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Molecular dynamics and DFT study of 38-atom coinage metal clusters

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ABSTRACT

The thermal behavior of 38-atom mono-, bi-, and trimetallic clusters consisting of Cu, Ag, and Au atoms, is analyzed employing molecular dynamics simulations and DFT calculations for selected cluster compositions. Low-energy structures were singled out to perform NVT molecular dynamics simulations at several temperatures, using the Andersen thermostat for temperature control. The caloric curve is used to estimate the melting temperature and the specific heat. The pair distribution function g(r) of the solid and liquid-phase clusters is examined at different temperatures. When comparing the estimated melting points (T_m) among the monatomic clusters, the order becomes $T_m^{Cu_{38}} > T_m^{Au_{38}} > T_m^{Au_{38}}$. For bimetallic clusters, an increase of T_m is observed for Cu-Au compared to their monatomic counterparts, while the opposite occurs for Cu-Ag clusters. For trimetallic clusters, two low-energy isomers of the $Cu_{36}Ag_1Au_1$ cluster are investigated. In this case, T_m is estimated to be 475 K, for the two isomers with the lowest-energy and second-to-lowest energy, respectively. For all the clusters studied, the pair distribution function g(r) shows that the first peak position is not shifted as an effect of temperature and its maximum value varies with composition, while the second peak essentially vanishes upon melting. The common-neighbor analysis (CNA) technique is used to analyze the local structural changes for the trimetallic clusters, again demonstrating a clear structural change upon melting. The HOMO-LUMO energy gap indicates that the trimetallic isomers' behavior is metallic, while the average binding energy show these clusters' energetic stability to be similar.

1. Introduction

Nanomaterials frequently differ in their chemical properties from their bulk counterparts, and thus open new possibilities for technological applications. In particular, transition and noble metal clusters of the 3d (Fe, Co, Ni, Cu), 4d (Rh, Pd, Ag), and 5d (Ir, Pt, Au) metals, have been employed in a variety of catalytic processes of economic importance, such as in the control of severe pollution [1–4], and numerous theoretical and experimental studies have been performed on such clusters and nanoparticles. Mono- and bimetallic clusters and nanoparticles have been found to be relevant for catalytic processes like oxidation of methane or reduction of CO_2 , among other reactions [5–12], and recently, trimetallic clusters have also been studied [13]. Many investigations focus on the thermal and chemical stabilities, which are important properties that determine the clusters' catalytic performance [14]. The structural transformation of the catalyst and the evolution of active sites can occur when varying the temperature [15,16]; hence the importance of having thermally stable catalysts, with well-defined active sites dispersed on the (usually) metallic surface [17]. In particular, melting temperature changes have been analyzed in metal clusters, showing a size-dependent melting point depression compared to the corresponding bulk material [18,19]. Furthermore, a detailed understanding of the structural properties of metal clusters as a function of temperature is crucial for applications in catalytic processes [14,20]. Besides monatomic and bimetallic clusters, the structure and thermal properties of trimetallic nanoparticles have been investigated [21-33], using various synthesis techniques to obtain morphologically diverse Ag-Au-Pd, Pt-Ru-Co, Au-Pd-Pt, Au-Ag-Cu, and many other ternary clusters [34-38], in alloy or core-shell configurations. Such trimetallic clusters are often more active than their mono- and bimetallic counterparts [39], with structural characteristics that make them candidates to be multifunctional catalysts, with the possibility of having different

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types of active sites. To gain insight into the behavior of active metal sites of trimetallic clusters, the effect of temperature changes, and the role of doping atoms that are inserted in a host metal cluster [15,40], theoretical investigations are highly valuable.

Earlier experimental studies providing evidence on the importance of the thermal effects on cluster properties, such as melting point depression, were conducted on Au and Ag clusters employing electron microscopy [19,41,42]. This dynamical behavior was also examined in supported Au and Ag clusters [43], which showed that the shapes of some clusters were stable on a time scale of minutes before changing. The experimentally observed quasi-melting phenomenon [44] and the fluctuations in the shape of the particles [45] have been analyzed using a continuum model. The change in the particles' morphology was interpreted in terms of the crossing of energy barriers between local minima of a multidimensional potential energy surface (PES), and experimental evidence of cluster surface melting was provided by Ayajan and Marks [46] for free small Au particles, using the dynamic high-resolution electron microscopy technique. Moreover, Ugarte [47] showed that premelting and structural fluctuations occur well below the melting point for small gold particles. The melting process usually begins on the cluster's surface and subsequently extends homogeneously throughout the cluster volume, where the latter step sometimes takes place long after the surface melting has occurred [48].

Nevertheless, the experimental determination of the melting point depression is still difficult [49], and therefore computational approaches are called upon to reveal the mechanism of the melting process in nanosize mono- and multi-metallic clusters. Extensive computer simulation studies of clusters employing various schemes at different levels of theory [50] have been performed, where atomic clusters have been studied as isolated atomic aggregates [51], deposited on substrates [52], or embedded in hosts [53], at different size scales and composition [54]. These calculations have contributed to the understanding of nanomaterials, both for free clusters and those subject to interactions with the environment. Both empirical potentials (EP) - that can only approximate the quantum aspects of the atomic interactions present in real physical systems - and, preferably, more sophisticated electronic structure methods such as density functional theory (DFT) have been used. But since the computational cost of the DFT approach in large-scale simulations of medium- or large-size clusters is often prohibitively high, reliable EPs that are transferable to a variety of metal clusters (pure or alloyed) are often used for large simulations; however, one needs to keep in mind that the quantitative value of, e.g., the melting temperature can strongly depend on the choice of empirical potential.

