## AFM TIP-GRAPHENE-SURFACE INTERACTIONS

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#### ABSTRACT

Graphene has high mobility of its charge carriers. It is the thinest and strongest material ever found. These extraordinary properties made graphene the most interesting and promising novel material. It has attracted great interest in recent years for various technological applications. For these applications graphene is placed on surfaces such as  $SiO_2$  and SiC. Here, we present theoretical investigations of graphene on SiO<sub>2</sub> surface. Employing geometrical optimization and molecular dynamics simulation method at the atomic level, we studied AFM tip-graphene-surface interactions. Single (or double) layer and layer graphene with the sharp and the blunt tips were considered in our studies. Using the total energy calculations, we show that the interaction between bilayer graphene and  $SiO_2$  surface is stronger than mono-layer graphene and surface. Similarly we show that the interaction between the blunt tip and the surface is stronger than the sharp tip and surface. From energy minimization method, we found that there are periodic waves in graphene when it is placed in SiO<sub>2</sub>. By applying both energy minimization calculations and molecular dynamics simulation we show the structural changes in both monolayer and bilayer graphene in the presence of tip over graphene sheet. We believe these studies provide invaluable insight for graphene nanodevice applications.

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## CHAPTER I

### INTRODUCTION

#### 1.1 Graphene

Graphene is one of the most interesting and promising novel materials in nanotechnology. Recently A.K Geim and K.S. Novoselov used a mechanical technique to peel graphene from graphite [1]. They won Novel prize in physics in 2010 due to this discovery. Graphene is a flat monolayer of carbon atoms packed in a two dimensional honey comb lattice as shown in figure 1.1. Carbon has four valence electrons. Three of them form  $\sigma$  bonds with their nearest neighbors. These are covalent bond and they make graphene as strong as diamond. The forth valence electron is in  $2p_z$  orbital and gives rise to conducting  $\pi$  band. The electron band structure of graphene is as shown in figure 1.2 [2]. It is unique in a way that it has two conical points per Brillouin zone where the band structure crosses. The Fermi level passes through these points those are called Dirac Points and this band structure makes graphene a gapless semiconductor [2].

By adding one more layer on monolayer graphene (MLG) bilayer graphene (BLG) is formed. There are two types of BLGs according to the placement of second layer above the first. If the top layer is mirror reflection of the bottom layer then it



Figure 1.1: Monolayer graphene sheet



Figure 1.2: Band structure of monolayer graphene.

is said to be AA-stacking BLG. If we label one atom of graphene sheet as A-atom and the neighboring atom as B-atom then in AA-staking BLG, all the A and B atoms of the top layer are directly above the atoms in bottom layer. If in the top layer A-atom is located right above B-atom in the bottom layer and B-atom in the top layer is located above a hexagonal hollow site of the bottom layer, as shown is figure 1.3 then the BLG called AB-staking BLG or simply AB-graphene. AB-stacking is found in HOPE graphite. The band structure of BLG is different then MLG's. BLG has gap between valence and conduction bands and it has parabolic dispersion where as the MLG has linear dispersion [2]. Due to its extraordinary electrical and mechanical properties [1-5] graphene has various potential applications. For example high mobility of its charge carriers it can be used in transparent conductor [4] in new electronic devices such as touch screens, thin film photovoltaics etc. Since BLG have significant band gap it can replace the semiconductor devices more effectively. Giving sutible circumstances graphene sheet can be used as field effect transistor down to nanometer sizes [1].

In many application, graphene lies on a surface thus it is important to understand the morphology of graphene on a surface. Many experimental as well theoretical studies have been performed to find the substrate effect and/or the tip effect on MLG and BLG [6–14]. Chao Tang et al. [6] studied the interface morphology of graphene on 6H–SiC(0001) surface. By performing molecular dynamics study, they reported that there is a periodic rippling of MLG on the substrate. The periodicity of the ripple is 12.3 Å. They found that random ripples occur at high temperatures (T = 3000K).



Figure 1.3: AB-stacking bilayer graphene.

T. Filleter et al. studied the friction and dissipation in MLG and BLG films epitaxially grown on SiC [15]. Their results show that the friction on SiC is reduced by MLG and it is further reduced by factor of 2 by BLG. In the experiments they grew MLG and BLG on SiC using thermal deposition. Kelvin probe force microscope was used to identify the thickness of the films. Frictional force microscopy (FFM) mode of atomic force microscopy in ultrahigh vacuum (UHV-AFM) was used to measure the frictional force. Similar results were reported by T. Filleter and R. Bennewitz by using atomic force microscopy. They have also studied the structure of graphene films on SiC substrate and reported that graphene films reveal corrugation with  $6 \times 6$  periodicity of the SiC lattice [7].

