

Melting Behaviour of Core-Shell Structured Ag–Rh Bimetallic Clusters *

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The melting behaviour of four typical core-shell structured 309-atom Ag–Rh bimetallic clusters, with decahedral and icosahedral geometric configurations, is investigated by using molecular dynamics simulation, based on the Sutton–Chen potential. The initial atomic configurations are obtained from semi-grand canonical ensemble Monte Carlo simulations. It is found that the melting point temperature T_m increases with the mole fraction of Rh in the bimetallic clusters, and T_m of Ag–Rh icosahedral clusters is higher than those of Ag–Rh decahedral clusters with the same Rh mole fraction. It is also found that the Ag atoms lie on the surface of Ag–Rh bimetallic clusters even after melting.

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Nanoscaled metallic clusters possess some unique chemical, optical, magnetic, electronic, physicochemical properties from their distinct structural characteristics. Recently, interest in both experiment^[1–3] and theory^[4–6] has focused on bimetallic clusters, which exhibit characteristics that are not just the sum of the properties of the constituent metals.

Unlike bulk metals, nanoscaled metallic clusters can present various crystalline and non-crystalline structures. Decahedra (Dec) and icosahedra (Ico) are considered as two of the most commonly accepted multiply twinned particles (MTP) with the face-centred-cubic (*fcc*) local environments.^[7] Bimetallic clusters are known to take various kinds of structures, covering a high entropy situation of a solid solution random alloy, and a low entropy product as a cluster-in-cluster, a layered compound, a heterobondphilic structure, and a core-shell structure. In particular, the core-shell structured bimetallic clusters can present unusual catalytic properties, due to their novel electronic properties and favourable surface/volume ratios.^[8] As a result, perfect core-shell structures were found in several bimetallic clusters by both experimental^[3,9] and theoretical investigations.^[8,10–14]

Ag–Rh bimetallic catalyst shows a high activity and selectivity, compared with mono-metallic Rh catalyst, in the $N_2O + CO$ reaction,^[15] the N_2O decomposition^[16] and the selective catalytic reduction of NO by propylene.^[17] Earlier theoretical studies suggest that the Ag atoms generally segregate on surface of Ag–Rh bimetallic clusters,^[18,19] which can lead to the core-shell structures. However, there are few data focused on the core-shell structures of Ag–Rh clusters with MTP configurations in detail. Furthermore, little attention has been paid to the melting behaviour of such Ag–Rh clusters, which is very important for further catalysis study.

In this Letter, based on the molecular dynam-

ics (MD) simulations, the melting behaviour of the core-shell structured 309-atom Ag–Rh bimetallic clusters, with decahedral and icosahedral configurations, is investigated. Four typical core-shell structures, obtained from Monte Carlo (MC) simulations, are employed as the initial configurations for the MD simulation. The dependence of the melting point on Rh mole fraction is discussed.

The initial atomic configurations of the core-shell structured Ag–Rh bimetallic clusters were obtained from the semi-grand canonical ensemble Monte Carlo (SEMI-GCMC) simulations.^[20–23] The details of the simulation can be found in our previous work.^[24–26] In this MC simulation, the total number of atoms ($N = N_{Ag} + N_{Rh}$), temperature T and chemical potential difference ($\Delta\mu = \mu_{Ag} - \mu_{Rh}$) between the two species are fixed. N_{Ag} and N_{Rh} are allowed to vary in our algorithm. The chemical composition at a given temperature (100 K for this work) is therefore obtained by performing the MC simulation at a fixed value of $\Delta\mu$ between the two species in a cluster.

MD simulations are carried to study the melting behaviour of Ag–Rh bimetallic clusters. All the MD simulations in this work are performed by using the DL.POLY programme developed by Smith and Forester,^[27] based on the Sutton–Chen potential.^[28,29] The potential parameters for the different interactions (Ag–Ag, Rh–Rh and Ag–Rh) used in the MD simulation can be found in the literature.^[28,29] The MD equations of motion are integrated based on the Verlet leapfrog scheme.^[30] The time step in all calculations is 1.0 fs, which leads to quite stable dynamics trajectories for the system. Each cluster is isolated in a free space without periodic boundary conditions. In this way, we simulate the clusters in MD simulation with constant temperature (using the Berendsen method to control the temperature), and constant N . The clusters are first re-

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laxed for 1000 ps at 100 K. Then, they are heated from 100 K to temperatures over the melting points, with steps of $\Delta T = 50$ K. At each temperature point, the simulation is carried out for 1000 ps, while the first half is used for equilibration, and the second half for average. For the temperature region near the melting point, smaller temperature increment $\Delta T = 10$ K, along with shorter simulation time 200 ps, is used to obtain the detailed information on the melting transition. The heating rate is fixed to 1 K per 20 ps during the whole heating process.