Molecular dynamics (MD) simulations are a popular choice for the study of the effect of temperature on the structure and the dynamical properties of metal clusters. In particular, such calculations are needed to understand the dependence of the melting temperature on the cluster size as well as on the chemical ordering and composition in nanoalloys. For instance, MD simulations incorporating a many-body glue Hamiltonian [55] were employed by Ercolessi et al. [56] to analyze the melting behavior of small particles composed of hundreds of Au atoms. The melting point was reported to be smaller than in the bulk, and a precursor liquid state was also observed in the simulations. An embedded-atom method (EAM) potential [57] was employed by Lewis et al. [58] to study melting, freezing, and coalescence of Au nanoclusters. They find a size-dependent behavior of the melting temperature as function of the number of atoms. The *n*-body Gupta potential [59,60] was used to simulate the solid-liquid transition of small Cu-Au clusters [61]. The melting temperature (T_m) estimated in Ref. [61] was consistent with the experimental findings, i.e., a temperature reduction to T_m \sim 441 K for the Au₁₃ cluster. Several free and supported metal clusters were studied by Mottet et al. using canonical MD combined with the Gupta potential [62]. For free Ag clusters, their simulation results demonstrate that T_m depends on both size and shape of the isomer that served as starting point of the simulations. They also found that the effect of support is to shift T_m toward higher temperatures compared to

those of the free clusters. In a recent study, Zhang et al. [63] performed MD simulations using both the empirical (Gupta) potential and DFT. They found that the Cu₃₈ cluster is solid-like below 380 K, and liquidlike above 520 K, respectively, suggesting that the premelting stage is located in the temperature range 380 K - 520 K. Their analysis showed the importance of considering several low-energy isomers as starting points. In particular, they observed that the pre-melting stage was dominated by dynamical isomerization between the two lowest-energy structures, i.e., by the structural competition between the truncated octahedron and the incomplete Mackay icosahedron. The melting point for the Cu₃₈ cluster should be inside the estimated pre-melting range, which is significantly lower than the melting temperature obtained by Li et al. [64], who found a value of 776 K for a 55-atom copper cluster. However, this discrepancy is in agreement with the fact that the melting point varies in an irregular manner, as was pointed out by Schmidt et al. [65].

Analogously to the monatomic clusters, many experimental and theoretical investigations have analyzed the structural stability of bimetallic clusters, as well as their thermal response to external stresses [66–69]. The structural richness arising from the existence of two or more chemical elements in the clusters is reflected in the complexity of their PES. Thus, global optimization techniques have been used to analyze their complex energy landscapes [70], where the search for lowenergy structures is more complicated than in monatomic clusters because of the existence of a large number of homotops [66,71]. Thermal stability and melting point predictions of bimetallic clusters obtained with the help of global optimization techniques have attracted considerable attention [33,72-76]. Specifically, the melting point depression phenomenon, the structural change induced by temperature, and the effect of this change on the physical and chemical properties, have been the focus in a number of computer simulations. Most of these studies have again found that melting initiates at the cluster's surface and is followed by the homogeneous melting of the core atoms. For bimetallic clusters, Nelli and Ferrando [76] have also shown that phase separation and surface segregation are favored for a class of bimetallic clusters, AgCu clusters among these.

Similarly, the thermal stability of trimetallic clusters has been estimated using theoretical (via thermodynamics based models) and computational approaches. In the latter case, a number of MD simulations have been performed at different thermodynamic conditions and for a variety of chemical compositions. To date, the thermal evolution of trimetallic nanoalloys has been extensively examined for several trimetallic nanoalloys, among which Pd-Ag-Pt, Co-Ag-Fe, Au-Ir-Pd, Cu-Al-Ni, Ag-Cu-Au, Au-Cu-Pt, and Ag-Pd-Pt, were analyzed through molecular dynamics simulations [69,77-83]. For example, the role of composition on the thermal properties was analyzed for 55-atom Pd-Ag-Pt clusters [77], implementing a basin-hopping strategy to obtain the initial configurations with the best chemical ordering. As expected, the critical T_m value depends in a complex manner on the composition and, importantly, unlike mono- and bimetallic clusters, in this study the surface premelting is not present for the analyzed compositions. The effect doping binary alloys has on the melting point, has also been systematically assessed using computational techniques [78], where it was shown that the addition of Co to Ag-Fe alloys produces more stable ternary Ag-Co-Fe nanoclusters. In the case of the AgPd@Pt nanoalloy, studies reported by Akbarzadeh et al. [80] showed the importance of the chemical ordering of the core structure to obtain more stable ternary metal nanoalloys, i.e., with a higher melting temperature.

In the present study, we focus on the investigation of the structural and thermal properties of coinage metal clusters. The simple electron configuration of monatomic clusters, and their remarkable catalytic properties, have motivated extensive experimental studies [39,84]. Several experimental techniques for fabrication and analysis of trimetallic Cu-Ag-Au nanoalloys are well established, and their catalytic properties have also been investigated. The role of composition in thermal stability has been extensively examined in bi- and trimetallic clusters [77,78,80,82,83]; however, the influence of doping has barely been studied [73,78]. The aim of this work is understanding the thermal stability of coinage metal clusters as function of composition. To this end, low-energy configurations have been singled out for 38-atom clusters with selected compositions. We explore the melting temperatures of 38-atom noble metal (Cu, Ag, Au) clusters employing classical MD, and analyze their structure as function of temperature using the pair distribution function and the common neighbor analysis (CNA). We complement this by an analysis of the reactivity of isomer structures of $Cu_{36}Au_1Ag_1$ cluster using DFT.

2. Computational details

2.1. The Gupta potential

The empirical many-body Gupta potential is derived within the tightbinding second-moment approximation. In this model, the general expression of the configurational energy for a two-component cluster is written as the sum over all the atoms of attractive and repulsive energy terms, corresponding to the second moment approximation of the *d*band density of states and a Born-Mayer type pairwise interaction model, respectively:

$$V_{cluster} = \sum_{i}^{N} \{ V^{r}(i) - V^{m}(i) \}$$
⁽¹⁾

where the Born-Mayer pair repulsive term V'(i) is expressed as:

$$V^{r}(i) = \sum_{j \neq i}^{N} A(\alpha, \beta) e^{-p(\alpha, \beta) \left(\frac{r_{ij}}{r_{0}^{(\alpha, \beta)} - 1}\right)}$$
(2)

and the many-body attractive term $V^{m}(i)$ is expressed as:

$$V^{m}(i) = \sqrt{\sum_{j \neq i}^{N} \xi^{2}(\alpha, \beta) e^{-2q(\alpha, \beta) \left(\frac{r_{ij}}{r_{0}(\alpha, \beta)} - 1\right)}}$$
(3)

 α and β represent the atomic nature of atoms *i* and *j*, respectively. *A*, ξ , *p* and *q* are the potential parameters, that are usually fitted to experimental properties of bulk metals and alloys, such as the cohesive energy, lattice parameters, and independent elastic constants for the reference crystal structure at 0 K; r_0 denotes the nearest neighbor distance of the pure bulk elements, the value of r_0 for the mixed interaction ($\alpha \neq \beta$) is often taken as the average of the pure metal distances but it can also be taken as the experimental nearest-neighbor distance in some specific ordered bulk alloy; and r_{ij} is the distance between atoms *i* and *j*. Values of the Gupta potential parameters describing interatomic interactions taken from the work of Rapallo et al. [60] are listed in Table 1:

2.2. Molecular dynamics simulation

Classical molecular dynamics (MD) simulations are performed to analyze the thermal behavior of 38-atom noble metal clusters. This scheme consists in solving Newton's equations of motion for a system of many particles, whose classical motion is described by numerically

Table 1

Gupta potential parameters used in this work for each of the different cluster types.