Wang et al. [8] presented the Raman studies of MLG and few layer graphene fabricated by mechanical cleavage on different substrates including  $SiO_2$ . They also presented the Raman feature of epitaxial MLG on SiC. In the experiment they transferred the MC MLG on different substrates and epitaxial graphene was grown on SiC. Their results show that the effect of substrate is negligible on the structure of graphene made by MC but Raman feature of epitaxial MLG grown on SiC shows that the interaction between MLG and the substrate is much stronger.

Masa Ishigami et al. [10] reported that graphene corrugates on  $SiO_2$  substrate which is due to the interaction between the graphene and  $SiO_2$  surface. Using combined SEM/AFM/STM technique they showed that graphene partially conforms to the underlying  $SiO_2$  substrate and it is about 60 percentage smoother than  $SiO_2$ surface.

#### 1.2 Atomic Force Microscope (AFM)

AFM is very high resolution type of scaning probe microscopy (SPM) with the resolution order of fraction of nanometer. Bining et al. invented it in 1986. SPM refers to a techinque that use the interaction of the probe (a sharp tip) with a sample surface to measure the characteristics of sample. Thus AFM consist of a tip supported by cantilever. To measure the certain porperty the tip is scaned over the sample surface. The stiffness of cantilever and the distance of samle from the tip determine the force between the tip and surface. In our current study we have study the interaction of tip with surfaces without the cantilever. AFM tip can be shrap or blunt as desired. Figure 1.4 shows the typical sharp tip and blunt tip.



1.4A: 1.4B: Figure 1.4: (A)A sharp tip with a single atom at its apex. (B)A Blunt tip.

## 1.3 Summary of the Thesis

In this research study, we perform theoretical investigations of AFM tip, MLG/BLG and  $SiO_2$  surface interactions. We study the morphology of graphene sheet on the surface and its structure in the presence of sharp and blunt AFM tips.

In second chapter of this thesis we present the model used in this work. The methods such as the energy minimization and molecular dynamics simulation method are also described. In chapter three, we present the results from the total energy calculations of sharp and blunt tips on the bare  $SiO_2$  surface. We also present the total energy calculation results for MLG and BLG on  $SiO_2$  surface. MLG and BLG structures on the surface after energy minimization calculations are also presented in this chapter.

In chapter four, we present our investigations on sharp tip-graphene-surface interactions. The sharp tip is placed over MLG or BLG, which was already placed on the SiO<sub>2</sub> surface. Then the energy minimization calculations are performed while moving the tip towards the surface. In a similar way we performed the molecular dynamics simulation of the structures. In this chapter we also present the variation of the total potential energy and sum of tips-graphene and tips-surface interaction energies as a function of the displacement of tip obtained from molecular dynamics simulation and energy minimization calculations. We discussed the change in structure of graphene in presence of tip. In chapter five, we present the results for blunt tip, graphene and surface combined structures. In final chapter we present our conclusions.

## CHAPTER II

#### THE MODEL AND THE ATOMIC SCALE SIMULATION METHODS

In this chapter present about the model we used in the current work and the simulation methods we adopted.

#### 2.1 Model

In present work the model is developed by using Materials Studio (MS) Visualizer. MS provides various tools to develop the model for different purpose. We used the crystal builder tools most of the time to develop our models.

#### 2.1.1 Sharp tip, Graphene and Surface

A model containing sharp tip (ST), MLG and SiO<sub>2</sub> surface as a substrate and the same model with BLG are constructed. The lattice parameters of graphene are a = 2.46Å, b = 4.26 Å. Using these values the unit cell of graphene and its supercell with the cell dimensions a = 71.32 Å, b = 85.2 Å are created. The lattice parameters of SiO<sub>2</sub> are a = 7.12 Å, b = 7.12 Å, c = 7.12 Å. The unit cells of SiO<sub>2</sub> with these parameters is prepared and its supercell with cell dimensions a = 71.32 Å, b = 85.2Å, c = 7.12 Å is formed matching the cell dimensions exactly with that of graphene. To fit the cell dimensions of graphene and SiO<sub>2</sub> the unit cell dimensions of SiO<sub>2</sub> is changed to a = 7.131 Å, b = 7.1 Å, c = 7.12 Å. Then by using layer builder tool (one of the tool of material studio) a layer of Graphene-SiO<sub>2</sub> having cell dimensions a = 71.32 Å, b = 85.2 Å, c = 13.25 Å is prepared. The MLG is placed above SiO<sub>2</sub> surface at a distance 3.468 Å at which the total energy of the structure is minimum. This structure was then minimized so that it would correspond to minimum total



2.1A:

2.1B:

Figure 2.1: (A)Model of ST-MLG-SiO<sub>2</sub> surface in a cell with cell dimensions a = 71.31 Å, b = 85.2 Å, c = 89.74 Å. (B) Model of ST-BLG-SiO<sub>2</sub> in a cell with cell dimensions a = 71.31 Å, b = 85.2 Å, c = 92.75 Å. The red atoms are fixed and the gray atoms are relaxed.

