REVIEW

from

Prof. Olympia Roeva, PhD
Institute of Biophysics and Biomedical Engineering - BAS
Bioinformatics and Mathematical Modeling Department

for awarding of the educational and scientific degree "Doctor of Philosophy"

Professional field:
4.6 Informatics and computer sciences,

with a candidate
Rossen Mikhov Mikhov

PhD thesis title
"Monte Carlo Approach for Optimization of Bimetallic Nanostructures"

1. Relevance of the problem developed in the PhD thesis in scientific and scientific-applied terms.

The problem of numerical modeling and optimization of bimetallic nanostructures is highly relevant due to their extensive applications in catalysis, energy, nanomedicine, and optoelectronics, where physicochemical properties are strongly dependent on size, shape, and surface configuration. Classical deterministic and continuum models often prove inadequate at the nanoscale, as they fail to accurately account for fluctuations, stochastic transitions, and the multi-scale nature of the underlying processes. Monte Carlo (MC) approaches provide a natural framework for describing thermodynamic behavior, rare events, and stable configurations of nanostructures, enabling the exploration of vast configurational spaces at an acceptable computational cost. Particularly in bimetallic systems, where interactions and energy landscapes are highly non-linear, MC methods outperform classical Molecular Dynamics in the optimization and analysis of equilibrium states. In this context, a PhD thesis

dedicated to a Monte Carlo approach for the optimization of bimetallic nanostructures is scientifically significant and aligns with current global research trends.

The PhD student aims to develop a Monte Carlo approach based on Simulated Annealing, utilizing tight-binding potentials for the optimization of various types of bimetallic nanostructures, including nanoparticles, nanowires, and nanofilms.

To achieve this objective, the following six tasks have been defined:

1: to propose a method for optimization of bimetallic nanostructures, including nanoparticles, nanowires and nanofilms;

2: to investigate the effectiveness of the proposed method;

3: to propose an appropriate approach for choosing and adjusting the parameters of the method;

4: to determine which of the following factors most significantly affect the optimal choice of initial temperature for simulated annealing: chemical element, nanoparticle size, lattice type, lattice size;

5: to propose a software architecture and to develop a software system implementing the new method that allows a high degree of optimizability for performance of the computations, flexibility for varying the algorithms and their parameters and good compatibility with external applications for analysis and visualization of the results;

6: to conduct an investigation applying the proposed method to the study of a specific class of gold-silver nanocages with 3000 atoms, which are of interest for many applications, in order to establish how the differences in the Au:Ag ratio and the symmetry of the lattice affect the atomic ordering and the processes of surface segregation.

2. Degree of knowledge of the state of the problem and creative interpretation of the literature

The PhD thesis cites 149 references, and I would like to highlight the impeccable bibliographic description of the sources. The PhD student provides a very thorough analysis of the methods for modeling and numerical optimization of the atomic configurations of metallic and bimetallic nanostructures. The steps and approaches employed in investigating the stability of metallic nanostructures through optimization problem-solving, the methods for optimizing metallic and bimetallic nanostructures, and the modeling of diffusion in bimetallic nanostructures are presented both systematically and analytically.

Rosen Mihov demonstrates a high level of expertise regarding the state-of-the-art in the field, as well as the appropriate tools and approaches required to address the research tasks and achieve the overall objectives of the PhD thesis.

3. General analytical characteristics of the PhD thesis

The PhD thesis is well-structured and logically consistent with the defined research tasks. The work comprises 124 pages and includes: acknowledgments, an introduction, Chapter 1 (literature review); Chapters 2-6, which present the core theoretical framework, research results, and applications; and a conclusion providing a summary of findings, scientific contributions, a list of publications and citations, participation in research projects, a declaration of originality, and a bibliography of 149 sources.

Chapter 1 provides an overview of existing methods for modeling metallic and bimetallic nanostructures. It defines the problem formulation and outlines the development of global optimization algorithms. The choice of energy functional and the efficacy of Monte Carlo simulations as a data-processing tool are also discussed.

Chapter 2 explores two approaches for optimizing bimetallic nanostructures, including a mathematical model, three standard algorithms, and an evaluation of their performance based on simulation results. The proposed two-stage method is detailed in five steps: the first stage is based on Simulated Annealing on wide-lattice configurations, while the second stage employs Simulated Diffusion.

Chapter 3 presents the testing results of the two-stage method compared to a single-stage approach. The optimal allocation of computational resources between the two stages is analyzed, and experimental data for determining method parameters are provided. These results serve to evaluate the efficiency of the methods in nanostructure optimization.

Chapter 4 investigates the correlation between initial temperature and the performance of the wide-lattice Monte Carlo algorithm. Extensive tests were conducted on various nanostructures of two chemical elements (Silver and Cobalt) under different sizes and conditions. The results presented by R. Mihov demonstrate that the Monte Carlo algorithm is well-suited for bimetallic nanostructure optimization and allows for flexible parameter adaptation during simulations.

