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Monomolecular adsorption on nanoparticles with repulsive interactions: A Monte Carlo Study

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Abstract

In the present work, we study the adsorption of different monomolecular species on nanoparticles with different sizes and geometries using a Gran Canonical Monte Carlo method. These species are characterized by repulsive lateral interactions between themselves as it take place in the case of the adsorption of partially charged atoms or molecules. Nanosize effects are analyzed in terms of adsorption on edge and facet sites. The energy minimization in these systems comes out as a complex conjugation of repulsive lateral interactions between the adsorbates and attractive interactions of the adsorbates with the nanoparticle. The phenomenon is analyzed as a function of the occurrence of different ordered structures being formed on the surface of the nanoparticle. It comes out that layers with different structures may coexist on different facets of the nanoparticle. Finally, a discussion of the deposition on flat surfaces and in finite systems is given.
1. Introduction

In real surfaces, crystallographic defects such as impurities, dislocations or borders make thermodynamic properties differ from those of flat surface materials [1]. In the nanoworld, this behavior is even more extreme. Nanoparticles (NPs) are systems characterized by a high curvature and a large heterogeneity in interatomic interactions. The latter causes large deviations from the bulk thermodynamic behavior [2,3]. Different physical and chemical properties have been found depending on the size and shape of the nanostructure such as diffusivity [4], sintering [5], chemical reactivity [6], melting [7,8] latent heat of fusion [9], magnetism [10] and the under/over potential deposition transition [11,12].

The special behavior of systems made of a relatively small number of particles was recognized in the 1960s by Hill [13], who described the basis of the thermodynamics that he called “of small systems.” Hill described in a visionary way how size could affect various thermodynamic properties of these systems. Keeping the pace of “nano times”, this theoretician extraordinarius [14] gave this area of study a new name; he called it nanothermodynamics [15]. A remarkable result of that, is the need to specify the size of the system for a proper (and correct) thermodynamic characterization, so that “small systems” have one more degree of freedom than large ones [13,15,16].

In the case of a very large flat surface, the thermodynamic properties of typical lattice gas models such as adsorption isotherms and energy per site do not show size effects. On the contrary, in the case of adsorption on NPs, nanoeffects were reported in several adsorption thermodynamics properties on both using Grand Canonical Monte Carlo (GCMC) simulations [17] and/or analytic approaches [18]. So, it is not hard to consider the size as a new parameter that allows the understanding of adsorption properties at the nanoscale.

From the theoretical electrochemical point of view, typical oxidation-reduction voltammetric curves can be obtained through the simulation of ion adsorption on electrodes in the GCMC scheme. Typical current densities in voltammetric curves can be obtained from the derivative of the adsorption isotherms or by computation of the
fluctuations of the ad-particles (see Section 2). The electrode potential is related with
the chemical potential of the adsorbate, which is the characteristic variable on GCMC
simulations. Rikvold has used this scheme to study several experimental systems such
as urea on Pt(100) and bisulfate on Rh(111) by ground-state calculations and GCMC
simulation [19]. Similar schemes were also used to study the underpotential deposition
of Cu on Au(111) in the presence of sulfate [20] and the electro sorption of Br on
Ag(100) [21,22].

The deposition of ions or capping molecules generally shows repulsive interactions,
which induce the formation of ordered structures on two-dimensional substrates such as
(100) or (111) faces of metals. For example, in the special case of repulsive first nearest
neighbors (NN) interactions, the deposition results in two-ordered structures: the (√3 x
√3) one, where each ad-particle does not have any NN occupied and the (√3 x √3)* one,
which only has three of the NN occupied in triangular lattices [23]. The repulsive effect
of lateral interactions has been analyzed for bromide adsorption on Ag(100) and sulfide
adsorption on Pt(111). Experimental systems were used to adjust parameters within the
simulation. Remarkably, a good fit was only possible introducing long range
interactions [24,25]. Following with repulsive interactions, the influence of the range
and type of lateral interactions in different adsorption geometries has been studied in the
case of flat surfaces [26].

DFT calculations have been used to reproduce voltammograms for H adsorption on
Pt(100) and Pt(111). The authors analyzed the reactions of protons from aqueous
solution on Pt surfaces to form adsorbed hydrogen. The results of the model agreed very
well with experiment [27].

Dynamic information was obtained using Kinetic Monte Carlo (KMC) simulations to
study CO oxidation on steeped surfaces of Rh(111) [28] and on the Pt(111)–electrolyte
(sulfuric acid) interface [29]. CO oxidation on Pt surfaces has been modeled using
Monte Carlo simulations and mean-field theory, to understand the phenomenon of bulk
CO electro-oxidation and stripping voltammetry [30].

