Molecular dynamics simulation of graphene formation on 6H–SiC substrate via simulated annealing

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Single layer graphene formation

How we construct the unit cell and supercell for 6H-SiC substrate

- We refer to
- http://cst-www.nrl.navy.mil/lattice/struk/6h.html to construct our 6H-SiC substrate.

The snapshots from the above webpage

- Prototype: CSi
- Pearson Symbol: hP12
- Space Group: $P6_3mc$ (Cartesian and lattice coordinate listings available)
- Number: 186
- Reference: Villars and Calvert, *Pearson's Handbook* Vol. II, p. 2006.
- Primitive Vectors:

$$\mathbf{A}_1 = \tfrac{1}{2}\,a\,\mathbf{X} - \tfrac{1}{2}\,3^{1/2}\,a\,\mathbf{Y}$$
$$\mathbf{A}_2 = \tfrac{1}{2}\,a\,\mathbf{X} + \tfrac{1}{2}\,3^{1/2}\,a\,\mathbf{Y}$$
$$\mathbf{A}_3 = c\,\mathbf{Z}$$

- Basis Vectors:

$\mathbf{B}_1$	=		0		(Si-I)	(2a)
$\mathbf{B}_2$	=	$\tfrac{1}{2}\,\mathbf{A}_3$	=	$\tfrac{1}{2}\,c\,\mathbf{Z}$	(Si-I)	(2a)
$\mathbf{B}_3$	=	$z_1\,\mathbf{A}_3$	=	$z_1\,c\,\mathbf{Z}$	(C-I)	(2a)
$\mathbf{B}_4$	=	$(\tfrac{1}{2} + z_1)\,\mathbf{A}_3$	=	$(\tfrac{1}{2} + z_1)\,c\,\mathbf{Z}$	(C-I)	(2a)
$\mathbf{B}_5$	=	$1/3\,\mathbf{A}_1 + 2/3\,\mathbf{A}_2 + z_2\,\mathbf{A}_3$	=	$\tfrac{1}{2}\,a\,\mathbf{X} + 12^{-1/2}\,a\,\mathbf{Y} + z_2\,c\,\mathbf{Z}$	(Si-II)	(2b)
$\mathbf{B}_6$	=	$2/3\,\mathbf{A}_1 + 1/3\,\mathbf{A}_2 + (\tfrac{1}{2} + z_2)\,\mathbf{A}_3$	=	$\tfrac{1}{2}\,a\,\mathbf{X} - 12^{-1/2}\,a\,\mathbf{Y} + (\tfrac{1}{2} + z_2)\,c\,\mathbf{Z}$	(Si-II)	(2b)
$\mathbf{B}_7$	=	$1/3\,\mathbf{A}_1 + 2/3\,\mathbf{A}_2 + z_3\,\mathbf{A}_3$	=	$\tfrac{1}{2}\,a\,\mathbf{X} + 12^{-1/2}\,a\,\mathbf{Y} + z_3\,c\,\mathbf{Z}$	(C-II)	(2b)
$\mathbf{B}_8$	=	$2/3\,\mathbf{A}_1 + 1/3\,\mathbf{A}_2 + (\tfrac{1}{2} + z_3)\,\mathbf{A}_3$	=	$\tfrac{1}{2}\,a\,\mathbf{X} - 12^{-1/2}\,a\,\mathbf{Y} + (\tfrac{1}{2} + z_3)\,c\,\mathbf{Z}$	(C-II)	(2b)
$\mathbf{B}_9$	=	$1/3\,\mathbf{A}_1 + 2/3\,\mathbf{A}_2 + z_4\,\mathbf{A}_3$	=	$\tfrac{1}{2}\,a\,\mathbf{X} + 12^{-1/2}\,a\,\mathbf{Y} + z_4\,c\,\mathbf{Z}$	(Si-III)	(2b)
$\mathbf{B}_{10}$	=	$2/3\,\mathbf{A}_1 + 1/3\,\mathbf{A}_2 + (\tfrac{1}{2} + z_4)\,\mathbf{A}_3$	=	$\tfrac{1}{2}\,a\,\mathbf{X} - 12^{-1/2}\,a\,\mathbf{Y} + (\tfrac{1}{2} + z_4)\,c\,\mathbf{Z}$	(Si-III)	(2b)
$\mathbf{B}_{11}$	=	$1/3\,\mathbf{A}_1 + 2/3\,\mathbf{A}_2 + z_5\,\mathbf{A}_3$	=	$\tfrac{1}{2}\,a\,\mathbf{X} + 12^{-1/2}\,a\,\mathbf{Y} + z_5\,c\,\mathbf{Z}$	(C-III)	(2b)
$\mathbf{B}_{12}$	=	$2/3\,\mathbf{A}_1 + 1/3\,\mathbf{A}_2 + (\tfrac{1}{2} + z_5)\,\mathbf{A}_3$	=	$\tfrac{1}{2}\,a\,\mathbf{X} - 12^{-1/2}\,a\,\mathbf{Y} + (\tfrac{1}{2} + z_5)\,c\,\mathbf{Z}$	(C-III)	(2b)