potential energy structure. The sharp pyramidal tip is formed from silicon (111) surface and is placed above the minimized graphene-SiO<sub>2</sub> layer in a cell with cell dimensions a = 71.31 Å, b = 85.2 Å, c = 89.74 Å. In this model there are 456 silicon atoms in ST, 2320 carbon atoms in MLG and 2902 atoms (960 Oxygen atoms and

1942 Silicon atoms) in the substrate. Thus there are total 5678 atoms present in the model. In the same way anther model containing ST, BLG and SiO<sub>2</sub> surface is formed in a cell with the cell dimensions a = 71.31 Å, b = 85.2 Å, c = 92.75 Å. This structure contains total 7998 atoms (456 Si atoms in tip, 4640 C atoms in double layer graphene sheet and 2902 atoms in the substrate). Periodic boundary condition has been used to simulate infinitely large system. Thus duplicates of the system were generated in all directions. The bottom two layers of atoms of the substrate and upper three layers of atoms of the ST are chosen to be fixed. ST-MLG-surface and ST-BLG-surface models are shown in figures 2.1A and 2.1B, respectively.

#### 2.1.2 Blunt tip, Graphene and Surface

The blunt tip (BT) is constructed by cutting the tip of ST. The models containing BT, MLG and surface and BT, BLG and the surface are constructed exactly in the same way as ST model. The lattice parameters of the cell containing BT, MLG and substrate are chosen to be a = 71.31 Å, b = 85.2 Å, c = 91.98 Å and those for the model containing BT, BLG and the surface are chosen to be a = 71.31 Å, b = 85.2 Å, c = 95.41 Å. In this model the BT contains 684 Si atoms. The number of atoms in MLG, BLG and surface are same as in ST model. Thus the system of BT-MLG-surface contains 5906 atoms and the system of BT-BLG-surface contains 8226 atoms. The upper three layers of atoms of the BT are chosen to be fixed. The BT-MLG-surface and BT-BLG-surface models are shown in figures 2.2A and 2.2B, respectively.





2.2B:

Figure 2.2: (A)Model of BT-MLG-SiO<sub>2</sub> surface in a cell with cell dimensions a = 71.31 Å, b = 85.2 Å, c = 91.98 Å. (B) Model of BT-BLG-SiO<sub>2</sub> in a cell with cell dimensions a = 71.31 Å, b = 85.2 Å, c = 95.41 Å. The red atoms are fixed and the gray atoms are relaxed.

#### 2.2 Methods

We adopted two methods, Geometry Optimization and Molecular Dynamics simulation method, in this work.

#### 2.2.1 Geometry Optimization

In Geometry Optimization atomic coordinates and if desired the cell parameters are adjusted until the total energy of the structure is minimized. Geometry optimization is based on reducing the magnitude of calculated forces and (where appropriate) stresses until they become smaller than defined convergence tolerances. Thus the optimized structure corresponds to a minimum energy surface.

In current work the 'Universal forcefield' has been used. The convergence criteria of energy is  $1 \times 10^{-4}$  kcal/mol, and atomic force cut off is  $5 \times 10^{-3}$  kcal/mol/Å. The calculation of total potential energy of the structures is performed by using the 'Forcite' (a classical molecular mechanics tool) module, one of the modules of Material Studio 4.3. Valecne energy, bond, angle, torson, inversion, non-bond energy ven der Waals energy contribute to the total energy of the structure. Forcite offers number of different algorithms such as Steepest Descent, Conjugate gradient, Quasi-Newton, Adjusted Basis set Newton-Ralphson (ABNR) and Smart for the geometry optimization. In the simulation the smart algorithm which is a cascade of the steepest descent, ABNR, and quasi-Newton methods has been used.

In present work the geometrical optimizations of ST/BT-surface, ST/BT-MLG-surface and ST/BT-BLG-surface structures are performed lowering the tips from 7 Å, 11.4 Å and 15 Å from the surface respectively. These distances are with respect to the top atomic layers of the surface. In all three cases, the tip is moved towards the surface in the increments of 0.1 Å.

#### 2.2.2 Molecular Dynamics

Molecular Dynamics (MD) is one of the atomic computer simulation methods which calculates the static as well as dynamic properties of systems using equations of motion. It provides understanding the properties of assemblies of atoms or molecules in terms of their structure and the microscopic interaction between them. Thus it acts as the bridge between microscopic length and time scale and macroscopic world of laboratory. MD involves the simultaneous numerical solution of the equations of motion which for a simple atomic system of N particles with coordinate  $r_i$ , can be written as [16]:

$$\vec{F}_i = m_i \ddot{\vec{r}_i}, \qquad \vec{F}_i = -\frac{\partial u}{\partial r_i}$$
(2.1)

where  $F_i$  is the force acting on the atoms *i* and  $u(\vec{r})$  is the total potential energy,  $\vec{r} = (\vec{r_1}, \vec{r_2}...\vec{r_N})$  representing the complete set of 3N atomic coordinates. Thus the force acting on the atoms is derived from the total potential energy.