As can be seen from the above paragraphs, no reference has been made to a systematic
study of the variation of the adsorption thermodynamic properties in finite surfaces with
repulsive interactions. In this respect, the present paper aims to perform the
characterization of the thermodynamics of size effects in NPs and its implications for
electrochemical measurements. We will consider different degrees of repulsion,
emulating systems ranging from anion adsorption to hard steric effects of capping
molecules and the different kinds and sizes of NPs. In the case where the distance between NPs becomes small (concentrated NP systems), the effects of confined spaces between two adjacent NPs could become important. These effects are neglected in the present studies.

The paper is organized as follows. Section 2 describes the lattice-gas model and some basic definitions. Section 3 shows the results for the thermodynamic behavior obtained from GCMC simulations. Finally, in Sec. 4 the conclusions and future perspectives are given.

2. Model and basic definitions

In its simplest, most usual form applied to represent infinite surfaces, the lattice-gas (LG) model describes a layer of type-$B$ adsorbates on a lattice of type-$A$ adsorption sites, where the substrate is assumed to be homogenous. The Hamiltonian of the adsorbed phase is defined by:

$$H_{LG} = w_{BB} \sum \sum_{i,j=i}^{NN} c_i c_j + \sum_{i=1}^{M} (\varepsilon_i - \mu) c_i \quad (1)$$

where $c_i$ corresponds to the occupation number of the $i$-th site that takes the value 1, if the site is occupied or 0, if it is empty. $w_{BB}$ is the interaction energy between adsorbates at neighboring sites, $\mu$ is the chemical potential and $\varepsilon_i$ is the interaction of a single adsorbate with the substrate. The first and second sums on the right side of Eq. (1) run over all $B$ nearest-neighbors (NNs) pairs and all lattice sites ($M$), respectively. While simulations are usually carried out for a finite network with periodic boundary conditions, the thermodynamic properties are currently evaluated in the limit $M \to \infty$.

In the LG model, the coordination number, i.e. quantity of NNs, of each lattice point is not an effective parameter, because adparticles “see” everywhere the same coordination with the substrate and the same number of neighbors. This is clearly an idealization of the surface. Conversely, a real surface has imperfections such as steps, edges, corners,
kink, adatoms, etc., which give a distribution of adsorption energies. In these cases, the surface is considered as a heterogeneous substrate. Thus, the heterogeneity can be energetic or geometric. The presence of inhomogeneities generally shifts the adsorption isotherms towards more negative chemical potentials, thus increasing the stability with respect to that predicted for a perfect surface [31].

In the case of NPs, the LG model given in Eq. (1) needs to be adapted, because the lattice representing the adsorption sites can no longer be considered as a homogeneous surface. Here, the coordination number of each point becomes a key parameter. To solve this problem, a modification of the Hamiltonian given in Eq. (1) allows taking into account this heterogeneity simply assuming an effective interaction $w_{AB}$:

$$
\sum_{i=1}^{M} \varepsilon_i c_i = w_{AB} \sum_{i=1}^{M} N_i c_i \quad (2a)
$$

Then,

$$
H_{NP} = w_{BB} \sum_{(i,j)} N_{ij} c_i c_j + w_{AB} \sum_{i=1}^{M} N_i c_i - \mu \sum_{i=1}^{M} c_i \quad (2b)
$$

where, as stated above, $w_{AB}$ is a unique parameter representing the average interaction energy between adparticles and substrate sites and $H_{NP}$ denotes the nanoparticle-adapted hamiltonian. In fact, $w_{AB}$ is an effective energy per bond. $N_i$ is the coordination with the substrate, of the $i$-th site. We emphasize that the present model involves different kinds of adsorption sites. For example, in the case of an icosahedral NP, the adsorption sites on facets correspond to hollow sites. On the other hand, the borders contain bridge adsorption sites and the vertices contain on-top adsorption sites. Fig. SI1 of supplementary information shows some snapshots illustrating the different types of adsorption sites within the present model.
By introducing a variable that depends on the coordination number with the substrate via the term $N_i w_{AB}$, it is possible to model different NPs. Then, we can analyze the effect of different shapes and the size in an independent way. As we will see, $w_{AB}$ is a constant, and the heterogeneity will be introduced via the quantity $N_i$. This definition implies that the effective contribution of $i$-th site is configuration dependent. Thus, we can introduce information from the NP morphology in the Hamiltonian in Eq. (2b). For example, $N_i = 3$ corresponds to adsorption on a triangular facet (such as (111)-surface) and $N_i = 4$ on a square one (such as (100)-surface). It is important to observe that $1 \leq N_i \leq 9$, because on the surface of a NP there may exist edge and vertex sites with low coordination and also vacant sites with high coordination. For simplicity, we will consider regular NPs.

For the present case, we consider a pre-existing substrate, let us say a seed-NP, with given size and geometry at a temperature $T$ and a chemical potential $\mu$. This seed-NP is formed by atoms of type A (so-called substrate), on which the particles of type B are deposited (adsorbate). The decorated NP, that is the seed-NP plus the deposited particles, will be characterized by the numbers of constituent particles, say $N_A$ and $N_B$.

