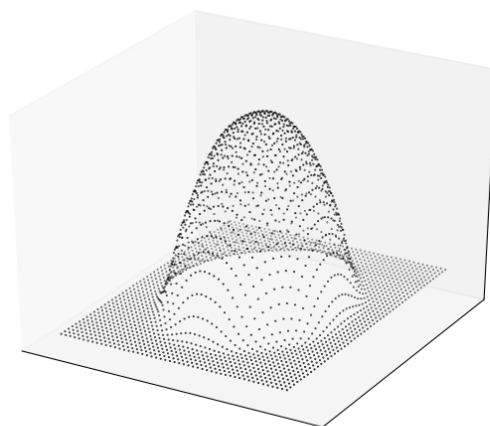


BACHELOR THESIS

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Atomistic simulations of the shape of bubbles in graphite



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Introduction

Since its discovery in 2004[1] graphene attracts a huge amount of interest, amongst other reasons because it is a very strong material[2]. An interesting application is to use graphene in van-der-Waals (vdW) heterostructures, which consist of a stack of several graphene and other two-dimensional (2D) sheets. These materials can be formed with tailored properties. But when a 2D sheet is deposited on other 2D materials, often some gas is trapped between the sheets. This creates protrusions in the sheets. These protrusions are called bubbles.

There are many applications for bubbles in graphene. One of those is that in many situations the nanoscale confinement of the gas in a bubble can change the properties of the graphene and the gas[3]. Khestanova et al.[3] also demonstrated that bubbles in graphene are smaller and more sparsely distributed due to the stiffness of graphene. This implies that there are relatively large areas of the structure that are perfectly clean. Another use was demonstrated by Bunch et al.[4], when they used bubbles in graphene to prove the impermeability of graphene to gas molecules and to measure the elastic properties of graphene. Zabel et al.[5] also used bubbles, and they did so to study the Raman spectrum of graphene under biaxial strain. A less scientific way to use bubbles is by storing gases in them.

Khestanova et al.[3] show that the shape and dimensions of the bubble conform closely to predictions of elasticity theory, completely depending on the elastic properties of one sheet and its attraction to the sheet below it. The ratio between the height of the bubble (h) and the radius of the base of the bubble (R), denoted as aspect ratio, is approximately 0.11 for $R > 50$ nm, and seems to decrease with R for smaller R . In this computational work we will investigate this ratio for several conditions. Even though in our models the investigated bubbles are necessarily smaller because we use atomistic simulations and cannot have too many atoms, we can hopefully still observe whether the trend holds and make predictions for (very) small bubbles.

In this thesis, we will perform atomistic simulations, based on accurate interatomic potentials (section 1.2.1) for carbon and molecular hydrogen. We start with a brief introduction to graphene in general (Section 1.1.1), then we deal more specifically with bubbles in graphene (Section 1.1.2) and finally we describe the modeling of the bubbles obtained by trapping a variable number of hydrogen molecules between graphene sheets (Section 1.1.3). To find their equilibrium structure we will perform Monte Carlo simulations as briefly described in Section 1.2.2. In Section 1.3.1 we describe our method for obtaining h , R and aspect ratio of the bubble from the simulations. Following that, we will discuss the measure of convergence (Section 1.3.2) we use and we briefly describe the radial distribution function (rdf) in Section 1.3.3. We present our results in Chapter 2. We discuss the dependence of the bubble aspect ratio as a function of the number of trapped molecules and temperature (T). The main result is that the aspect ratio increases with number of hydrogen molecules trapped in the bubble (N_{H_2}) but not with T . More elaborate conclusions are drawn in Chapter 3, in which we also discuss some ways to continue this research.

Chapter 1

Numerical methods and theory

In Section 1.1 we give a short introduction to graphene in general (1.1.1), to bubbles, more specific to graphene bubbles (1.1.2) and finally we describe the geometry of our sample with the graphene bubble (1.1.3).

The computational methods used for our simulations are described in Section 1.2, starting with a brief overview of the model in terms of potentials (1.2.1) and then explaining the Monte Carlo method (1.2.2).

In the last section of this chapter (1.3) the methods to analyse the data are explained.

1.1 Graphene

1.1.1 General

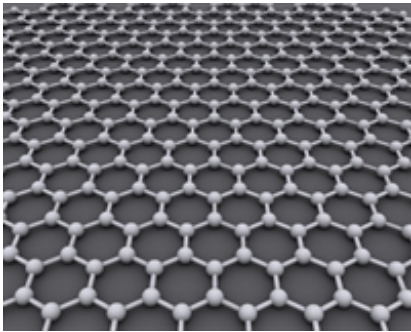


FIGURE 1.1: **Honeycomb structure of graphene.**

Graphene is a two-dimensional (2D) form of carbon. It consists of aromatic hexagons, leading to its typical 'honeycomb' structure as seen in Figure 1.1. The distance between individual atoms a_{CC} at $T = 0$ K is

$$a_{CC} = 1.42 \text{ \AA} = 0.142 \text{ nm} \quad (1.1)$$

The lattice constant of graphene a , is related to a_{CC} as

$$a = \sqrt{3}a_{CC} \quad (1.2)$$

The unit cell of the structure is defined by the vectors \vec{a}_1 and \vec{a}_2 :

$$\vec{a}_1 = a \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \vec{a}_2 = \frac{a}{2} \begin{pmatrix} 1 \\ \sqrt{3} \end{pmatrix} \quad (1.3)$$

Each cell contains two atoms at $\begin{pmatrix} 0 \\ 0 \end{pmatrix}$ and $\frac{a}{\sqrt{3}} \begin{pmatrix} \sqrt{3} \\ 1 \end{pmatrix}$ relative to the origin[6]. Each atom forms strong covalent bonds to its three neighbours. This, among other things, makes graphene a strong material that can withstand a pressure difference of 130 GPa[2] before breaking apart in its purest form. In the real world we are often dealing with defects in the structure, for example carbon atom changed with another atom like nitrogen, missing atoms, extra atoms etc. More complete descriptions can be found in articles (e.g. Geim and Novoselov[7]) and books (e.g. Graphene[8]).

Graphite can be described as many sheets of graphene stacked together. Because the only force holding the sheets together is the van-der-Waals interaction a single sheet of graphene can be isolated from it with something as simple as sticky tape[9].

1.1.2 Bubbles in graphene

When placing a graphene layer on a bulk substrate (e.g. graphite) it is commonly occurring some gas is trapped between the graphene and the bulk. The strong van-der-Waals forces between the

graphene and the bulk causes these gases to gather in little, nanoscale bubbles, leaving large parts of the surface atomically clean.