In the simplest case the number of atoms or molecules (N) the total energy,(E) and the volume (V) of the system are kept constant and we have microcanonical (NVE) ensemble. In this case Hamiltonian is given by [16]

$$H = \sum_{i} \frac{p_i^2}{2m_i} + u(\vec{r})$$
 (2.2)

where  $p_i$  are the momenta of the particles.

In practical simulations however it is desirable to investigate a system with the number of particles N, the volume of the system V and the temperature T fixed and we have canonical (NVT) ensemble. In this case the Hamiltonian is modified in such a way that the system should be coupled with a heat bath which introduces the energy fluctuations keeping the temperature constant. In the current work, NVT ensemble has been used for the simulation environment. And we used Varlet Algorithm a time step  $\Delta t = 1 f s$  and the temperature is 4K. The simulations of ST-surface, ST-MLG-surface and ST-BLG-surface is started keeping the tips at 12 Å, 16.4 Å and 20

Å from the surface respectively and that of BT-surface, BT-MLG-surface and BT-BLG-substrate is started keeping the tips at 7 Å, 11.4 Å and 15 Å from the surface respectively. The system is allowed to equilibrate for 30000 steps initially and there are 1000 step between each increment of displacement of tips.

## CHAPTER III

#### MORPHOLOGY OF GRAPHENE ON SUBSTRATE

In this chapter, we present the results of total energy variation of MLG/BLG/ST/BTon SiO<sub>2</sub> surface obtained from total energy calculations and investigate the morphology of graphene on substrate through energy minimizations.

#### 3.1 Tip/Graphene-Surface interactions

In this section we present the result of the total energy variation of MLG, BLG, ST and BT on the SiO<sub>2</sub> surface obtained form the total energy calculations. The total energy calculation of the model containing the MLG/BLG and surface is started keeping MLG/BLG at 12 Å from the surface. In both the cases the graphene sheets are moved towards the surface in increments of 0.1 Å. The results obtained from the total energy calculation are shown in figure 3.2A. In the figure it is seen that the interaction between BLG and surface is stronger then the interaction between MLG and surface. The equilibrium separation between MLG and the surface in 3.4 Å and between BLG and substrate is 3.5 Å. Similarly the total energy calculations of the ST and BT on the surface are performed. In this case, the tips were at 12 Å from the surface and they were moved towards the surface in the increments of 0.1 Å. The results are shown in figure 3.2B. The interaction is stronger in case of BT as there are



Figure 3.1: Variation of total energy of MLG and BLG on substrate with the distance from substrate.



Figure 3.2: Variation of total energy of ST and BT on substrate with the distance from substrate.

more atoms in the tip of BT. The equilibrium separation of BT from the substrate is 3.3 Å and that of ST is 3.6 Å.

#### 3.2 Morphology of Graphene on the Surface

Here we investigate the structures of MLG and BLG on  $SiO_2$  surface after energy minimizations. MLG is placed at a distance 3.4 Å and BLG is placed at a distance 3.5 Å from the substrate. These distances are the equilibrium separations between MLG/BLG and the surface. The energy minimizations are performed up to a maximum 5000 iteration steps. The MLG-substrate system is minimized in 3155 iteration steps and BLG-substrate system is minimized in 3765 iteration steps. Thus the minimum energy configurations of MLG and BLG are obtained. The results show that both MLG and BLG on  $SiO_2$  surface are not perfectly flat but exhibit a wavy structure. Moreover, we found that the wave have regular periodicity of 21.3 Å along y-direction as shown in the figures 3.3 and 3.4. The lattice parameters of unit cell of SiO<sub>2</sub> surface are a = 7.131 Å, b = 7.1 Å, c = 7.12 Å i.e along y-direction the lattice constant of unit cell of  $SiO_2$  is b = 7.1 Å which is exactly 3 times the periodicity of ripples in the graphene sheets. The length of C-C covalent bond in graphene is 1.42 Å and hence 15 honeycombs of graphene are in a wave and 5 honeycomb are in between Si-Si interatomic distance  $SiO_2$  surface. This shows that the corrugations in MLG and BLG are due to the lattice coincidence of graphene and  $SiO_2$  surface.



Figure 3.3: Wavy structure of MLG on  $SiO_2$  surface.



Figure 3.4: Wavy structure of BLG on  $SiO_2$  surface.