Composition	<i>A_{ij}</i> (eV)	ξ _{ij} (eV)	Pij	q ij	$r_{ij}^0(\text{\AA})$
Cu-Cu (in Cu-Au)	0.0855	1.2240	10.960	2.2780	2.556
Cu-Au	0.1539	1.5605	11.050	3.0475	2.556
Au-Au (in Cu-Au)	0.2061	1.7900	10.229	4.0360	2.884
Ag-Ag (in Ag-Au)	0.1031	1.1895	10.850	3.180	2.8921
Ag-Au	0.1488	1.4874	10.494	3.607	2.8885
Au-Au (in Ag-Au)	0.2096	1.8153	10.139	4.033	2.8850

solving:

$$m_i \frac{d^2 r_i}{dt^2} = f_i \tag{4}$$

where m_i is the atomic mass of the i-th atom, and f_i is the force acting on that atom, which is derived from the model potential function (Eqs. (1)–(3) in this work). This classical description usually has an acceptable predictive power when the model potential adequately describes the interatomic interactions and the cluster size is ~2 nm. This type of potential has been successfully employed to study nanoparticles with tens and hundreds of atoms. In the present study, the velocity version of the Verlet algorithm [85] is used to integrate Newton's equations of motion, introducing the Andersen thermostat to perform computer simulations in the canonical ensemble, i.e., the cluster temperature is controlled through a simple scaling of velocities, thus reaching the different target thermal states for each of the nanoalloys studied. In this approach, the melting point is obtained by heating the cluster from a solid cluster at low temperature to a high-temperature melted state [86]. No other boundary conditions were prescribed during the simulations.

In a first set of runs, the temperatures were raised from 0 K in intervals of 100 K; subsequently smaller temperature step sizes (10 K) were employed in the neighborhood of the melting transition temperature, in order to locate the melting point more precisely. For each simulation, the time-step is 1 fs with total simulation time of 6000–12000 ps. The calculated properties are stored every 1 ps, taking time averages every 1000 ps after the system has reached equilibrium. In all clusters, the phase transition is identified through the calculation of the caloric curve [87] thus obtaining an estimate of the melting temperature. Structural changes in the different thermodynamic states are characterized by the inspection of the pair distribution function, g(r), which is a measure of the probability of finding a pair of atoms separated a certain distance r, in a given volume. For all the metal clusters studied, the initial configurations are obtained from global exploration searches performed through the basin-hopping (BH) method in combination with the Gupta potential. BH is a methodology devised to explore a complex PES, which is transformed into a step-type function. This transformation does not affect the minima of the PES but the number of barriers encountered is reduced [88]. All the lowest energy structures exhibit a truncated octahedron (TO) geometry except that of Cu₁Au₃₇ cluster, which shows an amorphous structure.

2.3. Common neighbor analysis

The common neighbor analysis (CNA) is employed to study the evolution of the atomic structure, allowing a more refined picture than the standard pair distribution function. This technique has been successfully used in the study of trimetallic Ag-Au-Pt clusters [26]. This is a simple method based on defining three indices, ijk, that result from counting the number of atoms separated by a distance $r < r_0$, where r_0 is the position of the first minimum of g(r), the nearest-neighbor distance. It provides information on the atomic arrangement surrounding selected pairs of bonded atoms, also referred to as root pairs. The first index (i) indicates the number of shared nearest-neighbors to a pair of bonded atoms, the second index (j) represents the number of bonds between shared neighbors. The third index (k) is the number of bonds in the longest bond chain formed by the shared neighbors [89]. Crystalline FCC, HCP, and BCC order is characterized by 421, 422, 444, and 666 indices. Icosahedral order is typically represented by 555 and 322 pairs, the latter being associated with the tetrahedral coordination of the icosahedron and the former with the presence of pentagonal planes, respectively, as typical elements of symmetry belonging to this structure [90].

2.4. DFT calculations

A common strategy to elucidate the energetic, structural, and electronic properties of structures optimized globally with empirical potentials is to perform a local minimization with DFT [91]. Here, we have reoptimized two low-energy isomers of the trimetallic clusters of TO geometry, obtained from Gupta-based basin-hopping global optimization, and have calculated the relative energy and the HOMO-LUMO energy gap (E_{r}) for each.

Structural minimization with DFT is performed using the Vienna *ab initio* simulation package (VASP) [92–95]. The Perdew-Burke-Ernzerhof (PBE) formulation is used to calculate the exchange–correlation energy [96]. The Kohn-Sham orbitals are expanded with plane waves, truncated at a kinetic energy of 550 eV. The core-valence electron interaction is described with projector augmented wave potentials (PAW) [97,98]. Cu, Ag and Au are described with eleven valence electrons, each. The Brillouin zone integration is approximated using the Monkhorst-Pack scheme with a $1 \times 1 \times 1$ k-mesh [99], and a Methfessel-Paxton smearing of 0.1 eV is applied to all systems. Structural reoptimizations are performed in a $20 \times 20 \times 20$ Å³ simulation cell. The total energy is converged when the difference between steps in the electronic optimization is smaller than 10^{-6} eV. Structural optimization is performed by use of the conjugate gradient method and convergence is assumed when forces are smaller than 0.01 eV/Å.

The relative energy and HOMO-LUMO energy gap (E_g) is calculated for two of the trimetallic isomers in a single point calculation using GAUSSIAN 09 [100]. The PBE functional is used together with the triple- ζ Stuttgart-Dresden basis set (SDD) [101], which includes an effective core potential (ECP) and valence basis including relativistic effects for the description of noble metal atoms. It is worthwhile mentioning that the calculated E_g value using the PBE functional may differ from the experimental observations. However, the affordability of this functional in terms of computational cost as well as the reliability shown over the years to describe transition and noble metal clusters, makes it an ideal exploratory tool for the trimetallic isomers under investigation.