The $M$ adsorption sites for the B particles are located on the surface of the seed-NP. Each site on this surface is assumed to be linked only to its NNs. This defines a sphere of coordination, which depends on the kind of site, the size and the geometry of the NP. The B particles can be linked with B-type particles (lateral NNs) and with A-type particles belonging to the seed-NP. We define two different interaction energies: $w_{AB}$ and $w_{BB}$ for A-B and B-B bonds, respectively. Repulsion between adsorbates is introduced setting $w_{BB} > 0$ and attractive interaction between A and B particles are introduced by $w_{AB} < 0$. Along all this work, we will be referring the energies in units of $k_B T$. In particular, $w_{AB}/k_B T = -3.86$ and $k_B T = 1.0$ are held fixed. A change of $w_{AB}/k_B T$ only implies a shift of the curves along the abscissa axis, and would not affect the overall coverage vs chemical potential behavior.

The deposition process is simulated by the Monte Carlo technique in the Grand Canonical ensemble using a typical adsorption-desorption algorithm [32,33]. The Metropolis scheme [34] is used to satisfy the principle of detailed balance. A MC Step
(MCS) is achieved when each of the $M$ sites has been tested to change its occupancy state. Typically, the equilibrium state can be well reproduced after discarding the first $5 \times 10^6$ MCS. Then, the next $2 \times 10^6$ MCS are used to compute averages. Evaluation of different thermodynamic quantities follows standard procedures, as described below.

The mean coverage, $\theta$, is obtained as a simple average of the simulations:

$$\theta(\mu, T) = \frac{\langle N_B \rangle}{M}$$

(4)

The differential heat of adsorption, $q_d$, is obtained from [35]:

$$q_d(\theta) = \frac{\langle H_{NP} N_B \rangle - \langle H_{NP} \rangle \langle N_B \rangle}{\langle N_B^2 \rangle - \langle N_B \rangle^2}$$

(5)

The differential heat of adsorption is a property experimentally accessible by means of thermal desorption spectra. The physical interpretation of this quantity is the energy associated with the removal of a particle from the surface at a given coverage. $q_d$ contains information on the binding energy. Therefore, it could reflect the different adsorption conditions, i.e. at terraces, steps, etc. In this way, thermal desorption spectra could be performed to check some of the predictions of the present modeling.

While in the present calculations the chemical potential fixed in the Grand Canonical simulation determines the coverage degree, in electrochemical systems, this role is played by the electrode potential. In fact, the electrode potential difference, $\Delta E$, is linearly related to the chemical potential of the B species according to:

$$\mu = C - ze_0 \Delta E$$

(6)
Where \( z \) is the number of electrons transferred in the electrochemical reaction, \( e_0 \) is the elemental charge and \( C \) is a constant that depends on the activity of B species in solution and the nature of the reference electrode. The physical reason for the minus sign is due to the fact that, in electrochemistry, an increase of the electrode potential will destabilize the adsorbate, since we are taking away their electrons. While the previous argument seems to suggest that some electronic device is necessary to set the potential difference, we have shown in a previous work that this can be achieved by a redox system in the case of free-standing nanoparticles \([11,12,16]\). Then, the present results may be also of interest for electrochemical systems.

An interesting electrochemical property to simulate and compare with experiments is the fluctuation in the number of B-particles on the surface of the NP, so-called compressibility of the adlayer. This quantity is defined as \( \beta \frac{\partial \theta}{\partial \mu} \) \([36]\) and is proportional to the current measured in a voltammetric experiment. On the other hand, the dimensionless chemical potential \( \beta \mu \) is proportional to the electric potential difference applied between working and reference electrodes \([24]\). Then, \( \beta \frac{\partial \theta}{\partial \mu} \) plotted versus \( \beta \mu \) resembles a voltammogram, if the latter was obtained at equilibrium conditions \([24,36]\). The derivative \( \frac{\partial \theta}{\partial \mu} \) can be computed in the Grand Canonical ensemble via the normalized mean square fluctuations:

\[
\beta^{-1} \left( \frac{\partial \theta}{\partial \mu} \right) \approx \left\langle N_B^2 \right\rangle - \left\langle N_B \right\rangle^2
\] (7)

where \( \beta = (k_B T)^{-1} \) and \( k_B \) is the Boltzmann constant. Eqs (5) and (7) result from the thermodynamics fluctuation theory \([37,38]\). We should note that the quantities given in Eqs. (5) and (7) cannot be predicted theoretically. However they can be obtained using computer simulations.

3. Results and Discussion
Firstly we introduce briefly our work considering adsorption on infinite flat surfaces. In lattice gas models, the deposition on flat surfaces, the adsorption isotherms, its derivative, energy per site, etc. do not show size effects when the size is changed, as long as the system is large enough. This is because the adsorption isotherm involves an intensive property, *i.e.* coverage can be envisaged as a surface density of ad-particles.

