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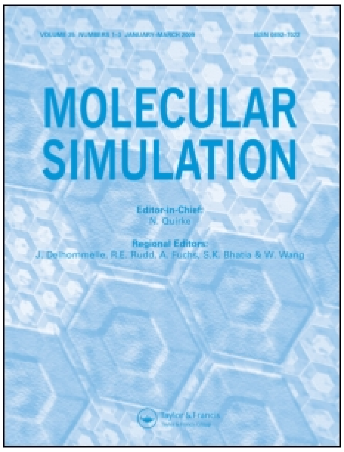

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Size effect on the stability of Cu-Ag nanoalloys

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Size effect on the stability of Cu–Ag nanoalloys

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Classical molecular dynamics (MD) simulations are used to study the phase stability of Cu–Ag nanoalloys based on the analysis of their thermodynamic mixing properties for both random and core-shell clusters as functions of nanoparticle size, temperature and composition. At 298 K, results for nanoalloys of increasing size at fixed composition suggest that alloying Cu and Ag is thermodynamically feasible only for a nanocluster size range, excluding very small (< 1.8 nm) and large clusters ($\gtrsim 4$ nm). In the size range of favourable alloy formation, Cu–Ag core-shell structures are more stable than random configurations, and the same conclusion holds for most of the composition range at fixed cluster size and 298 K. Varying temperature at fixed nanocluster size and fixed composition, core-shell structures are preferred up to the melting temperature of the nanoparticle. Also, we test an analytical model to predict the thermodynamic properties of mixing of nanoalloys using bulk enthalpies of mixing of the pure components and those of the corresponding bulk alloy. The enthalpies and Gibbs free energies of mixing obtained from the analytical model qualitatively agree with those obtained from MD simulations, especially when the nanoparticle size increases above 2.8 nm.

Keywords: molecular dynamics; nanoalloys; Gibbs energy of mixing

1. Introduction

A lot of attention is currently focused on the field of nanoparticles since the nanoscale behaviour of substances differs greatly from its macroscale behaviour, providing new opportunities for technological applications. Bimetallic clusters are of particular interest in applications ranging from catalytic to optic and electronic applications [1–3] because the cluster properties can vary dramatically not only with size, as occurs in pure nanoclusters, but also with chemical composition.

Advances in the synthesis and experimental characterisation of nanoparticles, and also in first-principles computational methods like *ab initio* and classical molecular dynamics (MD), allow the investigation of many nanocluster physical and chemical properties [4]. Nevertheless, there are aspects of nanoalloy behaviour, such as alloy formation and phase separation as a function of temperature, that are not well characterised. Previous reports have shown that the phase diagram of nanoparticles differs from that of the bulk material [5–7] in the solid regions, the interrelation among the effects of size, nucleation, phase transitions and depletion in first-order phase transitions have been studied using models of ideal and regular solutions [8,9]. Transitions from a single-phase state to two-phase structures are illustrated in Figure 1. Thermodynamic models of the transition process in nanoparticles usually involve significant contributions of interfacial tensions to the Gibbs free energies of these various phases. The condition that the Gibbs free energy of the total system for a new (two-phase) system be lower than that of the starting (single-phase) system is the transition criterion.

Surface segregation phenomena play an important role in the behaviour of solid-state bimetallic systems, and can lead to the formation of core-shell structures. For instance, Cu–Ag nanoalloys are found to be stable in the core-shell configuration at certain conditions [10,11], and this behaviour has been correlated with both the lower surface energy and larger atomic size of Ag [12–14] and also with the miscibility gap present in Cu–Ag bulk [15]. On the other hand, the properties of the Cu–Ag nanoalloys are expected to make this a suitable catalyst for processes such as the synthesis of methyl glicolate [16]. and selective oxidation of ammonia [17]. However, in order to design and synthesise efficient nanocatalysts, a better understanding has to be achieved of the stabilities of core-shell and random configurations for these nanoalloys.

In this work, we use classical MD simulations to study the phase stability of Cu–Ag nanoalloys through the analysis of thermodynamic mixing properties for both random and core-shell clusters, as functions of nanoparticle size, temperature and composition. Also, we test an analytical model to predict the thermodynamic properties of mixing of random systems using bulk enthalpies of mixing of the pure components and those of the corresponding bulk alloy.

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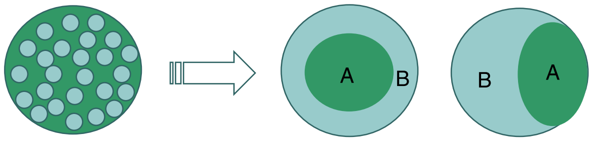

Figure 1. Schematic illustration of possible structures that may arise from phase separation in nanoalloys composed by elements A and B.

