Communication

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# Study of the Structure of Monoatomic Adsorbates on Metal Surfaces Using the Sphere-in-Contact Model

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**Abstract:** We have recently shown that the sphere-in-contact model can be used as an educational and research tool in various contexts, such as the visualization of carbon structures (e.g. graphene, carbon nanotubes, carbon nanocones and graphite), heterogeneous catalysts, metal nanoparticles and organic molecules. In this communication we present how it can be used to model the adsorbate structure of a monoatomic element on the hexagonal close-packed surface of the metal. We have used atoms of varying radius to represent the metal surface atoms and the adsorbate atoms. The study reveals that many surface symmetries are possible for a fixed adsorbate coverage by the movement of the adsorbate atoms in response to surface adsorbate-adsorbate repulsions. The movement of the particles (e.g. particle diffusion) can be seen directly in the model and this is caused by the user intervention. This has great educational but also research value as one can directly see how the adsorbate atoms reorder on the surface of a metal. We believe that this model will be useful in the rational design of catalytic materials and materials coatings with new technological applications.

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## 1. Introduction

Rational design of catalytic surfaces is of paramount importance in heterogeneous catalysis and nanotechnology.[1,2] This is because the tailored design of adsorbate-surface systems can find applications in catalysis, nanotechnology and materials science.[3] Particularly when these systems are composed of monoatomic adsorbates and the surface is made from transition and noble metals.[4] Therefore the better understanding of possible surface structures of adsorbates on metal surfaces and the design of new materials, with particular surface termination and therefore tailored properties, is desirable in many fields.[5] Thus far the understanding of adsorption on metal surfaces on the microscopic level has relied on computer models and DFT calculations to which experimentalist do not have readily accesibility.[6] We have previously shown that physical molecular models can have some advantages with respect to computer models as the teacher, researcher or student can manipulate the physical molecular model in ways that is currently not possible in computer simulations.[7] Perhaps in the future there will be some computer models of catalytic surfaces where the structure of adsorbates can be altered during the course of the calculation by the influence of a user action. Such efforts are currently underway via virtual reality teachniques. [8] Nevertheless, the use of inexpensive physical molecular models is desirable in research and education. For this reason we have used the sphere-in-contact model to study the structure of monoatomic adsorbates on the surface of close-packed metals.

The sphere-in-contact model is a molecular model in which the atoms are represented by their atomic radius.[9] These spheres are in contact at a single point, where also the chemical bond is centered. This model has been shown to have certain advantages over other molecular models such as the ball-and-stick model where the electron density volume of the molecular structure is underestimated. Also in the wireframe model (e.g. stick model) the volume that the electron density has is completely absent and we can only see the connectivity of the atoms. The other model broadly

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used in chemistry was developed by Robert Corey, Linus Pauling, and Walter Koltun and is called the space-fill model (also known as CPK model).[10] In this model the atoms have their van der Waals (VdW) radius. This model is useful when we want to understand the packing of molecules in self-assembled molecular structures, as the molecules or particles have the correct separation due to weak interactions such as London dispersion forces.[11–15] However it does not allow the proper modelling of doped materials and intercalation compounds as the void space in the structures is smaller than the actual space due to the electron density, which is correctly represented better in the sphere-in-contact model.

We have shown previously that the sphere-in-contact model can be used in research for example to understand the structure of carbon on curved surfaces, such as the hemispherical cap of carbon nanotubes.[7,16] It has also been used to reveal the molecular channels in rhombohedral graphite structures, which can find use as a radiation filter.[17] We have also used sphere-in-contact models to model the complete reaction mechanism of heterogeneous catalytic reactions, where the adsorbates, the metal nanoparticle and the substrate are explicitly shown.[18] When the sphere-in-contact model uses different radius for the atoms of structure then we can model almost anything with atomic precision. This could be organic molecules, organometallic complexes, biomolecules and doped materials. It has also been used to understand the position of nanoparticles on metal close-packed surfaces.[18] We have also recently shown that sphere-in-contact models can be used to understand the number of (100) and (111) sites that a nanoparticle has on its exposed surface when such NPs are deposited on flat hexagonal, trigonal and cubic surfaces.[19]

In this communication we show how the sphere-in-contact models can be used to model surface interactions during the adsorption of monoatomic elements (e.g. H, C, N, S, O etc) on hexagonal metal surfaces. The question we address with these models is what are the possible structures of monoatomic adsorbates for a given surface coverage (θ). This is a question with great interest in surface chemistry, heterogeneous catalysis and nanotechnology.