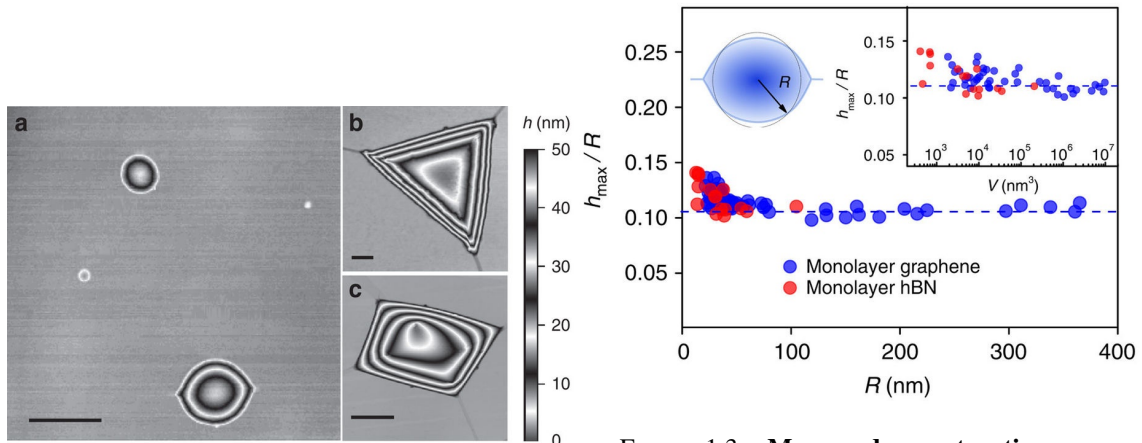


FIGURE 1.2: **Atomic Force Microscope images of bubbles in graphene of different sizes.** The vertical scale bar on the right indicates h . The horizontal scale bar correspond to **a)**: 500nm, **b)**: 100 nm and **c)**: 500 nm.

Figure taken from Khestanova et al.[3].

FIGURE 1.3: **Measured aspect ratios as a function of the base radius of the bubble.** The bubble is in graphene (blue dots) or monolayer hBN (red dots). The dashed line shows the mean value. Top left inset: sketch of a nearly round bubble and its effective radius R determined as $R = \sqrt{A/\pi}$, where A is the measured area of the base of the bubble. Top right inset: aspect ratio of the bubbles as a function of their volume. Figure taken from Khestanova et al.[3].

In Figure 1.2 we show an Atomic Force Microscope picture of bubbles which spontaneously occur when graphene is placed on a substrate with the same hexagonal structure like graphene, e.g. hexagonal boron nitride (h-BN), graphite or other 2D crystals. Bubbles with a radius not larger than 500 nm have a round base[3]. Recent research[10] showed that the shape of the bubble can also depend on the properties of the trapped substance.

There are several properties of a bubble that are interesting to investigate. Inspired by Khestanova et al.[3], in this work we mainly look at h , R and the aspect ratio h/R of the bubble. In Figure 1.3 we show the experimental measurement of the aspect ratio of circular bubbles reported in Khestanova et al.[3]. One can see that the aspect ratio is nearly constant. It is thus argued that the shape of the bubbles follows a universal pattern.

It is interesting to look at the influence of several external factors on the properties of the bubble. For example we expect T and N_{H_2} to have an effect on the bubble because of the ideal gas law. Other interesting factors are the external electric field[11] or the materials of the substrate. In this study we only investigate the first two.

1.1.3 Atomistic model of the bubble

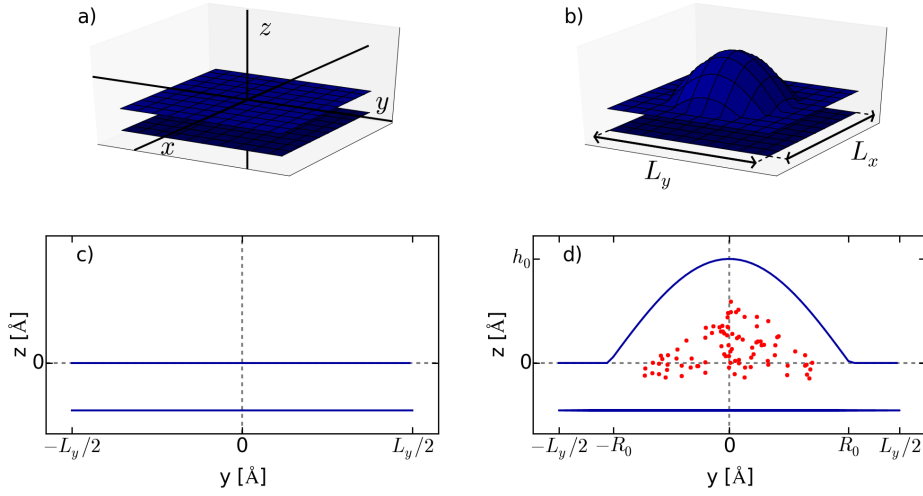


FIGURE 1.4: **Process of generating the sample.** **a)** 3D view of the initially generated sample before adding the bubble. Note that the origin of the coordinate system is in the center of the graphene, top sheet. The bottom sheet represents the bulk of graphite. **b)** 3D view of the sample after deformation of the top graphene sheet according to equation 1.4. L_x (L_y) is the length of the sheets in the x (y)-direction **c)** cross-section of a) at $x = 0$ Å. **d)** cross-section of b) at $x = 0$ Å showing where the hydrogen molecules (red dots) are in the bubble. R_0 (h_0) is the initial radius (height) of the bubble. See text for more details.

In the experiments by Khestanova et al.[3] a bubble is often formed when a single sheet of graphene is placed on a bulk substrate (graphite). In our simulations we simplify the bulk as one sheet of graphene and then add the sheet we study on top of it as shown in Figure 1.4a. This simplification saves computational time and has only minimal influences on the outcome, as shown in section 2.4.

We try to get the sample as good as possible into a square shape. Because of the hexagonal structure of graphene, see equation 1.3, it cannot be exactly a square. The amount of unit cells in the x -direction is b_x , in the y -direction b_y and in the z -direction b_z . To be able to apply periodic boundary conditions in the x (y)-direction b_x (b_y) has to be an integer. In this study we will vary b_x and b_y , b_z is 1 unless stated otherwise. The length of the sheets in the x -direction is called L_x and in the y -direction L_y as shown in Figure 1.4b. For a given b_x we calculate the optimal b_y to have L_x is as close as possible to L_y , such that the top view of the sample is almost a square while maintaining integer b_x and b_y . Next we lifted the top sheet from the middle in an artificial, circular bubble (Equation 1.4). Our final sample thus contains two more or less squared sheets of graphene and the top sheet has a circular bubble (see Figure 1.4b).

