Stabilized jellium model and structural relaxation effects on the fragmentation energies of ionized silver clusters

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Abstract

Using the stabilized jellium model in two schemes of ‘relaxed’ and ‘rigid’, we have calculated the dissociation energies and the fission barrier heights for the binary fragmentations of singly-ionized and doubly-ionized Ag clusters. In the calculations, we have assumed spherical geometries for the clusters. Comparison of the fragmentation energies in the two schemes show differences which are significant in some cases. This result reveals the advantages of the relaxed SJM over the rigid SJM in dynamical processes such as fragmentation. Comparing the relaxed SJM results and experimental data on fragmentation energies, it is possible to predict the sizes of the clusters just before their fragmentations.

1 Introduction

Metal clusters are one of the building blocks of the nano-structured systems. The stability of these systems is of great importance in nano-technology. One of the mechanisms which can destroy the stability of metal clusters is charging. These systems have been extensively studied in the context of jellium model (JM). In the JM, the discrete ions are replaced by a uniform positive charge background of density \( n^B = 3/4\pi (r_s^B)^3 \) in which \( r_s^B \) is the bulk value of the Wigner-Seitz (WS) radius of the valence electrons in the metal. A more realistic version of the JM, the stabilized jellium model (SJM), which was introduced
by Perdew *et. al.* in 1990, has improved some drawbacks of the JM. The SJM calculations for the fragmentation processes of metal clusters reported so far [3], were based on the assumption that the density parameter $r_s$ takes its bulk value $r_s^B$, which we call ‘rigid’ SJM. However, since the surface effects have large contributions in the energetics and sizes of small clusters, a more sophisticated use of the SJM is needed to predict the correct energetics of the clusters in the study of the fragmentation processes. This method, ‘relaxed’ SJM, has already been used to predict the equilibrium sizes and energies of neutral as well as the charged [5] metal clusters (This method is also called self-compression method). In contrast to the JM and the rigid SJM in which the $r_s$ value is borrowed from the bulk system, in the relaxed SJM, the density parameter of the jellium sphere assumes a value such that a cluster with a given number of electrons and specific electronic configuration achieves its equilibrium state. Comparing the relaxed SJM results with the rigid SJM results on the one hand, and the experiment on the other hand, provide information on the possible structural relaxations of the clusters in the fragmentation processes.

In this work, we have studied the binary decay processes of positively charged silver clusters Ag$_Z^Z$ ($Z=1, 2$) containing up to 100 atoms, in all possible channels, using the relaxed and the rigid SJMs. The possible decay channels for singly-ionized Ag clusters are

$$\text{Ag}^{1+}_N \rightarrow \text{Ag}^{1+}_{N-p} + \text{Ag}^0_p, \quad p = 1, 2, \cdots, N - 2.$$ (1)

For doubly charged clusters, the decays can proceed via two different processes. The first one is the evaporation process

$$\text{Ag}^{2+}_N \rightarrow \text{Ag}^{2+}_{N-p} + \text{Ag}^0_p, \quad p = 1, 2, \cdots, N - 3,$$ (2)

in which one of the products is neutral; and the second one is fission into two charged products

$$\text{Ag}^{2+}_N \rightarrow \text{Ag}^{1+}_{N-p} + \text{Ag}^{1+}_p, \quad p = 2, 3, \cdots, \lfloor N/2 \rfloor.$$ (3)

In the evaporation processes, the negativity of the difference between total energies before and after fragmentation in a specific channel, $D^Z(N, p) = E^Z(N - p) + E^0(p) - E^Z(N)$, (4)
is sufficient for the decay in that channel to take place. In the above equation, $E^Z(N)$ and $E^0(N)$ are the total energies of $Z$-ply ionized and neutral $N$-atom clusters, respectively. However, in fission processes a negative value for the difference energy is not a sufficient
condition for the decay of the parent cluster. This is because the competition between the short-range surface tension and the long-range repulsive Coulomb force may give rise to a fission barrier. The height of the fission barriers are calculated using the two-spheres approximation\[6\]. The situation in a fission process is shown in Fig. 1. In figure 1, the fission of a Z-ply charged N-atom cluster into two clusters of respective sizes \(N_1\), \(N_2 = N - N_1\) and respective charges \(Z_1\), \(Z_2 = Z - Z_1\) is schematically shown. \(Q_f\) is the energy release, \(B_c\) is the fusion barrier which is the maximum energy of the Coulomb interaction of two positively-charged conducting spheres, taking their polarizabilities into account. \(B_f\) is the fission barrier height which is defined as

\[
B_f = -Q_f + B_c.
\] (5)