## 2. Materials and Methods

We have used marbles of different size and colour and a template that would hold the marbles in a hexagonal close packed structure. The marbles are transparent so that we can observe the underlying structure beneath the adsorbates, such as the three-fold hollow sites and four-fold hollow sites. Therefore the marbles in the metal (111) surfaces are colourless and the marbles of the adsorbate layer are blue. Also the marbles have the natural tendency to arrange in a hexagonal close packed pattern by lateral repulsive interactions, which can be enforced by a lateral movement of the template frame. As far as we know this modelling technique using spheres of different size to model surface adsorption phenomena through physical molecular models has not been previously employed elsewhere.

The adsorbate surface coverage (θ) was calculated by the assumption that we have a full coverage (e.g. θ = 1) when each surface metal atom has one adsorbate atom bound to it. This equation is,

$$\theta = \frac{number\ of\ adsorbate\ atoms\ in\ surface}{number\ of\ metal\ atoms\ in\ surface} \qquad \text{Eq. 1}$$

## 3. Results and Discussion

We have placed 81 colorless marbles in a rectangular template and allowed them to obtain their minimum energy configuration, which is a hexagonal closed packed structure. This hexagonal closed packed structure is the surface termination of both hexagonal closed packed (HCP) and face centered cubic (FCC) crystals. However, similar models can be built for the body centered cubic (BCC) structure. This means that all metals which have usually one of these three crystal structures can be modelled this way and the structure of adsorbates can be studied. Furthermore, steps and adatoms can be modelled within the sphere-in-contact model by adding a second layer of metal atoms or by adding an atom on the terrace of the metal surface, respectively. We have also prepared sphere-in-contact models with atom vacancies (e.g. defects). However, the adsorption at the surface defect is difficult to model with these models as the actual bonding is not present between the metal and the adsorbate atoms, at the vacancy site. Therefore there is no force holding the adsorbate in place. Therefore the modeling of adsorbates to vacancy sites has to rely on computer simulations primarily using density functional theory (DFT). However, these attributes suggest that this simplistic and inexpensive physical molecular model can help us in the study of most adsorbate – metal surface systems and it can have a great visual advantage over computer simulations when it comes to teaching the adsorption of monoatomic elements on the surface of metal surfaces and nanoparticles.

We have then added blue marbles and let them obtain various surface structures by moving them manually with our hands. This process is not entirely dictated by the user-marble interaction but also by the adsorbate marble-marble interaction that in some cases results in a simultaneous movement of the marbles in a row. Also due to repulsion the adsorbates cannot reside in the nearest neighbhour three-fold hollow sites. This of course depends on the atomic radius of the adsorbate and smaller atoms such as hydrogen may actually reside at nearby 3-fold hollow positions.

When placing the adsorbate atoms onto the metal surface the adsorbates obtain structures that are based on the fact that they want to reduce the repulsive interactions between them. Therefore new geometries for the adsorbate adsorption arise from the user-marble interactions that affect the marble-marble interactions, in the sphere-in-contact model. These interactions and they way the adsorbate atoms move on the surface to obtain new low energy positions is educationally very interactive and interesting. We have modelled in this way about 11 surface adsorbate structures that have different symmetries (only 4 of these structures are shown) and all had an adsorbate coverage of θ = 0.39. These sphere-in-contact surface models are shown in Figure 1.

