PhD report

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Research activity

During my first year as a PhD student, I focused on two main objectives. The first one was the study of some of the properties of specific systems of physical and chemical interest, which I list below. As a group, we successfully cooperated with Dr. Chloé Minnai (Experimental Physicist at the Okinawa Institute of Science and Technology) for the theoretical description of an interesting phenomenon regarding AuPd nanoparticles produced in the gas phase (i.e. conditions of low contamination). Pure Pd nanoparticles, in the size range that we studied, exhibit octahedral structural motifs. However, when a little percentage of palladium is replaced with gold (around 20%), these bimetallic nanoparticles (often referred to as nanoalloys) change their shape towards the icosahedral motif. The key aspect to understand this phenomenon is the anisotropic surface stress, which relaxes when gold atoms (bigger than palladium atoms, and also with a lower surface energy) are placed on the surface of the nanoparticles: this new configuration is lower in energy than the pure Pd counterpart, thus making this shift towards the icosahedral motif possible. The details of this research are published in [1]. The second publication instead, is about the composition dependent growth of PtPd nanoalloys produced in gas phase. Here we showed, supporting with Molecular Dynamics (MD) simulations and global optimizations what was observed experimentally, that Pt rich nanoparticles grow with sharper tips, whereas Pd rich ones are more rounded. Moreover, we established that in the conditions of the experiment, this kind of growth is mainly due to kinetic effects, rather than being an equilibrium growth. More details can be found in [2]. Another collaboration in which I am currently taking part is that with Prof. Richard Palmer (Experimental Physicist at the Swansea University). His experimental results about the evolution of small gold nanoparticles (around N=309 atoms) deposited on an amorphous carbon substrate showed that, at room temperature, these nanoparticles are continuously changing their shape between icosahedral, decahedral and crystalline motif. In particular he was able to give us some probabilities for those transitions (i.e. the fractions of times some transitions were observed over all the transitions). We successfully recovered these results by means of the application of Harmonic Superposition Approximation (HSA), which is an approximation for the partition function of a collection of atoms, on a data set obtained after the global optimizations of Au nanoparticles structures in the range N=300-320 atoms. Global optimization are performed with our own code. Atomic interactions are modelled with a Gupta potential, and the search for the best structure (i.e. atoms coordinates) is done with a Markov chain Monte Carlo over the local minimization of the potential energy surface induced by the Gupta potential. Performing Molecular Dynamics simulations, we observed the same transitions observed experimentally, in particular that there are two kind of transitions: solid-solid transitions and solid-liquid-solid transitions. We are currently preparing all the material for a publication. Finally, I am also taking part in another collaboration of our group with Dr. El Yakout El Koraychy, about the growth mechanisms of decahedral Au nanoparticles. It is in fact very well known in the literature that decahedral nanoparticles can

grow from tetrahedral seeds, however, the mechanisms behind this evolution were not yet understood. Thanks to MD growth simulations, we showed that the formation of the fivefold axis (leading then to a decahedral structure) is guaranteed whenever there is a stabilization of two island in stacking faults on two facets of the tetrahedral seed. This collaboration also gave me the opportunity to get in touch with Density Functional Theory (DFT), thanks to which we could calculate the adsorption energy of gold atoms on different surface sites for the tetrahedral facets. This kind of calculation allowed us to confirm at a more advanced level an essential part of our explanation for the formation of the fivefold axis. Also for this collaboration, we are preparing all the relevant material for a publication.

The second objective is the application and development of Machine Learning (ML) algorithms for systems such as those described above. The two major problems that one has to face when dealing with such systems are the often inadequate amount of available data and the choice of a clever description of nanoparticles in terms of variables that will be used by the algorithms. I first tried to address these problems to a data set I build myself by performing global optimizations with our code for AgCu nanoalloys with N=100 atoms, for each composition (i.e. all 101 possible choice of m atoms of one metal and n atoms of the other one, given that m+n=100) and for AgCu nanoalloys with N=200 for only 1 composition over two. Given the relative small number of atoms, there is a good amount of variety of different structural motifs appearing in the pool of all global minima found. Our goal was to prepare a pipeline for the automatic separation of each structure in the group it belongs to. We found that it is sufficient to describe nanoalloys with a two dimensional vector given by the Common Neighbor Analysis (CNA), which is a simple yet powerful method to describe the local environment of atoms in a nanoparticle. In particular we discovered that by using the 422 and 555 signatures, one is able to recover the correct grouping of structures, when an unsupervised learning algorithm such as K-Means or Gaussian Mixture Model (GMM) is used. The automatic separation into different structural families also allowed us to include an application of HSA to determine the temperature dependent probabilities of each structural motif. This pipeline (global optimization $\rightarrow$ automatic separation with ML and CNA $\rightarrow$ probability with HSA) is therefore a relatively simple and automatic procedure to obtain useful and physically meaningful information about similar systems to those we analysed. The material for this research has been accepted in publication [3]. Even though we successfully found a simplification in the description of nanoalloys (for an object with N atoms, from 3N variables to 2), we believe that a finer representation in the space of CNA signatures could improve the performance of our pipeline. Our code is able to distinguish at least among 50 different signatures, however it is not so simple to apply the already mentioned algorithm in such a high dimensional space, since in such a space points tend to move apart from each other. We are then trying to define our own distance in this space in such a way that it will be possible to use all the information available to build a finer algorithm for classification of nanoalloys. Work in this direction is in progress

List of attended courses

- Advanced Machine Learning (2 slots - exam given)
- Advanced Computational Physics (1 slot)
- Density functional theory (1 slot)

List of publications

[1] Nelli, D.; Roncaglia, C.; Ferrando, R.; Minnai, C. Shape Changes in AuPd Alloy Nanoparticles Controlled by Anisotropic Surface Stress Relaxation. *The Journal of Physical Chemistry Letters* **2021** *12* (19), 4609-4615. https://doi.org/10.1021/acs.jpclett.1c00787

[2] Nelli, D.; Roncaglia, C.; Ahearn, S.; Di Vece, M.; Ferrando, R.; Minnai, C. Octahedral Growth of PtPd Nanocrystals. *Catalysts* **2021**, *11*(6), 718. https://doi.org/10.3390/catal11060718

[3] Roncaglia, C.; Rapetti, D.; Ferrando, R. Regression and clustering algorithms for AgCu nanoalloys: from mixing energy predictions to structure recognition. *Phys. Chem. Chem. Phys.*, **2021**, 23, 23325-23335. https://doi.org/10.1039/d1cp02143e

List of attended conferences

I presented a poster, entitled "Regression and Clustering algorithms for nanoalloys: from energy predictions to structure recognition", about publication [3], at the two following conferences:

- International Meeting on Nanoalloys (IMN 2021 - April 14 to 16, 2021) Virtual conference. Link: https://nanoalloys-irn.cnrs.fr/IMN-2021/
- CECAM Workshop on nanoalloys - "Multi-approach modeling of alloy nanoparticles: from non-equilibrium synthesis to structural and functional properties" - July 07, 2021 / July 09, 2021 - On-line event. Link: https://www.cecam.org/workshop-details/1068

I gave a short talk, entitled "Structural transitions in metal nanoparticles: equilibrium-driven processes in Au and AuPd", about publication [1], at the following conference:

- DySoN-ISACC 2021 Conference (October 18-21, 2021). Link: https://www.dyson-conference.org/