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Determination of the threshold of nanoparticle behavior: Structural and electronic properties study of nano-sized copper

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ABSTRACT

In the present work we determine the threshold of the nanoparticle behavior of copper nanoparticles by studying their structural and electronic properties. The studied nanoparticles contain from 13 to 8217 atoms and were obtained by molecular dynamics simulations using the Johnson potential for copper based on the embedded atom method. The results indicate that for small copper nanoparticles (<1000 atoms, ~ 2.8 nm) the surface plays an important role in their physical properties. Whereas, for large nanoparticles (>2000 atoms, ~ 3.5 nm), with spherical-like external shape and large percentage of fcc-like local structure, this effect is negligible and their electronic character are similar to such expected in solid copper. Finally, it has also been shown that copper nanoparticles change their electronic character, from metallic to insulating, after increasing the strength of the chemical disorder.

1. Introduction

During the last two decades metallic nanoparticles have been subject of extensive theoretical and experimental investigations due to their peculiar physical and chemical properties which strongly depend on their size, structure, composition, and defects [1–7]. For instance, nickel, cobalt, and iron nanoparticles acquire a superparamagnetic behavior when their size is reduced [1]. Moreover, it is well known that gold and silver nanoparticles change their color after reducing their sizes [3], and that small copper nanoparticles have large surface which induces high reactivity [8]. Thus, there are many studies about the influence of these factors on the structural and electronic properties of copper nanoparticles under different situations [7–14]. The reason for these intense studies is because these systems are relevant for potential technological applications in different fields which include optics, magneto-electronics (magnetic discs), and catalytic systems [15–17]. However, it is sometimes difficult to carry out these kinds of experimental studies in nanoparticles. Fortunately, computer simulations (e.g., molecular dynamics) are an effective tool to perform these studies, at an atomic level, from a theoretical point of view.

One of the main reasons because nanoparticles have unusual properties is the strong influence of the surface which is a consequence of the reduction of the system size. This effect is relevant for systems at the nanoscale, whereas it is usually negligible for solids (macroscopic scale) [13]. Thus, it is important to know for which size this influence is considerably reduced so that the nanoparticle properties resemble those of their corresponding macroscopic counterpart. In this sense, an experimental study performed by Monot et al. [8] has showed that copper nanoparticles, grown by homogeneous nucleation from the vapor, undergone a structural transition, from icosahedral to fcc structure, around an average size of ~ 3.8 nm. It is noteworthy that they have found, under similar preparation conditions, large silver nanoparticles (~ 13.0 nm of diameter) with icosahedral-like structure [18]. Moreover, it has been reported that the surface influences the melting temperature of Cu nanoparticles (embedded in a silica matrix) [4], and the cohesive energy of Mo and W nanoparticles [19]. In the case of the electronic properties it has been found that when the size of metallic nanoparticles decreases, the electronic density of states (EDOS) is affected [5,12], and the resistivity reaches a complex behavior [20]. All these effects are also influenced by the conditions employed to obtain the nanoparticles (e.g., atmosphere, cooling rate, pressure) [7,13,14]. It is also worth mentioning that apart from the surface there is another factor: the chemical disorder, which strongly influences the electronic properties of several (simple and complex) systems [21–25], e.g., producing in some cases the metal–insulator transition [22,23]. Nevertheless, the influence of this kind of disorder on metallic nanoparticles has been poorly studied [25].

Inside the context explained above, in order to determine the threshold above which the nanoparticle behaves like its solid counterpart, in the present work we study the structural and

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electronic properties of small and large copper nanoparticles, which contain atoms ranging from 13 to 8217 (these numbers belong to the icosahedral magic numbers sequence [26]). These nanoparticles were obtained by molecular dynamics (MD) simulations and using a Johnson potential, which is based on the embedded atom method (EAM) [27]. Additionally, the influence of chemical disorder on the nearest-neighbor electronic level spacing distribution (NNELSD) [28–31] of copper nanoparticles will also be studied. The paper is organized as follows. In the next section we discuss about the formation process of copper nanoparticles. We will also describe the details of the structural analysis, and the tight-binding Hamiltonian employed for the calculation of EDOS and NNELSD. In Section 3 we present the results and discussion. Finally, the main conclusions are outlined in Section 4.

2. Model and methods

2.1. Molecular dynamics simulation

The molecular dynamics calculations were carried out employing a force field derived from Johnson's potential for Cu [27], which is based on the Embedded Atom Method (EAM) originally developed by Daw and Baskes [32]. This potential has been successfully used to study the binding energy and atomic structure of copper nanoparticles [9,10] and nanowires [33]. Within this framework, the total energy of the system, E_{tot}, is given by

$$E_{tot} = \sum_i F(\rho_i) + \frac{1}{2}\sum_i \sum_{j(i\neq j)} \phi_{ij}(r_{ij}), \tag{1}$$

with

$$\rho_i = \sum_{j(i\neq j)} f(r_{ij}),$$

where ρ_i is the electron density at atom i due to all other atoms, $f(r_{ij})$ is the electron density at atom i due to atom j as a function of the distance r_{ij} between them, $F(\rho_i)$ is the embedded energy of atom i in an electron density ρ_i, and $\phi(r_{ij})$ is a two-body potential between atoms i and j. The parameters F, f and ϕ corresponding to copper were taken from Ref. [27].