The Coulomb interaction energy, \(E_c\), as a function of their separations, \(d\), for two charged metal spheres can be numerically calculated using the classical method of image charges \[6\]. Our calculations show that the maximum of the interaction energy, \(B_c\), is achieved for a separation \(d_0 \geq R_1 + R_2\). The equality applies for equal cluster radii and charges. The electrostatic interaction energies of pairs of equally charged \((Z_1 = Z_2 = 1)\) clusters as functions of the pair separation are shown in Fig. 2 for different pair sizes. The radii of the clusters in this figure are calculated from \(R = N^{1/3}r_B\). In Fig. 3 the values of the Coulomb barrier, \(B_c\), are plotted for different pair sizes but equal charges \(Z_1 = Z_2 = 1\) in the rigid SJM. As is seen, when both of the cluster sizes are small, the barrier is higher than the case when at least one of them is larger.

The most favored decay channel in evaporation processes is defined as the channel for which the dissociation energy attains its minimum value

\[
D^Z(N, p^*) = \min \{D^Z(N, p)\},
\] (6)

and the most favored decay channel in fission processes is defined as the channel for which the fission-barrier height attains its minimum value

\[
B_f(N, p^*) = \min \{B_f(N, p)\}.
\] (7)

2 Total energies of clusters

The total energy of an N-electron Z-ply charged cluster is obtained by solution of the self-consistent Kohn-Sham (KS) equations \[7\] in the density functional\[8\] theory (DFT) with local spin density approximation (LSDA) for the exchange-correlation energy functional. The SJM energy for a cluster in the LSDA is given by\[5\].
\[ E_{\text{SJM}}[n_\uparrow, n_\downarrow, n_+] = E_{\text{JM}}[n_\uparrow, n_\downarrow, n_+] + (\varepsilon_M(r_s) + \tilde{w}_R(r_s, r_B^c)) \int d\mathbf{r} n_+(\mathbf{r}) \]
\[ + (\delta v)_{\text{WS}}(r_s, r_B^c) \int d\mathbf{r} \Theta(\mathbf{r}) [n(\mathbf{r}) - n_+(\mathbf{r})], \tag{8} \]

where
\[ E_{\text{JM}}[n_\uparrow, n_\downarrow, n_+] = T_s[n_\uparrow, n_\downarrow] + E_{\text{xc}}[n_\uparrow, n_\downarrow] \]
\[ + \frac{1}{2} \int d\mathbf{r} \phi([n, n_+]; \mathbf{r}) [n(\mathbf{r}) - n_+(\mathbf{r})] \tag{9} \]

and
\[ \phi([n, n_+]; \mathbf{r}) = \int d\mathbf{r}' \frac{[n(\mathbf{r}') - n_+(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|}. \tag{10} \]

Here, \( n = n_\uparrow + n_\downarrow \) which satisfies \( \int d\mathbf{r} n(\mathbf{r}) = N - Z \), and \( n_+ \) is the jellium density which satisfies \( \int d\mathbf{r} n_+(\mathbf{r}) = N \). \( \Theta(\mathbf{r}) \) takes the value of unity inside the jellium background and zero, outside. The first and second terms in the right hand side of Eq. (8) are the non-interacting kinetic energy and the exchange-correlation energy, and the last term is the Coulomb interaction energy of the system. \( \varepsilon_M \) is the average Madelung energy. All equations throughout this paper are expressed in atomic units \((\hbar = e^2 = m = 1, \) the units of length and energy are bohr and hartree, respectively). The quantity \( \langle \delta v \rangle_{\text{WS}} \) is the average of the difference potential over the Wigner-Seitz cell and the difference potential, \( \delta v \), is defined as the difference between the pseudo-potential of a lattice of ions and the electrostatic potential of the jellium positive background [2].

The SJM ground-state energy [Eq. (3)] for a cluster with \( N \) electrons is a function of \( N, r_s, \) and \( r_B^c \). In the rigid SJM, \( r_s \) takes the bulk value \( r_s^B \), whereas in the relaxed SJM, it takes the equilibrium value, \( \bar{r}_s(N) \), which for a cluster in the ground state electronic configuration, is obtained by the solution of the equation
\[ \frac{\partial}{\partial r_s} E_{\text{SJM}}(N, r_s, r_B^c) \bigg|_{r_s = \bar{r}_s(N)}, \tag{11} \]
where, the derivative is taken at fixed values of \( N \) and \( r_B^c \). The total energies of the cluster in the relaxed SJM and the rigid SJM are given by \( \bar{E}_{\text{SJM}} = E_{\text{SJM}}(N, \bar{r}_s(N), r_B^c) \) and \( E_{\text{SJM}}(N, r_s^B, r_B^c) \), respectively.

