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Chapter

Graphene Exfoliation from HOPG Using the Difference in Binding Energy between Graphite, Graphene and a Substrate

Yannick A.F. Kamta

Abstract

Since its discovery in 2004, the graphene global market had a huge/considerable growth. Such growth can be explained by the use of graphene in specific or targeted applications where it has a huge and clear advantage. Although graphene is growing and has many possible applications, its market fraction is insignificant compared to the carbon global market. This is simply explained because the industry still has challenges related to quality, costs, reproducibility and safety. In this chapter, we propose a new look on the mechanical exfoliation. Basically, based on the difference in binding energy between graphite, graphene and a substrate we can exfoliate. The binding energy is the energy between materials at equilibrium. When 3 materials A-B-C are interacting, if the binding energy between A-B is superior to B-C, then by moving A in the opposite direction, B will follow. Based on that, we calculated the interaction potential between graphite, graphene and a substrate using the standard Lennard-Jones potential. Conventional substrates like silicon and silicon dioxide cannot exfoliate while gold, silver and copper can at 3.2 to 3.3 Å. This difference may be because of their higher atomic density and modest lattice parameter compared to others substrates used in this study.

Keywords: graphite, graphene, binding energy, cohesive energy, exfoliation

1. Introduction

Graphene, the world's thinnest material, was first introduced theoretically in 1947 by PR Wallace [1] to understand the properties of graphite. From this theoretical study, many scientific tried to isolate a single layer of graphite without success. It always resulted in few layers of graphene [2]. Graphene (single layer of graphite) becomes a reality in 2004 [3] when Andre Geim and Konstantin Novoselov isolated for the first time graphene using an adhesive scotch tape to exfoliate graphene and test its properties. The outstanding properties of graphene attracted a lot of interest in the scientific community and in the industry, opening a large range of opportunities and applications in electronics, medicine, etc. From 2004, the goal became then to find a

reliable method to produce graphene layers. Today, we have many synthetics methods [4] that can be reliable in many aspects such as: Chemical Vapor Deposition (CVD), Liquid Phase Exfoliation (LPE) and reduction of graphene oxide. These methods allowed the transition from laboratory to industrial production.

In 2014, the global graphene market was projected to reach 190 million by 2022 [5], but recent studies by Report Link [6] shows that the graphene market will grow from 600 million USD (2020) to 1479 million in 2025. This huge grow in such a small time is really high, but compared to the carbon global market [7] (272 billion in 2020), it is almost insignificant. This is mostly because graphene is in its incubation phase and there is not yet a precise control on synthesis method. What could then be responsible for such growth? According to Li Lin and co-workers [8], the use of graphene in specific or targeted applications where it has a huge and clear advantage over other materials like in composites and electronics is the reason of graphene fast growth. More than that, the notable success of graphene in applications where chemical processes are required is because of its irregularities or defects [9]. This is to say that even though perfect flat graphene is hard to get, the small defective graphene plays a huge role in its growth.

Graphene has a large range of applications, but because of challenges related to quality, cost, reproducibility, processability and safety, we cannot really exploit it. So how, how to overcome these limits? Should we focus on enhancing the existing methods? Should we find new targeted applications? Should we focus more on standardization? Etc. The graphene industry still has a lot of work to accomplish, and anyone can work on something particular.

The aim of this project is to propose a new model of graphene exfoliation from Highly Oriented Pyrolytic Graphite (HOPG). Here, we gave a new look at the mechanical exfoliation by Andre Geim and Konstantin Novoselov [3]. Basically, using a scotch tape, they applied a force on top of graphite surface, graphite (many layers) sticks to the scotch, and by peeling it off using another scotch, they were able to get graphene. Why they did not get graphene the first time they put the scotch on graphite? Simply because the applied force was too superior to the interlayer force (cohesive or cleavage energy of graphite) that hold graphite layers together. Considering F as the interlayer force of graphite, if the applied force Fa was superior to F and inferior to $2F$, then they would have got a single layer, but it is really difficult to achieve such small forces. Just like intermolecular forces like VDW forces are holding graphite layers together, putting a substrate to a certain distance from the graphite surface will create such forces. Using a substrate on top of graphite, our first goal is to show that we can exfoliate a single layer by controlling the resulting force (binding energy) between F and $2F$. Thanks to the standard Lennard-Jones (LJ) potential we will calculate the binding energies of graphite surface/substrate and compare it to the interlayer binding energy of graphite (cleavage energy) to show that we can exfoliate. This work is divided into 3 parts. The first part is a review of exfoliation principles. The second part discusses our model and the calculations equations and finally the third part is about results and discussions.

2. Review on exfoliation principles and calculus

2.1 Exfoliation principles

Like gravitational forces acting on earth, there are intermolecular forces acting between all atoms and molecules. These forces have been variously known as

dispersion forces, London forces, induced-dipoles forces, etc. but they are all referred as Van der Walls forces (VDW). As we know, these forces are present between graphite layers. In fact, the carbon layers are dipole-induced dipole that created forces between layers. These VDW forces created between two layers form a potential energy which is known as the bonding energy of graphite (binding energy). In order to exfoliate a graphene layer then, the cohesive energy has to be overcome. Exfoliation of graphite is a top-down method which consists in finding ways to surpass these interlayers forces, to breakdown or overcome that cohesive energy, hence the name of cleavage energy. We distinguish two types of exfoliation techniques for graphene: mechanical and chemical exfoliation.

In mechanical exfoliation a longitudinal or transversal stress is generated on the surface of the layered material by a scotch, AFM tip or a substrate [10]. The goal here is to overcome the energy between the layers. The difficulty in mechanical exfoliation is that the energy between layers is too small and by consequent easy to overcome resulting in many layers which is not graphene. Mechanical exfoliation is a simple and easy method for small lab experiments and cannot be used for industrial purpose. It is irreproducible, it has no control in layers, defects and size. Our goal is to change that, to make mechanical exfoliation reproducible and predictable by using intermolecular forces to exfoliate (**Figure 1**).