3. Results and discussion

In the case of metal clusters comprising several atomic species, multielement clusters have a large structural diversity and the physical properties change depending on the chemical composition. Furthermore, temperature effects are also relevant in modifying the physicochemical properties, for example causing a change in the positions of the atoms that act as active sites in the cluster. A massive change in this regard is expected to occur at the melting point; the melting temperature is characteristic for each cluster and depends on a variety of particle attributes such as size, composition, and geometry. Here, we are particularly interested in estimating of the melting temperatures for ternary nanoalloys. For a reliable estimate of the melting transition, we first calculate the melting temperatures of mono- and bimetallic coinage metal clusters. In all cases, and for the range of temperatures studied here, the total energies in the MD trajectories show fluctuations characteristic of thermodynamically equilibrated systems.

3.1. Thermal stability of monatomic clusters

Fig. 1 depicts the initial geometry (T = 0 K) for the 38-atom Cu, Ag, and Au clusters with the TO shape. This structural motif has six square faces and eight hexagonal faces, and the symmetry properties are characterized by the O_h point group. For each metal cluster, the starting structures of the MD simulations correspond to the lowest-energy configurations obtained through the basin-hopping global exploration.

A comparative analysis of results shows that the Cu₃₈ cluster has a more compact structure than the Ag₃₈ and Au₃₈ ones. The shortest interatomic distance for Cu₃₈ is ~2.5 Å and the longest is about 7.9 Å. The compactness of Ag₃₈ and Au₃₈ clusters is slightly lower than that of



Fig. 1. Structural motif of the lowest-energy 38-atom Cu, Ag, Au, monatomic clusters.

Cu₃₈ but the overall structure is similar. For Au and Ag clusters, the shortest interatomic distance is 2.73 and 2.77 Å, while the longest distance is about 8.73 and 8.83 Å, respectively. This trend in the shortest distance of the three coinage metal clusters is similar to the one observed for the bond length of Cu₂, Ag₂, and Au₂ dimers, namely $d_{Cu_2} < d_{Ag_2}$ [102], according to both experimental and theoretical DFT/PBE results.

The caloric curve is constructed for each cluster by computing the average potential energy per atom ($\langle V \rangle$) of the MD trajectory after equilibration, at each temperature. The corresponding caloric curve is given in the left panel of Fig. 2 (a-c). Typically, three regions are observed. Firstly, a linear increase is observed for temperatures below the phase transition, with a discontinuity around the melting point in a second stage, and finally observing again a monotonic (nearly linear)



Fig. 2. Calculated caloric curves and g(r) plots for the 38-atom (a) Cu, (b) Ag, (c) Au, clusters.

increase with temperature. This jump in the potential energy is an indication of a first-order melting transition. The energy gap between the lower $\langle V \rangle$ point in the solid-like region of the energy landscape and the higher $\langle V \rangle$ point in the liquid-like region represents the release of latent heat during the "solidification" process of the coinage metal clusters when we are approaching the melting point from the liquid state. The location of this rapid increase/decrease in the average potential energy allows us to estimate the melting temperature. It is interesting to note that, in the case of the Ag cluster, the phase change occurs more abruptly than in the Cu and Au clusters.

From the caloric curve, we can also approximately compute the specific heat of the system on the simulated time scale via the definition

$$C_V = \frac{\partial E}{\partial T} \approx \frac{\Delta E}{\Delta T} = \frac{3}{2} k_B + \frac{\Delta \langle V \rangle}{\Delta T} = C_V^{kin} + C_V^{pot}$$
(5)

of the specific heat/atom in the cluster. We note that for systems studied with classical MD simulations, the contribution of the kinetic energy to the specific heat is a constant $\frac{3}{2}k_B$ per atom, and that for a classical harmonic oscillator potential, the contribution to the specific heat due to the potential would also be $C_V^{pot} = \frac{3}{2}k_B$ per atom. Table 2 shows the specific heat $G_V^{pot} = \frac{\Delta(V)}{\Delta T}$ estimated from the caloric curves computed in this study for the various clusters. Since we do not have a very high resolution in temperature, we just give the specific heats for the two linear temperature regimes above and below the melting range, plus an average for the integrated value of the jump in average potential energy over the temperature range of the melting transition. As one would expect, for $T < T_{melt}$, $C_V^{pot} \approx \frac{3}{2}k_B$; in contrast, for $T > T_{melt}$, C_V^{pot} of the monatomic clusters (and also of most of the nanoalloys) is somewhat larger than $\frac{3}{2}k_B$, which is most likely due to the fact that now the landscape that is explored is richer than the one associated with a single isomer - which can be approximately treated as a (quasi-) harmonic oscillator -, and thus the fluctuations in the potential energy are larger. However, one needs to keep in mind that the average softening of the potential wells at higher energies can also lead to a countervailing effect resulting in a decrease in the specific heat for higher temperatures; thus, the final computed or measured specific heat will depend on details of the energy landscape accessible to the system at a given temperature range and, in principle, also on the time scales of observation. Finally, there is always a peak of the specific heat in the temperature range around the melting transition. The height of the integrated peak over the

Table 2

Contributions of the potential energy to the specific heat/atom C_V^{pot} for all clusters investigated via MD simulations, for temperatures above, below and at the melting range, in units of k_B . Note that for $T < T_{melt}$ and for $T > T_{melt}$, we compute the specific heat for the linearly increasing portions of the caloric curve, while for the temperature range around the melting temperature, the value of the specific heat is computed for the integrated change in potential energy within the small temperature interval where the caloric curve shows a rapid increase in the average value of the potential energy. Since Fig. 6(a) shows that the caloric curve of the trimetallic clusters fluctuates more strongly around an average linear increase of $\langle V \rangle$ with temperature than those for the monatomic and binary clusters, we show not only the average value for $T > T_{melt}$, but also the instantaneous value of C_V^{pot} right above the melting temperature (in

brackets), which is actually smaller than $\frac{3}{2}k_B$.

