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Thesis Changes Log

Name of Candidate: Evgeny Iakovlev

PhD Program: Mathematics and Mechanics

Title of Thesis: Multiscale modeling of graphene nanobubbles

Supervisor: Prof. Iskander Akhatov, Dr. Petr Zhilyaev

The thesis document includes the following changes in answer to the external review process.

Dear Reviewers,

I would like to express my gratitude for your comments and suggestions to all of you! I found them very useful and it helped to significantly improve my thesis.

Sincerely,
Evgeny Iakovlev

The change log:
- Deleted title, author, date and "submitted … " part before abstract.
- Reduced the number of usage of this/these etc.
- Some misprints are corrected. Some of them: p. 16: "large pokets", p. 17: "useful to use", "this values", p. 27: "nobel gases", p. 32: "phenomenon of universal shape scaling is approved", "elastic modules", p. 85: "the formation of graphene nanobubbles are disclosed".
- Deleted section 1.1 (Thesis structure) and 1.8 (Points to discuss).
- Changed the beginning of the section 2.3 to more logical one.
- Deleted the first sentence in Chapter 4.
- The MD limitations in section 3.1 are explained in more details.
- The contribution sections are added.
- The imprecise wording on pages 11, 19 is corrected. Also, text is proofread more thoroughly.
- The red text on pp. 81-82 is fixed.
- The glossary is extended.

The comments:

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?

The "forbidden region" effect is detected for large nanobubbles, where gas or liquid states are assumed to be found. However, there is still no DFT model developed to describe the solid state in complex geometry confinement. That is why our continuum model has a lower limit in radius. In our calculation, the minimal radius is 50 nm (for graphene nanobubbles at 300 K with trapped argon). For smaller radii (30 nm and less), we found a solid state inside the bubbles using MD simulations.

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?

Indeed, it is not right to use our model for small nanobubbles, where strong confinement leads to the deviation in behaviour of the matter from bulk matter. That is why we used for small nanobubbles direct MD simulations and continuum model for bigger bubbles. Of course, it is necessary to use chemical potential and equation of state, which takes into account solid state to model small nanobubbles. And it is a great topic for further research.

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?

I used the method implemented in LAMMPS (https://docs.lammps.org/compute_cnp_atom.html). This method calculates the Common Neighborhood Parameter (CNP) for each atom, and according to the CNP value, it is possible to attribute an atom to one of the lattices, or none. So, in order to calculate the attribution validly, the atom has to have all the nearest neighbors specific for the lattice (in the case of FCC/HCP it is 12). Thus, it is necessary to have at least 3 layers. In this case, we can calculate the CNP values for the middle layer, as all atoms in this layer have all their neighbors present in the calculation.

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?

We used the value from the reference [Wei, Yujie, et al. Nano letters, 2013] – 1.44 eV. Depending on the experimental study or calculation, the value varies from 1 to 1.6 eV. Nevertheless, in [Khestanova Ekaterina, et al. Nature communications, 2016] it is shown that for graphene nanobubbles the bending rigidity can be neglected.

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?

The Poisson ratio of the graphene monolayer cannot be measured directly experimentally [Cao, Guoxin. Polymers, 2014], and usually the thickness of graphene is assumed to be equal to 3.35 Å as in graphite. But we can estimate the possible contribution from [Landau, Lifshits, 1987]: $E \sim 1/(1 - \nu^2)$, taking the Poisson ratio to be equal to 0.14 [Cao, Guoxin. Polymers, 2014], the contribution to elastic energy $< 2\%$. Taking Poisson ratio into account does not qualitatively change the results.

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?

Indeed, the dependence on the Z-axis only is an assumption in our model. However, we apply the continuum model only for large graphene nanobubbles, where the main contribution to the fluid energy is from the central part of the trapped matter, not affected by the graphene surfaces. The comment is very important and taking into account the boundary effects in X,Y- axis is a great topic for further research.