**Grégory Guisbiers, Ph.D.**
**Assistant Professor-Tenure Track**

# Proposed research project: "Nano-alloys: from theory to applications"

## 1. Overview

Metallic nano-alloys possess excellent physico-chemical properties in catalysis, magnetism, optics and medicine. They have been applied with success in ultra-high density magnetic recordings [1], anti-bacterial coatings [2] and as catalysts [3]. These exciting properties are obtained and controlled by a fine tuning of size, shape, composition and segregation. The purity of the surface and the nature of the segregated element are tremendously important for nano-alloys used in medicine and in catalysis.

Particularly, in catalysis, a lot of improvement has been done by developing nanoparticles of noble metals (gold, silver, platinum, palladium,…). However, and in spite of these advances, the high demand of these materials make their prices high and their sustainability at risk [4]. Therefore, one possible solution to reduce prices without affecting their catalytic properties is to synthesize core-shell nanomaterials where the core is an inexpensive metal (Fe, Cu, etc.) and the shell is only a few atomic layers of Au, Ag, Pt or Pd. The synthesis of these heterogeneous core-shell nanoparticles is challenging and requires of a deep understanding of the chemical and physical properties of the alloy at the nanoscale. In general, alloys are studied from their phase diagram which is needed in order to tune their structure. However, at the nanoscale, the experimental determination of these phase diagrams is almost impossible because it requires calorimetry measurements which are very challenging to perform because of the small mass involved. In this area, theoretical modelling is very often the only tool that can be used to infer the thermodynamics of nano-alloys.

In order to tackle this problem, my future research will be focused on; **1) the determination of phase diagrams at the nanoscale** and **2) the synthesis of those materials at the nanoscale**. To do this, I have developed a theoretical model based on the thermodynamics of small systems, called nano-thermodynamics, which consider size and shape effect on material properties and allow to determine the phase diagrams at the nanoscale. Then, the nano-alloy can be synthesized for a specific application.

The model I developed is based on the modification of the Gibbs potential at the nanoscale to consider the importance of the atoms present at the surface [5]. It calculates the size and shape dependencies on melting temperature and melting enthalpy of mono-metallic nanoparticles. By precisely applying a Gibbs energy minimization, the phase diagram of bi-metallic nano-alloys can be predicted. Different phase transitions (solid-liquid, order-disorder, amorphous-crystalline, ferromagnetic-paramagnetic) of nanomaterials can be considered within this model. The power of the model is illustrated in Figure 1 where the phase diagram of gold-

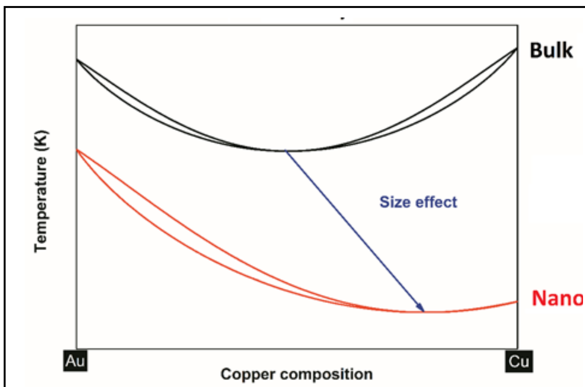


***Figure 1.*** *Phase diagram of the gold-copper alloy at the bulk scale and at the nanoscale for an icosahedral shape at 4 nm.*

copper is calculated at the bulk and nanoscale. The results show that size effect changes the congruent melting point to larger copper concentrations. This is due to a stronger size effect on copper than on gold. This type of result will definitively impact and speed up the synthesis of nano-alloys.

Here, the precision of the model in predicting the order-disorder phase transition was experimentally confirmed by Transmission Electron Microscopy (TEM). The experiment led on gold-copper nanocubes show that the order-disorder phase transition can be carefully controlled by adjusting the annealing temperature (Figure 2). Indeed, after being annealed at 120°C the cubes are ordered while being annealed at 200°C they are disordered in very good agreement with the theoretical calculations. In this experiment, the theory was used to predict the temperatures to apply to the cubes to induce ordering or disordering.

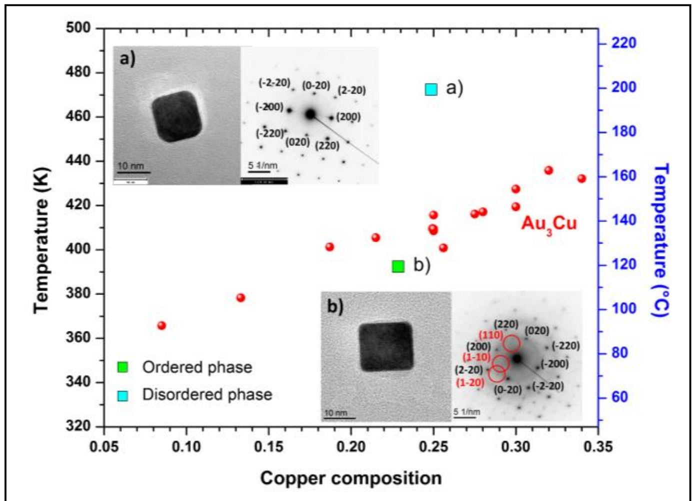


***Figure 2.*** *Order-disorder phase transition calculated for a gold-copper cube having a side length equal to 10 nm. A) and B) TEM image showing the nanocube with its corresponding diffraction pattern.*

Reflections shared between ordered and disordered structures are known as *fundamental reflections*. Extra reflections found in the ordered phase are called *superlattice reflections* (red circles in Figure 2). They arise when the primitive cell of the ordered structure is larger than that of the disordered structure.