On the other hand, chemical exfoliation mostly known as liquid phase exfoliation (LPE) is almost the same as mechanical exfoliation. In LPE, transversal and longitudinal stress are provided by sonication, high shear mixing or micro fluidization [11] and it is happening in a liquid. LPE is a cheap, easy and scalable method to produce nano-flakes of graphite, but it has its challenges. Depending on the type of solvent used, we can face problems like aggregation, pollution, conservation and washing problems to some degrees. It also has a low yield (**Figure 2**).

2.2 Cohesive energy and implications

The first challenge for exfoliation technique is the requirement of an energy close to the cohesive energy of graphite, and we need to know its value first. In 1956, L. Girifalco and Lad [12], calculated the binding energy (cohesive energy) of graphite using the summation lattice with the LJ potential. They found the binding energy was approximately $-0.33 \, J/m^2$ ($-53.96 \, meV/atom$). They confirmed this result by comparing it to values got from Heat wetting experiment. Since the expansion of
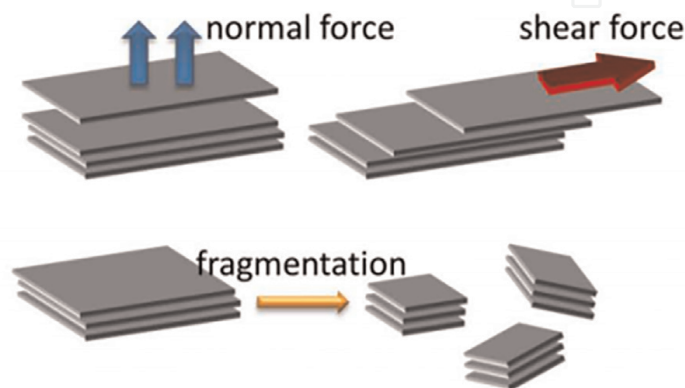

Figure 1.
Mechanical exfoliation principle. (reprinted from reference Yi and Shen [25] with permission of CCC Inc.).
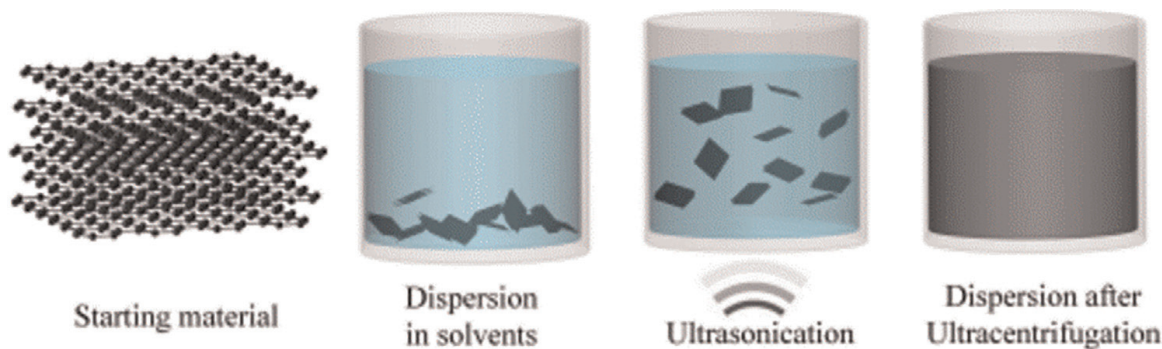
Figure 2.
LPE using sonication (reprinted from reference [26]).

graphene, the cohesive energy of graphite has attracted a lot of attention to under-stand better its properties for better exfoliation experiments design.

Xiaobin and colleagues calculated the interlayer potential by combining the Mobius inversion method with ab initio calculation [13]. They found the binding energy to be between 55 and 60 $meV/atom$. According to them, the binding/cohesive energy is between 50 and 60 $meV/atom$. They also found the interlayer space to be 3.1 Å. In the same way, using Quantum mechanics orbital occupancy approach and second order perturbation theory, Y.J Dappe and colleagues obtain a binding energy of 60–72 $meV/atom$ and interlayer space distance of 3.1–3.2 Å [14]. Throughout our literature review, we can say that the binding energy of graphite *Eg* lies between 50 and 72 $meV/atom$ and the interlayer distance is 3.34 Å as confirmed by XRD studies of graphite. So the goal of all exfoliation technique is to provide an energy *Ex* (by many means) which is: $Eg < Ex < 2*Eg$ to exfoliate a single graphene layer. When *Ex* exceeds, we can have bilayers and more.

2.3 Exfoliation methods

Using this knowledge about the cohesive energy, Zhang et al. [15] while working on transport measurements of microscopic graphite devices, fabricated their samples using a micromechanical cleavage process. With a silicon cantilever with a normal force between $10 - 2000nN$ (**Figure 3a**), they could exfoliate few layers of graphite. These small VDW forces between graphene layers (2 eV/nm^2) are not easy to achieve for graphene exfoliation but is required. For instance, Hernandez et al. [16] while working on LPE, found that by using a solvent with similar surface tension like graphene, the exfoliation was easier and single layers were obtained.

The requirement of such small forces made researchers to look for more sensible methods. For example, Seunguen Lee and Wei [17] simulate the exfoliation of graphene from HOPG on a SiO2 substrate and called it friction-induced exfoliation (**Figure 3b**). In that process, they used the lubrication properties of HOPG, the corrugation of HOPG combined with the roughness of the substrate. Another similar article is the exfoliation of graphene using the adhesive energy of few layers of graphene on a silicon substrate, while applying an upper velocity force on top of graphite to exfoliate the top layer (**Figure 3c**) [18]. In that study, based on the number of layer and the velocity, they could exfoliate the top layer.