Figure 1: Snapshot from http://cst-www.nrl.navy.mil/lattice/struk/6h.html. The 6H-SiC belongs to the hexagonal class. For crystal in such a class, the lattice parameters and the angles between these lattice parameters are such that $a = b \neq c$; $\alpha = \beta = 90$ degree, $\gamma = 120$ degree.

Figure 2: Snapshot from http://cst-www.nrl.navy.mil/lattice/struk.xmol/6h.pos

```
Primitive vectors
a(1) =   1.54035000 -2.66796446   .00000000
a(2) =   1.54035000  2.66796446   .00000000
a(3) =    .00000000   .00000000 15.11740000


Volume = 124.25290558


Reciprocal vectors
b(1) =    .32460155  -.18740879   .00000000
b(2) =    .32460155   .18740879  -.00000000
b(3) =   -.00000000   .00000000   .06614894


Basis Vectors:
Atom    Lattice Coordinates                Cartesian Coordinates

C     .00000000   .00000000   .12540000      .00000000   .00000000  1.89572196
C     .00000000   .00000000   .62540000      .00000000   .00000000  9.45442196
W     .00000000   .00000000   .00000000      .00000000   .00000000   .00000000
W     .00000000   .00000000   .50000000      .00000000   .00000000  7.55870000
C     .33333333   .66666667   .79190000     1.54035000   .88932149 11.97146906
C     .66666667   .33333333   .29190000     1.54035000  -.88932149  4.41276906
C     .33333333   .66666667   .45840000     1.54035000   .88932149  6.92981616
C     .66666667   .33333333  -.04160000     1.54035000  -.88932149  -.62888384
W     .33333333   .66666667   .66670000     1.54035000   .88932149 10.07877058
W     .66666667   .33333333   .16670000     1.54035000  -.88932149  2.52007058
W     .33333333   .66666667   .33320000     1.54035000   .88932149  5.03711768
W     .66666667   .33333333  -.16680000     1.54035000  -.88932149 -2.52158232
```

Structure of the unit cell

- Each unit cell of the 6H-SiC has a total of 12 basis atoms, 6 of them carbon, and 6 silicon.
- Figure 2 display:
- (1) The coordinates of these atoms (listed in the last 12 rows in Figure 2). We note that only the Cartesian coordinates are to be used when preparing the input data for LAMMPS.
- (2) Primitive vectors *a*(1), *a*(2), a(3) in the {**X**, **Y**, **Z**} basis (i.e. Cartesian coordinate system).

Procedure to construct our rhombus-shaped 6H-SiC substrate

- First, we determine the lattice constants, *a* , *b* (= *a*), *c* :
- From Figure 2, the primitive vectors, *a*(1), *a*(2), *a*(3) are given respectively (in unit of nanometer) as
- *a*(1) = (1.54035000, -2.66796446, 0 .00000000)
- *a*(2) = (1.54035000, 2.66796446, 0.00000000)
- *a*(3) = (.00000000, .00000000, 15.11740000).
- Squaring *a*(1) and adding it to *a*(2) squared, we could easily obtain the value for the lattice parameter *a*, which is also equal to *b* by definition of the crystallographic group.