The idea is to look experimentally for structures predicted on a theoretical basis. I have already used this approach with success in my previous publications. The most common method used to synthesize nano-alloys is wet-chemistry. With this method, the uniformity of the nanoparticles can be controlled by using in the synthesis phosphoric acids, polymeric chains or thiolated groups as surfactants. The ligands play an important role in the synthesis of bi-metallic nanoparticles because they influence the final shape and size of the nanoparticle. By varying the capping agent different polyhedral morphologies can be obtained. For example, in order to obtain Au-Cu nanocubes, a modification of the Brust method was performed. This method is generally used to produce nanoparticles in organic solutions. Tetraoctylammonium bromide (TOAB, transfer agent) was dissolved in an organic solvent and mixed with Au and Cu ions in

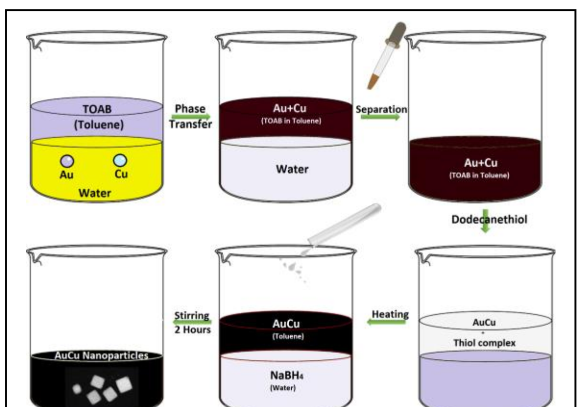


***Figure 3.*** *Synthesis protocol to get Au-Cu nanocubes by wet-chemistry.*

aqueous solution, starting the transfer indicated by the coloration of the solution; then followed by the addition of dodecanethiol (DDT) and sodium borohydride ($NaBH_4$) as a reducing agent. The solution was finally heated and cooled down to room temperature (Figure 3). Then in order to control the chemical ordering, the annealing temperature was determined by my theoretical predictions (Figure 2).

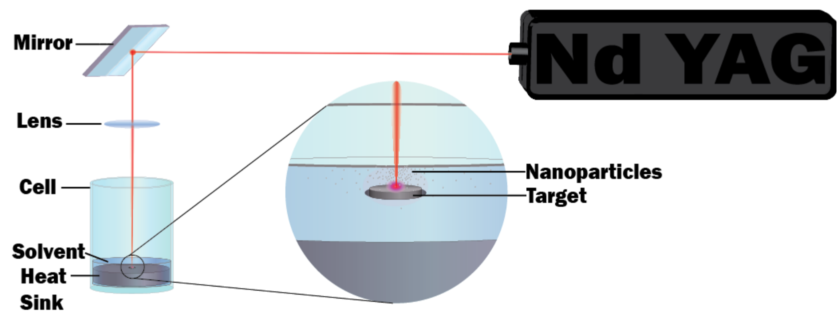


***Figure 4.*** *Synthesis protocol to get nanostructures by laser ablation in liquids.*

In order to have more flexibility concerning the shape of nanostructures, another synthesis methodology is considered i.e. laser ablation in liquids (Figure 4). This last methodology is more adapted to obtain spheres, core-shell structures, rods or nanowires and even quantum structures [7]. Depending on the final application, one of the two methodologies will be preferred. Furthermore, laser ablation in liquids may be used to synthesize metastable structures that are hardly achievable by wet-chemistry.

**Therefore, this association between nano-thermodynamics, synthesis and TEM characterization is an original approach to create and design new materials that do not exist naturally!**

## 2. Previous experience

I have extensive experience in studying and have published on the size and shape effect of material properties [8, 9] and on the phase diagrams in particular [10, 11]. I have used a broad spectrum of characterization techniques such as transmission electron microscopy, energy dispersive spectroscopy, and electron diffraction to confirm my theoretical predictions. I can synthesize nanoparticles myself either by wet-chemistry or laser ablation in liquids [12, 13]. I acquired those experimental skills during a two years stay in the industry sector as project manager.

I have a vast experience with transition metals, III-V and II-VI semiconductors [14]. In my previous positions, I studied size and shape effects on thermal, mechanical and optical properties of various nanostructured materials.