To illustrate this behavior in the Fig. 1a, adsorption isotherms for square lattice for several lattice sites $M$ are shown. For simplicity we define $\delta E = |w_{BB}/w_{AB}|$, where the only energy changed is $w_{BB}/k_BT>0$. A flat plateau is observed at half coverage in concordance with the formation of the c(2x2) structure. The inset shows the fluctuations for a square lattice with different numbers of lattice sites $M$, calculated from Eq. (6), where no shifts are observed with the size of the system. In Fig. 1b the simulations are repeated for triangular lattices. Two broad plateaus are shown in correspondence with the structures formed at $\theta = 1/3$ and $2/3$. As in the previous case, the derivate shown in the inset is size independent.

We turn now to consider surfaces defined in a three-dimensional space, like of NPs. Depending on the shape of the NPs under consideration, it comes out that they can be classified into three groups, depending on the nature of the adsorption sites found at their facets and at their edges. In the first group, we include those NPs having one type of adsorption sites at the facets and one type of adsorption sites at the edges. This is for example the case of icosahedral (ICO) NPs, see Fig. 2a, where all the facets exhibit the $\{111\}$ structure and all edges present equivalent adsorption sites. In the second group, we include those NPs having two types of adsorption sites at the facets and one type of adsorption site at the edges. The NPs belonging to this group can be observed in Fig. 2b. Examples of this type are cuboctahedral (CO) NPs, which present two types of facets: $\{111\}$ and $\{100\}$, sharing only one type of edge. Finally, in the third group, we include those NPs having two types of adsorption sites at the facets and two types of adsorption sites at the edges. NPs with the shape of a truncated octahedron (TO) belong to this group, see Fig. 2c.

3.1. First NPs group
We begin describing an ICO NP. The total number of atoms of an icosahedron can be characterized by a natural number \( n \), which is related to the size of the seed, and to the number of surface sites. For example, if \( n = 1 \), the NP has \( N_s = 1 \) and \( M = 12 \), the smallest value of the number of surface sites. From the energetic point of view, the adsorbate-substrate interaction energies are : \( w_{AB} \) for vertex, \( 2 w_{AB} \) for edge and \( 3 w_{AB} \) for \{111\}-facet sites. The adsorbate-adsorbate interaction energies are: \( 5 w_{BB} \) for vertex, \( 6 w_{BB} \) for edge and \( 6 w_{BB} \) for facet sites. We consider simulations for a seed-NP with \( N_s = 1415 \) ( \( n = 7 \) ) and \( M = 492 \). Fig. 3 shows the adsorption isotherms ( \( \theta \) versus \( \mu / k_B T \) ) for several \( \delta E \) values. The isotherm changes its shape from a sigmoid to the occurrence of two plateaus, as the lateral repulsion becomes stronger. The plateaus appear at \( \theta = 1/3 \) and \( 2/3 \) and become wider as \( \delta E \) increases. It is important to note that the plateaus show a fine structure, this will be analyzed later. The surface structure generated at the first plateau reminds the \((\sqrt{3} \times \sqrt{3})\) structure found in infinite planar surfaces, where each ad-particle has no NNs occupied. In the second plateau, a \((\sqrt{3} \times \sqrt{3})^*\) structure is formed, where each ad-particle has only the half of its coordination fulfilled. In Fig. 4a, we present the differential heat under the same conditions as those of Fig. 3. Steps are found at the coverages, where the plateaus are formed in the isotherms of Fig. 3. These steps present small arrests, marked with black ellipses, reflecting the fine structure of the plateaus discussed above. These are particularly remarkable in the case of \( \delta E = 4.0 \). The dotted lines indicate the coverages 1/3 and 2/3.