In this paper, we present a new way of graphene exfoliation based on binding and interaction energy between graphene, graphite and a substrate.
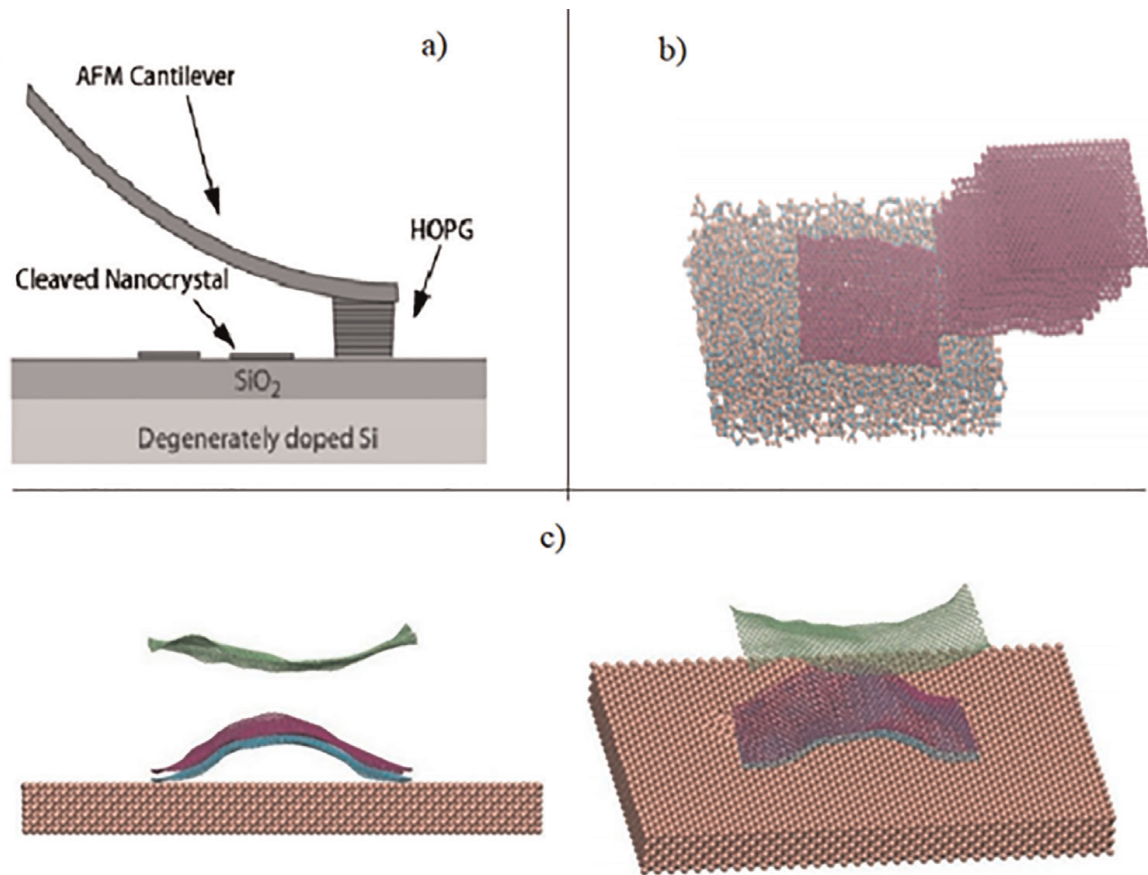
Figure 3.
a. Cleavage process using the adhesion energy between graphite and substrate (reprinted from [15] with permission of AIP publishing) b. Friction induced exfoliation (reprinted from [17] with permission of AIP publishing) c. Top layer exfoliation based on velocity and adhesion.

3. Proposed exfoliation and principle

3.1 Exfoliation model

When two materials (atoms, material made of atoms) are brought together, we can distinguish two types of energy: adhesive and interactive energy. The adhesive energy describes the forces when two materials are in contact (when they adhere) while the interaction energy describes the forces exerted by each material on the other. The interactive energy can be described by the Lennard-Jones (LJ) potential in **Figure 4**. When we look at the interactive energy curve, there is a minimum which is known as the binding energy ε. It is obtained at equilibrium. The broader and deeper it is, the stronger is the bond between the materials (mostly for non-covalent bonds). σ is the distance at which the potential is 0. It can be taken as the repulsive core.

