General segregation and chemical ordering in bimetallic nanoclusters through atomistic view points

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Abstract

We predict general trends for surface segregation in a binary metal cluster based on the difference between the atomic properties of the constituent elements. Considering the attractive and repulsive contributions of the cohesive energy of an atom in a cluster, energetically most favorable sites for a guest atom on a pure metal cluster is determined. It is predicted that for adjacent elements in a row of the periodic table, the bimetallic system would be more stable if the component with smallest valence electron density is placed on the surface. On the contrary, for well separated components in the periodic table, the bimetallic cluster would be more stable if the component with the smallest core electron density is placed inside. Such chemical ordering trends in the lowest energy configurations of Pt-Au, Pt-Pd and Pt-Ni binary alloy clusters are verified for their 561 atom systems through simulated annealing process. It is predicted that the Ir, Rh, Ni, Pd atoms would tend to be located inside the Ir-Pt, Rh-Pd, Ni-Cu and Pd-Ag bimetallic nanoclusters, respectively.

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Surface segregation mechanism in nanoalloy clusters is of great importance for controlling their morphology, composition and catalytic activities. Though, current understanding of this phenomenon, based on some theoretical calculations \[1, 2, 3, 4, 5, 6, 7, 8, 9, 10\] and discrete experimental observations \[11, 12, 13, 14\] highlights the general trend of this process in some particular systems, there exist no generalized convention and physical explanation to suit for all the binary systems till now.

Understanding of surface segregation in alloy systems based on the properties of component elements and composition has been addressed in the pioneer works of Friedel \[1\]. For bulk alloys, several groups \[2, 3, 4, 5, 6\] at different theory levels have confirmed the otherwise intuitively general physical trend that surface segregation energy in a transition metal (TM) alloy is given by the difference in the surface energies of the pure alloy components \[7\]. The present understanding of this phenomenon is based on empirical and thermodynamic models, although there have been attempts to predict both the surface alloy extent \[2, 3\] and crystalline structure of an alloy from quantum mechanical perspectives \[8\].

Motivated by practical applications in heterogeneous catalysis, surface segregation process has also been addressed in metallic nanoparticles (NPs). Baletto and coworkers \[10\] have explored the idea of atomic size mismatch between the components to shed light on the core-shell structure formation of different TM alloys, where the size mismatch between the atoms is one of the driving forces for the formation of such structures. On the other hand Bozzolo et al. \[7\] have adapted a simple semiempirical method based on the concept that energy of formation of a given atomic configuration is the sum of strain and chemical energies of the individual atoms in the cluster, to calculate the heat of formation of binary alloys. However, though these criteria highlight the general trends of surface segregation, they do not give any physical explanation of the phenomenon. Alternatively, Hwang et al. have implemented a general methodology for the quantitative determination of the extent of alloying or atomic distribution in bimetallic NPs, based on local coordination parameters extracted from X-ray absorption spectroscopy (XAS) data \[9\]. Although, the method provides a good qualitative description of the experimental results, it is applicable to bimetallic NPs prepared under certain conditions, which have not fully reached their thermodynamic equilibrium.

In general, the cohesive energy of an atom in a cluster is the sum of the energies corresponding to its attractive and repulsive interactions with the other atoms of the system:

\[
U_{coh} = U_{atr} + U_{rep} \] [15]. Also, the interaction of an atom with the others of the system
is mainly determined by its nearest neighbors. Thus, the magnitude (absolute value) of
the changes $\Delta U_{atr}$ and $\Delta U_{rep}$ at a site of a pure cluster induced by the replacement of its
original atom with a guest one (guest-replacement), fundamentally depends on the coordi-
nation number of the site. The magnitudes of both the changes reach their minima when
the guest-replacement is done at a cluster surface and maxima when the replacement site is
inside the cluster. Because the values of $U_{atr}$ and $U_{rep}$ are negative and positive respectively,
the most energetically favored site for the guest-replacement process is the replacement site
in which both $\Delta U_{atr}$ and $\Delta U_{rep}$ reach their minimum values.