## CHAPTER IV

### SHARP TIP-GRAHENE-SURFACE INTERACTIONS

Here, we present our investigations on the ST-MLG/BLG-  $SiO_2$  surface interactions. The structures obtained from energy minimizations and MD simulations are also presented.

4.1 Energy Minimizations of Sharp Tip-Graphene-Surface System

The energy minimization calculations of ST-surface and ST-MLG/BLG-surface system has been performed. In ST-surface, ST-MLG-surface and ST-BLG-surface systems the calculations are started keeping the tip at 7 Å, 11.4 Å and 15 Å from the substrate respectively. In all three cases the tip is moved towards  $SiO_2$  surface in the increment of 0.1 Å. The bottom two layers of the atoms of the surface and upper three layers of atoms of tip are chosen to be fixed. The total potential energy and sum of tip-graphene and tip-surface interaction energy are plotted as a function of displacement of tip in z direction [figure 4.1 and 4.2]. The tip-graphene/tip-surface interaction energy is calculated by

$$E_{interaction} = E_{total} - (E_{tip} + E_{graphene/surface})$$
(4.1)

where  $E_{total}$  is the total energy of the system including interactions,  $E_{tip}$  is the energy of the bare tip and  $E_{graphene/surface}$  is the energy of graphene/surface. Sample calculations of tip-graphene and tip-substrate interactions in the case of ST-BLG-surface system are shown in table 4.1. In the table  $\Delta z$  is the displacement of tip along z direction,  $E_{total}^{\dagger}$  and  $E_{total}^{\ddagger}$  are the total energy of tip-graphene and tip-surface system including the interactions and  $E_{interaction}^{\dagger}$  and  $E_{interaction}^{\ddagger}$  are the total energy of tip-graphene and tip-surface and tip-surface interactions and  $E_{interaction}^{\dagger}$  are the total energy of total potential energy [figure 4.1]

Table 4.1: Tip-graphene and tip-substrate interaction energy calculation.

$\Delta z$ (Å)	15	11.3	6	4
$E_{tip}(kcal/mol)$	-924.14	-925.56	-893.43	-719.02
$E_{graphene}(kcal/mol)$	4713.62	4135.57	4208.97	4258.33
$E_{surface}(kcal/mol)$	-1015.52	-1051.62	-1010.65	-949.84
$E_{tip} + E_{graphene}(kcal/mol)$	3757.86	3180.41	3267.16	3506.61
$E_{tip} + E_{surface}(kcal/mol)$	-1937.16	-1973.21	-1902.07	-1801.02
$E_{total}^{\dagger}(kcal/mol)$	3789.48	3210.01	3315.53	-1667.95
$E_{total}^{\ddagger}(kcal/mol)$	-1939.66	-1977.19	-1904.09	-1668.86
$E_{interaction}^{\dagger}(kcal/mol)$	-31.62	-29.59	-48.37	-32.70
$E_{interaction}^{\ddagger}(kcal/mol)$	2.5	3.98	2.01	0.91
$E_{interaction}^{\dagger} + E_{interaction}^{\ddagger} (k cal/mol)$	-29.11	-25.61	-46.36	-31.79

shows that the equilibrium separation of tip from the surface in ST-surface system is



Figure 4.1: Energy minimization results of variation of total potential energy of STsurface, ST-MLG-surface and ST-BLG-surface systems with the displacement of tip along z direction when the tip is pointing the crest of BLG.

1.9 Å, in ST-MLG-surface system it is 5.2 Å and in ST-BLG-surface system it is 8.5 Å. The equilibrium separation is increasing in ST-MLG-surface and ST-BLG-surface system because of the presence of MLG and BLG between the tip and the surface. The interaction energy plot [figure 4.2] shows that the equilibrium separation in ST-surface system, ST-MLG-surface and ST-BLG-surface system are 1 Å, 4 Å and 6 Å respectively.

The morphology of ST-MLG-surface system at different position of the tip (obtained from energy minimizations) are shown in figure 4.5. When the tip is placed above the graphene and the structure is minimized, the wavy nature of graphene on SiO<sub>2</sub> surface is destroyed. Side surface facets of the tip attracts the part of graphene



Figure 4.2: Energy minimization results of variation of sum of tip-graphene and tipsurface interaction energy with the displacement of tip along z direction when the tip is pointing the crest of BLG.

sheet creating humps approximately around the tip as shown in figure 4.5A. As the tip is moved nearer to the sheet the humps get closer narrowing down the flat area below the tip and covering the tip and hence decreasing the total potential energy of the system. When the tip crosses the equilibrium separation (5.2 Å), bottom of tip still attracts the sheet but the top starts to repel the graphene sheet resulting with a concave surface right below it [figures 4.5E and 4.5F]. Because of this total potential energy is increased.