The working principle of our exfoliation model is shown in the next figure and can be viewed here (**Video 1**: https://drive.google.com/file/d/1eE48rBa0de_vzHd_zfxd QN940se1UqBj/view?usp=drivesdk). It is based on the interaction energy between three materials: graphite (HOPG), graphene (the bottom layer of HOPG) and a substrate. As we can see in the **Figure 5**, we consider HOPG as graphite and graphene. So our goal is to study the interaction between these materials.
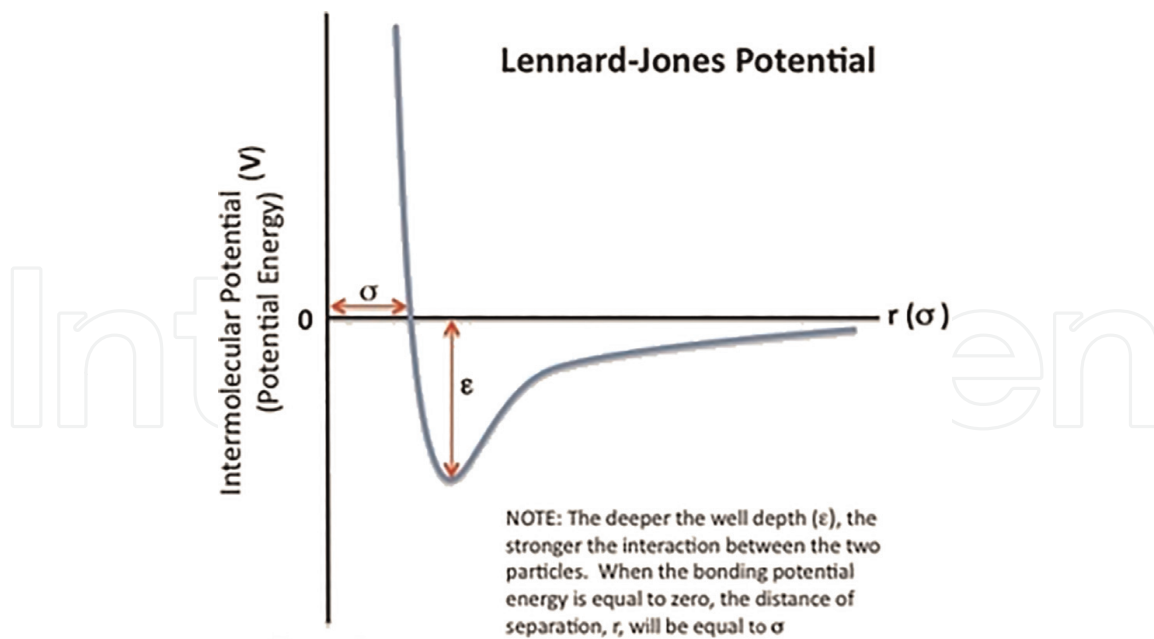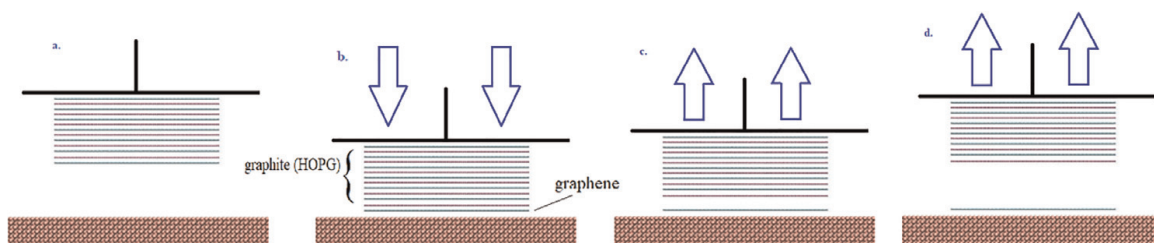
Figure 4.
Lennard Jones potential curve.

Figure 5.
Exfoliation of graphene based on interaction energy.

Here is a small description of the working principle.

a. The HOPG graphite and the substrate are separated considerably. The substrate is stable while the HOPG can move up and down.

b. The HOPG is pushed down to the substrate at a certain distance (the distance at which we have the binding energy between graphene and the substrate)

c. We pull up the HOPG and because the binding energy between the bottom layer graphene and the substrate is superior to the binding energy of graphite, the bottom layer will stay and adhere on the substrate.

d. Finally, the system is back to the normal and the HOPG is reduced by one layer and we can pass another substrate.

We simulated first the interaction energy (binding energy) between graphene and graphite. Then we determine the interaction energy between graphene and a couple of materials to see what materials can exfoliate and finally a study of the results to see how we can make the process more effective.

3.2 Calculation of the interaction energy using the LJ potential

To calculate the interaction energy between materials in this project, we used the standard LJ 6–12 potential expressed as:

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{1}$$

where $V(r)$ is the interaction energy between two atoms. The first term of the potential $\left(\frac{\sigma}{r}\right)^{12}$ is the repulsive term, and the second term $\left(\frac{\sigma}{r}\right)^{6}$ is the attractive term. ε *and* σ are the minimum value of the potential, and the distance at which the potential is zero respectively. r is the distance between the atoms interacting. We opted for this potential because it is easy to manipulate, good for non-covalent bonds like VDW forces and more used for qualitative purpose.

3.2.1 Potential in terms of material

The potential energy is the sum of a long range attractive contribution and short range repulsion as we saw in the potential curve. One thing about this LJ potential is that the bond strength increase with the atomic number/atomic mass (molecular weight). This is because atoms with large atomic numbers have high number of electrons that will then increase the VDW forces to get stronger. Second, the shape of the molecules also plays a role in the VDW bond strength. The shape will dictate the spread of the electrons, whether they are widely distributed or centered. For example, molecules of the same molecular weight have greater bond strength if they have larger aspect ratio shapes.

These understanding helps us in the designing or the choice of the materials that we are going to use to exfoliate graphene from graphite. From the previous paragraphs, we asked the following questions:

- What would be the material composition (atomic composition)?

- What could be the shape, size and aspect ratio?

- What should be the perfect material density to exfoliate just one graphene layers without causing defects or anything else?

- Is it possible to manufacture the material size that we want? Atomic thickness for example!

3.2.2 Parameters ε, σ

The LJ potential is a pairwise potential. Atoms parameters of ε *and* σ are mostly defined by experiments. The parameters values ε, σ for different atoms combinations were obtained through Rappe et al. [19], and the references [20, 21] by using the formulas:

$$\sigma_{A-B} = \frac{\sigma_{A-A} + \sigma_{B-B}}{2} \tag{2}$$

$$\varepsilon_{A-B} = \sqrt{\varepsilon_{A-A}\varepsilon_{B-B}} \tag{3}$$

Pair_style	$\sigma(A)$	ε(meV)
C – C	3.431	4.55
Si – Si	3.826	17.4
Ag – Ag	2.648	350.6
Au – Au	2.646	412.9
Cu – Cu	2.338	409.32
Si – C	3.629	8.91
O – C	3.275	3.44
Cu – C	2.8845	43.156
Au – C	3.0385	43.3439
Ag – C	3.0395	39.9403

Table 1.
Lennard Jones parameters of atoms and pair of atoms.