For the present study we have considered copper nanoparticles of sizes ranging from 13 to 8217 atoms. The sizes have been selected so that all nanoparticles belong to geometric magic numbers with icosahedral symmetry [13]. In this way, structural stability is promoted [26]. Thus, the number of atoms in a nanoparticle is obtained from the relation [13]:

$$N_{Ih}(k) = \tfrac{10}{3}k^3 - 5k^2 + \tfrac{11}{3}k - 1, \tag{2}$$

with k as the number of shells of the icosahedron (Ih). Hereafter, we will use N instead of N_{Ih} to refer us to the number of atoms in the nanoparticle.

Standard MD method is used in the simulation: the Newtonian equations of motion are integrated using the fifth order predictor–corrector algorithm with a time step of 2 fs. To obtain optimized structures for the nanoparticles we proceed as follows. A nanoparticle of desired size was prepared by filling a spherical region with N atoms distributed in a fcc-like lattice. Then, the temperature of the nanoparticle (T) is raised close to the melting point (T_M^N), which is different for each size. At this temperature the system was equilibrated for 200 ps, and then after every 50 steps 1000 different configurations were saved. Thereafter, each configuration is quenched to 0 K and kept in this temperature for 100 MD steps. Hence, the positions are unfolded at the temperature $T_i = T_{i-1} - 20$ K (for $i > 1$, $T_1 = T_{initial} = T_M^N$) for 200 MD steps. This process is carried out until it reaches $T_i = T_{final} = 0$ K. Finally, we choose the nanoparticle configuration with the lowest energy minimum.

2.2. Structural analysis methods

2.2.1. Geometric analysis

Considering that the nanoparticle is almost spherical, we can define its average radius as

$$R_N = r_{Cu} + \frac{1}{6}\sum_i d_i, \tag{3}$$

where d_i $(i = x, y, z)$ is the maximum separation between the centers of two atoms along the x-, y- or z-axis, and r_{Cu} is the theoretical radius of a copper atom ($r_{Cu} = 1.28$ Å). This relation will be compared to an ideal spherical model, where $R_N^{ideal} = r_{Cu}N^{1/3}$, by means of a least square fitting procedure. It is worth mentioning that the relation given by Eq. (3) is only valid for close packed nanoparticles, which is the case in this study as will be shown in the next section. Besides, in order to quantify the error percentage, $S_\Delta(\%)$, by assuming that the nanoparticle is spherical, we define

$$S_\Delta = \sum_i [d_i - \langle l\rangle]^2,$$

with $\langle l\rangle$ as the average over d_i. Then

$$S_\Delta(\%) = \frac{S_\Delta}{2R_N} \times 100\%. \tag{4}$$

2.2.2. Pair analysis technique

The common neighbors analysis (CNA) technique, introduced by Honeycut and Andersen [34], allows us to analyze the local structural environment of an atom in a given structure. Thus, a set of four indices (i, j, k, m) is defined to identify the local structure between pairs of atoms in the system. The most important indices, employed in this work, are 1421, 1422, and 1551, which correspond to fcc-like, hcp-like, and icosahedral-like local structures, respectively [35]. In this work, we define the quantity $A(\%)$ as the percentage of a specific local structure.

2.2.3. Surface–volume ratio

In order to study the influence of the surface on the physical properties of the nanoparticles, we classify the atoms as a core or surface one following this criterion: if the atom has twelve neighbors (fcc local symmetry) within a given distance d_0 (see below) this atom is considered a *core atom*, else it is considered a *surface atom*. Thus, taking into account the number of surface atoms, N_s, we define the surface–volume ratio as

$$r_{sv} = \frac{N_s}{N}.$$

2.3. Electronic structure

Considering that the electronic configuration of copper is $[Ar]4s^1 3d^{10}$, where the d orbital is filled and there is only one s orbital, and that many body effects are already considered in the MD simulation, we can define a local basis of atomic orbitals $|\vec{R}\rangle = |\vec{R_s}\rangle$ employing only one orbital per atomic site. In this basis the *tight-binding* Hamiltonian (considering only first neighbors contributions) is described by [5]

$$H = \sum_{\vec{R}}\sum_{\vec{R}'} |\vec{R}\rangle H_{\vec{R},\vec{R}'} \langle \vec{R}'|, \tag{5}$$