3 Results and discussion

To obtain the relaxed SJM properties, we have performed an extensive self-consistent solutions of the KS equations along with Eqs. (8)-(11), and have calculated the equilibrium
$r_s$ and the energy values of $\text{Ag}_N^Z$ clusters ($Z = 0, 1, 2$) for different cluster sizes ($N \leq 100$). To show the main differences in the equilibrium $r_s$ values of these clusters, which are appreciable for small clusters, we have plotted in Fig. the corresponding values only up to $N = 34$. As is obviously seen in the figure, the neutral and singly-ionized clusters are self-compressed for all values of $N$. However, for doubly-ionized clusters, the values cross the bulk border (i.e., $r_s^B = 3.02$) at $N = 7$.

Figure shows the relaxed SJM energies per atom in electron volts for neutral, singly-ionized, and doubly-ionized silver clusters with $N \leq 34$. For comparison, we have also plotted the bulk value ($\varepsilon = -7.89$ eV) by a dashed line. Using these values of equilibrium energies and sizes, the relaxed SJM fragmentation energies are calculated by the Eqs. (5)-(7).

In Fig. we have plotted the dissociation energies of the most favored evaporation channels of the singly ionized clusters. We have shown the most favored value of $p$ by $p^*$. The solid small square symbols show the most favored values $p^*$ on the right vertical axis whereas, the corresponding dissociation energies, $D^{1+}(N, p^*)$, are shown on the left vertical axis by large open squares. As is seen in the figure, there exist some maxima and minima. The maxima of the $D^{z}(N, p^*)$ correspond to the closed-shell $\text{Ag}_N^+$ clusters with $N = 3, 9, 19, 35, 59, ...$. These clusters have high stabilities compared to their neighboring sizes. On the other hand, the minima correspond to the sizes which decay into two closed-shell clusters (for example, $\text{Ag}_{11}^+ \rightarrow \text{Ag}_9^+ + \text{Ag}_2$). A negative value for the dissociation energy implies that the cluster is unstable against the spontaneous decay.

In Fig. we have shown the most favored products $\text{Ag}_{p}^0$ and the dissociation energies $D^{2+}(N, p^*)$ for the decay of $\text{Ag}_N^{2+}$ via evaporation channel. It is seen that, here, the mean dissociation energy is higher than that in the evaporation of singly ionized clusters. That is, here, the number of clusters stable against the spontaneous evaporation is larger than that in the singly ionized case. However, evaporation is not the only decay mechanism for multiply charged clusters, and they can also decay via fission processes in which both fragments are charged.

Figure shows the barrier heights $B_f(N, p^*)$ for the most favored fission channels $\text{Ag}_N^{2+} \rightarrow \text{Ag}_{N-p^*}^+ + \text{Ag}_{p^*}^+$. Here, in the relaxed SJM, the Coulomb barriers are calculated using the equilibrium sizes of each $Z$-ply charged fragments i.e., $\bar{R}^Z(N) = N^{1/3}\bar{r}^Z_s(N)$. As is seen, for small clusters, the majority have negative barrier heights. That is, most of them are unstable against spontaneous fission. However, as $N$ increases, the number of clusters with negative barrier heights decreases and beyond a certain size range, all the barrier heights become positive. As before, the fragment sizes $p^*$ are shown in the left vertical axis.

As mentioned before, a doubly charged cluster can decay both via evaporation and
fission. To estimate at what sizes which decay mechanism is dominant, we have compared the dissociation energies and the fission barrier heights in Fig. 7(c). At small sizes (\(N < 21\)), the fission process dominates because, the barrier heights for the fission are lower than the dissociation energies for the evaporation. However, the competition between the evaporation and fission starts at \(N=21\). This competition continues with some fluctuations until the evaporation dominates completely. Ag clusters of sizes \(\sim 1\) nm and \(\sim 2\) nm contain \(\sim 40\) and \(\sim 300\) atoms, respectively. Knowing the fact that, in doubly ionized clusters, the induced evaporation is most favored for \(N > 21\), we conclude that the ionized clusters of nano-meter size undergo the fragmentation mostly via the evaporation processes.