System	$C_V^{pot}(T < T_{melt})$	$C_V^{pot}(T \approx T_{melt})$	$C_V^{pot}(T > T_{melt})$
Cu ₃₈	1.63	12.65	2.03
Ag ₃₈	1.66	14.58	2.12
Au ₃₈	1.63	11.37	2.72
Cu1Ag37	1.61	8.70	1.56
Cu ₃₇ Ag ₁	1.62	9.86	2.57
Cu1Au37	1.72	6.03	2.32
Cu ₃₇ Au ₁	1.65	13.93	2.56
Cu36Au1Ag1-Iso1	1.38	4.92	1,88 (0.93)
Cu36Au1Ag1-Iso2	1.39	4.04	2.25 (0.79)

melting range indicates how sharp the transition is; a low height suggests that the transition is smeared out over a large temperature interval, and thus, e.g., pre-melting may take place. For example, we see that the Au₃₈ cluster appears to exhibit a spread in the melting transition over a larger temperature interval than for the Cu₃₈ and Ag₃₈ cluster, resulting in a smaller peak of the specific heat compared the other two monatomic clusters.

It is worth mentioning that increasing the temperature permits the exploration of wider regions of the PES corresponding to each cluster. In this process, the average total energy is raised with temperature, and the instantaneous total energy (at each time step) presents the typical statistical fluctuations in the NVT ensemble. Thus, for each thermal state, the atomic configurations of clusters will have characteristics that essentially define their solid or liquid phase. This fingerprint is captured by the pair distribution function, g(r), shown in the right panel of Fig. 2 (a-c). Each g(r) plot corresponds to a single atomic configuration (snapshot) taken from the MD trajectory in the equilibration period for each temperature. We observe that the short-range order peaks of g(r)change with temperature. For example, the intensity of this second peak decreases as the temperature increases: the second peak is sharp at low temperatures, wider at intermediate temperatures, which is typical for disordered structures, and has clearly vanished at the higher simulation temperatures, which is characteristic of the cluster's liquid state. Similar results were recently reported by Delgado-Callico et al. in an exhaustive study on the melting of transition and noble metal nanoparticles [103], suggesting that the absence of the second peak can serve as a fundamental (structural) signature for the solid-liquid transition. We believe, however, that this signature should be complemented with the cluster's atomic mobility, in order to discard diverse alternative possibilities, such as amorphous states or potentially more complicated soft modifications of other metal structures. From these results and the caloric curve plots in Fig. 2 (a-c), the melting temperature is determined for each of the monatomic coinage metal clusters. The deduced values are listed in Table 3. Furthermore, in the Supplementary Material an animation of the trajectories (for the trimetallic cluster) at temperatures below and above the melting point is provided, clearly demonstrating the much higher mobility of the atoms above the melting temperature; analogous trajectories are observed for the monatomic and binary clusters.

The results show that the melting point of the 38-atom clusters decreases as the atomic number increases. This tendency is in agreement to that reported by Li et al. [64] for 55-atom coinage metal clusters with icosahedral geometry. Additionally, our simulation results for the monatomic 38-atom clusters predict lower T_m values compared to those of Li et al., which is also consistent with experimental measurements [104], phenomenological, and theoretical model predictions [105,106], which indicate a reduction of T_m as the cluster size decreases. Thus, on the basis of these observations we conclude that our simulation scheme is reliable, and we proceed to investigate the melting behavior for selected compositions of bimetallic Cu-Ag and Cu-Au clusters.

3.2. Thermal stability of bimetallic clusters

The changes in the melting temperature for bimetallic clusters were also analyzed regarding the effect of inserting impurities into monatomic metal clusters. Two different compositions are considered in

Table 3Melting tempersimulations forclusters.	ratures deduced from MD r Cu ₃₈ , Ag ₃₈ , and Au ₃₈	
Cluster T _m (K)		
Cu ₃₈	405	
Ag ₃₈	375	
Au38	315	

this work for Cu-M (M = Ag, Au) clusters. Fig. 3 shows the initial configuration of Cu1M37 and Cu37M1 clusters. As mentioned earlier, all the lowest-energy structures obtained through the global exploration search exhibit a TO geometry except the global minimum of the Cu1Au37 cluster, which is apparently amorphous. It is remarkable that introducing a single Cu atom modifies the morphology of the Au₃₈ cluster, for which the lowest-energy structure has an ordered TO geometry. To check, whether this was a fluke of the global optimization, we constructed other candidates for the lowest-energy configuration by hand, which exhibited more symmetric structures, and performed local relaxations. However, we found that the proposed structures correspond to higher energy isomers at the Gupta level, suggesting that the "amorphous" structure is really the global minimum.

To investigate the effect of temperature on the physical properties of the lowest-energy bimetallic clusters, we proceeded to perform MD simulations. The initial and final temperatures depend on the nanoalloy, being chosen to easily locate the sharp change occurring in the average potential energy around the melting transition. The melting temperature was estimated for each of the bimetallic clusters in this study. Results are shown in Fig. 4 for two different target compositions: Cu₁M₃₇, Cu₃₇M₁, with M = Ag, Au.

Again, we also analyzed the specific heat. The main observation was that the peak in C_V^{pot} was less sharp than for the monatomic clusters, indicating that the disorder by the presence of the foreign atom leads to a softening of the transition between the solid and the liquid state of the cluster. This also was suggested by the fact that in the "linear" regimes of the caloric curve above the melting point, C_V^{pot} for the binary clusters was slightly larger than for the monatomic clusters, again indicating an, on average, somewhat larger contribution to the energy fluctuations during the MD simulations.

The analysis of the results reveals that, as compared to the pure coinage metal clusters, the substitution of an atom by another one of a different chemical nature changes the melting temperatures of the clusters and softens the phase transition. The estimated melting temperature for the bimetallic clusters are listed in Table 4.

These results suggest that the presence of heteronuclear bonds strongly affects the thermal properties of bimetallic clusters, specifically the melting temperature. In particular, single-atom doping modifies the metal clusters' melting point, i.e., the melting temperatures of Ag1Cu37 and Cu1Ag37 decrease as compared to Cu38 and Ag38, respectively, while the doping leads to an increase in T_m for clusters Au₁Cu₃₇ and Cu₁Au₃₇ in contrast to Cu₃₈ and Au₃₈ clusters, in agreement with results obtained



Fig. 3. - Initial configurations of the 38-atom Cu-M bimetallic clusters (M = Ag, Au).



Fig. 4. Plot of the the caloric curve and the pair distribution function of the 38atom (a) Cu-Ag and (b) Cu-Au clusters.

Table 4								
Melting	temperatures	estimated	from	MD simulatio	ns for	Cu-based	nanoallo	ovs.