In ST-BLG-surface system, when the tip is placed above the crest of the wavy graphene, the tip attracts the graphene sheet creating a peak right below the apex of it [figure 4.6A]. As the tip is moved towards the graphene sheet, the apex of the



Figure 4.3: Energy minimization results of variation of total potential energy of ST-surface, ST-MLG-surface and ST-BLG-surface system with the displacement of tip in z direction when the tip is pointing the trough in BLG.

tip pushes the peak created earlier and hence the diminishes the height of the peak as it can be seen in figures 4.6B and 4.6C. Side-surface facets of the tip attracts the far ends of the graphene sheet thus graphene covers the tip. At certain position of the tip ( $\Delta z = 11.3$  Å in this case) self bending of graphene sheet occurs and the far end of it cover the tip. This causes the sudden drop of total potential energy [figure 4.1] and increase in the sum of tip-graphene and tip-surface interaction energy [figure 4.2]. As the tip is further moved towards the graphene sheet, the small hump created in a valley of the sheets is also repelled causing further decrease in the total potential energy and creating a flat surface below the tip [figure 4.6E]. When the tip crosses the equilibrium separation ( $\Delta z = 8.5$  Å in this case) the far bottom of the tip still



Figure 4.4: Energy minimization results of variation of sum of tip-graphene and tip-surface interaction energy in ST-surface, ST-MLG-surface and ST-BLG-surface system with the displacement of tip in z direction when the tip is pointing the trough in BLG.









4.5F:

Figure 4.5: Snapshots from energy minimization of ST-MLG-SiO<sub>2</sub> surface when the tip is at position (A) $\Delta z = 11.4$  Å (B) $\Delta z = 9.4$  Å (C) $\Delta z = 7.8$  Å (D) $\Delta z = 5.2$  Å(E) $\Delta z = 3.4$  Å (F) $\Delta z = 1.4$  Å

attracts the far end of the graphene sheet but the apex of the tip strongly repels it and creates the concave surface [figure 4.6F] as in case of MLG that causes increase in total potential energy.

Comparing the structures of MLG and BLG after the placement of the tip above them and after energy minimizations, we found that the BLG bends more then the MLG and cover the tip. This is because the BLG is stiffer then the MLG. The small hump in the valley of BLG is due to one of the edge of pyramidal tip facing it. If the tip is conical in stead of pyramidal we would expect the valley without the hump in it.

In the ST-BLG-surface system, if ST is place in such a way that its apex pointing at the trough of the wavy graphene at one side of the structure, it attracts the graphene sheet and make a peak as shown in figure 4.6A. As the tip is moved towards the graphene sheet it repels the hump near its apex. Since the graphene sheets in this case could not cover the tip all around, the equilibrium energy is increased compared to MLG and BLG when the tip is pointing the crest of graphene sheet. There is no big shape change of graphene sheets at this time, thus there is no abrupt change in the total potential energy [figure 4.3]. In this case the equilibrium separation is 8.8 Å from the total potential energy plot and it is 7 Å from the interaction energy plot [figure 4.4] The equilibrium separations when the tip is pointing the crest of BLG were 8.5 Å and 6 Å [figure 4.1 and 4.2].

#### 4.2 MD study of Sharp Tip-Graphene-Surface System

In this section, we present the total potential energy and tip-graphene and tip-surface interaction energies of ST-MLG/BLG-surface system obtained from the MD simulations of the system. we also discuss the ST and MLG/BLG morphology on SiO<sub>2</sub> surface resulted from MD simulations. We started the simulation of ST-surface, ST-MLG-surface and ST-BLG-surface systems putting the tip above the graphene. The separations of the tip were 12 Å, 16.4 Å and 20 Å with respect to  $SiO_2$  surface. In all three cases the tip is moved towards the surface in the increment of 0.1 Å as in energy minimization. The total potential energy and the sum of tip-graphene and tip-surface interaction energy of all three systems obtained from the MD simulation are plotted as a function of displacement of the tip [figure 4.8, 4.9]. The equilibrium separation of tip from the surface in this case from the total potential energy is 2 Å, 5.7 Å and 8.9 Å in ST-surface, ST-MLG-surface and ST-BLG-surface systems respectively. And those from interaction energy plot are 1.5 Å, 4.4 Å and 8 Å. The total potential energy curve for both MLG and BLG obtained from this method are not as smoother as those obtained from energy minimization method. In this case there are more fluctuations in MLG/BLG systems due to temperature. The structures of ST-MLG-surface and ST-BLG-surface systems at different position of tip are shown in figure 4.10 and 4.11. Form the figures it is clear that due to its flexibility MLG is not covering the tip where as BLG is covering the tip. Therefore the energy at the equilibrium position in BLG system is less then that in MLG system. As in the energy minimization simulations the equilibrium position in ST-surface, ST-MLGsurface and ST-BLG-surface systems are increasing due to the presence of MLG and BLG between the tip and surface. In both MLG and BLG systems, when the tip cross the energy equilibrium point, the apex of the tip repels the atoms in graphene sheets right below it and produces a concave surface [figure 4.10D and 4.11D]. This increases the total potential energy and the interaction energy.