An interesting property available from the present MCGC simulations is the compressibility. As mentioned before, this is proportional to the current of voltammograms obtained in electrochemical systems, where the current is plotted as function of potential. Fig. 4b shows \( \beta^2 \partial \theta / \partial \mu \), as a function of \( \mu / k_B T \) for the same system as above. The curve for \( \delta E = 0.5 \) shows three small maxima, which correspond to the inflexion points of the isotherms. The fluctuations decrease as the system approaches the coverages where the structures begin to form. On the other hand, the maxima present a sharp shoulder that corresponds to an increase in \( \langle \delta (N)^2 \rangle \), when the system passes from a disordered to an ordered state. Although the present system is finite, the fluctuations observed resemble the phase transition observed in an infinite...
A similar behavior has also been reported in simulated voltammograms for two-dimensional systems [24]. These sharp shoulders are marked with back arrows in Fig. 4b for \( \delta E = 4.0 \). We now return to the problem of the fine structure observed in the steps of Fig. 3. To understand these features, we study the dependence of the isotherms on the size of the ICO NPs in Fig. 5 for the particular case of \( \delta E = 10.0 \). The sizes considered range from \( N_4 = 147 \ (n=3) \) to \( N_4 = 2869 \ (n=9) \). It is remarkable that the first plateau presents no fine structure for \( n = 3, 6 \) and 9 but the opposite occurs for \( n = 4, 5, 7 \) and 8, as it can be better appreciated in the inset of Fig. 5. On the other hand, the second plateau presents a fine structure for all values of \( n \). To understand the phenomenon described above, it is necessary to analyze the role of the edges in the different surface structures. To build a adsorbate \((\sqrt{3}x\sqrt{3})\) structure, the NPs needs to be commensurate with this structure. Twelve vertices must be empty and the edges must be alternately filled. When this sequence is fulfilled, the \((\sqrt{3}x\sqrt{3})\) structure forms without defects and the isotherms show a unique plateau at coverage exactly 1/3 and a unique step at the differential heat. This geometrical situation can only occur in ICO NP where the index “\( n \)” is a multiple of 3. This is so because the number of adsorption sites at the edge is \( n+1 \). If a NP does not satisfy this condition, it leads to frustrations, in the sense that all adatoms cannot minimize its number of occupied NNs simultaneously. Fig. SI2 of supplementary information shows some snapshots illustrating this geometrical frustration. On the other hand, for the plateau around \( \theta \approx 2/3 \), we observe several subplateaus for all values of \( n \). The \((\sqrt{3}x\sqrt{3})^*\) structure, which occurs on a 2D triangular lattice, is not possible on an ICO. This is also due to the fivefold coordination of the vertices. This behavior can also be observed in Fig. SI2 (supplementary information), which shows the differential heats for the several values of \( n \). For \( n \) multiple of 3, only one step is visible at \( \theta = 1/3 \), but in the other cases multiple steps occur, in agreement with the behavior of the isotherms. In Fig. IS3 (supplementary information), we show an isotherm for a ICO-NP of size equal to \( n = 9 \) with \( \delta E = 7.0 \), an extreme situation (strongly repulsive interaction), where an effective separation of the 3 frustrated states at \( \theta = 2/3 \) can be observed. The previous behavior can be also analyzed taking into account the average number of links \( (L_k) \), that we define as the average number of occupied neighbors per adsorbate in the NP. For a two-dimensional substrate, the \((\sqrt{3}x\sqrt{3})\) structure has \( L_k = 0.0 \) for \( \theta \leq 1/3 \) because no adsorbed particle has occupied NNs sites. The \((\sqrt{3}x\sqrt{3})^*\) structure has \( L_k = 3.0 \) while at full coverage \( L_k = 6.0 \). Fig. 6a
show $L_k$ versus $\theta$ for several values of $n$ characterizing the ICO NP. At $\theta<1/3$ there are practically no links and $L_k=0.0$ and when the NP is filled $L_k=5.9$ because the adsorption sites at the vertices are linked with five NNs instead of six. In the zoom of the Fig. 6a, we can observe that for “$n$” non-multiple of three, the curve increases for $\theta<1/3$, showing that there are particles that are linked with each other at these coverages. This is induced by the geometry of the ICO. The change in the slope of $L_k$ is coincident with each sub plateau observed in the isotherms, (the black lines in the inset are a guide to the eyes). For $n=3, 6, \text{ and } 9$ no links are evident for $\theta<1/3$. In this case, the structure $(\sqrt{3} \times \sqrt{3})$ is completely formed in all the surface of NP, and the links begin to increase for values higher than $\theta=1/3$. Fig. 6b-d presents the normalized distribution of links ($D_{nk}$) versus NN, for a ICO of $n=9$. For a $(\sqrt{3} \times \sqrt{3})^*$ structure, we expect a distribution with a maximum at 3.0. However in all plateaus we observe sites linked with two, four and five NNs occupied. Thus, plateaus correspond to frustrated $(\sqrt{3} \times \sqrt{3})^*$ structures, something that also becomes evident in the differential heat. Fig. 7 shows the simulated voltammograms for different ICO NP sizes. Independent of $n$, all maxima occur at roughly the same chemical potentials. As expected, in the regions where the plateaus in the isotherm are flat, no evidence for the presence of peaks for $n=6$ and 9 is found. However, for $n=7$ and 8, two new small maxima appear; these correspond to the formation of sub-plateaus related with these frustrated $(\sqrt{3} \times \sqrt{3})^*$ structures. Inset shows a zoom of the first flat region.

Now we analyze other NP geometries but within the first group. Under the present approach, the adsorbates on the facets of regular decahedra (DH) and regular tetrahedra (TH) have the same type of repulsive lateral interactions as those of the facets of ICO NPs. The sites on the facets have a lateral coordination of six. The main difference resides in the different relative number of adsorption sites at edges and facets. Sub-plateaus are also present around $\theta=1/3$ and $2/3$ for values of “$n$” not compatible with the formation of the $(\sqrt{3} \times \sqrt{3})$ structure. Fig. SI4 illustrates this behavior.