Tabl

Cu-Ag	T (K)	Cu-Au	T (K)
Cu ₁ Ag ₃₇	295	Cu ₁ Au ₃₇	375
Cu ₃₇ Ag ₁	395	Cu ₃₇ Au ₁	455

by Cheng at al. [107] and Taherkhani et al. [108]. It is widely documented in the scientific literature that, among other properties of metallic clusters, the melting temperature depends on its shape, chemical composition and size. The dependence on size is particularly important, where both experimental and theoretical studies have found an approximately linear dependence on the inverse of the radius of the cluster. Therefore, it is expected that T_m will be, in general, considerably lower for smaller metal clusters than for the bulk material. Furthermore, with regard to the composition, several theoretical studies have shown changes in the melting point, upward or downward, when single-atom impurities doped the metal clusters (see refs. 40, 110 and references therein).

The theoretical limitations of our computational model do not allow a deeper explanation in terms of the clusters' electronic properties; however, it is possible to discuss the origin of this behavior in terms of the corresponding potential energy surface. Obviously, the single atom doping of a metal cluster modifies the main features of the PES, e.g., local and global minima, energy barriers, and minimum energy pathways for (isomerization) solid-solid or solid-liquid phase transformations. In this general context, the raising of the melting point can be understood in terms of the increase of the energy barrier for the solid-liquid phase transition to occur. One should note that the energy barriers compete with entropic barriers [109]: due to the likely formation of homotops in intermetallic clusters, the number of energetically and structurally very similar local minima rapidly increases with the introduction of impurities. Thus, the statistical contribution of lowenergy states to the configurational entropy of the system can greatly increase, favoring a possible decrease of the melting temperature when introducing monatomic impurities in a metallic cluster.

As noted for the 38-atom Cu-Au TO nanoalloys, the melting point is shifted to higher T_m values. This suggest that exploration of their chemical functionality is important due to the high structural stability up to relatively high temperatures. In order to learn more about the effect of doping with foreign atoms, it is interesting to study trimetallic clusters with the aim of exploring the effect on the melting behavior of Cu atom substitution in the Au₁Cu₃₇ cluster by a single Ag atom. The global optimization showed that the resulting Cu₃₆Au₁Ag₁ clusters with the lowest energies exhibited three different atom types on the surface, potentially giving an enhanced chemical functionality. In this regard, previous computational studies have shown that the melting temperature of Cu-Au-Pt nanoalloys is dependent on both composition and atomic distribution [28,30]. We will focus now on the two Cu₃₆Au₁Ag₁ isomers with the two lowest energies.

3.3. Thermal stability of trimetallic clusters

For trimetallic clusters the structural diversity is greater than in bimetallic or monometallic clusters because of the higher complexity of the PES, and finding the lowest-energy structures becomes a formidable computational task. For $Cu_lAg_mAu_n$ clusters, we performed several global explorations for different (*l*, *m*, *n*) compositions, finding the TO geometry in clusters with a major Cu concentration, with Ag and Au serving as dopant species. For trimetallic clusters, we have singled out minimum energy structures with TO geometry for this study. In this case, the PES is very complex and our global explorations identified several TO based low-energy isomer structures in the cluster $Cu_{36}Au_1Ag_1$; the two isomers with the lowest energies are shown in Fig. 5.

This cluster structure is obtained by substituting a Cu atom with a single Ag atom in the bimetallic cluster with the higher melting point (Cu₃₇Au₁). In both trimetallic isomers, the Au atom is located in the center of a hexagonal face and is bound to each of the Cu atoms forming a hexagonal plane, while the Ag atom is located on the corners of the isomers. To analyze their stability and thermal properties, we again performed MD simulations. A detailed inspection of the MD trajectories for temperatures near the melting temperature provides computational evidence on the structural stability of this cluster. For both isomers it is observed that, before melting, the cluster atoms strongly oscillate around their equilibrium positions, but the overall TO shape is still apparent for the whole simulation. Above melting, the TO geometry remains stable for a few time-steps until a structural rearrangement occurs and surface diffusion slowly occurs for the Ag and Au atoms. The MD results obtained for the structural and thermal characterization of $Cu_{36}Au_1Ag_1$ isomers are shown in Fig. 6 (a-c).

From the constructed caloric curves (Fig. 6(a)) we find that both isomers melt at the same temperature, which is about 475 K. Below this temperature, both isomers increase the energy following a straight line,



Fig. 5. Initial TO atomic configuration of trimetallic $Cu_{36}Au_1Ag_1$ isomers. (a) Structure with the lowest-energy; (b) Structure with the second-lowest energy.



Fig. 6. Plot of (a) the the caloric curve of isomers 1 and 2 and the pair distribution function of the 38-atom (b) $Cu_{36}Au_1Ag_1$ lowest-energy cluster and (c) $Cu_{36}Au_1Ag_1$ next low-lying isomer.

and after melting, the Au and Ag atoms move toward positions inside the clusters producing a different effect on the average potential energy. This explains the different behavior of the caloric curve in the molten state (see animation file in the Supplementary Material). Concerning the high thermal stability of these two homotop structures up to the melting point, we turn to their energetic properties, in particular, the average binding energy of the atoms in the clusters. Calculated for the two isomeric trimetallic structures under study, we find that the corresponding average binding energy ($E_b = -\frac{V_{min}}{N}$), is ~2.884 eV/atom for isomer 1 and ~2.883 eV/atom for isomer 2, respectively. This small difference in $E_{b}\ of \ about\ 0.001\ eV/atom\ explains the\ competition\ in\ the$ thermal stability of the trimetallic clusters under consideration. A similar result is obtained for the mixing (excess) energy (-0.301 eV for isomer 1 and -0.296 eV for isomer 2), in which case the difference between isomers is 0.005 eV. The results obtained for the trimetallic isomers show that the substitution of two Cu atoms for one Ag atom plus one Au atom enhances the structural stability of the Cu₃₈ cluster, thus allowing it to keep its morphology at higher temperatures. For the melting temperatures of selected globally optimized cluster structures we find the ranking: $T_m^{Cu_{38}}(405) < T_m^{Cu_{37}Au_1}(455) < T_m^{Cu_{36}Au_1Ag_1}(475)$, where the number in parenthesis is the estimated T_m in K.

The location of the Ag atom on different sites of TO-shaped clusters is not significant for the melting of these structures. However, changes in the Ag atom position may be relevant regarding other important physical or chemical properties, such as the chemical reactivity. Thus, prior to investigating such properties, it is necessary to carry out a local structure analysis to gain insight into the high stability of solid trimetallic clusters and the degree of ordering at finite temperatures, before and after cluster melting.