The next table shows the parameters values calculated for atoms combination we will use for simulations.

3.2.3 Computation process (pairwise summation)

The LJ potential $V(r)$ as described in Eq. (1) is the interaction between two atoms a and b. When we talk about the interaction energy of graphene with a substrate, we are referring to more than two atoms (100, 1000 atoms for example). In general, to determine the interaction energy between two bodies G (graphene or graphite) and S (substrate), we do the summation of the LJ potential $V(r)$ over all the possible combinations of atoms in the bodies. For instance, the interaction energy between G and S is given by:

$$U(a) = \sum_{i}\sum_{j>i} V(r_{ij}) \tag{4}$$

where r_{ij} is the separation distance between atoms i and j in the bodies G and S respectively. To compute the previous formula Eq. (4), we use the same method described by Giralfco and co-workers in their paper [12]:

- We calculate first the interaction between a carbon atom in graphene and all the atoms in the substrate. Since there is two type of carbon atoms in graphene, we have the following expressions

$$U_{1j}(a) = \sum_{j} V(r_{1j}) \tag{5}$$

$$U_{2j}(a) = \sum_{j} V(r_{2j}) \tag{6}$$

where a is the distance between the graphene surface and the substrate surface as we can see in **Figure 6**; r_{1j} and r_{2j} are the distance between a carbon atom 1 (or 2) and the j atom in the substrate.
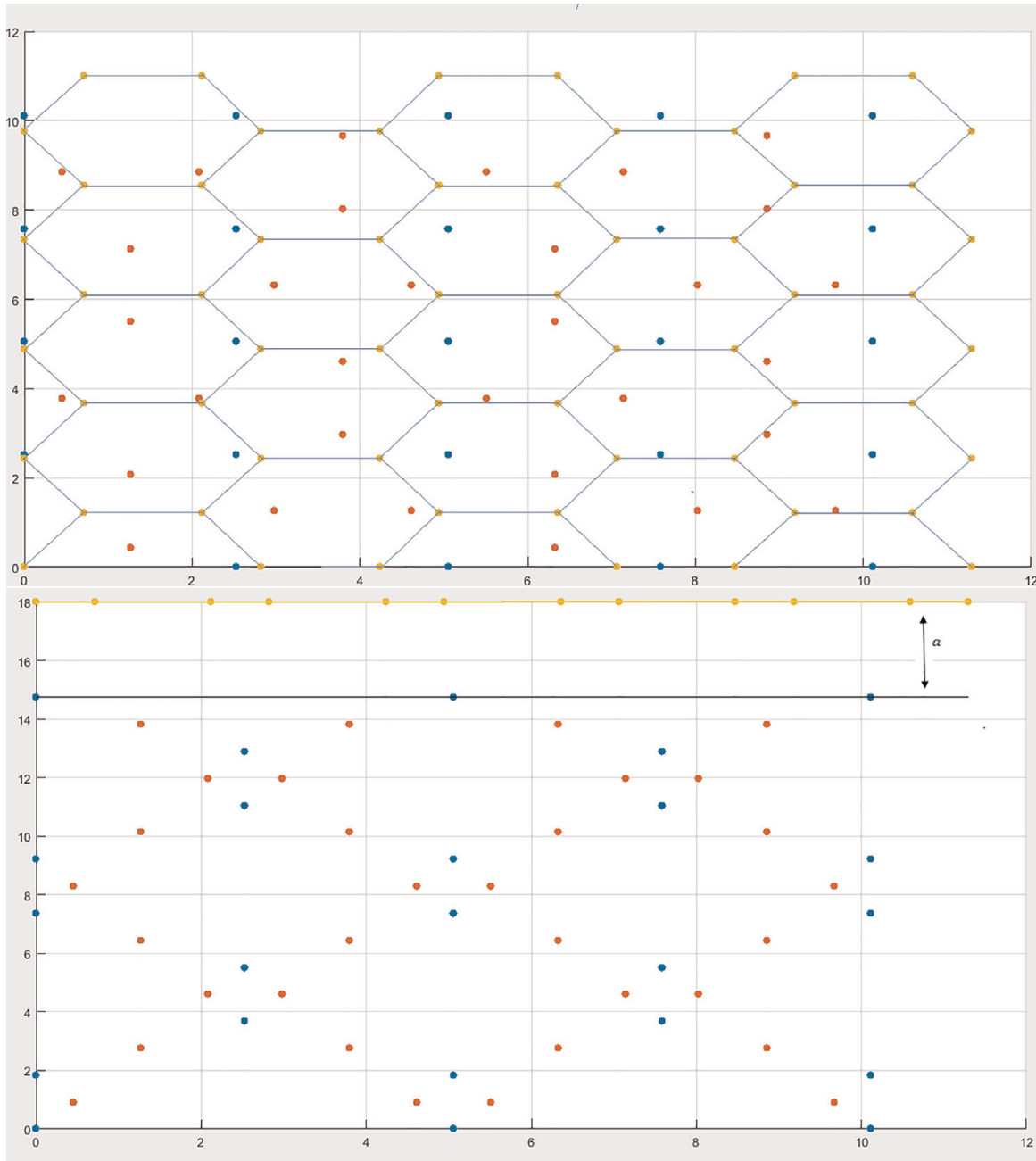
Figure 6.
Left – xy view of graphene/silicon dioxide interaction; right – xz view of graphene/silicon dioxide separated. The yellow, blue and red points are carbon, silicon and oxygen atoms respectively.