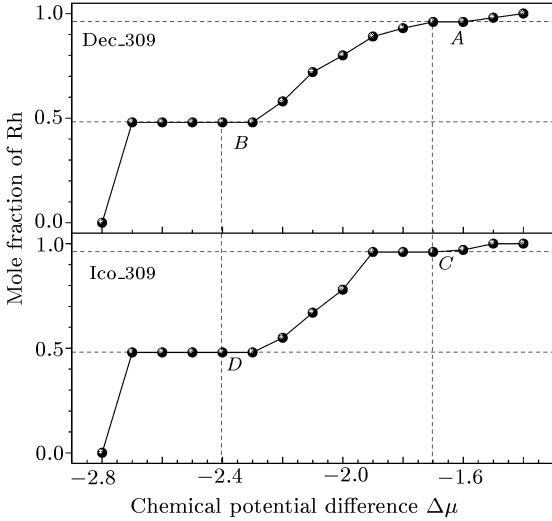


Fig. 1. Mole fraction of Rh for Ag-Rh bimetallic clusters versus the chemical potential difference $\Delta\mu$ ($\Delta\mu = \mu_{\text{Ag}} - \mu_{\text{Rh}}$) at 100 K. The symbols A, B, C and D represent the four typical core-shell structures for both Dec and Ico geometric configurations. In detail, A represents the Dec structured Ag-Rh cluster with 12 Ag atoms and 297 Rh atoms, shorted as Dec_Ag12-Rh297. B, C, D are shorted as Dec_Ag162-Rh147, Ico_Ag12-Rh297, and Ico_Ag162-Rh147, respectively.

The structural properties of Ag-Rh bimetallic clusters are investigated by using the SEMI-GCMC methods. Figure 1 shows the mole fraction of Rh changing with the chemical potential difference $\Delta\mu$ ($\Delta\mu = \mu_{\text{Ag}} - \mu_{\text{Rh}}$) for 309-atom Ag-Rh clusters, with Dec and Ico configurations, respectively. From Fig. 1, it is found that the mole fraction of Rh increases monotonically with $\Delta\mu$. The points A–D in Fig. 1 represent the four typical core-shell structures, whose snapshots are shown in Figs. 2(a)–2(d), corresponding to Dec_Ag12-Rh297, Dec_Ag162-Rh147, Ico_Ag12-Rh297 and Ico_Ag162-Rh147. From Figs. 2(a) and 2(c), it is observed that corresponding to the A and C phases shown in Fig. 1 at $\Delta\mu = -1.7$ eV, there are 12 Ag atoms at the 12 vertex sites of both the Dec and Ico clusters, while the other sites of the clusters are occupied by 297 Rh atoms. In addition, the perfect core-shell structures of the 309-atom Ag-Rh clusters, with Dec and Ico configurations, are shown in Figs. 2(b) and 2(d), corresponding to the B and D phases in Fig. 1 at $\Delta\mu = -2.4$ eV. In the perfect core-shell structures, the surfaces of the clusters are

preferentially occupied by 162 Ag atoms, and the core sites of the clusters are occupied by 147 Rh atoms. It should be mentioned that the surface segregation of Ag atoms in the Ag-Rh clusters was also found by using the genetic algorithm^[18] and other theoretical works.^[19]

In this study, the thermal properties of the four typical core-shell Ag-Rh clusters, represented by A, B, C and D in Figs. 1 and 2, and the 309-atom mono-metallic Ag and Rh clusters are studied. Figure 3 shows the temperature dependence of the potential energy for the four typical core-shell Ag-Rh clusters. It is found that a distinguishable abrupt increase in the potential energy curve occurs for each cluster, indicating the melting transition of the cluster. To confirm the occurrence of a solid-liquid transition, the rms bond-length fluctuation δ as a function of temperature is calculated. The rms bond-length fluctuation δ is defined as

$$\delta = \frac{2}{n(n-1)} \sum_{i=1}^n \sum_{j=i+1}^n \frac{\sqrt{\langle r_{ij}^2 \rangle_T - \langle r_{ij} \rangle_T^2}}{\langle r_{ij} \rangle_T}, \quad (1)$$