With the aim of understanding the local changes in the structure of trimetallic clusters and the corresponding degree of ordering during the MD simulations below and above the melting temperature, a commonneighbor analysis (CNA) [89] is carried out to explore the evolution of the atomic structure of trimetallic clusters in the temperature limits of solid and liquid phases. The relative abundance (RA) of the indices characteristic for the TO structure is shown in Table 5. For comparison, we have included in Supplementary Material the CNA indices for the 13and 55-atom icosahedra together with their relative abundances.

At temperatures below the molten state, strong structural distortions occur in both cases. However, the configurations along the MD trajectory at 450 K show that TO features are still present. Ten configurations were systematically chosen after the cluster had equilibrated with respect to the potential energy to monitor the local structure changes through the CNA indices. For both isomers at 450 K, it is observed that indices 211, 311, and 421 are the most abundant root pairs, summing to about 96%, on average. Nevertheless, small structural distortions are already manifest in the appearance of a small number of 411 pairs

Table 5

Relative abundances (RA) of the CNA indices characterizing the TO ${\rm Cu}_{36}{\rm Au}_1{\rm Ag}_1$ isomers.

Cu ₃₆ Au ₁ Ag ₁	INDEX	RA
TO Isomers	211	0.18
	311	0.36
	421	0.46

(~4%), and we also observe a change in the relative abundance of 211, 311 and 421 pairs. The fractions of pairs 211 and 311 increase to about 25% and 46%, respectively, while the fraction of 421 pairs decreases to ~25% (all these percentages are averages estimated from a reduced configurations sample; see Supp. Mat.).

For temperatures above the melting point, larger distortions produce the eventual appearance of configurations no longer typical for the TO based structure that exhibit the presence of 322 (tetrahedral coordination of icosahedron) and 543 (distorted icosahedral order) indices associated with (local) five-fold symmetries, as well as the 555 index, i. e., the more distorted structures become quasi-amorphous, similar to the five-fold coordinations often associated with the liquid state. For example, the analysis of both isomers for a temperature above melting (500 K) shows that the fraction of indices characterizing the crystalline local order (211, 311, 421, 422, 432) decreases to about 60-70%, while those indicating a non-crystalline order (322, 531, 532, 543, 555) increase to a percentage ranging from 30 to 40%. We expect that for higher temperatures these percentages can vary substantially. Just as had happened for the monatomic and binary clusters, the second peak of g(r)has completely vanished at 500 K, while the third and fourth peaks tend to merge (c.f. figure SM1 in the Supp. Mat.).

As mentioned earlier, the size dependence of the melting point of metal clusters has been extensively studied. Currently, two size regimes are recognized in the study of cluster phase transitions, namely, the nonscaling regime for clusters of very small size and the thermodynamic scaling regime [110]. In the latter one, the melting point decreases essentially monotonically from the high bulk value of the melting temperature. In the non-scaling regime, the overall trend to far lower melting points for smaller cluster size persists but the change in the melting temperature from one cluster size to the next is no longer smooth and small changes in cluster size and ground state morphology can have a strong effect on the associated change in the melting point. Similarly, the structural pattern of the obtained low-energy isomers can vary as a function of cluster size. Thus, for a given cluster geometry, the melting point decreases dramatically with size and this trend is observed in the literature and it not associated with specific empirical potentials. Discrepancies in the melting point values may occur among different classes of empirical potentials, but also when the same potential is employed yet different parameter sets are used. The clusters investigated in this study are in the range where these two regimes overlap.

However, in this context, it is worth emphasizing that molecular dynamics simulations with empirical potentials provide predictions regarding the general behavior of fundamental properties, not quantitatively accurate values. In our calculations, the results obtained are consistent with the general behavior of the melting temperature observed in the thermodynamic scaling regime (see Fig. SM2 in Supp. Mat. for 147-atom Au/Ag clusters). Furthermore, the predicted behavior exhibits a trend similar to the one found in calculations of clusters for other sizes and structures of the ground state. However, one should note that for such rather small clusters, the existence of many structurally varying low-energy minima that become accessible in the melting process of the metal clusters suggests to adopt a wider point of view: instead of trying to determine a unique fixed melting temperature, it might be more suitable to consider a temperature range over which the melting can occur. As mentioned by Zhang [63], premelting and solid-solid structural transitions may occur in a temperature range, preceding the melted state of metal clusters. In particular, not only energetic aspects, such as the potential energy and the specific heat, should be used to identify the onset of melting, but one would want to observe both structural and dynamical properties as function of temperature. In this fashion, one would gain a deeper understanding of the state of the system and the structural changes that occur when the phase change occurs. The analysis of dynamical properties as function of temperature, such as the diffusion coefficient, could serve as an additional indicator observable for the temperature of the melting phase transition. In particular, it would allow us to distinguish whether the system has

become a liquid-like melt or if the cluster is located in a thermodynamic glass-like state where the structure is disordered like a liquid but dynamically frozen with only slow hopping movement among the lowenergy isomers of the cluster taking place.

The former analysis can be reinforced by considering that, in atomic clusters, several investigations have shown that the phase transition can occur in two different ways [111]. One, where a single transition occurs abruptly, the solid-liquid transition, and another that proceeds following two stages. The first involves surface atom diffusion, known as premelting, and in the second stage a homogeneous spread of bulk diffusion activity takes place until all atoms including the core atoms participate. For the two trimetallic isomers considered in our work, the molecular dynamics simulation reveals that the entire melting proceeds in two stages. The animation provided in Supp. Mat. shows that the cluster structure remains stable in the temperature range below 450 K. It is also noticed that in the temperature range 460-470 K surface diffusion starts probably with the displacement of the Ag atom over the cluster surface. This displacement destabilizes the surface atom arrangement, and thus, the outer shell of the cluster becomes an amorphous (liquidlike) layer representing the premelting stage. The second melting stage is observed at 480 K, in which the entire cluster is involved in the melting process, leading to the metal cluster behaving like a homogeneous liquid.

More accurate calculations of the melting temperature are possible through ab initio molecular dynamics or BOMD computer simulations [112,113]. However, first-principles schemes have also model issues in, for example, the use of energy functionals that poorly describe the changes in the changes in the electronic structure occurring at the melting transition. Another well-known issue of these more realistic methods are their very large computational requirements. Thus, regardless of the level of theory used in our computations, obtaining the melting temperature remains an estimate, the validation of which will unquestionably require results from experimental investigations carried out on systems with the characteristics of the clusters (size, composition, morphology) used in the theoretical studies.