4.6A:

4.6B:



4.6C:







4.6F:

Figure 4.6: Snapshots from energy minimization of ST-BLG-SiO<sub>2</sub> surface system when the tip is pointing the crest of MLG and is a at position  $(A)\Delta z = 15$  Å  $(B)\Delta z = 13$  Å  $(C)\Delta z = 11.4$  Å  $(D)\Delta z = 11.3$  Å  $(E)\Delta z = 8.5$  Å  $(F)\Delta z = 5$  Å









Figure 4.7: Snapshots from energy minimization of ST-BLG-SiO<sub>2</sub> surface system when the tip is pointing trough of BLG and at a position  $(A)\Delta z = 15$  Å  $(B)\Delta z = 11$  Å  $(C)\Delta z = 8.8$  Å  $(D)\Delta z = 5$  Å



Figure 4.8: MD results of variation of total potential energy of ST-surface, ST-MLGsurface and ST-BLG-surface systems with the displacement of tip along z direction.



Figure 4.9: MD results of variation of sum of tip-graphene and tip-surface interaction energy with the displacement of tip along z direction when the tip is pointing the crest of BLG.









Figure 4.10: Snapshots from MD simulation of ST-MLG-SiO<sub>2</sub> surface system when the tip at a position (A) $\Delta z = 16.4$  Å (B) $\Delta z = 8.4$  Å (C) $\Delta z = 5.7$  Å (D) $\Delta z = 2$  Å











4.11D:

Figure 4.11: Snapshots from MD simulation of ST-BLG-SiO<sub>2</sub> surface system when the tip at a position (A) $\Delta z = 20$  Å (B) $\Delta z = 15.4$  Å (C) $\Delta z = 8.9$  Å (D) $\Delta z = 6.3$  Å

## CHAPTER V

### BLUNT TIP-GRAHENE-SURFACE INTERACTION

In chapter 4 we presented our investigations on the ST-MLG/BLG-surface interactions through energy minimization and MD simulation methods. In this chapter we present the BT-MLG/BLG-surface interactions through the same two methods.

5.1 Energy Minimization of Blunt Tip-Graphene-Surface System

We performed the energy minimization of BT-surface, BT-MLG-surface and BT-BLG-surface systems in the same way as the ST systems. In this section we present the results obtained from that method. The total potential energy and the sum of tip-surface and tip-graphene interaction energy obtained from this method are shown as a function of displacement of tip in figures 5.1 and 5.2. The equilibrium separations of the tip from the surface are 2 Å, 5.4 Å and 8.7 Å in BT-surface, BT-MLG-surface and BT-BLG-surface systems respectively. Different from the ST systems, the minimum energy positions obtained from total potential energy and interaction energy are the same in this case. As in the ST case, the total potential energy as well as the interaction energy at the point of equilibrium separation decrease in BT-surface, BT-MLG-surface and BT-BLG-surface systems. The resion for this is in the first system there are just BT and surface and hence there is a weak interaction



Figure 5.1: The energy minimization result of variation of total potential energy of BT-surface, BT-MLG-surface and BT-BLG-surface systems with the displacement of tip along z direction.



Figure 5.2: The energy minimization result of variation of sum of tip-graphene and tip-surface interaction energy of BT-surface, BT-MLG-surface and BT-BLG-surface systems with the displacement of tip along z direction.

between them. In MLG system, some of the facets of pyramidal BT is attracting the MLG but since the MLG is more flaxiable then BLG it is not covering the tip all around where as in BLG system, BLG is stiffer and it covers the tip approximately all around and the atoms in the tip and in the graphene sheet remain in such a way that there is minimum potential energy at the equilibrium position of tip. Therefore the BT-MLG-surface system has higher minimum energy than the BT-BLG-surface system.

The structure of MLG changes as the position of the tip changes as it can be seen in figure 5.3. When the BT is far away from the surface (11.4 Å) the apex of the tip attracts graphene sheet and creats a peak of graphene below it. If the tip is moved towards the surface, the peak of MLG is repelled. Due to the attraction of the top of the tip, the far ends of the sheet come closer to the tip [figure 5.3B] and reduce the total potential energy. At equilibrium separation the apex of the tip repels the hill completely on one side and makes flat surface below it [figure 5.3C]. The top of the tip still attracts some part of sheet giving the minimum total potential energy and the interaction energy. And as in ST case, when the tip crosses the equilibrium separation the atoms at the top part of the tip starts to repel the atoms below it giving rise to a concave surface on that part of the graphene sheet.