2. Theoretical background

2.1 *Properties of mixing*

The Gibbs free energy of mixing (ΔG_{mix}), which may be used to determine the relative stability of a binary system, is related to the enthalpy and entropy of mixing (ΔH_{mix} and ΔS_{mix}, respectively) by Equation (1):

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}. \tag{1}$$

Any transformation that results in a Gibbs free energy decrease is thermodynamically possible. Accordingly, the following is a necessary criterion for the formation of a bimetallic alloy:

$$\Delta G_{\mathrm{mix}} = G_{\mathrm{AB}} - X_{\mathrm{A}}G_{\mathrm{A}} - X_{\mathrm{B}}G_{\mathrm{B}} < 0. \tag{2}$$

The subscripts AB, A and B denote the A–B alloy and its A and B constituent elements, respectively. In solid nanoparticles, the mixed state may be in either random, core-shell or other ordered configuration. Surface segregation is a well-known effect that is influenced by the atomic sizes of the alloy components, their respective surface energies and the heat of formation of the alloy. Numerous first-principle studies have addressed this problem [18–23]. Ag segregates in Cu–Ag bulk alloys due to its larger atomic size and lower surface energy. For this reason, Cu–Ag alloys are usually found in core-shell structures, and in the following analysis, we only consider random versus core-shell structures. If both configurations show negative ΔG_{mix}, then both random and core-shell systems are thermodynamically possible, but the one with the more negative ΔG_{mix} is considered more stable and would be the preferred configuration of the system. Similarly, ΔH_{mix} of an A–B alloy nanoparticle can be expressed as follows:

$$\begin{aligned}&\Delta H_{\mathrm{mix}}\,(\text{nanoparticle size},\, X_{\mathrm{A}})\\ &\quad = H_{\mathrm{AB}} - H_{\mathrm{A}}X_{\mathrm{A}} - H_{\mathrm{B}}(1 - X_{\mathrm{A}}),\end{aligned} \tag{3}$$

H_{AB} is the enthalpy of a nanoalloy composed by N_{A} and N_{B} atoms with atomic fraction X_{A}, and H_{A} and H_{B} are the enthalpies of nanoparticles (of N_{A} and N_{B} atoms) of pure A and pure B, respectively. In this work, the values for these enthalpies are obtained via MD simulations as explained in the next subsection.

According to statistical thermodynamics, entropy is quantitatively related to randomness by the Boltzmann equation:

$$S = k \ln \omega, \tag{4}$$

where k is the Boltzmann's constant and ω is a measure of randomness. Using suitable mathematical tools it is possible to estimate ω as the number of ways in which the atoms can be arranged in the particle, yielding the following expression for the entropy change per atom in a random mixing process:

$$\Delta S_{\mathrm{mix}} = -R\,[X_{\mathrm{A}} \ln X_{\mathrm{A}} + (1 - X_{\mathrm{A}}) \ln (1 - X_{\mathrm{A}})], \tag{5}$$

where R is the universal gas constant. Since X_{A} and $(1 - X_{\mathrm{A}})$, are less than unity, ΔS_{mix} is positive, i.e. in a random mixture there is always an entropy increase after mixing. Compared with random structures, core-shell alloy nanoparticles have a much smaller number of ways to arrange the A and B atoms. For this reason, the entropy of mixing for core-shell systems is neglected in this study.

2.2 *Modelling mixing properties of nanoalloys from the corresponding bulk properties*

Computing enthalpies of mixing of nanoalloys by MD simulations is relatively expensive due to the need of performing simulations of alloy clusters with different sizes and compositions including the corresponding pure components. An alternative way to obtain the heat of formation of a nanoalloy is based on the enthalpies of the bulk pure components and on that of the bulk alloy and relating them to the nanoparticle size N (the total number of atoms of the nanoparticle) [24] by:

$$\begin{aligned}\Delta H_{\mathrm{mix}} =& H_{\mathrm{AB}}^{\mathrm{Bulk}}\left(1 - \sqrt[3]{\frac{1}{N}}\right) - X_{\mathrm{A}} \cdot H_{\mathrm{A}}^{\mathrm{Bulk}}\left(1 - \sqrt[3]{\frac{1}{NX_{\mathrm{A}}}}\right)\\ &- (1 - X_{\mathrm{A}}) \cdot H_{\mathrm{B}}^{\mathrm{Bulk}}\left(1 - \sqrt[3]{\frac{1}{N(1 - X_{\mathrm{A}})}}\right),\end{aligned} \tag{6}$$

where $H_{\mathrm{AB}}^{\mathrm{Bulk}}$ is the enthalpy of the bulk alloy with atomic fraction $X_{\mathrm{A}} \cdot H_{\mathrm{A}}^{\mathrm{Bulk}}$ and $H_{\mathrm{B}}^{\mathrm{Bulk}}$ are enthalpies of the bulk alloys of pure components A and B, and N is the number of atoms of the nanoparticle. We used Equation (6) to calculate the enthalpies of mixing of nanoalloys, where $H_{\mathrm{AB}}^{\mathrm{Bulk}}$, $H_{\mathrm{A}}^{\mathrm{Bulk}}$ and $H_{\mathrm{B}}^{\mathrm{Bulk}}$ were obtained using MD simulations. Entropies and free energies of mixing were calculated with Equations (1) and (5).

3. Computational methods

3.1 Evaluation of enthalpies of mixing of Cu–Ag nanoalloys

Firstly, MD simulations of Ag_xCu_{1-x} clusters with random and core-shell structures were performed to study the size effect on phase separation at fixed composition and 298 K; the Ag atomic fractions were fixed between 0.4 and 0.5. Table 1 lists the studied systems.

Secondly, the temperature dependence of phase separation was investigated at fixed cluster size for the 321 and 642 atom systems at 298, 400, 500, 600, 700 and 800 K. Finally, for systems with 321, 642 and 1289 atoms at 298.15 K, the effect of varying composition was investigated in the whole range from pure Ag to pure Cu, as shown in Table 2.