where n is the total number of atoms in the bimetallic clusters (309 for this work), r_{ij} is the distance between atoms i and j , and the brackets represents the ensemble average at temperature T . Figure 4 shows the temperature dependence of δ for the four Ag-Rh clusters. It is obvious that a giant jump appears in the $\delta - T$ curve, indicating the appearance of the liquid phase for each cluster of the four typical core-shell structured Ag-Rh clusters. To identify the melting temperature, the heat capacity C_v is plotted in Fig. 3. The isotonic heat capacity C_v is defined as a function of the fluctuation of potential energy U ,^[30] given by

$$C_v = \frac{\langle \delta U^2 \rangle}{k_B T^2} + \frac{3}{2} N k_B, \quad (2)$$

where $\langle \delta U^2 \rangle$ is the potential energy fluctuation of the cluster, N is the total number of atoms, and k_B is the Boltzmann constant. Consistent with the literature,^[31–33] the melting point is defined as the temperature with the maximum of the peak in the heat capacity C_v . In Fig. 3, the maximum C_v peaks, combined with the distinguishable sudden increases in the potential energy $U - T$ curves and the giant jumps in the curves of the rms bond-length fluctuation δ , indicate the homogeneous melting of the Ag-Rh bimetallic clusters. The melting points T_m observed from Figs. 4(a)–4(d), along with the calculated temperature T_m of the 309-atom mono-metallic Ag and Rh clusters, are listed in Table 1. From Table 1, it is found that the melting points T_m increase with the mole fraction of Rh in the bimetallic clusters. Furthermore, compared to the difference of T_m between Dec and Ico structured clusters, i.e. $T_m(\text{Ico}) - T_m(\text{Dec})$, it can be concluded that values of T_m of Ag-Rh Ico structured clusters are higher than T_m of Ag-Rh Dec structured clusters at the same Rh mole fraction.

Table 1. Melting points T_m of 309-atom Ag-Rh bimetallic clusters and mono-metallic Ag and Rh clusters, with Dec and Ico geometric configurations.

	Ag309	Ag162-Rh147	Ag12-Rh297	Rh309
Dec structured	790 ± 10 K	1220 ± 10 K	1460 ± 10 K	1500 ± 10 K
Ico structured	830 ± 10 K	1300 ± 10 K	1560 ± 10 K	1580 ± 10 K
$T_m(\text{Ico}) - T_m(\text{Dec})$	40 K	80 K	100 K	80 K

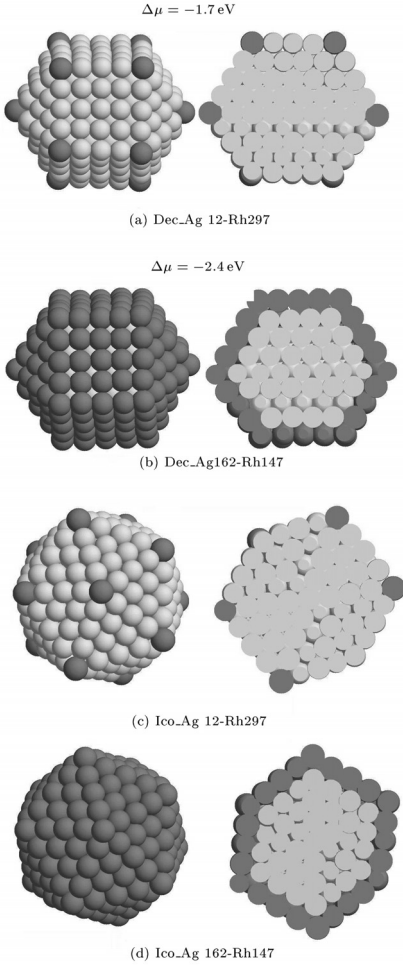


Fig. 2. Snapshots of 309-atom Ag-Rh bimetallic clusters (dark grey dots represent Ag atoms, and light grey dots represent Rh atoms) when $\Delta\mu = -1.7$ and -2.4 eV at 100 K, corresponding to the symbols A, B, C and D in Fig. 1.

