Obtaining the state of matter inside graphene nanobubble from its shape

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Abstract. Graphene nanobubble (GN) is a system consisting of the substrate, the graphene sheet and the substance trapped between them. Radius of GN regulates the pressure inside the bubble and for small GN with radius of several nanometers extreme pressures up to 1 GPa due to the van der Waals interaction can be observed. Therefore trapped substances inside GN can exist in a number of different states of matter. In this study we theoretically establish the connection between the shape of GN and the state of the trapped material inside. Both atomistic and continuum models are used to describe mechanical and thermodynamic properties of GN. Atomistic approach is applied to calculate the elastic constants and the adhesion energies. These parameters are used as inputs for the following analyses in terms of continuum media.

1. Introduction

Two-dimensional (2D) heterostructures allow to develop materials with adjustable properties [1]. Such structures are assembled by layer-by-layer stacking of 2D crystals, for example, graphene, hexagonal boron nitride, molybdenum disulphide (MoS$_2$), other dichalcogenides and layered oxides.

While creating such structures some substance can be trapped between layers [2] that leads to formation of the surface bubbles [3]. It was shown that such bubbles possess number of interesting properties such as universal shape scaling [3], i.e. the ration of the height of the nanobubble ($H$) to the radius of the footprint ($R$) remains constant for various radii, giant pseudo magnetic field [4], extreme pressure insight [5]. In particular case when outer layer is graphene such nanobubbles are called graphene nanobubbles (GN). In this study we consider the graphene nanobubbles for which the substrate is the graphite and the trapped material is argon (figure 1).

Due to large graphene stiffness and strong van der Waals (vdW) interaction between the outer graphene sheet and the graphite substrate sufficiently large pressure is built inside GN. The smaller the radius of GN the larger the pressure is created by vdW interaction. Extreme pressures up to 1 GPa are experimentally observed for GN with radius of several nanometers [5]. Inside GN on the graphite substrate with radii of the order of 400 nm the experimental estimation of pressure is 2 MPa [3]. Therefore the state of matter inside the GN may exist in various phases: gas, liquid or solid depending on the type of molecules and size of the GN.

From the experimental perspective direct investigating of the state of matter inside GN is rather complex problem. One have to use cutting edge and expensive experimental techniques...
such as transmitting electron microscopy (TEM) or synchronizing-based photoemission electron microscopy (XPEEM) [6]. On the other hand obtaining information about the shape of GNs is routine task done by atomic force microscopy (AFM). Thus it is of particular interest to establish the relation between the shape of the GN and the state of matter inside, so one can obtain information about the matter directly from AFM experiments.

In this study we theoretically establish the relation between the shape of the GN and the phase of the trapped material inside. Atomistic modelling is used to calculate the elastic constants and the adhesion energies. These parameters are used as inputs for the following analyses in terms of continuum media.

2. Methods

In our molecular dynamics part of this research software package LAMMPS [7] (the Large-scale Atomic/Molecular Massively Parallel Simulator) is used.

To calculate the elastic properties of graphene the adaptive intermolecular reactive bond order potential (AIREBO) [8] is used to describe the carbon–carbon interaction. It was shown that this potential describe well the mechanical properties of graphene [9].

Graphene layer is generated using software package VMD [10]. The boundary condition are set to periodic in order to model continuous graphene crystal. Then it is statically elongated in two different directions (zigzag and armchair) [9] and stresses are measured.

Lennard-Jones potential is used to evaluate the adhesion energy between argon and the graphite substrate. For argon–argon interaction the parameters are $\sigma_{\text{Ar–Ar}} = 3.405 \text{ Å}$, $\varepsilon_{\text{Ar–Ar}} = 10.34 \text{ meV}$ [11]. Lorentz–Berthelot combining rules [12] are used to define carbon–argon interaction: $\sigma_{\text{C–Ar}} = 3.4025 \text{ Å}$, $\varepsilon_{\text{C–Ar}} = 5.42 \text{ meV}$. To apply these rules the carbon–carbon parameters are taken from Lennard-Jones part of AIREBO potential [8]: $\sigma_{\text{C–C}} = 3.4 \text{ Å}$, $\varepsilon_{\text{C–C}} = 2.84 \text{ meV}$.

To calculate the adhesion energy we modeled three cases: argon–graphite system, only argon system, only graphite system. To evaluate the adhesion energy we measure the potential energy per unit area difference between combined graphite–argon system and separated systems. Thus the adhesion energy can be calculated as $\gamma_{SB} = (U_{\text{graphite+argon}} - (U_{\text{graphite}} + U_{\text{argon}}))/S$.

In graphite–argon system three graphene layers represent substrate. They are generated using VMD. The size of graphene layer is $L_x = 100.698 \text{ Å}$, $L_y = 102.098 \text{ Å}$, where $L_x, L_y$ are lengths in $x$ and $y$ directions. The $z$-length of the simulation box is $L_z = 107 \text{ Å}$, the substrate fills 6.7 Å, the remaining space is filled by argon. Initially the argon atoms are inserted into the simulation box in simple cubic lattice. Different initial densities are set to study pressure dependence of the adhesion energy. Then the argon atoms are allowed to move in the NVT
ensemble. The temperature is set to 300 K for all cases. The carbon atoms in graphite are fixed. After the energy of the system stabilizes, we assume that equilibrium is achieved, and statistical information can be gathered.