- After, to determine the interaction energy between a graphene sheet and the substrate, we integrate the previous terms Eqs. (5) and (6) over all the graphene sheet. Since here we are interested in general results, we are dividing the previous terms by the surface of the atoms (δ: surface of one carbon atom).

$$U_{GS}(a) = \frac{1}{2\delta}\left(U_{1j}(a) + U_{1j}(a)\right) \tag{7}$$

where δ is the area occupied by a carbon atom in a graphene sheet. $\frac{1}{2\delta}$ is the number of atom of each type per square unit area in the monolayer.

3.2.4 Simulation set-up

For the simulation, we are using 2–3 supercells depending on the length of the lattice of the substrate. For example, silicon has a lattice parameter of $5.43°A$. So, we are using two supercells for a total dimensions of 10.86*10.86*10.86. Based on those dimensions, we define the dimensions of graphite $11*11°A^2$ for this case. We choose such a small set up to gain in simulation time and performance of the algorithm.

There are 5 simulations. Cupper, silicon, gold and silver have a face-centered cubic (fcc) lattice structure. So we will not show all the figures. By showing only one system we can guess how the other ones will look like since they have the same lattice structure with different lattice parameter. For instance, we have: Silicon $(5.43°A)$, Cupper $(3.625°A)$, Silver $(4.09°A)$ and Gold $(4.08°A)$.

The other simulation is with silicon dioxide (**Figure 6**). SiO2 is a complex structure that can be found in many structures. In this project, we consider silicon dioxide as a crystal in a simple tetragonal structure. Here the dimensions of the system are $10.5*10.5*14°A^3$.

There are five simulations. The principle of our algorithm is to calculate the interaction energy as a function of the separation distance a between the substrate and the graphene/graphite.

4. Results and discussions

Most of the researches that has been done between graphene and a substrate is more concerned about the adhesive energy. Few papers are actually about the inter-action energy or binding energy. For this reason, we first verified the acceptance of our algorithm by calculating the cohesive energy of graphite (cleavage energy) and compare the result to see if it is similar to others in the literature. From the computed interaction potential between graphite and graphene, we found the cohesive energy of graphite or the binding energy between graphite and graphene to be $-0.3060 \, J/m^2$ at $3.6°A$ (**Figure 7**). This result is closed to those got by Girifalco [12] and some practical experiments [22]. Now that we know our algorithm is acceptable, our goal is to compare the interaction between graphite – graphene and graphene – substrate. In the next figures, the blue curve represents the energy potential of graphene/graphite and the orange curve, the potential of graphene/substrate.

Using the same algorithm, we computed the interaction potential between silicon and graphene. We found the binding energy to be $-0.1014 \, J/m^2$. This result agrees with the one obtained by Norio Inui and Sho Iwasaki [20]. As we can see from the **Figure 8**, the cohesive energy of graphite is much more superior to the binding energy between graphene and silicon. From this energy difference, it is clear that silicon cannot exfoliate graphene from graphite.

For silicon dioxide, we found the binding energy with graphene to be $-0.090 \, J/m^2$ at $3.45°A$ (**Figure 9**) which is the value got by Ishigma et al. [23] in their work. By comparing it to the cohesive energy of graphite, silicon dioxide cannot exfoliate graphene using this principle. However, a study by Wei Gao and coworkers shows that the interaction strength is strongly influenced by changes in the silicon dioxide surface structure due to surface reaction with water [24]. By reconstructing a SiO_2 surface, they could increase the interaction energy. In this project, we used silicon dioxide simple
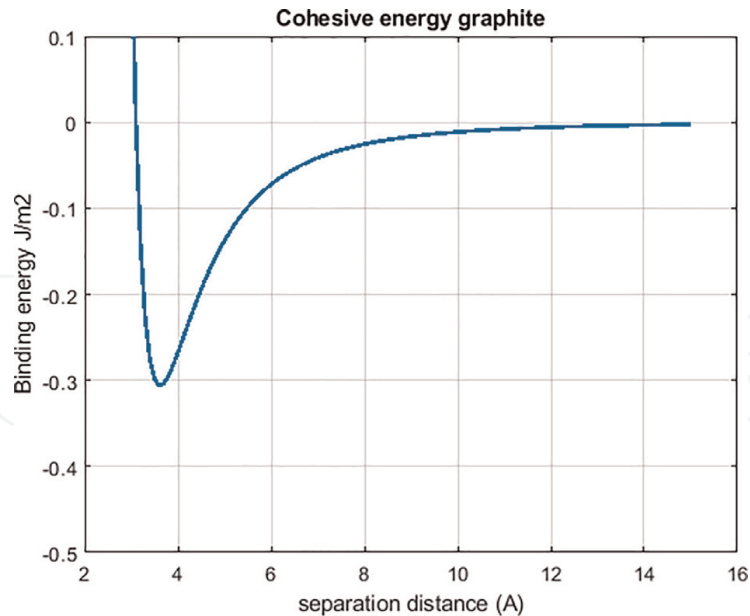
Figure 7.
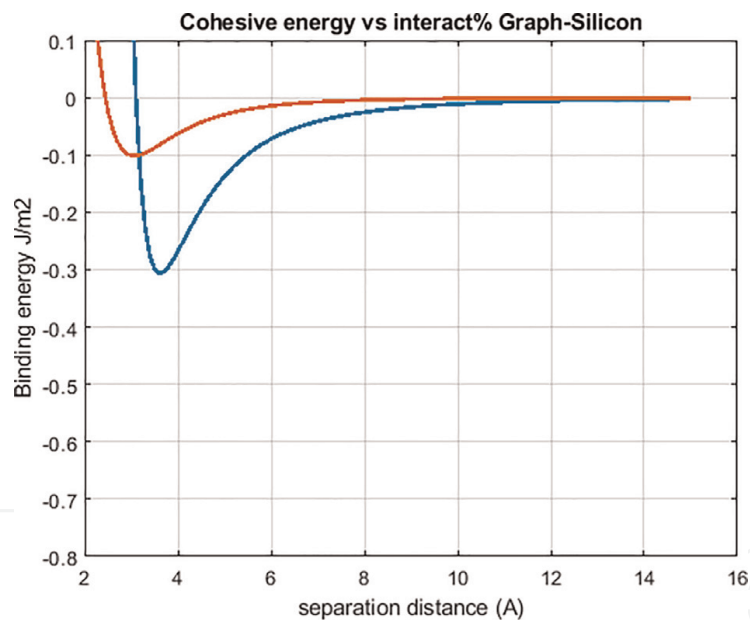*Graphite graphene interaction energy.*

Figure 8.
Graphene silicon interaction (orange), graphene/graphite interaction (blue).

tetragonal structure without surface modification. This is to say that we can increase the binding energy by surface modification.