### 3.2. Second NPs group

In this section, we describe the behavior a NP with cuboctahedral (CO) geometry. A CO NP has six $\{100\}$ and eight $\{111\}$ facets. The CO has four types of adsorbate-substrate
energies; \( w_{ab}, 2w_{ab}, 3w_{ab}, \) and \( 4w_{ab} \) that correspond to adsorption on vertex, edge, \{111\} and \{100\}-facet sites, respectively. It is important to note that all edges connecting \{111\} and \{100\} facets, present the same coordination. Fig. 8a shows isothersms calculated for a CO with \( N_A = 2057 \), \( w_{ab} / k_B T \) was settled like as the ICO and \( \delta E = 0.0, 1.0, 2.0, \) and \( 3.0. \) As lateral interactions increase, several plateaus are formed.

For \( \delta E = 0.0 \), the calculated isotherm is in agreement with the Langmuir conditions. In the first plateau (i) at \( \theta \approx 0.40 \), the typical structures c(2x2) and (\( \sqrt{3} \times \sqrt{3} \)) are formed at the \{100\} and \{111\}-facets, respectively. Due to repulsion, all sites prefer not to have any lateral link. Fig. 8b shows a representative snapshot of the CO for this first plateau.

The second plateau (ii) is formed at \( \theta \approx 0.44 \). When the vertex sites change their status, there is an inversion in the occupation in the edge sites. This induces a reorganization of the occupation on the \{111\} facet and a complete inversion at the \{100\} facet. It is worth remembering that vertex sites are sites with a higher energy. The \{111\} facet now shows the presence of dimers and trimers, always starting at the edge sites (see Fig. IS5). This corresponds to a new type of frustration; we mean all ad-particles cannot satisfy their energetic requirements. The filling sequences of the edge and vertex sites induce frustration on all NPs. This is shown in the Fig. 8c. There, we show the corresponding snapshot for the (iii) plateau at \( \theta \approx 0.82 \), where the \{100\}-facets are filled, see Fig. 8d. Simultaneously, at the \{111\} facets the structure \( (\sqrt{3} \times \sqrt{3})^* \) is formed.

The last plateau (iv) at \( \theta \approx 0.91 \) is characterized by the filling of the remaining edge sites. The corresponding snapshot is shown in Fig. 8e. The voltammogram for the present geometry is shown in Fig. IS6.

### 3.3. Third NPs group

Finally, we consider a truncated octahedron (TO) geometry. Like in the CO, in this geometry there are two different facets: \{111\} and \{100\} (see Fig. 2c). However, in this NP type there are also edge sites of different types, with different coordination numbers: those connecting \{111\} facets with each other and those connecting \{111\} with \{100\} facets. Thus, the TO NP has four types of adsorbate-substrate energies; \( w_{ab} \) (vertex and \{111\}-\{111\} edges), \( 2w_{ab} \) (\{100\}-\{111\} edges), \( 3w_{ab} \) (\{111\} facets), \( 4w_{ab} \) (\{100\} facets) and three types of adsorbate-adsorbate energies; \( 5w_{bb} \) (\{111\}-\{100\} edges), \( 4w_{bb} \) (\{100\} facets), \( 6w_{bb} \) (\{111\} facets and \{111\}-\{111\} edges). Fig. 9 shows the
isotherms for the TO using $N_A = 405, 976, 1925$ and $3348$ for $\delta E = 3.0$, here $w_{AB} / k_B T$

has the same value as before. The behavior is similar to that of the CO geometry: two principal plateaus are formed. The first corresponds to the case where each particle has no NNs. On the \{100\} and \{111\} facets the structures c(2x2) and (\sqrt{3}x\sqrt{3}) are formed, respectively. In the second plateau, the \{100\}-facets are filled and on the hexagonal facets each particle is linked with other three, forming the (\sqrt{3}x\sqrt{3})* structure. For all sizes, the formation of sub plateaus is observed. The insets b) and c) present snapshot of the structures at the first and second plateaus respectively.

Fig. IS7a presents the simulated voltammogram for several sizes of TO NPs with the same set of parameters of Fig. 9. Three main maxima are observed, which become better defined as size increases. The sub plateaus in the isotherms appear here as small peaks. The differential heat show steps and sub steps, in correspondence with the behavior of the isotherms as is shown in the Fig. IS7b.