#### 5.2 MD Simulation of Blunt Tip-Graphene-Surface System

In this section we present the results obtained from MD simulation of BT-MLG/BLGsurface system. We discuss the variation of total potential energy and interaction



5.3A:





5.3C: 5.3D: Figure 5.3: Snapshots from energy minimization of BT-MLG-SiO<sub>2</sub> surface when the tip is at position (A) $\Delta z = 11.4$  Å (B) $\Delta z = 8.4$  Å(C) $\Delta z = 5.4$  Å (D) $\Delta z = 1.4$  Å

energy pattern and changes in the structure of the systems. The total potential energy and sum of tip-graphene and tip-surface interaction energy are plotted as a function of displacement of tip [figure 5.5 and 5.6]. The equilibrium separations of the tip from surface are 1.9 Å, 5.4 Å and 8.9 Å in BT-surface, BT-MLG-surface and BT-BLG-surface systems respectively. These results are very close to those obtained from energy minimizations. The equilibrium separation values from the interaction energy curves are 1 Å, 5.4 Å and 8.9 Å. In the minimum energy calculations all



5.4A:



5.4D:





Figure 5.4: Snapshots from energy minimization of BT-BLG-SiO<sub>2</sub> surface when the tip is at position (A) $\Delta z = 15$  Å (B) $\Delta z = 12$  Å(C) $\Delta z = 8.7$  Å (D) $\Delta z = 2$  Å

three values were equal but in this case tip-surface interaction energy is minimum when the apex of the tip is at 1 Å from the surface. However in BT-MLG-surface system and BT-BLG-surface system the positions of the tip are same from both minimum potential energy and interaction energy curves. The structures of graphene sheet/sheets were similar to those in energy minimization calculations



Figure 5.5: The MD simulation results of variation of total potential energy of BT-surface, BT-MLG-surface and BT-BLG-surface systems with the displacement of tip along z direction.



Figure 5.6: The MD simulation results of variation of sum of tip-graphene and tipsurface interaction energy of BT-surface, BT-MLG-surface and BT-BLG-surface systems with the displacement of tip along z direction.



5.7A:







5.7D:

Figure 5.7: Snapshots from MD simulation of BT-MLG-SiO<sub>2</sub> surface when the tip is at position (A) $\Delta z = 11.4$  Å (B) $\Delta z = 8.4$  Å(C) $\Delta z = 5.4$  Å (D) $\Delta z = 1.4$  Å



40





5.8D:

Figure 5.8: Snapshots from MD simulation of BT-BLG-SiO<sub>2</sub> surface when the tip is at position (A) $\Delta z = 15$  Å (B) $\Delta z = 13$  Å(C) $\Delta z = 8.9$  Å (D) $\Delta z = 5$  Å

## CHAPTER VI

#### CONCLUSION

In this research work we investigated  $ST/BT-MLG/BLG-SiO_2$  surface interaction through the total energy calculations, energy minimization and MD simulation methods. From total energy calculations we studied the  $ST/BT/MLG/BLG-SiO_2$  surface interaction and we were able to show the BLG (or BT)-surface interaction is stronger than MLG (or ST). Employing the energy minimization we studied the morphology of MLG/BLG on SiO<sub>2</sub> surface and found that graphene exhibit wavy structure when placed on the surface. The wave have regular periodicity of 21.3 Å along y-direction. We show that the rippling in graphene is due to the lattice matching between graphene and underlaying surface.

The variation of total potential energy and the sum of tip-graphene and tipsurface interaction energy of ST/BT-MLG/BLG-surface systems were studied with the displacement of tip above the graphene sheet placed on SiO<sub>2</sub> surface using both energy minimization calculations and MD simulation methods. We show that the position of minimum total potential energy or the equilibrium separation of the tip from the surface is increasing in ST/BT-surface, ST/BT-MLG-surface and ST/BT-BLG-surface due to the presence of graphene sheet between the tip and the surface. We found that the minimum energy positions of the BT from the total energy curve and interaction energy curve are same in all three cases (BT-surface, BT-MLG-surface and BT-BLG-surface). But those values in ST systems are different. The equilibrium separation from the interaction curve is always less than that from total potential energy curve. We suspect in case of BT systems the region of graphene sheet below the tip is always flat but in ST system there is more deformations of graphene sheet. Due to the more deformations in graphene sheet more interactions has taken place and hence the minimum energy positions decreases in this case.

We also investigated the interactions of the ST with BLG on the surface placing the tip at different point of wavy BLG by energy minimization method. We were able to show that when the ST is pointing at the crest of wavy BLG around it center, at certain position of tip, graphene suddenly bends to cover the tip and hence the total potential energy abruptly decreases. But if the tip is placed in one side of graphene pointing the trough of wavy BLG it does not get chance to cover the tip all around. Hence the equilibrium separation of tip from the surface increases and become more than that of ST-MLG-surface system.

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