Silvia Fasce - First Year Ph.D. Report

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Research overview

I am a member of the Nanobiocomp research group, where we use computational tools to investigate the behavior and properties of materials at the nanoscale. My research focuses on the atomistic mechanisms that regulate the formation and evolution of topological defects in metal nanoparticles.

Force field validation

The tool I use the most is Molecular Dynamics (MD). In MD simulations, Newton's equations of motion are numerically solved by discretizing time in small steps whose duration is a few femtoseconds. To model the interactions between atoms in noble metal nanoparticles, we use the Gupta potential, a semi-empirical many-body potential. To obtain an improved atomistic model of Au suitable for defect studies, I tested a new parametrization of the Gupta potential obtained using machine-learning techniques implemented in [1]. The parametrization aimed to improve agreement with measured energetic differences between common crystal motifs (fcc–bcc and fcc–hcp) and with the elastic constants of bulk Au; these properties are particularly important when studying defects because they determine the relative stability of local coordinations and the energetic cost of lattice distortions.

I have followed these validation steps:

- Global minimization using the Basin Hopping algorithm (BH) of clusters of different sizes and structures using the new Gupta parameters, comparing the resulting structures and total energies with those obtained with the reference potential [2] and with the available density functional theory (DFT) data.
- Heating MD simulations to estimate melting temperatures of selected clusters in order to compare them with the reference potential [2] and experimental ones.
- Coalescence MD simulations to compare the results with those obtained using the reference potential [2].

Our results show that this Gupta parametrization yields better agreement with experimental melting temperatures than the reference potential [3], while producing cluster geometries consistent with both the reference potential [2] and DFT where available.

Systematic study of twinning and de-twinning

The core of this year's work was a systematic computational investigation of the mechanisms leading to twinning and de-twinning in decahedral Au nanoparticles. A decahedral nanoparticle can be seen as being formed by five tetrahedra sharing a common edge along the fivefold axis. Each tetrahedron also shares one facet (which is also a twin plane) with each of the two neighbor tetrahedra. When five regular tetrahedra are packed around an axis, an angular gap remains, so that the atoms in the tetrahedra must adjust their mutual distances to fill the gap. This amounts to distorting the tetrahedra, thus introducing some strain in the structure. This intrinsic strain and the high density of topological defects (twin planes), influence their optical, mechanical and chemical properties, making them markedly different from single-crystal FCC nanoparticles. Therefore, understanding the underlying evolution mechanisms of multiply twinned structures enables control of their configuration and thus the capability to tailor their properties. Thanks to advances in electron-microscopy techniques, which now enable three-dimensional reconstruction and precise mapping of local strain fields, many recent experimental studies shed some light on the formation mechanisms of multiple twinned nanoparticles, however these processes remain not fully understood. Molecular dynamics and other computational approaches allow us us to follow entire transformation pathways, test hypothetical mechanisms, and generate statistically significant ensembles of structural transitions that complement and extend experimental observations.

We proceeded as follows:

- We selected five stable Marks decahedral clusters of different sizes (between 348 atoms and 766 atoms) and aspect ratios.
- We introduced "cuts", removing several atomic layers from the decahedra, creating both concave and convex structures, to reduce symmetry and bring the five-fold axis closer to the nanoparticle surface; these cuts lower the energetic stability thus facilitating structural evolution.
- Starting from these configurations, constant-temperature molecular dynamics simulations in the canonical ensemble, common-neighbour analysis, and local pressure monitoring were performed in order to identify rearrangement mechanisms.

Two main behaviors were identified:

1. Atoms rearrange to re-center the five-fold axis beneath the nanoparticle surface, reducing the surface energy. This mechanism is more likely to occur in the concave structures, both in the ones with only one layer and even when the five-fold axis is on the surface (zero layers).
2. In convex structures with the axis beneath a single surface layer, the de-twinning occurs after few nanoseconds: the surface layer "glides", eliminating the five-fold symmetry and leaving a planar twin boundary, reducing the local strain. Subsequent evolution may preserve the twin plane, proceed to full de-twinning to pure fcc, or re-twin forming a new five-fold axis.

These results indicate that nanoparticle surface geometry influences twinning and de-twinning when the axis is peripheral, providing insights that may help the engineering of clusters with targeted structures and therefore preferred properties.

This research will be presented at the International Meeting on Nanoalloys (IMN 2025) in Barcelona in December, and the results will be compiled into a scientific article in order to arrive soon at publication.

Implementation of the Nudged Elastic Band algorithm

In addition, I implemented the Nudged Elastic Band (NEB) algorithm with Climbing-Image refinement, a method to find minimum-energy paths (MEP) and transition states between known initial and final configurations on a potential-energy surface. To validate the implementation, I will use it to calculate saddle-point energies for several known processes that can be modeled with the Lennard-Jones potential, which is the only potential I have currently implemented. I plan to extend the code by adding metal force fields, integrate it into the group's simulation software and apply it to find MEPs and saddle-point energies for de-twinning mechanisms.

References

[1] L. Benzi et al. *In preparation*. In preparation. 2025.

[2] D. Nelli et al. "Structure and orientation effects in the coalescence of Au clusters". In: *Nanoscale* 12 (2020).

[3] D. M. Foster et al. "Atomic-resolution imaging of surface and core melting in individual size-selected Au nanoclusters on carbon". In: *Nature Communications* 10 (2019), p. 2583.

Attended courses, schools and conferences

- Atomistic simulations with machine learning based interatomic potentials (exam passed, 1.5 credits)
- Advanced computational physics (attended, 3 credits)
- Introduction to nano photonics and nanofabrication (attended, 3credits)
- CINECA HPC Molecular Modelling course, 2024 Casalecchio Di Reno, Italy (3 credits)
- CINECA Advanced School on High Performance Computing with GPU Accelerators, online, 2024 (3 credits)
- International Meeting on Nanoalloys, 2024, Genova, Italy (member of the organizing commettee)