NPs pristine with perfect geometries such as those discussed in the previous sections are rarely found in experiments. Surface defects such as adatoms, vacancies and other sites are the generality rather than the exception. It is even possible to find domains with different crystallinities present in the same NP. It is very common to find NPs of different geometries within the same set of synthesized NPs. Despite this complex scenario, is possible to extract valuable information by analyzing the behavior of perfect NPs. For example, Fig. 10 shows the normalized mean square fluctuations as a function of chemical potential at $T = 300$ K for ICO, TH, CO and TO NPs of a similar sizes, such as may be obtained in an experimental histogram. The convolution of all fluctuations shown in the figure can be used to give an idea of "experimental noise" in the voltammograms, caused by different shapes but similar sizes of NPs. For the convolution shown in Fig. 10 we have assumed a population of NPs composed of the same proportions of ICO, TH, CO and TO. The number of sites available on the facets, edges and vertices determine the height of each peak. Then, it is clear that the convolution is not unique. The line in Fig. 10 shows three well defined regions; the first where expanded structures such as (\sqrt{3}x\sqrt{3}), (2x2) and their frustrated structures coexist; the second where expanded and compact structures of type frustrated (\sqrt{3}x\sqrt{3})* and (1x1) coexist; and finally a third region where only compact structures coexist. Because the extent of the separation of these three regions exhibits a strong dependence on the magnitude of the repulsion between the adsorbates (as shown qualitatively in Fig. 4), for
relatively weak but repulsive interactions, adsorption may yield a broad shoulder in the voltammograms, where all structures coexist simultaneously.

In the light of the present results it is interesting to remark the main differences between these nanostructured systems and flat surfaces. Adsorption on flat surfaces does not show size effects for relatively large systems. For example, in 2D lattices the main thermodynamics properties do not change when tend to the thermodynamics limit \( M \rightarrow \infty \). In all cases the ordered structure involved a continuous phase transition for repulsive interactions. Even the related derivatives do not show differences in the intensity or shift of their peaks.

In the nanosystem analyzed here, there are a few features such as sites with different coordination on facets, borders, and vertices that play an important role. These features induce the nanoeffects observed. These nanoeffects are manifest in a shift in the isotherms, in the different intensities in the compressibility peaks, etc, at several NP sizes.

The repulsive character of the lateral interactions is responsible for the ordered structures formed on the facets. The size of the NP is directly related to the size of each facet and the commensurability of the ordered structures depend on the quantities of adsorption sites. The frustrations and the subplateaus observed are consequences of this.

### 4. Conclusions

In the present work we have studied size and shape effects for the formation of adsorbates presenting repulsive interactions, on the surface of a nanoparticle. Nanosize effects were analyzed, considering adsorption at edge and facet sites within a lattice gas model and Monte Carlo simulations. The energy minimization results from the complex conjugation of repulsive lateral interactions and attractive links between the adsorbates and the seed nanoparticle. Several geometries were considered, emphasizing on icosahedra, cuboctahedra, and truncate octahedra. The properties calculated were adsorption isotherms, differential heats of adsorption, and compressibility with the methods of fluctuations. Depending on the kind of substrate, different types of behavior were found:
• For icosahedral nanoparticles the \((\sqrt{3}x\sqrt{3})\) structure is formed on the whole surface only when the index “n” is a multiple of 3. At these indices the NP size is commensurate with this structure. For others values of n, subplateaus are observed in the isotherms in correspondence with frustrations related to the occurrence of the mentioned structure.

• On the other hand, the \((\sqrt{3}x\sqrt{3})^*\) structure cannot be completely formed on ICO structures of any size. Then, frustration related to subplateaus are always observed.

• Compressibility plots show peaks associated with ordered structures, which appear and depending on nanoparticle size.

• For cuboctahedral nanoparticles, \(c(2x2)\) and \((\sqrt{3}x\sqrt{3})\) or \((1x1)\) and \((\sqrt{3}x\sqrt{3})^*\) structures were formed on the \{100\} and \{111\} facets, respectively. Geometrical frustrations were found too.

• For truncated octahedral nanoparticles, the existence of \{111\}-\{111\} edges, allow the perfect connection of both \(c(2x2)\) and \((\sqrt{3}x\sqrt{3})\) structures, where no frustration was observed.

• In two dimensional adsorption phenomena the ordered structures like \(c(2x2)\), \((\sqrt{3}x\sqrt{3})\) and \((\sqrt{3}x\sqrt{3})^*\) are characterized by order-disorder phase transitions. For each transition, a critical exponent may be determined. These systems have the peculiarity that in the vicinity of criticality the correlation length tends to infinity. This means that in two dimensional lattice-gas models the correlation length reaches the size of the system. Finite size effects are the manifestation of a phase transition and are useful to define the critical temperature. Monomolecular decoration of nanostructures such as nanoparticles or nanoholes is different. A new behavior is observed, corresponding to nano effects. These are manifested in a shift of thermodynamics properties when the size of the nanostructure is changed. These effects tend to hide the size effects associated with the phase transitions taking place on the different facets of the NP. One technique than can help to identify the transition and could allow to obtain the critical temperature is the thermodynamic integration method in the canonical ensemble. With this technique it is possible to analyze the structural disorder in the vicinity of the transition through the calculation of the configurational entropy. In this ensemble other critical functions can be used to help to classify the structural changes found on the surface of NPs.
These functions are fourth-order cumulants of energy, order parameters, specific heat, etc. These studies are in progress.

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7. Figures Caption

Figure 1: Adsorption isotherms on flat surfaces, for several quantities of adsorption sites M. a) Square lattices, b) Triangular lattices. The respective inset shows the corresponding derivative.