Cross sections of the 3D samples are helpful to show more details. Figure 1.4c is a cross section at $x = 0$ Å of the bulk and the graphene sheet without bubble and shows clearly that the origin of the coordinate system is defined in the center of the graphene sheet before the bubble was added. To create an artificial bubble we deform the upper graphene sheet as follows:

$$z(x, y) = \begin{cases} h_0 \cos\left(\frac{\sqrt{x^2 + y^2}\pi}{2R_0}\right) & \text{if } x^2 + y^2 < R_0^2 \\ 0 & \text{otherwise} \end{cases} \quad (1.4)$$

with R_0 the radius of the base of the initial bubble and h_0 its height (see Figure 1.4d). Because of the limited size of the sample R_0 cannot be larger than half the minimum of L_x and L_y . We chose

R_0 to be well under this limit: 35 % of the average of L_x and L_y . The aspect ratio, h/R is initially set to 0.15, a value comparable to experimental values [3], so $h_0 = 0.15R_0$.

In this artificially formed bubble we place a specified number of hydrogen molecules (N_{H_2}) as shown by the red dots in Figure 1.4d. The distance between the center of mass of these hydrogen molecules is supposed to be at least 2.4 Å and at least 3.0 Å between the center of mass of the hydrogen molecules and the carbon atoms. In section 2.5 we will discuss mistakes we made for these distances and their consequences.

1.2 Computational method

1.2.1 Potentials used in the model

Our model describes the interactions between the atoms in the sample, which contains two different species of atoms: carbon (C) and hydrogen (H). Within the model we choose the total binding energy, which consists of a short-range, a middle-range and a long-range potential energy. Covalent interaction between the atoms are described by the short-range potential. The long-range potential describes the nonbonded van-der-Waals interactions at long range. A middle-range potential is added to describe the reactivity and possible changes of bonding (for example from sp^2 to sp^3) that can occur at high temperature or in presence of defects. The value for the potentials depends on the distance and angles between neighbouring atoms as well as their species. For the middle-range potential only the carbon-carbon interactions were implemented in the version of the model we used. The model, called long-range carbon hydrogen bond-order potential (LCHBOP), is a general model for any system consisting of C- and H-atoms. It is based on LCBOPII ([12]), which itself is an improvement of long-range carbon bond-order potential (LCBOP). In this version we added (started to at least) the interactions of C- and H-atoms and of H-atoms with each other. The middle-range potential is not extended to these interactions with the H-atoms yet.

1.2.2 Monte Carlo

We use Monte Carlo (MC) simulations to find the equilibrium values the system converges to at a given temperature and pressure.

First we pick a random atom (i). Then we randomly choose one of the three coördinates ($v \in x, y, z$) and move it:

$$v_{i,n+1} = v_{i,n} + \delta(2\alpha_1 - 1) \quad (1.5)$$

with n the number of steps already made and α_1 a random number between 0 and 1. δ is dynamically chosen so that about 40% of the moves are accepted.

To check whether the move is accepted, we calculate the energy of the system after the move (E_{n+1}) and compare it to the energy before (E_n).

If

$$\alpha_2 < e^{-\beta(E_{n+1}-E_n)} \quad (1.6)$$

the move is accepted, otherwise it is rejected. α_2 is a random number between 0 and 1. β is $\frac{1}{k_B T}$ with k_B the Boltzmann constant and T the temperature of the system. This means a move that decreases energy is always accepted, while a move that increases energy has larger chances to be accepted if the increase is small. Whether accepted or rejected we move on to the next atom which is again randomly chosen. This model is based on an ensemble in which the amount of atoms (N) and temperature (T) is set.

Usually a MC step is defined as N individual moves, with N the number of moveable atoms, in the following however, for convenience, we will define a MC step as $500N$ moves. We only save the configuration after each MC step. MC does not give a realistic time evolution of the sample, but many MC steps together are a good approximation of the ensemble. Because of that we always have to average over many MC steps to get a reliable result.

In our model the energy is only calculated locally, not globally. For this we assume a move does not affect the energy further away. This assumption saves a lot of computational time. We also do not allow the bottom sheet of the bulk to move. This is usually also the only sheet of the bulk. The rigidness is done to simulate more graphite under it, and is a good approximation as will be shown in section 2.4 where we investigate the effect of two sheets in the bulk. We have constant N : $N = N_C + 2N_{H_2}$ and constant T : 100, 300 or 1000 K. We also have constant pressure: we chose 0 Pa. Apart from that we use periodic boundary condition in the x - and y -direction and do not allow the volume of the bounding box to change. The box is chosen so that the atoms can freely

expand in the z -direction, but cannot expand in x or y . We neglect the temperature dependence of the lattice parameter of graphene[13] and take it always equal to the value at $T = 0$ K.

1.3 Calculation of the relevant quantities

1.3.1 Evaluating one MC step

In this study we are mainly interested in h , R and the aspect ratio to which the simulations converge at equilibrium. We will determine these variables for each MC-step i , with

$$1 \leq i \leq N_{MC}$$

where N_{MC} is the total number of MC steps.

To calculate R_i and h_i we lay a 50×50 grid over the configuration of the sample at the end of the i -th MC step. In total there are N_g gridpoints. Then the weighted average of the height of the atoms surrounding a gridpoint for the top layer of carbon is calculated. The weight of an atom is defined as:

$$\frac{\Delta_x - \delta_x}{\Delta_x} \frac{\Delta_y - \delta_y}{\Delta_y} \quad (1.7)$$

with $\Delta_x(y)$ the distance in the $x(y)$ -direction between the gridpoints, and $\delta_x(y)$ the distance of the atom in the $x(y)$ -direction to the gridpoint that is being considered. Atoms more than one gridpoint away in the x - and/or the y -direction do not influence the height at all. Next we select all gridpoints with a height larger than 0.2 \AA . This amount is called N_{sel} . After that the average position of these N_{sel} gridpoints in the xy -direction is calculated and called the origin of the bubble xy_o .

Now we start an iterative process to determine the radius of the bubble. As a first guess for R_i we calculate the radius R_c of a circle around xy_o with these N_{sel} gridpoints in it. We use N_{sel} and the xy -density ρ_{xy} of the grid to determine R_c :

$$R_c = \sqrt{\frac{N_{sel}}{\rho_{xy}\pi}} \quad (1.8)$$

We then count all gridpoints which lie within a circle with radius R_c around xy_o and call this amount N_{sel2} . We then calculate their average xy -position (xy_{o2}). If $N_{sel} - N_{sel2} < \frac{1}{4}N_g$ we stop the iteration. We have verified that this procedure is sufficient to reach a stable final value of R_c . Otherwise we set $N_{sel} = N_{sel2}$ and $xy_o = xy_{o2}$ and repeat the iteration.