The initial systems were face centred cubic (FCC) structures built as explained in the legend of Table 1. Thus, the truncation pattern to approximate the spherical shape is dependent on the cluster diameter. Figure 2 shows such pattern for clusters of different diameters.

All of the MD simulations were carried out using the DL_POLY simulation package [25]. Preliminary tests using both the isothermal-isobaric NPT ensemble [26] and the canonical NVT ensemble [27] were performed on the Cu–Ag nanoalloys. These tests were designed to compare the enthalpies from the NPT simulations with the energies from the NVT simulations. However, given that these results were very similar to each other, we chose the NVT ensemble for all the simulations of the nanoalloy systems because the construction of the systems to be simulated is much simpler in the NVT ensemble. The reason is that the NPT ensemble requires the adjustment of the simulation box for each cluster size, which is not needed in the NVT simulations without periodic boundary conditions.

NPT simulations used only in the preliminary tests were carried out at 298.15 K and at 1 atm, the temperature and pressure being controlled through the Berendsen's thermostat and barostat [26], using the same value of 0.4 ps as relaxation time both for the thermostat and barostat, respectively. The equations of motion were solved using the Verlet Leapfrog integration algorithm with a Verlet width shell of 1.0 Å [27]. The simulation cell containing one metal particle was a cubic box of 60 Å side. Simulations were done using a cut-off radius of 25 Å to avoid particle–particle interactions between neighbouring cells; periodic boundary conditions were used in all directions, and interactions between the atoms in the clusters were modelled with the Sutton–Chen potential [28] with published parameters [29]. These simulations were considered acceptable when they showed small volume fluctuations (~ 1%).

Table 1. Parameters of the systems studied to evaluate size dependence at 298 K.

Systems random and core shell		
Diameter (nm)	Number of atoms	X_{Ag}
1.80	177	0.50
1.85	200	0.50
1.90	225	0.50
2.00	270	0.50
2.20	321	0.45
2.80	642	0.45
3.50	1289	0.40
4.00	2000	0.50

To build such systems, FCC cells were added successively around a central one until a spherical-like cluster of the desired diameter (left column) was obtained. The resulting number of atoms for each structure is listed in the central column along with the silver atomic fraction X_{Ag} in the right column.

Table 2. Compositions studied for each nanoparticle size at 298 K.

Atomic fraction of Ag		
321 atoms	642 atoms	1289 atoms
0.22	0.17	0.10
0.29	0.31	0.25
0.44	0.45	0.40
0.56	0.62	0.56
0.75	0.73	0.70
0.86	0.88	0.89

In the canonical NVT ensemble, the temperature was controlled through the Berendsen's thermostat, using a relaxation time of 0.4 ps. The equations of motion were solved using the Verlet Leapfrog integration algorithm with a Verlet width shell of 1.0 Å. Periodic boundary conditions were not used. The simulations were performed using a cut-off radius close to half the diameter of each cluster for the interatomic interactions that were modelled through the Sutton–Chen potential. The total energy of the system in equilibrium was used to approximate its enthalpy. Mixing enthalpies of the nanoalloys were calculated with Equation (3) using the MD simulation enthalpies of the bimetallic systems and those of their corresponding pure components.

For all simulations, the lengths were chosen in such a way that equilibrium was reached as determined by the stability of the total energy of the system as a function of time. Fluctuations defined as differences between the instantaneous total energy and its average were calculated for every 4000 steps; the system was considered stable when these fluctuations remained around zero, with a tolerance of $\pm 10^{-4}$ eV/atom. In most of the cases simulated at 298 K, the simulation length was equal to 20 ns with the first 19 ns for equilibration and the remaining 1 ns for data collection. However, for systems simulated at larger temperatures, the simulation length was mostly equal to 80 ns, the first 79 ns for equilibration and the remaining 1 ns for data collection. These long equilibration times are indeed needed for the Cu–Ag systems. This is apparently related with the large size mismatch between the metal constituents, since in most of the cases they have to find alternative energy-lowering

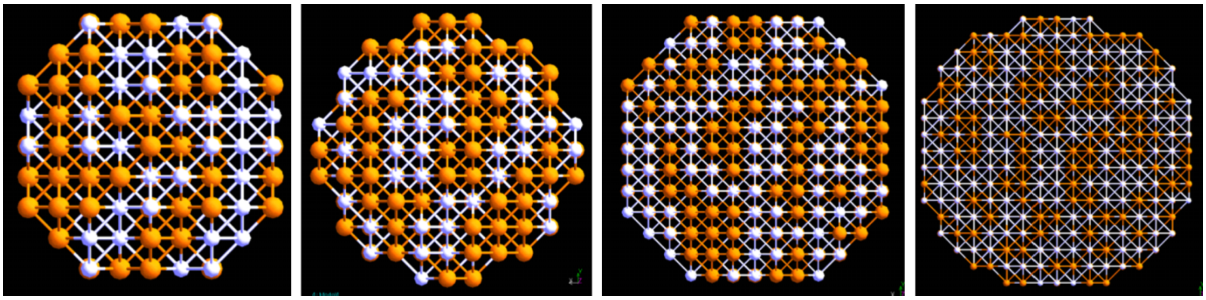

Figure 2. Examples of initial structures. From left to right: 225 atoms, $X_A = 0.50$; 321 atoms, $X_A = 0.45$; 642 atoms, $X_A = 0.45$; 1289 atoms, $X_A = 0.40$.

positions, which makes the equilibration time large. This finding is in agreement with previous studies that used MD simulations [11,30,31] to analyse the growth of Cu–Ag nanoclusters, where Ag atoms are deposited one by one on a Cu core and the equilibrium interval given to the system among subsequent depositions is between 2.1 and 7 ns to let the cluster find its minimum free energy configuration at the given temperature avoiding the formation of metastable structures attributed to kinetic trapping. These times are comparable with the equilibration times used in our simulations.