Now, the cohesive energy can be changed only by three ways: i) only one of its contribu-
tions changes, ii) both of them increase or decrease, and iii) one contribution increases and
the other decreases. According to the above described relation between these energy changes
and the coordination number, in the cases i) and ii) the best replacement site for the change
of one contribution is also the best for the change of the other. On the contrary, for the
situation iii) the change in attractive contribution reaches its minimum value at the same
site at which the repulsive one reaches its maximum. The best site for the change of one
contribution is the worst for the change of the other. Therefore, while the most energetically
favored replacement site by the guest-host replacement process can be a priori determined
in cases i) and ii), it is not possible in the case iii) and the changes in the cohesive energy
contributions must be calculated.

In addition, the differences between the properties of the guest atom and those of the host
atoms define the values of $\Delta U_{atr}$ and $\Delta U_{rep}$ at the replacement site. In a first approximation,
the core and the valence electron charge densities of the atoms determine the extent of their
repulsive and attractive interactions, respectively. If we assume that the electron charge
transfer between the atoms inside the cluster is practically negligible, the extent of the
energy changes induced at a given site can be a priori determined only from the core and
valence electron densities of the neutral host and guest atoms. Independently, each of
the two electron charge densities of the guest atom can be less, equal or higher than the
 corresponding one of the host atom. When the guest and the host atoms have adjacent
locations in a row on the periodic table, their core electron charge densities are similar, thus
$\Delta U_{rep} \approx 0$, and due to the difference between their valence charge densities, $\Delta U_{atr} \neq 0$.
Thus, this situation belongs to case i). The more energetically favored site for the guest-
replacement will be a surface site if the valence electron density of the guest atom is lower,
FIG. 1: Interaction energies needed to make up the model potential for each binary system. For
the $ij$-th pair of atoms, $V^{ij}(r)$ is the repulsive potential energy. The function $\tau^{ij}(r)$ represents the
attractive energy of the $i$-th atom in the presence of the $j$-th atom.

and it will be a core site if the valence electron density is the higher. On the contrary, if the
guest and the host atoms are far enough away on the periodic table, the difference between
their core electron charge densities will be more important than the difference between their
valence electron charge densities. Then, even in case $iii)$, the more energetically favored site
for the replacement will be a surface site if the core electron density of the guest atom is the
higher one, and will be a volume site if it is the smaller one.

Therefore, with respect to the relative location of the component atoms in the periodic
table, there are two situations at which the more stable chemical ordering in a binary metal
cluster alloy can be a priori determined. When they have adjacent locations in a row, the
component with smaller valence electron density will be on the surface. On the contrary, if
the alloy components have atomic numbers far enough away, the metallic atom with smaller
core electron density will be in the core. As immediate consequence of this result, stable
Pt-Au clusters can be obtained by putting the gold atom on the surface, and the tendency
of the Ni atoms to be located in the core is higher in the Pt-Ni alloy than for Pd atoms in
the Pt-Pd alloy.

In order to support these predicted results, the chemical ordering in Pt-Au, Pt-Pd and
Pt-Ni alloy clusters of 561 atoms are investigated. The atomic interaction in the alloy
nanoclusters is modelled by the many body Rafii-Tabar & Sutton version of the Sutton
& Chen potential that is based on the second moment approximation of a tight binding Hamiltonian \[16\]. In this model, the cohesive energy of the \(i\)-th atom is constructed from the repulsive \(V_{ij}(r)\) and the attractive \(\tau_{ij}(r)\) energies of its independent interactions with the \(j\)-th atoms \((j \neq i)\).

Atomic interactions in the alloy cluster are completely determined by these functions. Both the sets of functions depend on the nature of the \(i\)-th and \(j\)-th atoms. The \(\tau_{ij}(r)\) functions are explicitly given by:

\[
\tau_{AA}(r) = -d_{AA}^{AA} \left( \phi_{AA}(r) \right)^{\frac{1}{2}}, \quad \tau_{AB}(r) = -d_{AA}^{AB} \left( \phi_{AB}(r) \right)^{\frac{1}{2}},
\]
\[
\tau_{BA}(r) = -d_{BB}^{AB} \left( \phi_{AB}(r) \right)^{\frac{1}{2}}, \quad \tau_{BB}(r) = -d_{BB}^{BB} \left( \phi_{BB}(r) \right)^{\frac{1}{2}}.
\]

The superscripts specify the kind of the \(i\)-th and \(j\)-th atoms, and the \(\phi_{ij}(r)\) and \(V_{ij}(r)\) terms as well as the constants \(d\)'s are defined in Ref. \[16\].