Once we stop the iteration we set $R_i = R_c$. We then choose a small circle around xy_{o2} and calculate the average height of the gridpoints within the circle, we call this z_{top} . Next we select all gridpoints more than 0.5 \AA outside the circle of R around xy_{o2} and calculate their average height to average out random fluctuations of the terrace, that is the flat part of the sample outside the bubble. We call this height z_{terr} . After that we define h at the i -th MC step, h_i , as $h_i = z_{top} - z_{terr}$. Finally the aspect ratio is now calculated by h_i/R_i .

1.3.2 Convergence

The simulation starts with the initial configuration that we guessed, and then the system relaxes to its equilibrium structure. To get a reliable result we have to average over many MC steps as described in section 1.2.2. But we do not want to average over the MC steps if the system is not yet at equilibrium. In order to know from which MC step on we should average we introduce a way of quantifying convergence.

Firstly we divide the MC steps for each simulation in intervals with a fixed width (W) of 80 MC steps. We call μ_i the average height (or radius) of interval i , with

$$1 \leq i \leq N_I$$

where N_I is the number of intervals.

Then we check if

$$|\mu_i - \mu_{i-1}| < p \left(\frac{\mu_i + \mu_{i-1}}{2} \right) \quad (1.9)$$

for $i \in 2, \dots, N_I$ and p a scaling factor. If the condition is satisfied we say that interval i has converged. We take p as 0.015 for the height and 0.002 for the radius. We define the aspect ratio as converged only if both radius and height are converged. In case all intervals j with $j \geq i$ are converged we calculate the average of all μ_j 's.

The average of these μ_j 's will be shown in the figures which display h , R or aspect ratio. We choose to display the standard deviation of these μ_j 's as the error of the value. If there are not at least three μ_j 's that have converged, we plotted the average of the last interval, denoted it with a red circle and did not plot an error. In case the radius reaches a value as large as possible for that sample, we plotted a blue triangle without an error.

1.3.3 Radial distribution function

In this study we are also interested in the phase of the hydrogen molecules in the bubble. This can be studied by the radial distribution function (rdf), a function which gives the average probability of finding an atom at a given distance from another. Below we will describe only briefly how this rdf can be determined. For more details see for example chapter 7 of the book *Introduction to modern statistical mechanics* [14].

First one takes the joint probability distribution $p(\mathbf{r}_1, \mathbf{r}_2)$ for finding atom one at position \mathbf{r}_1 and atom two at \mathbf{r}_2 . There are N atoms in total, so there are N possibilities for atom one. Then there are $N - 1$ left for atom two. In this way the density of the atoms is found:

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = N(N - 1)p(\mathbf{r}_1, \mathbf{r}_2) \quad (1.10)$$

Under the assumption that ρ is isotropic we can simplify ρ by taking only the distance between the two atoms into account, $d = \|\mathbf{r}_1 - \mathbf{r}_2\|$ resulting in $\rho(d)$. After that we scale the function, such that the limit of $d \rightarrow \infty$ becomes one. This final function is the rdf. We note however that, when applied to the H_2 gas in the strongly anisotropic situation under a bubble this normalization does not apply.

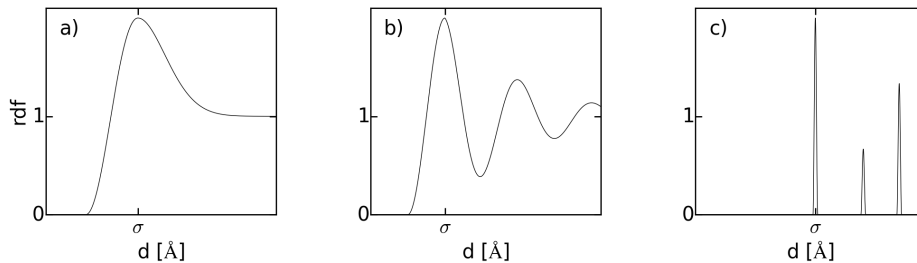


FIGURE 1.5: **Sketch of the radial distribution function (rdf) for different phases.** The rdf depends on the distance d between two atoms/molecules. σ is the distance of the nearest neighbour. Typical rdf for **a)**: a gas, **b)**: a liquid, **c)**: a solid. See text for more details.

From the form of the rdf one can determine the phase of the atoms/molecules. In case the atoms in the sample are in the gas phase the rdf shows just one peak at the distance of the nearest

neighbouring atom and then smoothly converges to a constant normalized to one (Figure 1.5a). For a liquid the rdf shows, as shown in Figure 1.5b, more than one peak at distances corresponding to broadened shells of neighbours and with decreasing amplitude. Figure 1.5c shows that the rdf for a solid consists of multiple peaks which would become deltafunctions at $T = 0$. Between the peaks the rdf is zero.

Chapter 2

Results

We will study samples of different sizes, with a different amount of hydrogen molecules (N_{H_2}) and temperatures (T). Most simulations are done for a sample, 245.951 x 247.08 Å with three values of N_{H_2} and each for three temperatures, as given by sample numbers 1-9 in table 2.1. Samples 10-13 are of different sizes all at room temperature ($T = 300\text{K}$) and with sample 14 we consider a bulk substrate with two sheets of which one mobile.

Sample Number	Bulk sheets	Lx (Å)	Ly (Å)	N_C	N_{H_2}	T (K)
1	1	245.951	247.08	46400	2500	100
2	1	245.951	247.08	46400	2500	300
3	1	245.951	247.08	46400	2500	1000
4	1	245.951	247.08	46400	5000	100
5	1	245.951	247.08	46400	5000	300
6	1	245.951	247.08	46400	5000	1000
7	1	245.951	247.08	46400	10000	100
8	1	245.951	247.08	46400	10000	300
9	1	245.951	247.08	46400	10000	1000
10	1	140.192	140.58	15048	750	300
11	1	199.22	200.22	30456	2500	300
12	1	285.303	285.42	62176	7500	300
13	1	314.818	315.24	75776	10000	300
14	2	140.192	140.58	22572	750	300

TABLE 2.1: **All simulated systems.** Samples 1-9 have the same sample size (L_x and L_y) and the same amount of carbon atoms (N_C). Samples 1-3 have the same amount of hydrogen molecules (N_{H_2}) but different temperature (T). Samples 4-6 and 7-9 have a different constant N_{H_2} and vary also in T just like 1-3. Samples 10-13 are at room temperature ($T = 300\text{ K}$) and differ in sample size whereby the density of the C-atoms is constant and the N_{H_2} is determined as a function of R_0 as described in 1.1.3. Sample 14 has an extra mobile sheet of graphene in the substrate.