3.4. Reactivity of trimetallic clusters

The role of clusters as model systems for active catalytic sites has recently been highlighted by Tyo and Vajda [114], emphasizing the importance of these nanomaterials as multifunctional catalysts. Hence, a detailed understanding of the influence of the system's composition on the structural stability of nanoparticles at high temperatures is essential for optimizing catalytic applications. Global explorations based on empirical potentials are known to reproduce the structural motifs obtained in experiments but can exhibit a different energetical ranking compared to that of the first-principles methods [115]. Thus, the structural motifs obtained in this work with the Gupta potential may be realistic, but the energetical ordering of these structures may be inaccurate. To gain further insight into the chemical properties of metal clusters, and to obtain a more accurate energetic ordering on the studied motifs, we have reoptimized the structure of the trimetallic (Cu₃₆Au₁Ag₁) clusters and explored the electronic structure of the isomers employing the DFT approach.

To examine the relative energy of the trimetallic isomers, singlepoint calculations were performed on the DFT reoptimized structures of the two trimetallic isomers studied, using GAUSSIAN 09 [100] and employing the PBE/SDD scheme. From the DFT calculations we find a different energetical ordering than with the Gupta potential, making isomer 2 the lowest-energy configuration. However, the relative energy ($E_{total}^{isomer2}$) between isomer 1 and isomer 2 at the DFT level is about 0.02 eV. This would correspond to an analogous "temperature difference" of $T_{\Delta} = 0.02 \times 11.600/38K \approx 6$ K, i.e., the two isomers are essentially equally likely to be present for, e.g., temperatures $T \ge 100K \gg T_{\Delta}$. Since the topology of the electron density is different, one could expect the chemical reactivity to be distinct for the different homotops. To elucidate the chemical behavior of the trimetallic ($Cu_{36}Au_1Ag_1$) clusters, we have calculated the energy gap (E_g) between highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) in each isomer, since the HOMO-LUMO gap (E_g) has been used as a reactivity descriptor in previous studies for several systems [112]. The calculated frontier molecular orbitals in isomer 1 and isomer 2 are shown in Fig. 7.

The calculated E_g for isomers 1 and 2 are 1.36 meV and 2.45 meV, respectively. Thus, for both isomers, the size of the HOMO-LUMO gap is negligible, suggesting that these trimetallic isomers should display metallic behavior. It is worthwhile mentioning here that the band gap obtained from VASP results also indicate a metallic behavior of these cluster isomers, which is consistent with the GAUSSIAN 09 prediction. These results are in agreement with the metallic behavior observed, both theoretically and experimentally, for Cu₃₈ [63]. Moreover, we find that isomer 1 and isomer 2 are electronically similar, as shown in Fig. 7. The contribution to the HOMO derives from copper and gold atoms located on the hexagonal (top and bottom) planes, as well as from the inner copper atoms, while the LUMO is mainly distributed over the atoms located on the middle planes of these clusters. In both isomers, there are no contributions from the Ag atoms to the frontier orbitals.

Another important property employed to assess the relative energetic stability is the average binding energy, E_b , defined by $E_b(Cu_{36}Au_1Ag_1) = \frac{36E_{Cu}+E_{Au}+E_{Ag}-E_{Cu_{36}Au_1Ag_1}}{38}$, where $E_{Cu_{36}Au_1Ag_1}$ is the total energy of the corresponding trimetallic cluster isomer, and E_{Cu} , E_{Au} and E_{Ag} are the energies of single Cu, Au and Ag atoms, respectively. For both isomers, the calculated values are ~ 2.71 eV/atom. This result indicates that the energetic stability is apparently not sensitive to the Ag atom position, as had already been indicated by the equal melting temperatures of the trimetallic cluster isomers. At this point, it is worth mentioning that, because the trimetallic isomers comprise atoms other than copper, it may be of interest to compare the results of our DFT calculations with those one would obtain with hybrid functionals, which are relevant when dealing with intermetallic systems, and, of course, an experimental validation would be highly valuable.

4. Conclusions

Systematic classical molecular dynamics simulations were carried out to determine the melting temperature of 38-atom metal clusters and to analyze the structural changes associated with the melting transition. In all cases, initial low-energy structures were obtained from basinhopping global explorations of the potential energy surfaces belonging to the cluster compositions investigated. Overall, our results show that the effect of doping coinage metal clusters is modifying the transition between the solid and the liquid state of clusters, as shown by the estimated heat capacities and the melting temperatures. For trimetallic clusters, our results predict that the analyzed isomers Cu₃₆Au₁Ag₁ possess a higher melting temperature compared with the mono- and bimetallic clusters studied here. For the trimetallic isomers, the second peak of g(r) is monitored as the temperature increases. This peak clearly vanishes when the system reaches the liquid state. We have also found that Cu₃₆Au₁Ag₁ clusters are stable up to the melting temperature, and the different low-energy isomers exhibit a comparable chemical reactivity, according to the theoretical calculations on DFT level. The computational strategy presented will aid in developing thermally stable metallic nanoalloys for applications in, e.g., catalysis and other technologically important applications where temperature is a key variable, and should be feasible for larger nanoparticles. And conversely, experimental studies of the melting behavior of clusters and the determination of their melting temperatures, will allow theorists to improve their tools for the study of the dynamics and thermodynamics of clusters and to elucidate the underlying concepts of melting in clusters.



Fig. 7. HOMO and LUMO frontier orbitals of the trimetallic $Cu_{36}Au_1Ag_1$ cluster isomers obtained through the DFT approach, utilizing the PBE functional and SDD basis set. Copper atoms are in brown, gold atoms are in yellow, and silver atoms are in white. Blue and red color represent the positive and negative phases of the molecular orbitals, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5. Data availability

All data are available upon request to the corresponding author.

CRediT authorship contribution statement

Oscar Alan Sanders-Gutierrez: Software, Visualization, Writing – original draft. Analila Luna-Valenzuela: Software, Validation. Alvaro Posada-Borbón: Software, Writing – original draft. J. Christian Schön: Conceptualization, Methodology, Writing – review & editing. Alvaro Posada-Amarillas: Conceptualization, Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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