3.2 Enthalpies of bulk alloys

Simulations of bulk systems were performed using cubic cells of side 22 Å, with FCC structure; the simulation cell consisted of 665 atoms. Periodic boundary conditions were applied in the three spatial directions. All of the MD simulations for bulk systems were carried out in the isothermal–isobaric NPT ensemble. The simulations were performed at 298.15 K and at 1 atm with the temperature and pressure being controlled through the Berendsen's thermostat and barostat, using 0.4 and 0.03 ps as relaxation times for the thermostat and barostat, respectively. Simulations were done using a cut-off radius of 8 Å, and interactions between the atoms in the clusters were modelled through the Sutton–Chen potential. Simulation lengths for bulk systems were 800 ps, the first 700 ps for equilibration and the remaining 100 ps for data collection. This length allowed the systems to reach equilibrium. Atomic fractions of Ag were varied from zero to one with increments of 0.1.

4. Results and discussion

4.1 Size effect on the stability of Cu–Ag nanoalloys

Figure 3 shows the energies of mixing of systems at fixed compositions (given in Table 1) as a function of nanoparticle size. Negative mixing enthalpies are found for systems between 200 and 1289 atoms, which indicates that alloying is an exothermic process for those nanoparticle sizes; on the other hand, alloying systems with less than 177 and more than 2000 atoms are endothermic processes.

As a first approximation, the heat of mixing is the result of interactions mainly between adjacent atoms, but since the Ag atom is 13% larger than Cu, the change in the energy of mixing must take into account a strain energy contribution, which generates repulsion between the atoms. Figure 3 also shows that alloying is thermodynamically feasible for system sizes between 200 (1.85 nm) and 1289 atoms (3.5 nm), as shown by the alloy Gibbs free energy being lower than the weighted sum of the Gibbs free energy of the pure components before mixing. The Gibbs free energies of mixing in the random alloys have the same behaviour as the enthalpies of mixing due to the relatively low temperature of 298 K, which makes the entropy term small relative to the enthalpy term.

Comparing configurations, only at very small sizes, such as a random system with 200 atoms (1.85 nm) has a lower Gibbs free energy of mixing than that of core shell, but larger clusters have lower Gibbs free energies of mixing with a core-shell configuration, indicating that the system is more stable in the two phase region when the number of atoms is 225 (1.90 nm) or larger. It is interesting that both ΔH and ΔG of mixing suggest a non-monotonic variation with size, with a minimum value (more exothermic and more stable) located near a cluster size of 350 atoms.

In summary, the results in Figure 3 suggest that for cluster sizes larger than 3.5 nm, Cu and Ag will not be alloyed at 298 K, as occurs in bulk. On the other hand, the results of small clusters (approximately below 200 atoms) must be taken with caution. Other studies have shown [32,33] that from growing noble metal clusters it is observed that they can adopt several different structures that may be classified as multiply twinned particles, such as icosahedra and decahedra, and FCC structures. These reports mentioned several studies that have found the icosahedral structure as the equilibrium shape for small sizes, especially in the range from 40 to 200 atoms. The size effect on the preferred structure can be understood from the energetic point of view [34] because icosahedral

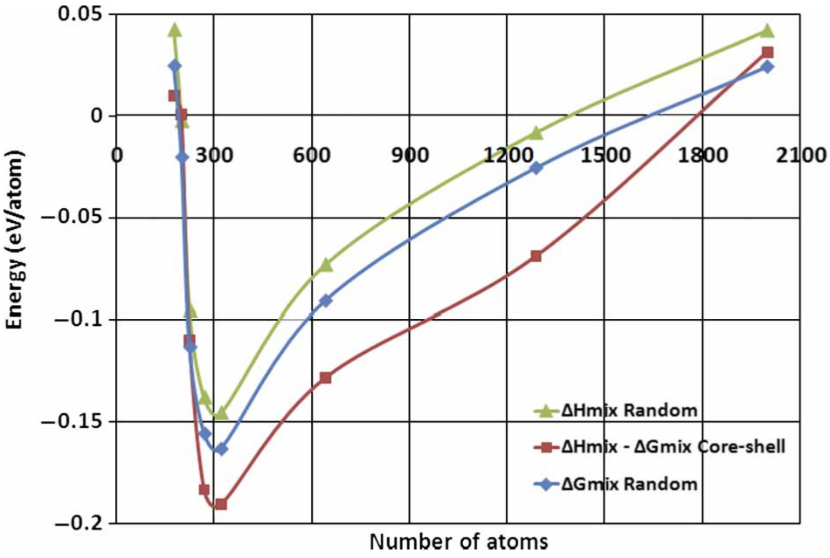

Figure 3. Enthalpies and free energies of mixing as a function of nanoparticle size at fixed atomic fraction (see Table 1) and 298 K. Symbols are MD data representing enthalpies of mixing calculated with Equation (3) and Gibbs free energies of mixing calculated using Equation (1). The solid line is a fit to the simulation data. Note that the same curve is used to describe the enthalpy and the Gibbs free energy of mixing in core-shell systems due to the negligible configurational entropy contribution in these systems.

structures are very compact, only exposing (111) facets on the surface, which is reflected by a surface energy gain with respect to FCC structures; however, this requires a distortion of the basic cubic lattice, increasing the internal stress. In the case of large clusters, the surface/volume ratio is smaller. Therefore, the stress involved in the core is no longer compensated by the surface energy gain, and icosahedral clusters become less stable than FCC structures. Since our study only includes FCC clusters, we consider that the results below 200 atoms are less reliable.