Lattice parameters

$$a(1)^2 + a(2)^2 = \left(\frac{1}{2}a\mathbf{X} - \frac{1}{2}3^{1/2}a\mathbf{Y}\right)^2 + \left(\frac{1}{2}a\mathbf{X} + \frac{1}{2}3^{1/2}a\mathbf{Y}\right)^2$$

$$2\left[(1.54035000)^2 + (2.66796446)^2\right] = 2\left(\frac{1}{4}a^2 + \frac{3}{4}a^2\right)$$

$$a^2 = (1.54035000)^2 + (2.66796446)^2$$

$$a = 3.08$$

$$a(3)^2 = (c\mathbf{Z})^2$$

$$15.11740000^2 = c^2$$

$$c = 15.11$$

$$b = a$$

- The lattice constants, after the above calculation, are *a* = 3.08 nm, *b*=3.08 nm, *c* = 15.11 nm.
- Since the 6H-SiC belongs to a hexagonal class, α = β = 90 degree, γ = 120 degree.

Translation of lattice parameters into LAMMPS-readable unit

- We refer to the instruction manual from the LAMMPS website in order to feed in the information of the lattice parameters into LAMMPS:
- http://lammps.sandia.gov/doc/Section_howto.html#howto_12, section 6.12, Triclinic (non-orthogonal) simulation boxes
- In LAMMPS, the units used are {lx, ly, lz; xy, xz, yz}. We need to convert {*a*, *b*, *c*; α, β, γ} into these units. This could be done quite trivially, via the conversion show in the right:

$$
\begin{aligned}
\mathrm{lx} &= a \\
\mathrm{xy} &= b\cos\gamma \\
\mathrm{xz} &= c\cos\beta \\
\mathrm{ly}^2 &= b^2 - \mathrm{xy}^2 \\
\mathrm{yz} &= \frac{b * c\cos\alpha - \mathrm{xy} * \mathrm{xz}}{\mathrm{ly}} \\
\mathrm{lz}^2 &= c^2 - \mathrm{xz}^2 - \mathrm{yz}^2
\end{aligned}
$$

Raw unit cell of 6H-SiC

- Based on the procedures described in previous slides, we constructed a LAMMPS data file for a raw 6H-SiC unit cell.
- It represents a unit cell of 6H-SiC comprises of six hexagonal layers repeating periodically in the *z*-direction.
- The resultant data file, named dataraw.xyz, is shown in Figure 4, to be viewed using xcrysdens or VMD.

Raw unit cell of 6H-SiC

- Each hexagonal layer consists of two sublayers, where each of these sublayers is comprised of either Carbon or Silicon.
- These sublayers are indicated in Figure 4.
- Note that the topmost atom is a Carbon. This means the (0001) surface of the 6H-SiC is Carbon terminated.
- The coordinates of these atoms are also shown in Figure 4.