## 3. Collaborations

I will leverage these studies through a variety of collaborations, which will provide expertise, equipment and other resources. These collaborations are already established and include researchers at the University of Texas at San Antonio, at Georgia Tech, at Northeastern University, at the Institute of Electronics, Microelectronics and Nanotechnology (CNRS, France) and at IPICYT (Mexico). Finally, I will promote research in nano-alloys through collaborations with different groups at Texas Tech University (Prof. Dr. L. G. de Peralta and Prof. Dr. Mahdi Sanati).

## 4. Student participation in this research proposal

As a scientific mentor at Texas Tech University, I am keen to help young researchers to develop their scientific thinking and acquire skills necessary for the analysis and evaluation of experimental data. The proposal, as described here, has well-defined objectives and methods with realistic potential outcomes. It also has a significant educational value for the next generation of scientists and engineers by providing them with the experience and opportunity to participate in interdisciplinary, international, cutting edge research.

The research projects I present have the flexibility of being divided into tasks. Each task has well-defined objectives and methods as well as requiring students to learn a variety of techniques, and engage with the current literature. General examples of tasks include commissioning of the theoretical calculation of the phase diagram of one specific alloy at the nanoscale, sample synthesis and characterization, and data analysis. Tasks can be assigned according to the student's interests, experience, and available time. By having group meetings weekly as well as individual meetings, I plan to track tasks and discuss short and long term goals. Whenever possible, I will foster the preparation of comprehensive written reports for their publication in undergraduate and peer reviewed journals. Finally, I am eager to sponsor my students to participate in outreach scientific activities at regional, national or international meetings.

## 5. External funding

This proposed research plan is flexible to change depending on available funding, joint equipment and other limitations. I intend to establish a vigorous externally-funded research program from different agencies: the National Science Foundation (NSF), the Department of Defense (DoD), the Department of Energy (DoE), the National Aeronautics and Space Administration (NASA) and the Mexican Council of Science and Technology (CONACYT, Mexico). Here are some recent calls on which I will focus:

- NSF, Division of Materials Research
  Program: Topical Materials Research
  Program Officer: Dr. Diana Farkas
  https://www.nsf.gov/funding/pgm_summ.jsp?pims_id=505447
- DoD, Army Research Office,
  Program: Synthesis and Processing of Materials
  Program Officer: Dr. Michael Bakas
  https://www.arl.army.mil/www/default.cfm?page=183
- DoD, Air Force Office of Scientific Research
  Program: Low Density Materials
  Program Officer: Dr. Jaimie S. Tiley
  https://www.grants.gov/web/grants/view-opportunity.html?oppId=305996
- DoE,
  Program : Physical Behavior of Materials
  Program Officer: Dr. Refik Kortan
  https://science.energy.gov/bes/mse/research-areas/physical-behavior-of-materials/

## References

[1] Sun S., Murray C. B., Weller D., Folks L. Moser A., Science (2000), vol. 287, 1989-1992

[2] Taner M., Sayar N., Yulug I. G., Suzer S., Journal of Materials Chemistry (2011), vol. 21, 13150-13154

[3] Luo W., Sankar M., Beale A. M., He Q., Kiely C. J., Bruijnincx P. C. A., Weckhuysen B. M., Nature Communications (2015) vol. 6, 6540.

[4] Hurd A. J., Kelley R. L., Eggert R. G., Lee M.-H., MRS Bulletin (2012), vol. 37, 405-410

[5] Guisbiers G., Buchaillot L., Journal of Physical Chemistry C (2009), vol. 113, 3566-3568

[6] Guisbiers G., Mendoza-Cruz R., Bazan-Diaz L., Velasquez-Salazar J. J., Mendoza-Perez R., Robledo-Torres J. A., Rodriguez-Lopez J.-L., Montejano-Carrizales J. M., Whetten R. L., José-Yacaman, M., ACS Nano (2016), vol. 10, 188-198

[7] Guisbiers G., Wang Q., Khachatryan E., Arellano-Jimenez M.-J., Webster T. J., Larese-Casanova P., Nash K. L., Laser Physics Letters 12 (2015) 016003.

[8] Guisbiers G., Buchaillot L. Physics Letters A (2009), vol. 374, 305-308

[9] Guisbiers G. Nanoscale Research Letters (2010), vol.5, 1132-1136

[10] Guisbiers G. Mejia-Rosales S., Khanal S., Ruiz-Zepeda F., Whetten R. L., José-Yacaman M., Nano Letters (2014), vol. 14, 6718-6726

[11] Guisbiers G., Wautelet M., Buchaillot L., Physical Review B (2009), vol. 79, 155426

[12] Guisbiers G., Mimun L. C., Mendoza-Cruz R., Nash K. L., Semiconductor Science & Technology 32 (2017) 04LT01

[13] Guisbiers G., Khanal S., Ruiz-Zepeda F., Roque de la Puente J., José-Yacaman M., Nanoscale 6 (2014) 14630-14635

[14] Guisbiers G., Kazan M., Van Overschelde O., Wautelet M., Pereira S., Journal of Physical Chemistry C (2008) vol. 112, 4097-4103