In section 2.1 we will investigate the effect of varying temperature for a fixed sample size. In section 2.2 we will investigate whether the aspect ratio is constant as a function of the radius in our model. In section 2.3 we will investigate boundary effects, varying either N_{H_2} (2.3.1) for a fixed sample size or sample size (2.3.2) for a fixed N_{H_2} . In section 2.4 we will investigate the effect of adding another sheet to the substrate.

2.1 Temperature effects

The ideal gas law predicts that if the temperature increases while the number of particles stays constant, the pressure times the volume of the gas increases. Although we are not dealing with an ideal gas, we still expect the temperature to have an effect on the pressure and/or volume of the bubble.

In this section we investigate the effect of temperature on h , R and aspect ratio of the bubble.

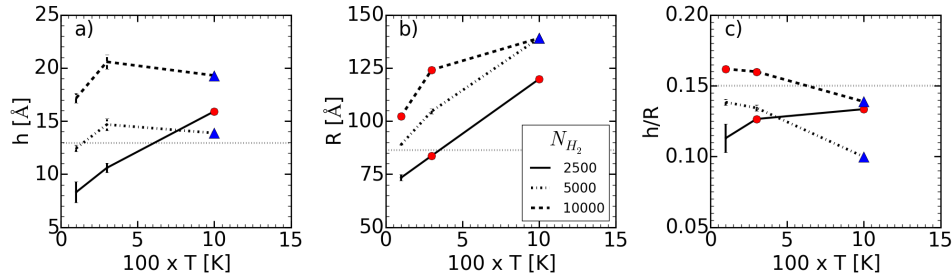


FIGURE 2.1: **Influence of temperature, T , on several dimensions of the bubble in graphene.** The simulations were all done for a sample size of $245.951 \text{ \AA} \times 247.08 \text{ \AA}$ (samples 1-9 of Table 2.1). The grey dotted horizontal line represents the initial value of the variable plotted in that panel. Red circles indicate that the value has not yet converged according to section 1.3.2. Blue triangles denote that the radius has reached its maximum possible value within the used sample size and are therefore not reliable. **a)** shows the effect of T on h , **b)** on R . The legend in this panel is valid for all three panels. **c)** Shows the effect of T on the aspect ratio, h/R .

We show the behaviour of h as a function of T for three values of N_{H_2} . The grey dotted line corresponds to the initial value of h , h_0 , which is the same for all temperatures. We see that for $N_{H_2} = 2500$ h increases with T . Also, for $N_{H_2} = 5000$ and $N_{H_2} = 10000$ there is an initial increase for h but at $T = 1000\text{K}$ h drastically drops because the sample is too small to contain the entire bubble: in that case the hydrogen molecules start to evenly spread between the graphene and the bulk, so h drops. For this reason these points tell us even less about what h would be than the red dots, at which h has not yet converged. The value and its error are determined as described in section 1.3.2.

R , also seems to increase with T (Figure 2.1b) for all N_{H_2} . Unfortunately for $T = 1000 \text{ K}$ and $N_{H_2} = 5000$ or 10000 , the bubble is too large for the chosen sample size, which results in the radius being the same. And for $N_{H_2} = 2500$ the radius has not yet converged for the higher temperatures, so we can only observe a trend but not determine the relation for certain. For $N_{H_2} = 5000$ the first two values have converged, and thus we can determine that radius increases with temperature. For $N_{H_2} = 10000$ none of the values have converged, but the relation seems to hold here too.

Figure 2.1c shows that for $N_{H_2} = 2500$ R only converged for 100 K . That means we can only determine the aspect ratio for 100 K accurately. And thus we cannot draw any definite conclusions about influence of the temperature on the radius as well as the aspect ratio for this N_{H_2} . For $N_{H_2} = 5000$ we have two values for the aspect ratio since R does only not converge for 1000 K . These two suggest that the aspect ratio is (almost) constant for difference in T . Finally, for $N_{H_2} = 10000$, none of the values have converged. Yet, when ignoring the last one where the bubble is too large for the sample, the aspect ratio seems pretty constant too.

It seems that both h and R increase with T , but aspect ratio is constant for difference in T .

2.2 Bubble size

The results of the experimental studies of Khestanova et al. (2016) [3] suggest that the aspect ratio is positive, even constant as a function of the radius of the bubble.

In this section we investigate whether the aspect ratio is also positive and constant as a function of radius in our model at room temperature ($T = 300$ K).

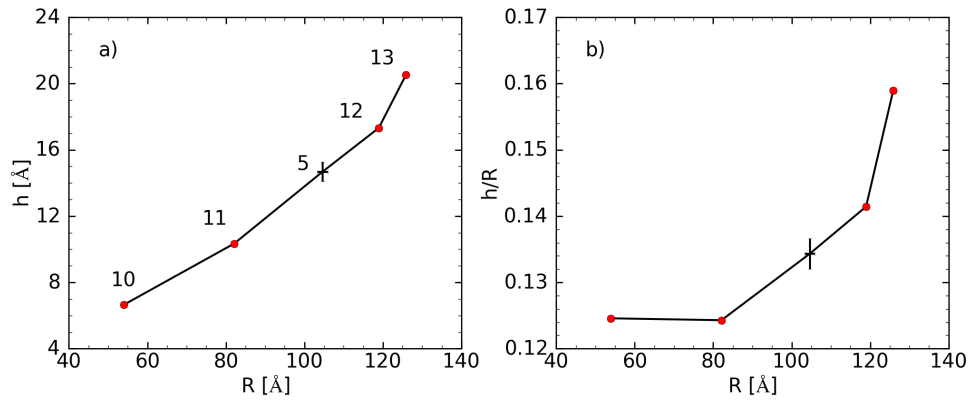


FIGURE 2.2: **Dependence of h and aspect ratio of the bubble in graphene on R .** The simulations are all done at room temperature ($T = 300$ K), see sample numbers 5 and 10-13 in Table 2.1 for more details. Red circles represent that the value has not yet converged according to section 1.3.2. **a)** shows the dependence of h on R . The numbers by the points represent the sample number in Table 2.1. **b)** shows the dependence of the aspect ratio on R .

Figure 2.2a suggests that h increases with its radius, R .

Note that both h and R should be converged in both panels of Figure 2.2 before the point can be marked as converged. Unfortunately only one of the five simulations has converged at the end of simulation. This means we cannot draw any conclusions about h as a function of R (Figure 2.2a).

Figure 2.2b suggests that the aspect ratio is not constant for these small radii. But again, because only one value has converged, no definite conclusions can be derived from these results.