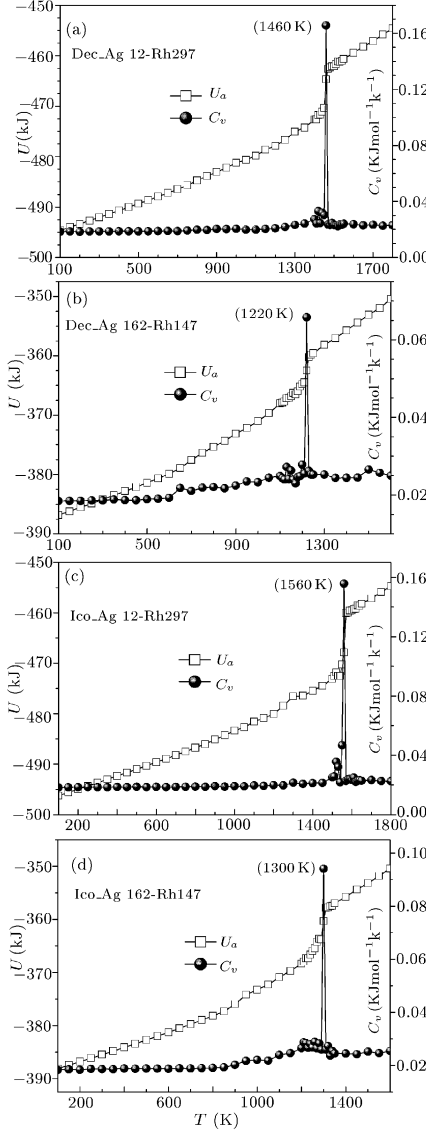


Fig. 3. Temperature dependence of potential energy U and isotonic heat capacity C_v of the four typical core-shell Ag-Rh bimetallic clusters in the heating process.

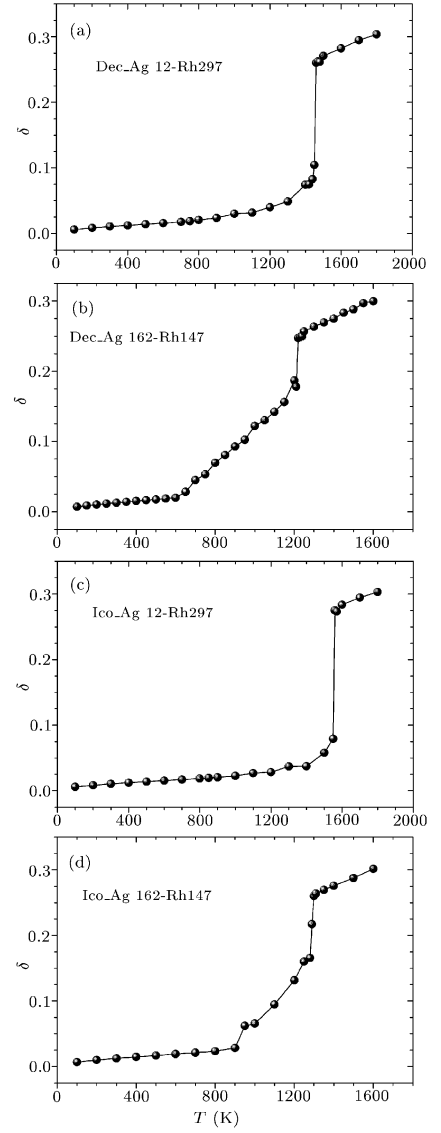


Fig. 4. Temperature dependence of the rms bond-length fluctuation δ of the four typical core-shell structured Ag-Rh bimetallic clusters.

The melting process of Ag-Rh bimetallic clusters can be further explored by the pair correlation functions of the clusters at the temperatures before and after melting. We define $g_{\text{cm}}(r)$ as the pair correlation function around the centre of mass for the bimetallic clusters. Here $g_{\text{cm}}(r)$ is calculated from trajectories of the MD simulation, i.e.

$$g_{\text{cm}}(r) = \frac{V}{N^2} \left\langle \sum_{i=1}^n \delta(\mathbf{r}_i - \mathbf{r}_{\text{cm}} - \mathbf{r}) \right\rangle, \quad (3)$$

where N is the total atom number of the whole cluster (309 for this work), V is a settled volume of a large enough cubic box, to ensure the isolation of the cluster, with fixed r_{cut} (12 Å for this work) in length, n is the atom numbers counted for the particular type of atom (Ag/Rh), and $\mathbf{r}_{\text{cm}}$ is the c.m. coordinates at each time step. We only discuss the pair correlation functions of the Dec_Ag162-Rh147 cluster. Figures 5(a)–5(f) show Ag and Rh $g_{\text{cm}}(r)$ at six chosen temperatures. At low temperature of 100 K, both Rh