4.2 Temperature effect on the stability of Cu–Ag nanoalloys

Figure 4 shows enthalpies of mixing as a function of temperature for systems with 321 (2.2 nm) and 642 atoms (2.8 nm) revealing in all cases exothermic formation of these alloys.

For systems with 321 atoms, alloying of core-shell clusters at temperatures between 298 and 500 K is more exothermic than that of random; however, at higher temperatures their enthalpies of mixing are very close,

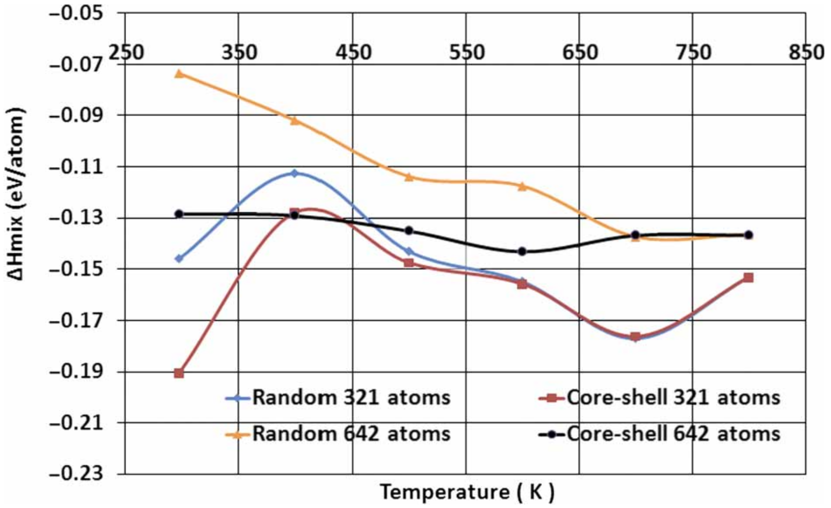

Figure 4. Enthalpies of mixing as function of temperature, systems with 321 and 642 atoms at fixed composition (see Table 1). Solid lines are fitting to the simulation data.

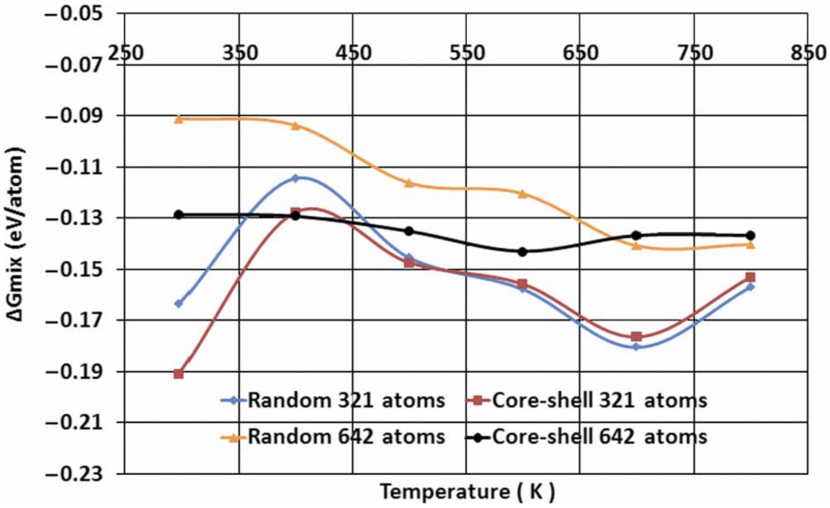

Figure 5. Gibbs free energies of mixing as a function of temperature, system with 321 and 642 atoms at fixed composition (see Table 1). Solid lines are fitting to the simulation data.

possibly due to the systems reaching their melting point. Similar behaviour is observed for systems with 642 atoms, but the transition point is approximately 700 K.

Figure 5 illustrates that alloying of Cu and Ag is thermodynamically possible at all the conditions studied for both the 321 and 642 atom systems, as suggested by negative values of their free energies of mixing. The Gibbs free energies of mixing of the systems with core-shell structures and 321 atoms are lower than the corresponding random ones at temperatures <500 K. Therefore, core shell is the most probable configuration for the systems at these conditions, but random mixing is favoured at higher temperatures. On the other hand, the Gibbs free energies of mixing of the systems with 642 atoms also prefer core-shell structures at low temperatures and random structures start to be preferred at 700 K and higher temperatures.

In summary, at constant particle size and fixed composition, the formation of core-shell alloys is more favourable than that of random mixtures at all temperatures up to the melting point of the nanoparticles; for the larger core-shell particle (642 atoms) ΔG_{mix} is practically independent of temperature, but for the smaller particle there is a significant variation as a function of temperature.