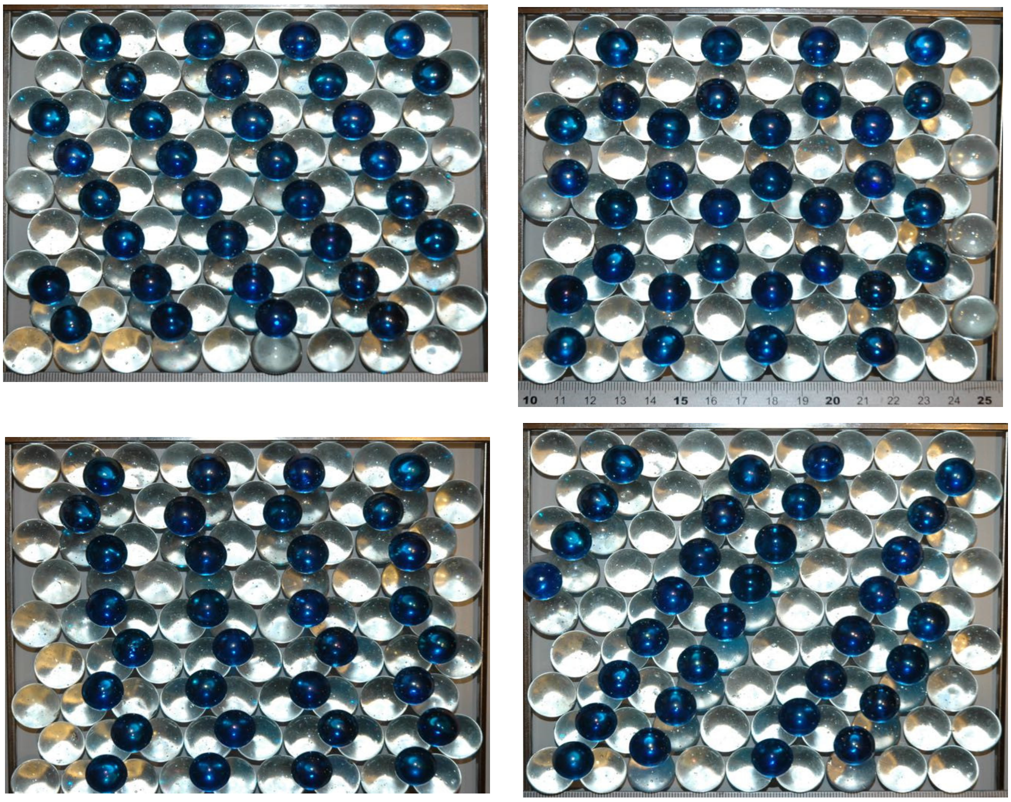

**Figure 1.** Sphere-in-contact models of various adsorbate metal surface structures where the adsorbate coverage was constant at θ = 0.39 in all models. We have found a total of 11 structures of different symmetry but only four are shown for convenience. Colourless atom is the surface metal atom and smaller radius blue atom is the surface adsorbate atom.

We note here that this model works better for the adsorption of adsorbates in three-fold hollow sites, which is also the site that has usually has the highest adsorption energy (e.g. the most exothermic adsorption energy) compared to bridged and atop adsorption, which is also a possibility especially when the adsorbate surface coverage increases and adsorbates are pushed due to repulsive interactions to these higher energy structures, that include both atop and bridged adsorption. We have previously studied the adsorption of CO on Pd nanoparticles and observed some of these trends in the adsorption energy of 3-fold-hollow being generally greater than the bridged and top CO bound to the surface of the NP.[20] If the crystal termination is due to a BCC crystal then the strongest adsorption site is usually the four-fold hollow site followed by the bridged and the atop. These trends in adsorption energy we have previously shown are similar in large NPs that have well defined surfaces and in small transition and noble metal clusters. However the smaller clusters usually have more negative adsorption energies due to the unsaturated nature of the metal atoms on the cluster.[21]

It is therefore evident that this sphere-in-contact model is useful in understanding and presenting the adsorption of monoatomic adsorbates on the surface of metals. It can show the formation of various adsorbate layers of different symmetry. It can help in the study of surface diffusion of adsorbates in a way that it minimises the repulsive intercations between adsorbates.

The fact that we use a different atomic radius for the adsorbates makes possible the measurement of the interatomic distances between the adsorbate atoms. It is conceivable that this maybe used computationally to estimate the relative energy of the surface adsorbate layer by a pair-wise interaction model, which is research in progress.

## 4. Conclusions

We have used the sphere-in-contact model to study the structure of monoatomic adsorbates on hexagonal close-packed surfaces of metals. This model contains atoms of different radius to represent the atoms of the metal surface and the adsorbate atoms. The study reveals that using this approach we can get the arrangement of the adsorbates on metal surfaces at various coverages and compare structures of different symmetry that were obtain for the same surface coverage. This has useful applications in an educational context but could also be used as a research tool. We anticipate that this approach will help teachers, researchers and students to visualize the structure of adsorbates on metal nanoparticles and surfaces in a practical way that allows real time manipulation and visualization of repulsive adsorbate-adsorbate interactions and the formation of adsorbate adlayers of different symmetry.

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