Chapter 5 describes methods for investigating the autonomous behavior and surface segregation processes in gold-silver (Au-Ag) nanocells consisting of 3,000 atoms. Emphasis is placed on the specifics of working with nanocells and the analysis of results across three primary Au:Ag crystal lattices. Experimental observations and an assessment of the influence of local order on the macroscopic properties of bimetallic nanostructures are also provided. The chapter concludes by systematizing the limitations of the two-stage method and outlining future research directions.

Chapter 6 details the software system developed as part of the PhD thesis. It presents a software architectural design for implementing the two-stage method, enabling high-performance optimization and the parallel execution of algorithms under varying conditions. The system is compatible with Linux and Windows and utilizes the standard XYZ format for the input and output of atomic configurations.

Each chapter concludes with systematized findings from the conducted research. A positive impression is made by R. Mihov's declaration that the results obtained in this PhD

thesis are being further utilized and developed for application across various types of bimetallic nanostructures.

4. Evaluation of contributions of the PhD thesis and their significance

I accept the contributions formulated in the PhD thesis, namely:

1: A two-stage lattice Monte Carlo method is proposed for optimization of bimetallic nanostructures, including nanoparticles, nanowires and nanofilms. The first stage is simulated annealing on a wide lattice and the second stage is simulated diffusion. The method is implemented with the help of data structures and a preprocessing strategy, which significantly increase its efficiency, and allow the optimization of nanostructures from several hundred to several thousand atoms on a standard personal computer.

2: Experimentally is established that an effective strategy for distributing computational resources between the two stages of the method is to use 30% of the time on the first stage and 70% of the time on the second stage.

3: Experimentally is established that the specific way in which the method is formulated in 5 steps is sound and leads to successful tuning of the parameters.

4: The influence of the initial temperature on the performance of the wide-lattice Monte Carlo algorithm is investigated for different lattices and chemical elements. Experimentally is established that the most important factor for choosing appropriate initial temperature is the lattice size, with the highest temperatures being required when placing a small particle on a large lattice. The type of chemical element is also of certain importance, while the type of lattice does not have a significant effect.

5: An adaptation of the two-stage method is made for nanocages. It is used for studying the atomic ordering and the processes of surface segregation in gold–silver nanocages with 3000 atoms. A comparative analysis of the results for three compositions (Au:Ag=1:1, 1:3, 3:1) and two lattices (fcc and icosahedral) shows that fcc nanocages have thinner walls, cavity with a larger radius, and more low-coordinated atoms on the surface in comparison to icosahedral cages. Ag atoms show a tendency to migrate to the two surfaces of the nanocage, as a result of which the interior layers of the Auenriched alloys are practically devoid of Ag and Au-Au bonds dominate. Ag-enriched alloys have a maximum number of mixed Ag-Au bonds and a more uniform local order on both lattices.

6: A software architecture is proposed for the implementation of the two-stage method, which allows a high degree of optimizability for performance of the computations, flexibility for concurrent execution and combination of the constituent algorithms in different conditions, and good compatibility with external applications for analysis and visualization of the results.

5. Assessment of PhD thesis publications

The results of the PhD thesis have been widely disseminated within the scientific community. The PhD student has presented four publications in international conference proceedings and the journal WSEAS Transactions on Electronics. One of the proceedings was published in the prestigious scientific series Studies in Computational Intelligence, which holds an SCImago Journal Rank indicator. Two of the publications are indexed in Scopus. Rosen Mihov is the first author of three of these publications. Two of the papers have accumulated a total of six citations in Scopus and one citation in another PhD thesis. R. Mihov's Scopus h-index is 3. All of this attests to the high level of the scientific research and results, as well as the significant personal involvement of the PhD student in the execution of the research tasks.

6. Assessment of the compliance of the autoreferate with the requirements for its preparation, as well as the adequacy of reflecting the main points and contributions of the PhD thesis

The autoreferate correctly reflects the content of the PhD thesis and gives an idea of the problems under consideration, the results obtained, and the thesis's contributions.

7. Critical notes on the PhD thesis

I have no critical remarks regarding the PhD thesis.

8. Conclusion with a clear positive or negative assessment of the PhD thesis

Given the proven scientific value of the research conducted and the contributory nature of the results achieved, I provide an exceptionally positive evaluation of the PhD thesis of Rosen Mihov Mihov.

The PhD thesis meets the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria, the Internal Regulations for its application, as well as the Regulations for the terms and conditions for acquiring scientific degrees and occupying academic positions at the IICT – BAS. The achieved scientific and scientific-applied results give me reason to propose to the respected Scientific Jury to award the educational and scientific degree "Doctor of Philosophy" to Rosen Mihov Mihov in the professional field 4.6 Informatics and Computer Sciences, PhD programme Informatics.

09.01.2026 Scientific Jury me

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