4.3 Composition effect on the stability of Cu–Ag nanoalloys

Figures 6–8 show exothermic processes for alloying Cu and Ag in clusters of 321, 642 and 1289 atoms, respectively, at various compositions. It was mentioned in Section 4.1 that the heat of mixing is the result of two contributions. One is strain energy, which generates a repulsion force; the other is the attractive interaction

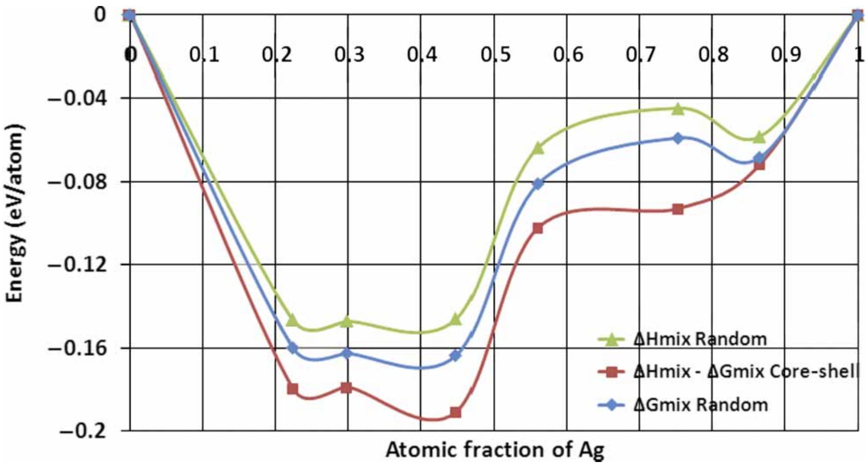

Figure 6. Energies of mixing as a function of composition, systems with 321 atoms at 298 K. Solid lines are fitting to the simulation data.

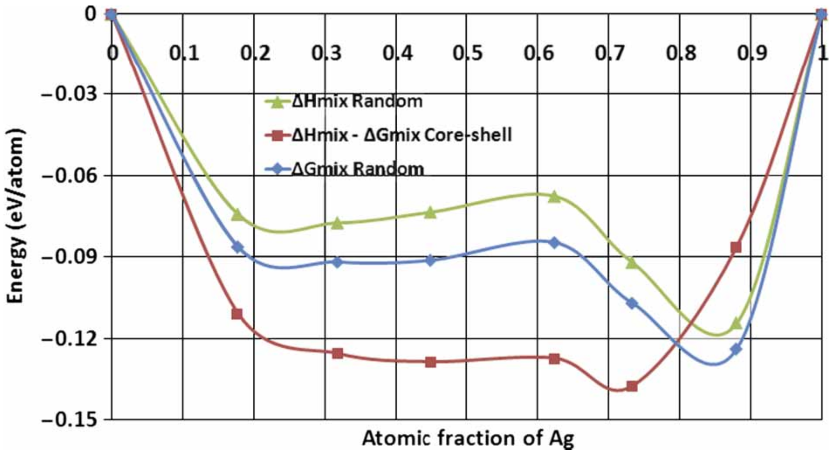

Figure 7. Energies of mixing as a function of composition, systems with 642 atoms at 298 K. Solid lines are fitting to the simulation data.

between adjacent Cu–Ag atoms, which in most cases favours the mixing process. However, at a fixed temperature, the relative contribution of each term on the heat of mixing changes with overall composition. For systems with 321 and 1289 atoms, the heat of mixing is more negative for core-shell alloys in the whole range of compositions. On the other hand, mixing enthalpies of core-shell clusters with 642 atoms are more negative than those of random systems for atomic fractions of Ag approximately lower than 0.7. In core-shell systems, partial alloying only exists at the interface; therefore, for the same atomic composition, the repulsion due to size differences of Cu and Ag atoms in core-shell clusters has a smaller contribution to the enthalpy of mixing than that in random alloys. Also, large compositions of Ag in core-shell systems mean a small Cu core and a smaller Cu–Ag interfacial area, therefore, with a reduced number of Cu–Ag pairs, resulting in less negative enthalpies of mixing in this region.

Random systems with 1289 atoms have the smallest negative enthalpies of mixing in the region close to 0.5 atomic fraction. In this region, the number of atoms of Cu and Ag is very similar, which increases the repulsion inside the cluster due to the difference in the atomic sizes. Random clusters with 321 atoms behave differently; in these particles more exothermic heats of formation are found in the region of $X_{\mathrm{Ag}} < 0.5$. The reason could be the smaller particle size, resulting in different relative contributions of the energies in these alloys.

Alloying is thermodynamically allowed in the three cluster sizes, as evidenced by the negative Gibbs free energies of mixing. In particles with 321 and 1289 atoms (Figures 6 and 8, respectively), core-shell structures are more stable than the corresponding random ones, and for nanoparticles with 642 atoms (Figure 7), core-shell structures are more stable for atomic fractions of Ag approximately lower than 0.7.