The rigid SJM fragmentation energies have been calculated by the self-consistent solutions of the KS equations for the system with the positive background density parameter of \(r_s^B\). In Figs. 8(a)-(c), the corresponding fragmentation energies of the relaxed and the rigid SJM are compared. As is seen, in some cases the energy difference is as large as 0.5 eV, indicating the significant effect of relaxation.

Improvements over our relaxed SJM results can be obtained by assuming that, at the instant the fragmentation takes place, the the parent and the products are not at their individual equilibrium state but that, the \(r_s\) values of the products are equal to that of the parent at that instant. Thus, in the equations used for the dissociation energies and the fission barrier heights this fact must be taken into account. The \(r_s\) value of the parent cluster at the fragmentation instant (i.e., at the instant the two pieces are created) is something which is between that of the neutral cluster with the same \(N\) and that of the relaxed \(Z\)-ply charged of the same \(N\). That is, \(r_s^0(N) \leq r_s \leq r_{s+}^2(N)\) for the fission of a doubly charged \(N\)-atom cluster. The reason for this fact lies in the probabilistic nature of the energy absorption in the ionization process of the neutral cluster as well as the energy absorption in the fragmentation process of the \(Z\)-ply charged parent cluster. If the fragmentation energy is absorbed as soon as the electrons are detached from the neutral cluster, then the parent charged cluster does not have enough time for structural relaxation due to its charging. Therefore, the appropriate \(r_s\) value would be that of the neutral cluster. On the other hand, if the absorption of the fragmentation energy takes place with enough delay relative to the ionization instant, then the parent charged cluster has a chance to arrive at its relaxed \(r_s\) value. These arguments lead us to conclude that the experimental fragmentation energies are highly dependent on the details of the experimental setup. This freedom in taking the \(r_s\) values of the clusters in a dynamical process such as fragmentation shows the advantages of the relaxed SJM over the rigid one. However, in cases where the relaxed and the rigid \(r_s\) values are more or less the same, one would expect that applying the time-saving rigid SJM would lead to the same estimates of the fragmentation energies.
4 Summary and conclusions

In this work, we have calculated the dissociation energies and the fission barrier heights of the fragmentations of singly and doubly ionized silver clusters in the two schemes of relaxed and rigid SJMs for different cluster sizes, $N \leq 100$. In our calculations, we have assumed spherical geometries for the clusters. In the rigid SJM, the density of the positive charge background is taken to be that of the bulk system, $n^B$. However, in the relaxed SJM, that density is obtained in a self-consistent way which corresponds to the equilibrium state of the cluster. The fission barrier heights are calculated using the two-spheres approximation and for the Coulomb interaction of the two metallic spheres we have employed the method of image charges numerically. The differences in the results of the two schemes show the advantages of the relaxed SJM over the rigid one in that, one is able to take into account the structural relaxations in dynamical processes such as fragmentations.
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Figure 1: Fission barrier in the two-spheres approximation. The parent $N$-atom $Z$-ply charged cluster decays into two clusters of sizes $N_1$ and $N - N_1$, with charges $Z_1$ and $Z_2$, respectively.

Figure 2: Coulomb energy in electron volts of two singly charged metallic spheres as a function of their separation distance.

Figure 3: Coulomb barrier heights in electron volts for two singly charged metallic spheres with different sizes.

Figure 4: Equilibrium $r_s$ values in atomic units for neutral, singly ionized, and doubly ionized silver clusters. The horizontal dashed-line shows the bulk value for silver, 3.02.

Figure 5: Equilibrium energies in electron volts of neutral, singly ionized, and doubly ionized silver clusters. The horizontal dashed-line shows the bulk value for silver, -7.89 eV.

Figure 6: Dissociation energies, in electron volts, of the most favored decay channels of singly ionized clusters, in relaxed SJM, are shown with respect to the left vertical axis. The right vertical axis shows the sizes of the fragments in the most favored channels.

Figure 7: Relaxed SJM results for doubly ionized silver clusters. a)- the same quantities as in Fig.4 for doubly ionized clusters; b)- the fission barrier height in electron volts for the most favored fission channel as a function of the cluster size. The right vertical axis shows the most favored product sizes of the neutral clusters; c)- comparison of the decay energies of via evaporation and fission mechanisms. Competition starts at $N = 21$.

Figure 8: Comparison of the most favored channel fragmentation energies, in electron volts, for the two schemes of the relaxed and rigid SJMs. a)- dissociation energies of singly ionized clusters; b)- dissociation energies of doubly ionized clusters; c)- fission barrier heights for the fission of doubly ionized clusters into two singly ionized clusters.
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