To simulate the argon system the separate calculations are performed. The number of argon atoms is the same as in corresponding case of the graphite–argon system. The size of the simulation box is $L_x = 100.698 \, \text{Å}$, $L_y = 102.098 \, \text{Å}$, $L_z = 100 \, \text{Å}$. Then argon atoms are allowed to move in the $NVT$ ensemble. The temperature is set also to 300 K.

### 3. Results and discussion

All continuum studies use macroscopic parameters as input in their models. In the case of graphene nanobubbles they are Young’s modulus of graphene and the adhesion energy between the bulk substance and the graphite. The precise values of these parameters allow to achieve better predictions of the shape of the nanobubble, the stresses of upper graphene sheet, the pressure inside the bubble. Also it gives more accurate value of the height to the footprint radius ratio, given by [3].

In theoretical part of the study [3] the free energy of the bubble is consist of tree parts: the elastic energy of the upper graphene sheet, vdW energy between the graphene, the substrate and trapped substance, and the free energy of trapped material. Minimizing the free energy with respect to the height and the radius, the $H$ to $R$ relation can be obtained:

$$\frac{H}{R} = \left(\frac{\pi (\gamma_{GS} - \gamma_{GB} - \gamma_{SB})}{5cY}\right)^{\frac{1}{4}},$$

where $\gamma_{GS}$, $\gamma_{GB}$, $\gamma_{SB}$ are graphene–substrate, graphene–bulk and substrate–bulk adhesion energies respectively, $Y$ is Young’s modulus of graphene sheet, $c$ is dimensionless coefficient depending only on the shape of the nanobubble, in the case of the round-shape bubbles $c = 0.7$. In our model $\gamma_{GB} = \gamma_{SB}$ as substrate (graphite) consists of graphene layers. Usually it is unknown [3] what kind of substance is trapped inside the bubble. Therefore it is especially important to have the additional information from the atomistic study.

#### 3.1. Young’s modulus

The Young’s modulus of graphene is calculated from strain-stress curves (figure 2). The zigzag and armchair directions are slightly differs for the large strains. However for the small strains graphene is isotropic and linear elasticity is observed. For the case of graphene nanobubbles the average strain is of order 1–2% [3]. Therefore in the continuum model we can assume graphene as linearly elastic material. Calculating the slope of stress-strain curve at point $(0, 0)$ we can get the value for two-dimensional graphene Young’s modulus $Y = 21.19 \, \text{eV/Å}^2$. Also we can divide this value by the average distance between layers in graphite 3.35 Å and derive the three dimensional modulus 1.01 TPa that is in agreement with previous molecular dynamics study [9], experiments [13] and ab initio calculations [14].

#### 3.2. Adhesion energy

Calculated adhesion energies at different pressures are presented in figure 3. The strong dependence is observed at low pressures where argon is in a gas phase. Thus one should carefully use the continuum approach while modeling large nanobubbles with the low pressure of the trapped substance. For high pressures the adhesion energy can be treated as constant.

In theoretical part of [3] when applying equation (1) it is assumed that the adhesion energy is constant. This assumption leads to the conclusion that the ratio $H/R$ is independent of the radius. But our results show that this conclusion is hold only if the trapped matter inside is in the condensed form such as incompressible liquid or solid. For gas phase inside the GN the adhesion energy strongly depend on the pressure (see figure 3) and as a consequence it is also
Figure 2. Stress-strain curve for single graphene layer modelled by AIREBO potential [8]. Both zigzag and armchair direction are presented. The Young’s modulus obtained from the slope of the curve equals 21.19 eV/Å².

Figure 3. Dependence of argon pressure on the adhesion energy to graphite. The approximate boundary between gas phase and liquid phase of argon in terms of pressure is 100 MPa.

depend on the radius of the GN. Therefore the findings from [3] is not true and there is no universal shape for GN with gas phase if one exist.
Adhesion energy for solid and liquid states typically has different values and, according to equation (1), the GNs with liquid or solid state inside should have also different \( H/R \) ratio. Unfortunately, if adhesion energies for liquid and solid states differ not significantly then root of the fourth degree in equation (1) will make this difference even more inconspicuous.

The figure 4 shows \( H/R \) ratio obtained with the help of equation (1) for two adhesion energies of gas and liquid phases of argon correspondingly. Dots in figure 4 present direct molecular dynamics modelling [15] of the GNs. In the study [15] argon inside the GN is in a solid state. Nevertheless the results of \( H/R \) value for both liquid and solid states of argon have very close values. We attribute this to the small differences in adhesion energies of liquid and solid argon.

4. Conclusion

This research provides insight into the importance of the accurate determination of the constants used in the continuum approach while modeling the graphene nanobubbles. The precise two-dimensional Young’s modulus of graphene is calculated. Also the strong dependence of the adhesion energy is detected at low pressures. Atomistic simulations can provide the crucial parameters for continuum approach particularly when it is impossible or problematic to measure them experimentally, for example, the adhesion energy.

Moreover this study shows that universal shape phenomenon [3] is only applicable in limited region of pressures and the dependence of adhesion energy on pressure should be taken into account when gas phase (if one exist) or liquid–solid phase transition is considered. The universal shape phenomenon is only valid in the thermodynamics regions where trapped material is either in liquid or solid state, and no phase transition occurs.

The result of this work can also be used as theoretical background for investigation of the phase state of the trapped material inside the graphene nanobubbles only using experimental information about their shape (\( H/R \) ratio).
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