At this point, it is useful to discuss the structures and especially the structural evolution of these systems obtained from the MD simulations. First, it is important to notice that starting from various ordered initial

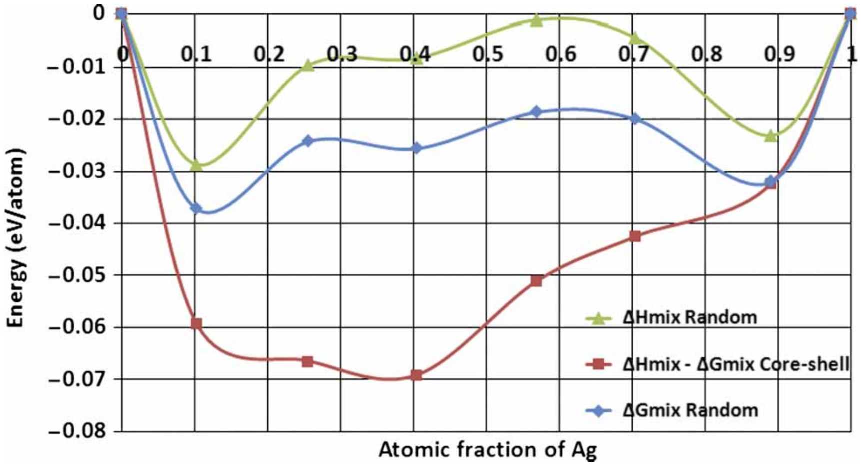

Figure 8. Energies of mixing as a function of composition, systems with 1289 atoms at 298 K. Solid lines are fitting to the simulation data.

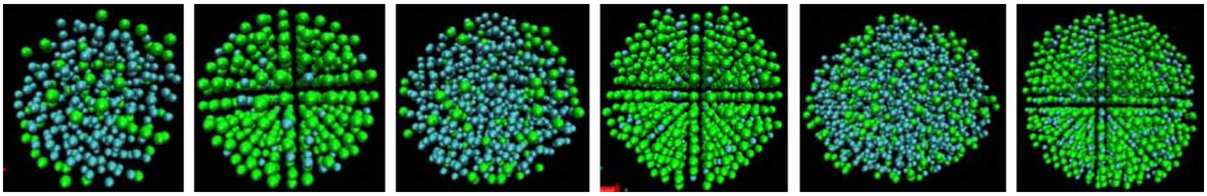

Figure 9. Snapshots of final configurations of random Cu–Ag systems at 298 K. From left to right: 321 atoms, $x_{Ag} = 0.224$; 321 atoms, $x_{Ag} = 0.866$; 642 atoms, $x_{Ag} = 0.177$; 642 atoms, $x_{Ag} = 0.88$; 1289 atoms, $x_{Ag} = 0.256$; 1289 atoms, $x_{Ag} = 0.89$.

configurations, the clusters with random distributions and low Ag atomic fractions, become disordered in few picoseconds, i.e. the atoms do not maintain the original lattice positions and find alternative locations that result in a lowest total energy for the cluster, although this is a disordered structure. Figure 9 illustrates this behaviour, which was previously observed for NiAg clusters at 300 K [35]. By contrast, large atomic fractions of Ag keep the ordered structure. Some disorder is also observed in core-shell structures, as depicted in Figure 10.

4.4 Analytical model of mixing properties based on the corresponding bulk properties

Figure 11 shows enthalpies of mixing obtained from Equation (6) as a function of composition for random systems with increasing number of atoms, using only enthalpies of the bulk systems obtained from MD simulations. Model data (symbols) were fitted with a Redlich–Kister expansion (solid lines) truncated after the third term [36].

Systems with 321 and 642 atoms display negative enthalpies of mixing in the whole range of compositions; however, some compositions of the system with 1289 atoms display positive heats of alloy formation. These results qualitatively agree with those obtained using data from with simulation of clusters (Figures 6–8). Although in Figures 6–8, all alloys showed negative heats of alloy formation, it is observed that the largest cluster (1289 atoms, Figure 8) has enthalpies of mixing close to zero in a range of Ag atomic fractions close to 0.5, which is the region, where Figure 11 displays positive heats of formation. Other details coming from the microscopic atomic arrangements such as variations at Ag-rich concentrations especially for the smallest cluster (321 atoms) cannot be captured by the mean field model given by Equation (6). Same observation relates to the comparison of the free energies of mixing of the cluster shown in Figure 12. Yet, this model can predict in an approximate way the relative stability of random Cu–Ag nanoclusters. In Equation (6), as the number of atoms approaches to infinite, the enthalpies of mixing of the alloy become equal to that of bulk system, as shown in Figure 11.

In agreement with the full simulation results, the systems become less stable (as denoted by the positive free energies of mixing in Figure 12) as the nanoparticle size increases. Systems with more than 1289 atoms (approximately 3.5 nm) are expected to be unstable, since the separated components are more stable than when alloyed; therefore, the analytical model predicts that thermodynamically it is not possible to alloy Cu and Ag forming clusters larger than 3.5 nm.