and Ag $g_{\text{cm}}(r)$ present solid-like well-separated sharp peaks. Up to 950 K, Rh $g_{\text{cm}}(r)$ maintains solid-like features with much lower and wider peaks, while Ag $g_{\text{cm}}(r)$ presents one peak curve with a slight shoulder to its left. At 1210 K, Rh $g_{\text{cm}}(r)$ loses solid-like features and three main peaks appear, with slight shoulders to their right. At 1220 K, both Rh and Ag $g_{\text{cm}}(r)$ shows similar features of the liquid-like radial distribution functions. The original slight shoulders disap-

pear, and the new obvious shoulder around $r = 2 \text{ \AA}$ is the effect of using the centre of mass as the zero point of $g_{\text{cm}}(r)$. At 1230 and 1600 K, the liquid-like features remain. Furthermore, it is observed that the Ag atoms prefer to stay at the surface region even at high temperature of 1600 K after melting. Similar features are found in the temperature dependence of the pair correlation function of the other three core-shell structured Ag-Rh bimetallic clusters.

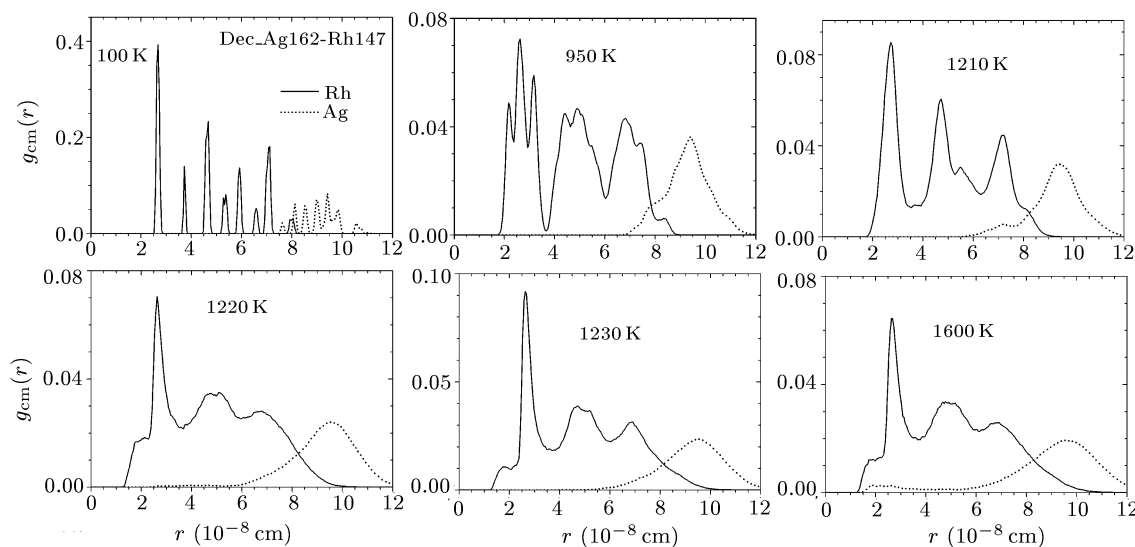


Fig. 5. The pair correlation functions around the c.m. $g_{\text{cm}}(r)$, for both the total and peculiar species of atoms (Ag/Rh) of Dec_Ag162-Rh147 clusters, at six chosen temperatures: (a) 100 K, (b) 950 K, (c) 1210 K, (d) 1220 K, (e) 1230 K and (f) 1600 K.

In summary, the melting behaviour of four typical core-shell structured 309-atom Ag-Rh clusters, including two perfect core-shell structures, have been investigated by using molecular dynamics simulation, based on the Sutton-Chen potential. The initial core-shell structures with decahedra and icosahedra geometric configurations are obtained by using the Monte Carlo simulation, performed in semi-grand canonical ensemble. Melting points T_m of the clusters are mainly identified by the change of the heat capacity C_v . The results show that T_m increases with the mole fraction of Rh in the bimetallic clusters, and T_m of Ag-Rh icosahedral clusters is higher than those of Ag-Rh decahedral clusters at the same Rh mole fraction. In addition, surface segregation of Ag atoms in Ag-Rh bimetallic clusters occurs even after melting of the clusters.

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