In the case of metals substrates, we find the binding energy between copper and graphene to be $-0.3792 \, J/m^2$ at $1.2 \, \mathring{A}$ (**Figure 10**). Here, we can notice that the equilibrium distance at which we obtain the binding energy is small. At first, it is tempting to say that copper cannot exfoliate graphene since at $1.2 \, \mathring{A}$, the cohesive energy of graphite is infinity. But in practice, the interlayer distance between graphene layer is fixed, so by approaching graphite at $1.2 \, \mathring{A}$ from the copper surface, we can see a weak exfoliation since they almost have the same energy. However, the distance is small.

The obtained binding energy between gold/graphene and silver/graphite is $-0.5924 \, J/m^2$ and $-0.5426 \, J/m^2$ both at $3.2 \, \mathring{A}$ respectively (**Figures 11** and **12**). They
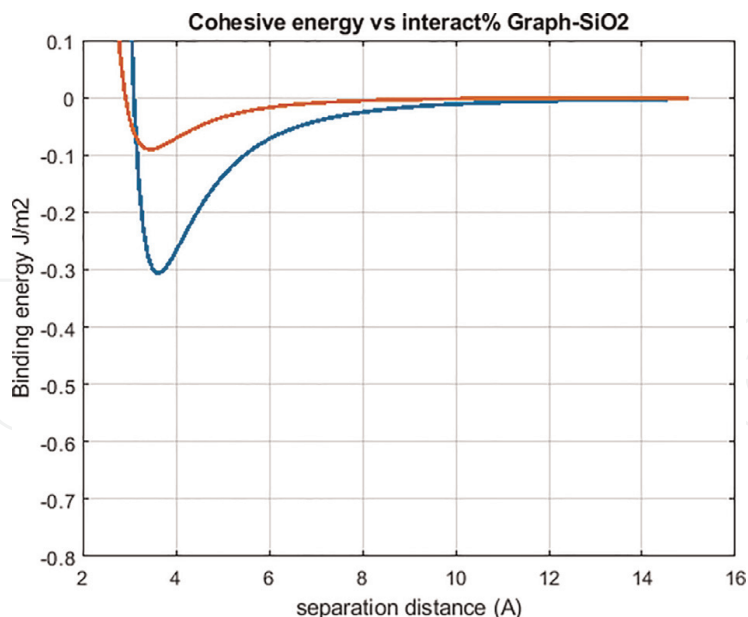
Figure 9.
Graphene/silicon dioxide interaction potential (orange curve), graphite/graphene interaction (blue curve).
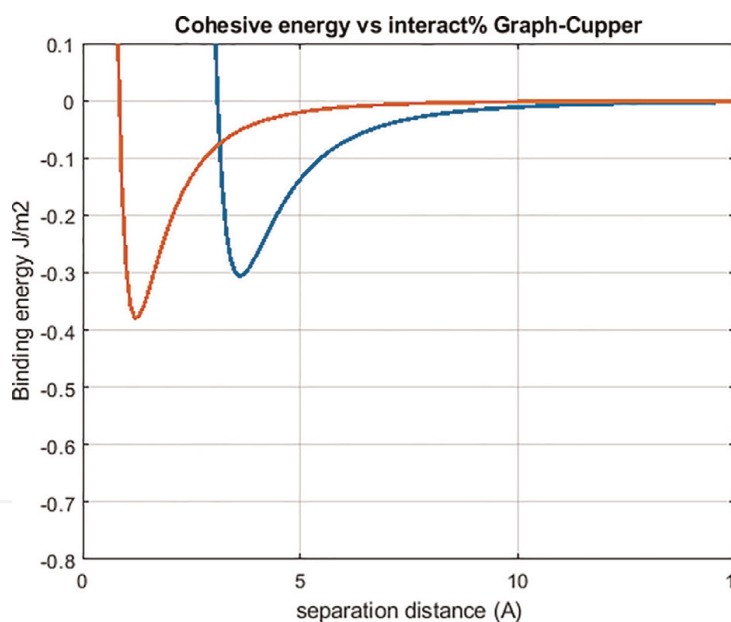

Figure 10.
Graphene/cupper interaction potential (orange curve), graphite/graphene interaction (blue curve).

both can clearly exfoliate graphene based on the principle described in **Figure 5**. These values of binding energy largely differ from copper and this may be because of the large atomic number and higher lattice parameter. From this result, we can agree that the atomic density has more influence on the binding energy.

