Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Evgeny Iakovlev

PhD Program: Mathematics and Mechanics

Title of Thesis: Multiscale modeling of graphene nanobubbles

Supervisor: Professor Iskander Akhatov

Co-supervisor: Petr Zhilyaev

Name of the Reviewer: Nikolai Brilliantov

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	 **Date: 05-08-2021**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The presented Doctoral Thesis “Multiscale modeling of graphene nanobubbles” by Evgeny Iakovlev is devoted to investigation of graphene nanobubbles with different types of trapped material. The work is aimed to provide models for analyzing the graphene nanobubbles: predict shape of the bubble and the state of matter inside. In order to achieve the aim two models are proposed. The first one is based on molecular dynamics calculations, which directly simulates the substrate, the graphene and the trapped matter. The second model is continuum approach, which is semi-analytical model based on the energy minimization of the system.

In the chapter one the motivation and goals of the work are provided. In the second chapter the comprehensive literature review is presented. In the first part the history of graphene nanobubbles as well as 2D heterostructures and vdW nanobubbles are described. Then there is a section with confined fluid unique properties and how it is connected with graphene nanobubbles. The background ends with molecular dynamics methods history and description as well as interatomic potential explanation. The third contains the thesis objectives. Each section in this chapter is represented by an article in a peer review journal; sections are logically connected.

Section three starts from the analysis of thermodynamic state of argon inside graphene nanobubles (GNBs). Firstly, the author study relatively small GNB (up to 34 nm), which may be modelled using Molecular Dynamic (MD) simulations. MD is rather powerful techniques to study nano size systems and widely used in modern science; still it has limitations with respect to the system size. An interesting effect is reported – the confined argon occurs to be in a solid state (with a mixture of two lattices), although it should be in liquid state at given temperatures and pressures. This effect indicates a high importance of the confinement on the state of matter. The author exploit combination of different potentials for different interactions, which enhances validation of the obtained results.

Next, much larger GNBs are investigated; here the continuum approach is applied, including classical elasticity theory, concepts of adhesion energy and equation of state for a bulk matter. The author uses semi-analytical model, based on the energy minimization of the whole system. To improve the accuracy of the theory and to account for the density inhomogeneity of the fluid inside the GNBs, a version of (local) density functional theory, in the RLST version, is applied. The author observes that for a given trapped mass not all GNBs footprint radii may realize for low temperatures. This effect is called the “forbidden region” for the GNB radii; it is associated with the existence of double-well of the total energy dependence on the GNB radius, with the area where GNBs are not stable.

To study GNBs with other organic fluids, the author undertakes a study of the adsorption of ethane on the graphite substrate. The specific adsorption energy has been obtained by means of MD, using two different approaches – by a direct measurement of the energy difference of covered and uncovered surface as well as by exploring the Langmuir adsorption isotherm. These methods of finding of the adsorption energy has been further used in the study of GNBs filled with ethane. Similar to the GNB with argon the GNBs with ethane also demonstrate the forbidden region in terms of GNB radii.

The last chapter is the Conclusion where the Thesis results are summarized and outlook on the future work is presented. Overall structure of the thesis is logical and easy to follow. The quality of the results is high, complying with the international standards. This is confirmed by the ranking of the journals, where the article of the applicant have been published (four papers in Q1 and two in Q3 journals). Hence, I conclude that Evgeny Iakovlev may be considered as a candidate for a PhD degree.

I advise to address the following issues in the Thesis before the defense:

1) As far as I understand, the effect of "forbidden region" has been detected only for the fluid state of matter in the GNBs, but not for the crystalline state. Is it possible to explain such an effect?
2) When you compute E_{bulk} in Eq. (7) in the Ref. [3] you integrate chemical potential, using the data from NIST, which corresponds to the bulk substance. At the same time, you have shown in Ref. [1], that the confined material differs by its structural properties from that of a bulk state (e.g. argon in GNBs may be in a solid phase, being liquid in unconfined). This seems to be inconsistent. Will the result change if you use the chemical potential not from NIST, but from you own simulations for smaller GNBs, with solid argon?
3) In Ref. [1] you reported that solid argon in the GNBs comprised two different lattice types. Here you exploited the so-called common neighbor analysis. This method, however, has been proposed for bulk crystals. How many layers are needed for this method to become valid? Can you provide an estimate for this?
4) In Eq. (6) of Ref.[3] you use the bending rigidity of a membrane. Where do you take it (I could not find it in the supplementary material)? I believe that this quantity is sensitive to the inter-atomic potential. Did you compute it by MD with AIREBO potential?
5) You assume that the Poisson ratio of the graphene membrane is zero. How it may be justified and what could be the possible impact if this assumption would be released?
6) Using the DFT, you assume that the density depends on Z only, which is fine, as this is the main dependence. Still, the density on the radial boundary is different due to the geometrical constraints. Is it possible to assess the density inhomogeneity in the radial direction and estimate its impact on the total energy?
7) I have a couple of comments which refer to the exposition of the thesis material:
    - The amount of pronouns – this, these, they etc. is overwhelming. Please, mention the subjects directly. Use synonyms where appropriate.
    - Thesis structure section 1.1 should go to the end of the Introduction, if not removed entirely. Also, no need for sub sections; they make it hard to read.
    - Start of the section 2.3 "Van der Waals nanobubbles". Text in a new section can't be direct continuation of the text in the previous one.
    - The MD limitations mentioned in section 3.1 of the literature review should be described in more details.
    - Delete the first sentence in Chapter 4.

Provisional Recommendation

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*