2.3 Boundary effects

2.3.1 Varying number of hydrogen molecules

In section 2.1 we described the effect of temperature on the bubble. But the ideal gas law also predicts an effect when varying the number of atoms and keeping the temperature constant. Under the assumption that the pressure in the bubble stays constant we expect an increase in the volume of the bubble. Since the volume is proportional to the product of h and R^2 we expect an increase in this product.

In this section we keep T , L_x and L_y constant and vary the number of molecules in the bubble. We then investigate the effect on h , R and aspect ratio of the bubble.

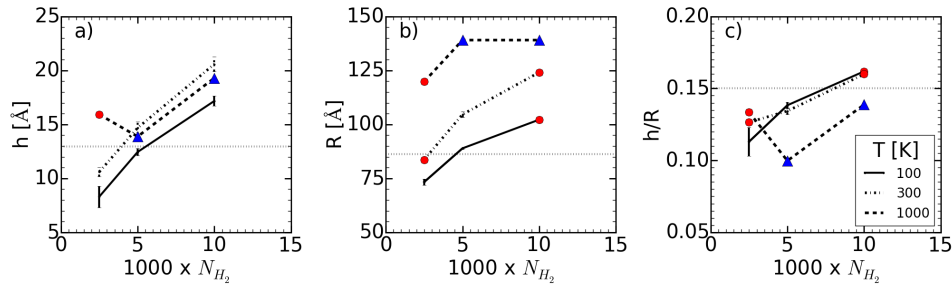


FIGURE 2.3: **Influence of the number of hydrogen molecules, N_{H_2} , on several dimensions of the bubble in graphene.** The simulations were all done for a sample of size $245.951 \text{ \AA} \times 247.08 \text{ \AA}$ (samples 1-9 of Table 2.1). The grey dotted line represents the initial value of the variable plotted in that panel. Red circles represent that the value has not yet converged according to section 1.3.2. Blue triangles denote that the radius has reached its maximum possible value within the used sample size. **a)** shows the effect of N_{H_2} on h . **b)** shows the effect on R . **c)** shows the effect of N_{H_2} on the aspect ratio, h/R . The legend in this panel is valid for all three panels.

Figure 2.3a shows that h increases if there are more hydrogen molecules in the bubble for several temperatures. Only the highest temperature of 1000 K does not seem to follow this relation, but none of the three values on that line are converged and additionally h takes a sharp dive when the radius reaches the maximum and the formed bubble is too large for the sample size.

As seen in Figure 2.3b the radius also seems to increase with N_{H_2} for all temperatures (T). For $T = 100 \text{ K}$ we can assume it since we have two values that have converged. For $T = 300 \text{ K}$ we unfortunately only have one value that has converged so no definite conclusion is possible, though the relation seems to hold. Lastly, for $T = 1000 \text{ K}$ the sample is just too small for the formed bubble.

Disregarding $T = 1000 \text{ K}$, the aspect ratio of the bubble seems to grow with N_{H_2} (Figure 2.3c), while, as shown in Figure 2.1, for varying temperature the aspect ratio seems to be constant.

2.3.2 Varying sample size

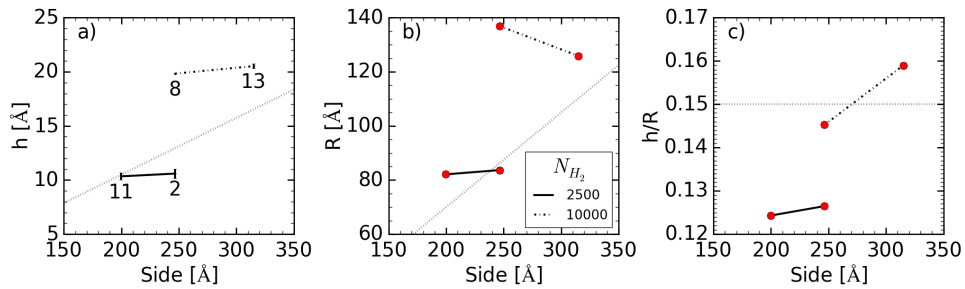


FIGURE 2.4: **Influence of the sample size on several dimensions of the bubble in graphene.** All simulations were done at room temperature. (samples 2,8,11 and 13 of Table 2.1). The x-axis is the average of L_x and L_y . The grey dotted line represents the initial value of the variable plotted in that panel. Red circles represent that the value has not yet converged according to section 1.3.2 and the numbers give the sample as in Table 2.1. **a)** shows the effect of the sample size on h , **b)** on R . The legend in this panel is valid for all three panels. **c)** shows the effect of the sample size on the aspect ratio, h/R .

As seen in Figure 2.4a h is nearly constant when changing the sample size for both $N_{H_2} = 2500$ and $N_{H_2} = 10000$ (constant means a difference of less than 10% of the average value between the values.)

R , also seems to be constant (Figure 2.4b) with the same definition of constant, but because none of the points have converged yet there is no certainty.

Because h and R seem constant, the aspect ratio h/R also seems to be constant (Figure 2.4c). Although the values are not completely reliable the fact that h , R and h/R remain constant by varying the sample size indicates that the shape of the bubble is an intrinsic property which does not depend on the extent of the flat terrace around it.

2.4 Effect of the number of sheets in the bulk

So far we have used the assumption that the bulk consists of one rigid sheet of graphene. In this section we investigate what happens if the bulk contains two sheets: the bottom sheet is still rigid, while the atoms in the top sheet can move.