5. Conclusion

The graphene industry still has a lot of rooms to improve in terms of standardization, conservation, synthesis, etc. The lack of a reliable and cost effective synthesis method avoids graphene to fulfill its potential. In this project, we proposed for the
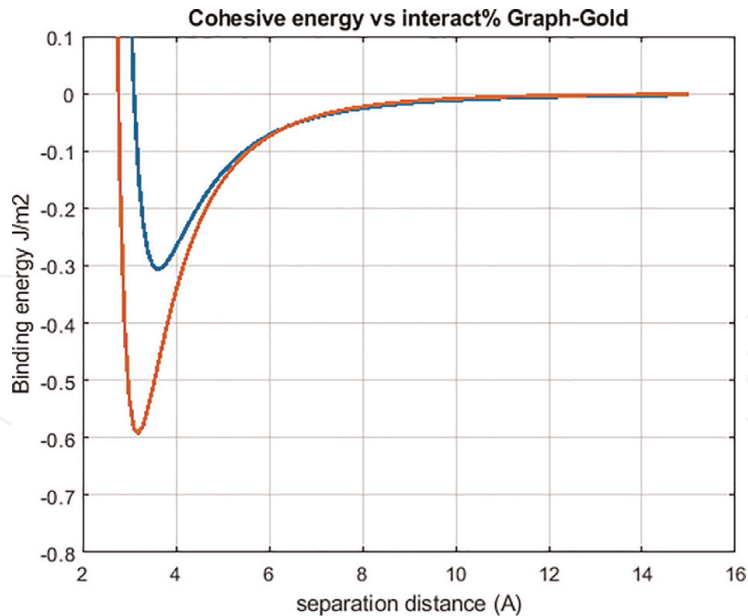
Figure 11.
Graphene/gold interaction potential (orange curve), graphite/graphene interaction (blue curve).
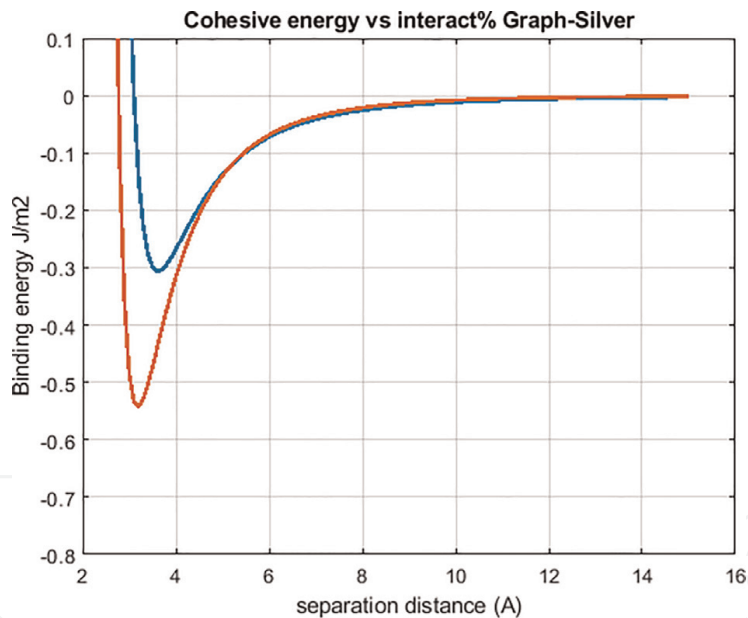

Figure 12.
Graphene/silver interaction potential (orange curve), graphite/graphene interaction (blue curve).

first time an exfoliation model of graphene from HOPG graphite based on the cohesive energy of graphite and the binding energy of the substrate with graphene. Calculations using the Lennard Jones potential and lattice summation showed metal substrate like gold, silver and copper can exfoliate graphene from graphite at 3.2 Å. Conventional substrate like silicon and silicon dioxide showed a binding energy inferior to the cohesive energy of graphite and cannot therefore exfoliate graphene. This result opens a new range of possibilities and opportunities for the graphene industry, notably in applications requiring first higher graphene quality. However further studies are still going on. First the distance at which the exfoliation can happen is small. 3.2 Å from the graphite or substrate surface is difficult to achieve. So the
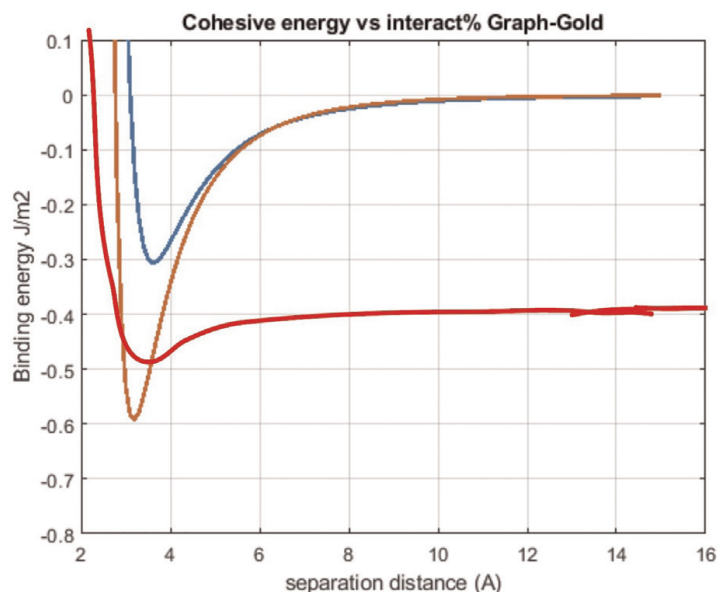
Figure 13.
Perfect substrate behavior (red curve).

challenge is to find or design a material that can exfoliate at an achievable distance which will make the process easier and effective. The perfect material curve looks like the one in **Figure 13**. where the red curve would be the behavior of the "perfect material". Second we need to find substrate materials that are polyvalent and can be used anywhere. Finally, we need to put more accuracy on our algorithm and do some practical tests. The truth is that this method is working, simply because by touching softly graphite or a pencil, there will be graphene layers in our finger and our goal was to understand it and automatized it. This model as shown in **Figure 5** can be easily scaled up to industrial manufacturing if we can achieve a good exfoliation distance. One thing is sure, a reliable, reproducible and effective synthesis technique could have a significant impact in the graphene industry.

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