5. Conclusions

Results of MD simulations of Cu–Ag nanoalloys at fixed composition indicate that at 298 K alloy formation is an exothermic and thermodynamically allowed process in nanoparticles with sizes between 1.85 and 3.5 nm (200 and 1289 atoms, respectively). Also, core-shell structures are preferred over random alloys in 1.9 nm or larger nanoparticles (number of atoms >225). Temperature effect at fixed particle size and fixed composition was examined in systems with 321 and 642 atoms; the results indicate exothermic and thermodynamically allowed alloy formation between 298 and 800 K, with core-shell structures being the most probable configuration until the systems reach their respective size-dependent melting

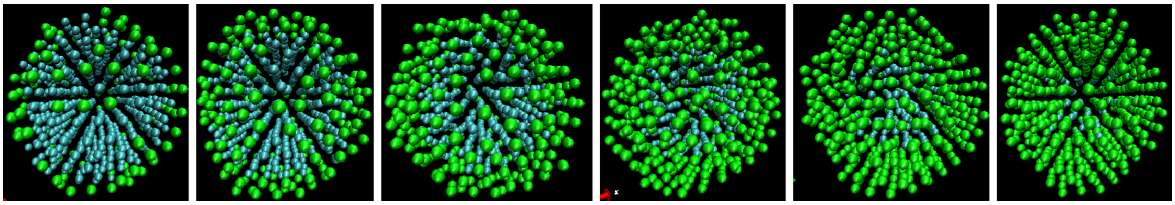

Figure 10. Snapshots of final configurations of core-shell Cu–Ag systems of 642 atoms at 298 K. From left to right: $x_{Ag} = 0.177$; $x_{Ag} = 0.318$; $x_{Ag} = 0.45$; $x_{Ag} = 0.625$; $x_{Ag} = 0.734$; $x_{Ag} = 0.88$.

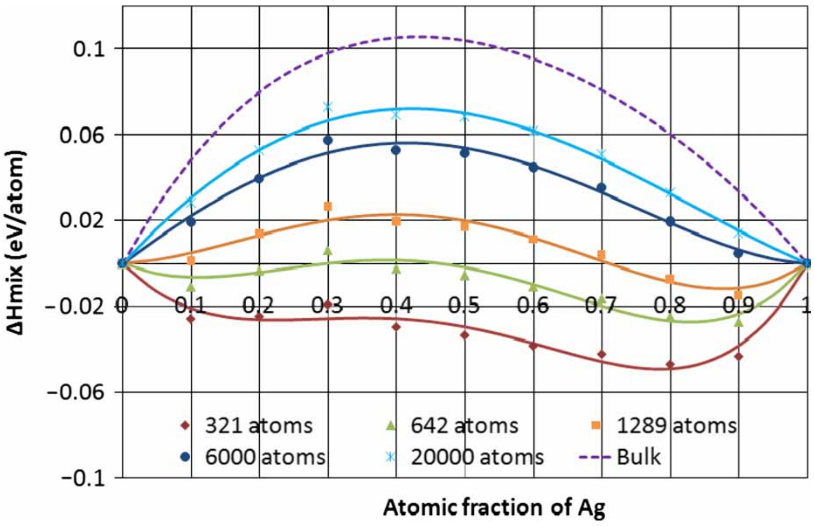

Figure 11. Enthalpies of mixing calculated from bulk properties using Equation (6). The dashed line was calculated with Equation (3) using the enthalpies of the bulk alloys from MD simulations.

point. Selected systems with 321, 642 and 1289 atoms were analysed in the entire range of compositions at 298 K; under these conditions, alloy formation is favourable and in most cases Cu–Ag systems prefer core-shell configurations.

An analytical model based only in bulk alloy properties was tested to obtain properties of mixing of nanoalloys. The model results qualitatively agree with those obtained using cluster simulations, and the agreement increases with the nanoparticle size; however, in all cases, the analytical model yielded less negative free energies of mixing. This model was used to study the relative stability of randomly mixed Cu–Ag particles of increasing size in the entire range of compositions at 298 K. It was found that stability decreases when the nanoparticle size increases. Predicted enthalpies and Gibbs free energies of mixing of particles with 321 and 642 atoms are negative in the whole range of compositions, which means that the formation of these alloys is an exothermic and thermodynamically allowed process. However, it is not thermodynamically feasible to alloy Cu and Ag with more than 1289 atoms at 298 K, which is in agreement with the results obtained via MD simulations. Thus, the simplicity of the analytical model may permit analysis of other alloys of technological interest.

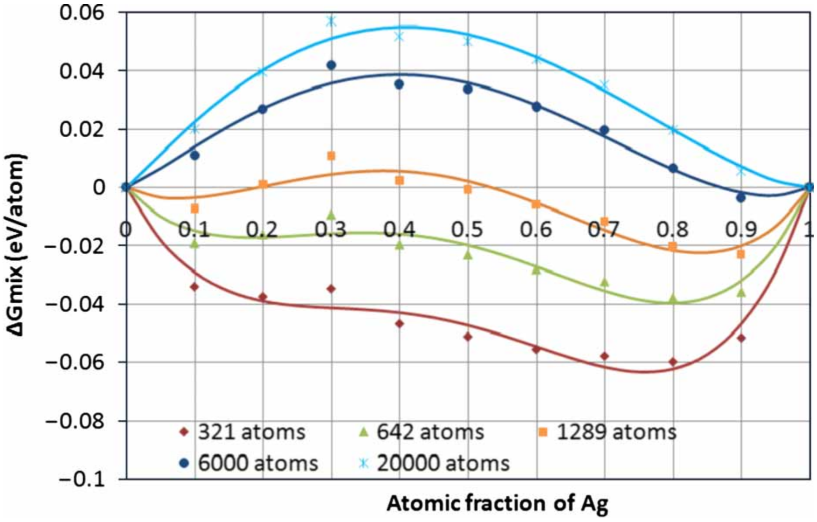

Figure 12. Gibbs free energies of mixing from bulk properties, calculated by Equation (6).

Acknowledgements

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