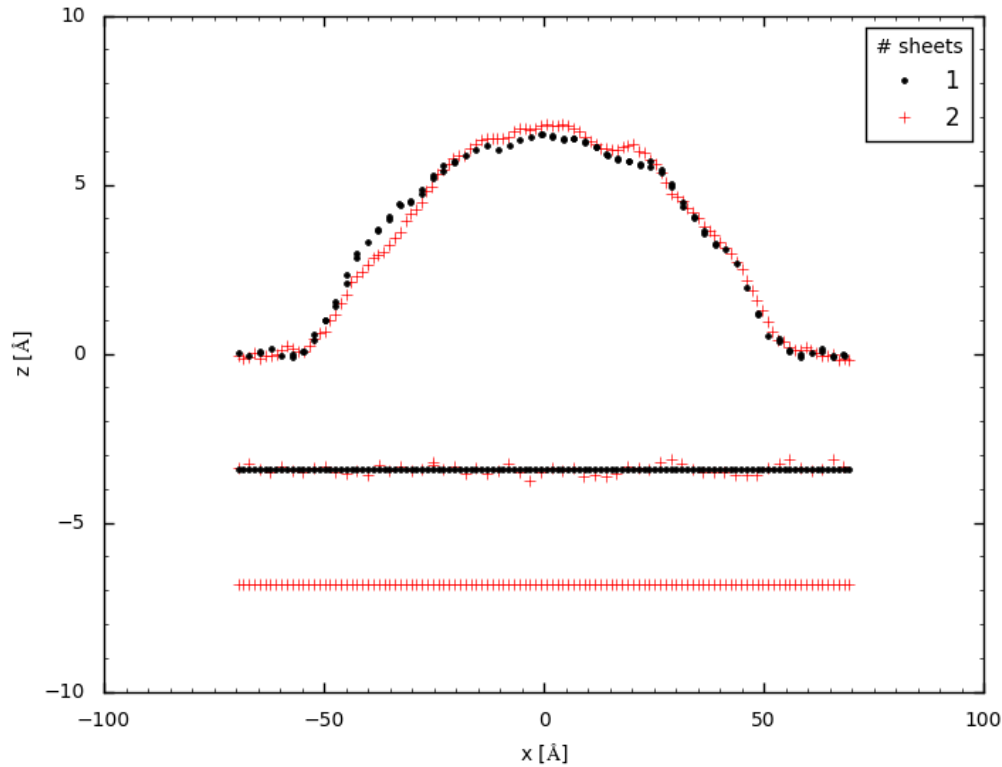


FIGURE 2.5: **Comparison of the crosssections at $y \approx 0$ for samples with one and two sheets in the bulk.** All simulations were done for a sample size of $140.192 \text{ \AA} \times 140.58 \text{ \AA}$, with 750 hydrogen molecules in the bubble, N_{H_2} , and at room temperature, $T = 300 \text{ K}$ (samples 10 and 14 of Table 2.1).

Figure 2.5 shows that after 2400 MC steps the top sheet of the bulk with non-rigid atoms is almost identical to the rigid sheet in the sample with only one sheet in the bulk. Therefore, it is not surprising that the shape of the bubble does not depend on how many sheets of graphene the bulk contains. This implies that the volume of the bubbles with one or two sheets in the bulk is also (almost) identical. From this we conclude that the simplification of the bulk as just one rigid sheet of graphene is justified.

2.5 Radial distribution function

The shape of the radial distribution function, rdf, can give us information about the phase the atoms are in (gas, fluid or solid). Another interesting way of using this function, although not done in this work, would be to compare the radial distribution function for hydrogen in the bubble with bulk hydrogen under pre-determined pressure to make a guess for what the pressure is.

In order to determine a reliable radial distribution function as described in section 1.3.3, we look at averages over the convergent section of sample 5 in Table 2.1. This is the only system plotted in Figure 2.2 that has converged. The components of the radial distribution function are shown in Figure 2.6.

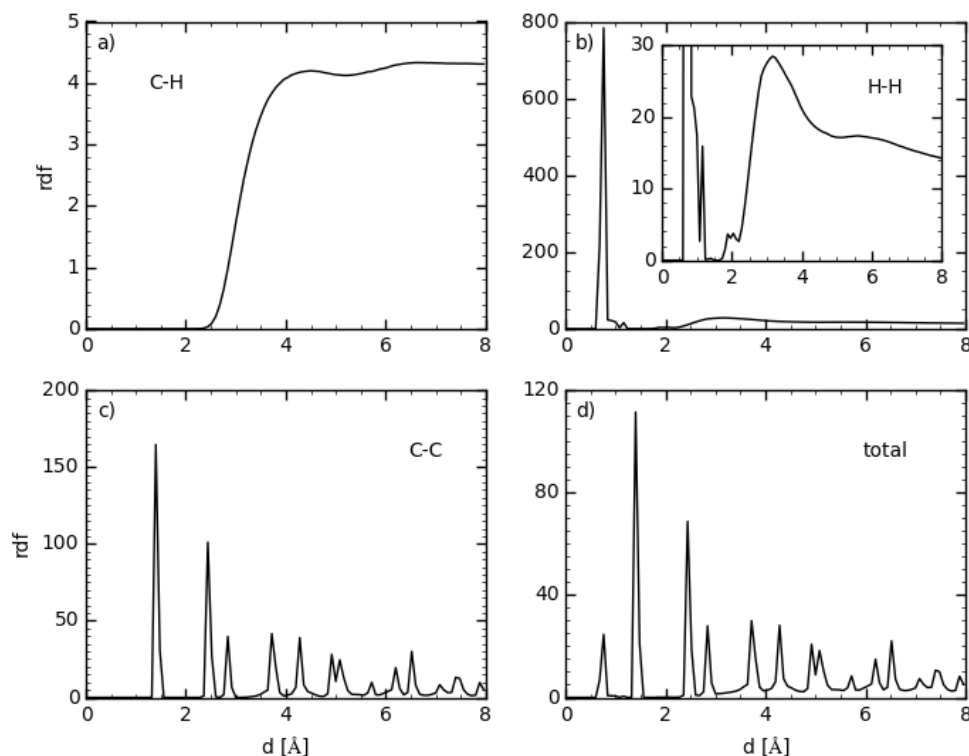


FIGURE 2.6: **Radial distribution functions of sample 5.** This sample has a size of $245.951 \text{ \AA} \times 247.08 \text{ \AA}$, 5000 hydrogen molecules in the bubble (N_{H_2}) and a temperature (T) of 300 K (sample 5 in Table 2.1). The radial distribution function is an average of the converged MC-steps according to section 1.3.2. **a)** shows the radial distribution function (rdf) for carbon vs hydrogen atoms, **b)** only for hydrogen atoms, **c)** only for carbon atoms, **d)** for all atoms in the sample. Note that the inset of panel b) is an enlargement of the interesting part of the graph in panel b).

Figure 2.6a shows the rdf of carbon and hydrogen. This tells us that in our model the minimum distance between carbon and hydrogen is 2.12 \AA .

The rdf of hydrogen has a high peak as shown in Figure 2.6b. The distance between hydrogen atoms at which the peak occurs corresponds to the distance between the two hydrogen atoms in a hydrogen molecule. Since the shape of the rdf for larger distances is more interesting, we have zoomed in at lower values of the rdf to be able to observe more details for larger distances (see the inset in Figure 2.6b). At this scale one notices the narrow peak immediately after the high

main peak. This means we made a mistake in the initialization of the initial configuration used in the simulations. The initial distance between the hydrogen molecules was too small, so there are always a few (less than 5%) chains of hydrogen longer than just two atoms (H_2 is the hydrogen molecule we originally wanted) spanning four atoms (so H_4) or more. Disregarding those peaks, the curve starting from 1.8 Å is somewhat intermediated between that of a gas and that of a liquid since there is a small second peak. While we did not determine the pressure exactly, it might be rather high if the hydrogen were indeed a liquid.