The sets of attractive and repulsive functions for each binary alloy clusters are displayed in the Fig. 1. For the \(ij\)-th atom pair, the attractive energy of the \(i\)-th atom due to the presence of the \(j\)-th atom is given by the \(\tau_{ij}\) term. The repulsive energy of any one atom of the pair is given by the function \(V_{ij}\). For the atom pairs Au-Pt, Pd-Pt and Ni-Pt, the function \(\tau_{ij}\) (taking Pt atom as \(j\)-th atom) is higher than for the atom pair Pt-Pt (see dotted and continuous curves in b), d) and f) sections of the Fig. 1), as an expression of the fact that the valence electron densities of the Au, Pd and Ni atoms are less than that of the Pt atom. On the other hand, the repulsive energy \(V_{ij}\) of the Pt-Pt atom pair is almost equals that of the Au-Pt, and greater than those of Pd-Pt and Ni-Pt atom pairs (see continuous line and dotted curves of the Figs. 1a-1c). The results are expected, as the core electron density of Pt is higher than those of Pd and Ni, and almost the same as that of Au.

Candidates for the lowest energy structure were found by means of constant energy MD simulations using the model potential. The clusters from five dynamic states (amorphous structure with uniform specie distributions) periodically extracted from a long simulation (\(\sim 0.1\) \(\mu s\)) of the liquid phase were frozen at a rate of 10 K/ns. The final configurations obtained from this simulated annealing process are described in Fig. 2. Although various morphologies were found like icosahedral, Mark’s decahedral and cuboctahedral, their species distributions are practically the same for the five homotops. For a uniform species distribution, the surface and global (the system as a whole) compositions are equal. Thus, according to the theoretical results, the values of the superficial composition for Au in Pt-Au must be greater than the global composition value. In addition, the superficial concentration of Ni in Pt-Ni must be less than that of Pd in Pt-Pd. The superficial composition values of
Au, Pd and Ni for the most stable structures of Pt-Au, Pt-Pd, and Pt-Ni alloy nanoclusters were found to confirm the predicted results. For the Pt-Au clusters, the values of the superficial composition of Au: 0.46, 0.79 and 0.95, are greater than their corresponding global concentration values: 0.25, 0.50 and 0.75 (see the values in the Fig. 2). In addition, for the Pt-Ni system the superficial composition values of Ni: 0.13, 0.28 and 0.63, are less than the ones corresponding to Pd in Pt-Pd system: 0.20, 0.56 and 0.84 (see the values in the second and third columns of Fig. 2). Thus, the theoretical predictions are completely supported by the model potential used to describe these three nanoalloy systems. However, the final proof of our predictions comes from the reported experimental results. Recently, using several experimental techniques, Yang and coworkers have shown that Pt-Au nanoparticles with core-shell structure can be obtained only when nanoparticles of Pt are used as seeds. On the contrary, only monometallic nanoparticles of each constituent metal are produced when the synthesis order is reversed using Au nanoparticles as seeds [14]. Though there are experimental evidences of existing stable Pt-Pd clusters with Pd enriched surfaces [12] and also the stable Pt-Ni alloys with Pt enriched extended surface [13], the nanostructures were grown through low temperature synthesis processes, where a complete thermodynamic equilibrium is not achieved. The experimental and theoretical evidences for the higher stability of Pd(core)-Au(shell) reported by Pal’s group [11] provide additional validity of the

|   | Pt-Au | Pt-Pd | Pt-Ni |
|---|-------|-------|-------|
| 3:1 | 0.54 0.46 | 0.80 0.20 | 0.87 0.13 |
| 1:1 | 0.21 0.79 | 0.44 0.56 | 0.72 0.28 |
| 1:3 | 0.05 0.95 | 0.16 0.84 | 0.37 0.63 |

FIG. 2: Candidates for the lowest energy structures of each binary system (columns), at the 3:1, 1:1 and 1:3 global compositions (rows). The superficial and cross sectional views of a particular cluster are shown in each block. Lighter spheres represent platinum atoms. The values presented in each block are the superficial compositions of the clusters.
present results. The Pd-Au system falls under the case iii). Thus, Pd with smaller core electron density will be in the volume. The two components of Ir-Pt, Rh-Pd, Ni-Cu and Pd-Ag clusters have adjacent locations in a row of the periodic table, and the earlier ones have the higher valence electron charge density for each system. Thus, it can be predicted that the earlier elements of the binary clusters would tend to be located inside the bimetallic cluster; just as it occurs for Pt-Au system.

