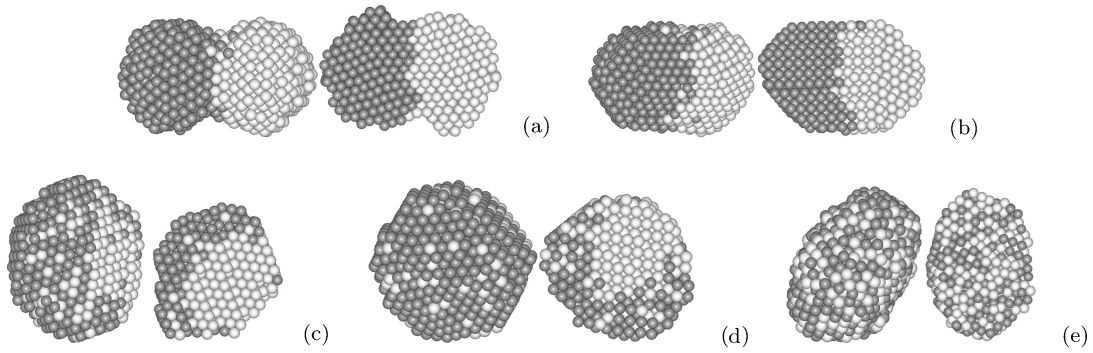


Fig.7. Snapshots of the coalesced cluster during the coalescence process when the temperature is (a) 300 K, (b) 500 K, (c) 700 K, (d) 715 K, and (e) 800 K. The left row in (a)–(e) is the entire cluster and the right row is cross section.

During the coalescence process, it is found that the centre of figure of the coalesced cluster shifts along x axis at different temperatures. Figure 8 shows that the displacement increases with the increase of the temperature. The shift of the centre of figure during the coalescence process has an important influence on the morphology of film. The reason for the shift of the centre of figure will be discussed somewhere.

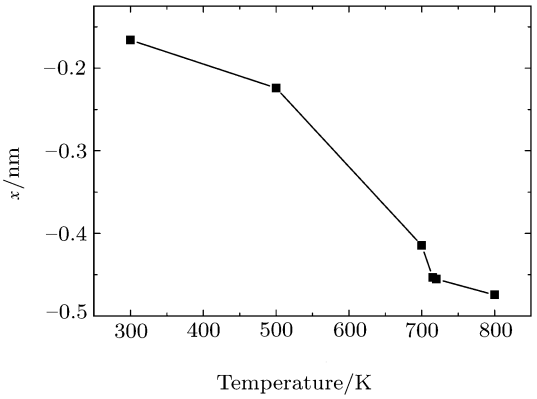


Fig.8. Displacements for the centre of figure along x axis with respect to different temperatures.

4. Conclusions

The coalescence of heteroclusters Au_{767} and Ag_{767} was studied by using molecular dynamics with the embedded atom method, where layer atomic energy was employed to describe the potential energy variation of per atom in different layers along radial direction. And the variation of layer atomic energy was investigated in order to reveal the coalescence mechanism. The results showed that:

(1) The coalescence of clusters was driven by releasing the atomic energy of coalesced zone.

(2) The coalesced cluster experienced liquid to solid ordering changes during the coalescence of a solid Au_{767} with a liquid Ag_{767} and a liquid Au_{767} with a liquid Ag_{767}.

(3) The centre of figure of the cluster system shifted during the coalescence process, and the displacement increased with the increase of the coalescence temperature.

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