The rdf of carbon is shown in Figure 2.6c. This clearly shows that the carbon has a crystalline structure. Since we are dealing with graphene there is nothing new about that.

Finally Figure 2.6d shows the rdf for the total system. Because there is so much more carbon than hydrogen, this graph strongly resembles the one of the pure carbon. The only clearly visible difference with it is the small peak at the beginning, which corresponds to the largest peak in the graph for pure hydrogen. The contributions of the rest of the graph and the carbon-hydrogen graph are too small to be seen by the naked eye.

Chapter 3

Conclusion and discussion

Atomistic simulations of graphene on graphite with hydrogen trapped within the bubble have been carried out to support model calculations with detailed predictions for graphene. We have performed Monte Carlo simulations to find the equilibrium structure of these carbon and hydrogen atoms and determined h , R and aspect ratio of the bubble in graphene at equilibrium for several conditions. Additionally, we made a tiny step in the direction of determining the pressure inside the bubble. Not many of our simulations have converged, but the ones that have suggest that the aspect ratio does not depend on temperature, but does depend on the amount of hydrogen molecules in the bubble. Also, the pressure in the bubble might be very high since the rdf of the H_2 -molecules suggests the formation of a liquid.

Both h and R increase with T and/or N_{H_2} . The aspect ratio of the bubble does not increase with T , but it does increase with N_{H_2} (see Figures 2.1 and 2.3). We suspect that the dimensions of the bubble do not noticeably change when two bubbles are close to each other as long as they are separated by a flat terrace as discussed in Section 2.3.2. We have also shown (Figure 2.6b) that the pressure in the bubble might be high enough to compress the hydrogen into a liquid.

From Figure 2.6b it is also seen that we made a mistake: we do not only have hydrogen molecules (H_2) in the bubble, but also a few longer chains (H_4 and on). The shapes of the bubble in Figure 2.5 show that the approach to treat the bulk as one rigid layer of graphene does not differ from a multiple layered bulk of graphite. It is seen in Figure 2.4 that the dimensions of the bubble do not depend on the size of the sample. However, the blue triangles in Figure 2.1 and Figure 2.3 indicate that the radius is more than twice the length of the sample so that the sample size does matter if the lengths of the sides of the sample are not larger than twice the radius of the bubble. On that note, we need to fiddle with the determination of radius some more so it gives more accurate results.

Maybe the most valuable result of this study is if we consider our obtained results as preliminary results. The preliminary results can be used to determine the initial conditions more accurate and thus save a lot of time. Each one of the simulations used for Figure 2.1 or Figure 2.3 took over eight weeks. If h_0 and R_0 are chosen closer to the expected equilibrium value (based on the results in Figures 2.1 and 2.3) convergence can be reached in less MC steps.

In follow-up studies it would be interesting to incorporate the middle-range potential for hydrogen, which in the current study is not taken into account as mentioned before in section 1.2.1. Further it would be wise to generate the hydrogen molecules less close together in order to prevent H_4 and higher order chains. It would be interesting to see if bubbles are formed spontaneously when just placing a bit of hydrogen molecules between a sheet of graphene and graphite. And finally, other simulations could look at different initial values - do they converge to the same bubble?

To analyse the results we need to improve the method of finding the radius. Our current method may give us an approximation, but it should be able to be determined with less bias. Also the radial distribution function needs to be looked at again, for the functions seem not to be properly normalized.

Also, to determine h and R , it might be better to first look at the convergence of the energy, and calculate h and R only for the configurations with converged energy.

Bibliography

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov. Electric Field Effect in Atomically Thin Carbon Films *Science*, 306(5696): 666-669, **2004**.
- [2] Changgu Lee, Xiaoding Wei, Jeffrey W. Kysar and James Hone. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science*, 321(5887): 386-388, **2008**.
- [3] E. Khestanova, F. Guinea, L. Fumagalli, A.K. Geim, and I.V. Grigorieva. **Universal shape and pressure inside bubbles appearing in van der Waals heterostructures**. *Nat. Commun.*, 7: 12587–12596, **2016**.
- [4] J. Scott Bunch, Scott S. Verbridge, Jonathan S. Alden, Arend M. van der Zande, Jeevak M. Parpia, Harold G. Craighead, and Paul L. McEuen. Impermeable Atomic Membranes from Graphene Sheets. *Nano Letters*, 8 (8): 2458-2462, **2008**.
- [5] Jakob Zabel, Rahul R. Nair, Anna Ott, Thanasis Georgiou, Andre K. Geim, Kostya S. Novoselov, and Cinzia Casiraghi. Raman Spectroscopy of Graphene and Bilayer under Biaxial Strain: Bubbles and Balloons. *Nano Letters*, 12 (2): 617-621 **2012**.
- [6] L. J. Karssemeijer. Thermal expansion of carbon structures Master's thesis, Radboud University Nijmegen, Heyendaalseweg 135, the Netherlands, **2010**.
- [7] A. K. Geim and K. S. Novoselov. The rise of graphene. *Nat Mater*, 6(3): 183–191, **2007**.
- [8] Mikhail I. Katnelson. *Graphene: Carbon in Two Dimensions* Cambridge U. Press, New York, **2012**.
- [9] K. S. Novoselov , D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim. Two-dimensional atomic crystals. *PNAS*, 102(30): 10451-10453, **2005**.
- [10] H. Ghorbanfekr-Kalashami, K. S. Vasu, R. R. Nair, François M. Peeters, and M. Neek-Amal. **Dependence of the shape of graphene nanobubbles on trapped substance**. *Nat. Commun.*, 8: 15844, **2017**.
- [11] T. Georgiou, L. Britnell, P. Blake, R. V. Gorbachev, A. Gholinia, A. K. Geim, C. Casiraghi, and K. S. Novoselov. Graphene bubbles with controllable curvature. *Appl. Phys. Lett.*, 99(9): 093103, **2011**
- [12] Jan H. Los, Luca M. Ghiringhelli, Evert Jan Meijer, and A. Fasolino. Improved long-range reactive bond-order potential for carbon. I. Construction. *Phys. Rev. B*, 72(21): 214102, **2005**.
- [13] K. V. Zakharchenko, M. I. Katsnelson and A. Fasolino. Finite Temperature Lattice Properties of Graphene beyond the Quasiharmonic Approximation. *Phys. Rev. Lett.*, 102: 046808, **2009**.
- [14] David Chandler. *Introduction to Modern Statistical Mechanics*. Oxford U. Press, New York, **1988**.