A quantitative description of the analysis presented here can be given through the energy changes shown in the Fig. 3. The change $\Delta U_{cohT}$ represents the difference in cohesive energy of the surface homotop (with a guest atom at the surface) of an icosahedral Pt cluster with respect to its central homotop (with the guest atom at the volume). According to the sign of $\Delta U_{cohT}$, the most stable homotop is the central one for Pd and Ni guest atoms, and the surface one for Au. This is why the superficial compositions of Pd and Ni atoms are less than 0.25, and that of the Au is higher than 0.25 for the Pt-Pd, Pt-Ni and Pt-Au nanoclusters with global atomic compositions 3:1, respectively (see the values presented in the first row of Fig. 2). The expression of $\Delta U_{cohT}$ as the sum of the cohesive energy changes at all the sites of the cluster; the replacement sites, the nearest sites to the replacement sites and so on, can be used to determine the sign of $\Delta U_{cohT}$. The first term of this sum is given by $\Delta U_{cohT}^0 = \Delta U_{coh}(S) - \Delta U_{coh}(C)$, where $\Delta U_{coh}(i)$ is the change of the cohesive energy induced at the replacement site $i$ through the guest-replacement; $S$ and $C$ denote the surface site and the center site, respectively.

The approximation $\Delta U_{cohT} \approx \Delta U_{cohT}^0$, is enough to obtain the sign of $\Delta U_{cohT}$ for Au and Ni, but for Pd it is insufficient (Compare the values of $\Delta U_{cohT}$ at the bottom of the Fig. 3 with those of $\Delta U_{cohT}^0$ at the top). Thus, for this guest, the next term must be added. The calculated changes of the repulsive and attractive energy contributions as well as the term $\Delta U_{cohT}^0$ are represented in the Fig. 3 by the continuous, dashed and bold arrows, respectively. The Fig. 4 shows the same quantities described in the Fig. 3, but now for three pure icosahedral hosts of 561 Au, Pd or Ni atoms with a single Pt guest atom. This figure shows that Pt is more stable at the center of the Au and at surface of the Ni hosts. The fact that $\Delta U_{cohT} \sim 0$ for Pd means that the changes $\Delta U_{atrT}$ and $\Delta U_{repT}$ almost cancel each other for this situation of case iii). Thus, for the most stable chemical ordering of Pt-Pd nanoclusters, the species distribution will be nearly homogeneous and the surface and global compositions must be similar (note that the superficial composition values of the column
FIG. 3: Energy changes at a site of a Pt cluster, induced by the replacement of its original atom with a guest one. The changes are calculated at the center (C) and a surface (S) site. The horizontal line represents the original energy of the site, the dashed arrow corresponds to $\Delta U_{atr}$ and the following continuous arrow to $\Delta U_{rep}$. The term $\Delta U_{cohT}^0$ (see the text) is represented by the bold arrow. Note that the sign of this term is the same as that of $\Delta U_{cohT}$ (see the text) for Pt-Au and Pt-Ni.

FIG. 4: Energy changes at a site of a pure Au, Pd, Pt cluster induced by the replacement of its original atom with a Pt guest atom. The same quantities as in Fig. 3, but now for three pure icosahedral hosts of 561 Au, Pd or Ni atoms and a Pt guest atom. Again the sign of $\Delta U_{cohT}^0$ is the same of $\Delta U_{cohT}$ for Pt-Au and Pt-Ni.

Pt-Pd in the Fig. 2 are close to the global composition values).

In summary, based on the fact that the cohesive energy is the sum of its attractive and repulsive contributions, it was shown that the trends of the most stable chemical ordering in a binary system are determined by the differences in the atomic properties of its elemental components. When they are adjacent in a row of the periodic table, the component with lower valence electron density will be on the surface. Moreover, if the alloy components have atomic numbers enough distant, the metallic atom with lower core electron density will be in the volume. MD simulations confirm the validity of these results for Pt-Au, Pt-Pd, and Pt-Ni systems. Finally, it is predicted that the Ir, Rh, Ni, Pd atoms would try to be located
inside the Ir-Pt, Rh-Pd, Ni-Cu and Pd-Ag bimetallic nanoclusters, respectively. We address that these predictions can be validated for any bimetallic nanocluster, and current research is underway.

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