Figure 2: (Color online) Representative pictures of nanoparticles presenting: a) one type of adsorption site at the facets and one type of adsorption site at the edges, in this case an icosahedron, b) two types of adsorption sites at the facets and one type of adsorption site at the edges, in this case a cuboctahedron, and c) two types of adsorption site at the facets and two types of adsorption site at the edges, in this case a truncated octahedron. Red lines denote edges. The facet types are marked at each structure.

Figure 3: (Color online) a) Adsorption isotherms obtained for an icosahedral NP made of 1415 type-A particles, for several $\delta E$ values as indicated.

Figure 4: (Color online) Results from GCMC simulations for the adsorption of particles with repulsive interactions on an icosahedral NP of 1415 type-A particles. a) Differential heat as a function of coverage degree and b) normalized mean square fluctuations as a function of chemical potential. The parameters of the simulations are the same as those of Figure 3.

Figure 5: (color online) Dependence of the isotherm on the size of an icosahedral NP, $n$, for $\delta E = 1.0$. The inset shows a zoom of the first plateau.

Figure 6: (color online) a) average number of links versus coverage for several values of $n$ charactering the size of the icosahedron. The vertical lines indicate the coverages $1/3$ and $2/3$, and the horizontal indicates $Lk = 3.0$. The inset shows a zoom around $\theta = 1/3$. The normalized distribution of links ($Dis$) for $n = 9$ is shown on the right for different coverage degrees, b) $\theta = 0.645$ c) $\theta = 0.667$ and d) $\theta = 0.6889$.

Figure 7: (Color online) Fluctuations obtained as a function of the normalized chemical potential for icosahedral NPs of different sizes.

Figure 8: (Color online) a) Adsorption isotherms on a CO with $N_a = 2057$ and several values of $\delta E$. The plateaus are labeled with “i’s”. Snapshot of the representative...
configurations at the plateaus, the black circles denote occupied sites and the colors are
empty sites: b) plateau \(i\), c) plateau \(ii\), d) plateau \(iii\) and e) plateau \(iv\).

Figure 9: (Color online) a) Isotherms obtained for Truncated Octahedra using different
values of \(n\), with \(\delta E = 3.0\). a) and b) present snapshots of the structures obtained at the
first and second plateaus respectively.

Figure 10: (Color online) Mean square fluctuations (MSF) as a function of chemical
potential for ICO(2057), TH(1771), CO(2057) and TO(1925) NPs at 300 K. The full
line is a convolution of the MSF of the four types of NPs with the same weight.
Figure 1

a) $\delta E = 0.5$

- $M$
  - ■ 14400
  - ○ 3600
  - ▲ 900
  - ▼ 100

b) $\delta E = 2.0$

- $M$
  - ■ 14400
  - ○ 3600
  - ▲ 900

$\langle N^2 \rangle - \langle N \rangle^2$

$\mu / k_B T$

$\theta$
Figure 2

a) Border {111}-{111}

b) Border {100}-{111}

c) Border {100}-{111}

Border {111}-{111}
Figure 3

\[ N_A = 1415 \]

\[ \theta \]

\[ \mu / k_B T \]

\[ \delta E \]

- 0.0
- 1.0
- 2.0
- 3.0
- 4.0
Figure 4a

![Graph showing the relationship between $q_d$ and $\theta$ for different values of $\delta E$.]

- $\delta E = 0.5$
- $\delta E = 1.0$
- $\delta E = 2.0$
- $\delta E = 3.0$
- $\delta E = 4.0$

The graph illustrates the change in $q_d$ with respect to $\theta$ for varying $\delta E$ values, with specific data points highlighted for the $\delta E = 0.5$ and $\delta E = 4.0$ cases.
Figure 5

$\delta E = 10.0$

The graph shows the dependence of $\Theta$ on $\mu/k_B T$ for different values of $n$. The inset provides a closer view of the transition points.

- $n = 3$
- $n = 4$
- $n = 5$
- $n = 6$
- $n = 7$
- $n = 8$
- $n = 9$
\[ \delta E = 10.0 \]

Figure 6

\[ \theta = 0.6458 \]
\[ n = 9 \]

\[ \theta = 0.6671 \]
\[ n = 9 \]

\[ \theta = 0.6889 \]
\[ n = 9 \]
Figure 7

$\delta E = 4.0$

$\langle N^2 \rangle - \langle N \rangle^2$

$\mu / k_B T$

$n$

- $6$
- $7$
- $8$
- $9$
Figure 9

\[ \delta E = 3.0 \]

\[ \mu / k_B T \]

\[ N_A \]

- 405
- 976
- 1925
- 3348
\[ \delta E = 2.0 \]
\[ w_{AB} = -0.1 \text{ (eV)} \]
\[ w_{BB} = 0.2 \text{ (eV)} \]
\[ T = 300 \text{ K} \]