Figure 4

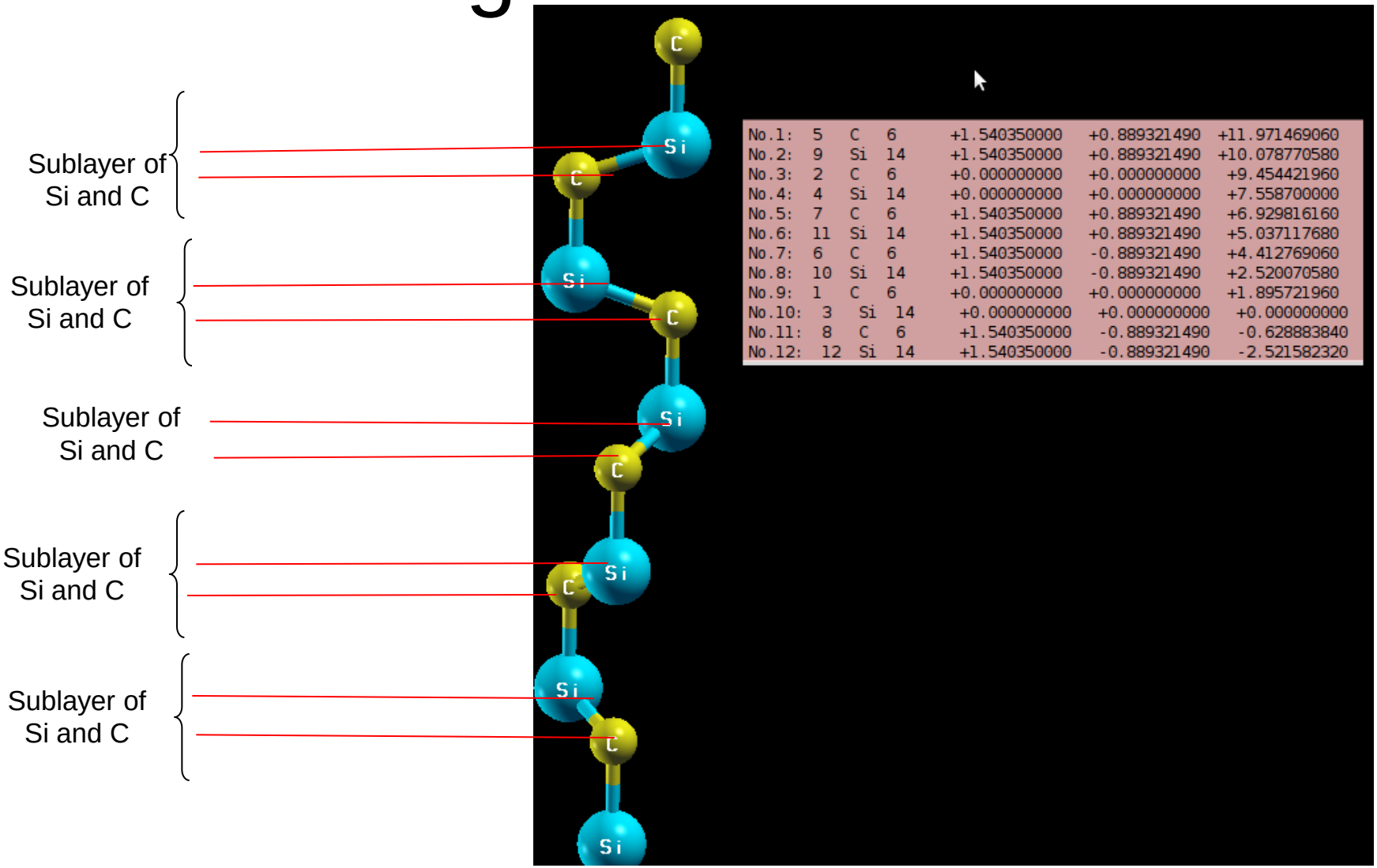


Figure 4: Visualization of the unit cell's atomic configuration as specified in data.raw. The coordinates of the atoms are also shown.

Modification for carbon-rich layer

- Next, we shall modify data.raw.xyz via the following procedure:
- The Si atom (No. 9) is removed. The atom C (No. 5) is now translated along the *z*–direction to take up the z-coordinate left vacant by the removed Si atom (while the *x*- and *y*-coordinate remains unchanged).

Content of data.singlelayer.xyz

```
Masses

1 12.0107

2 28.0855

3 12.0107

4 28.0855

 Atoms

1 1 0.00000000   0.00000000   1.89572196

2 3 0.00000000   0.00000000   9.45442196

3 2 0.00000000   0.00000000   0.00000000

4 4 0.00000000   0.00000000   7.55870000

5 3 1.54035000   0.88932149   10.07877058

6 1 1.54035000  -0.88932149   4.41276906

7 1 1.54035000   0.88932149   6.92981616

8 1 1.54035000  -0.88932149  -0.62888384

10 2 1.54035000  -0.88932149   2.52007058

11 2 1.54035000   0.88932149   5.03711768

12 2 1.54035000  -0.88932149  -2.52158232
```

- The content of data.raw is now modified and renamed as data.singlelayer.xyz, which content is shown in Figure 5, and visualised in Figure 6.

Figure 5: The content of data.singlelayer.xyz, detailing the coordinates of the atoms in a carbon-rich SiC substrate unit cell. Note that now only 11 atoms remain as one Si atom (atom 5).

Figure 6: carbon-rich unit cell of SiC

11 atoms per unit cell left as one Si atom (No. 9) has been removed.

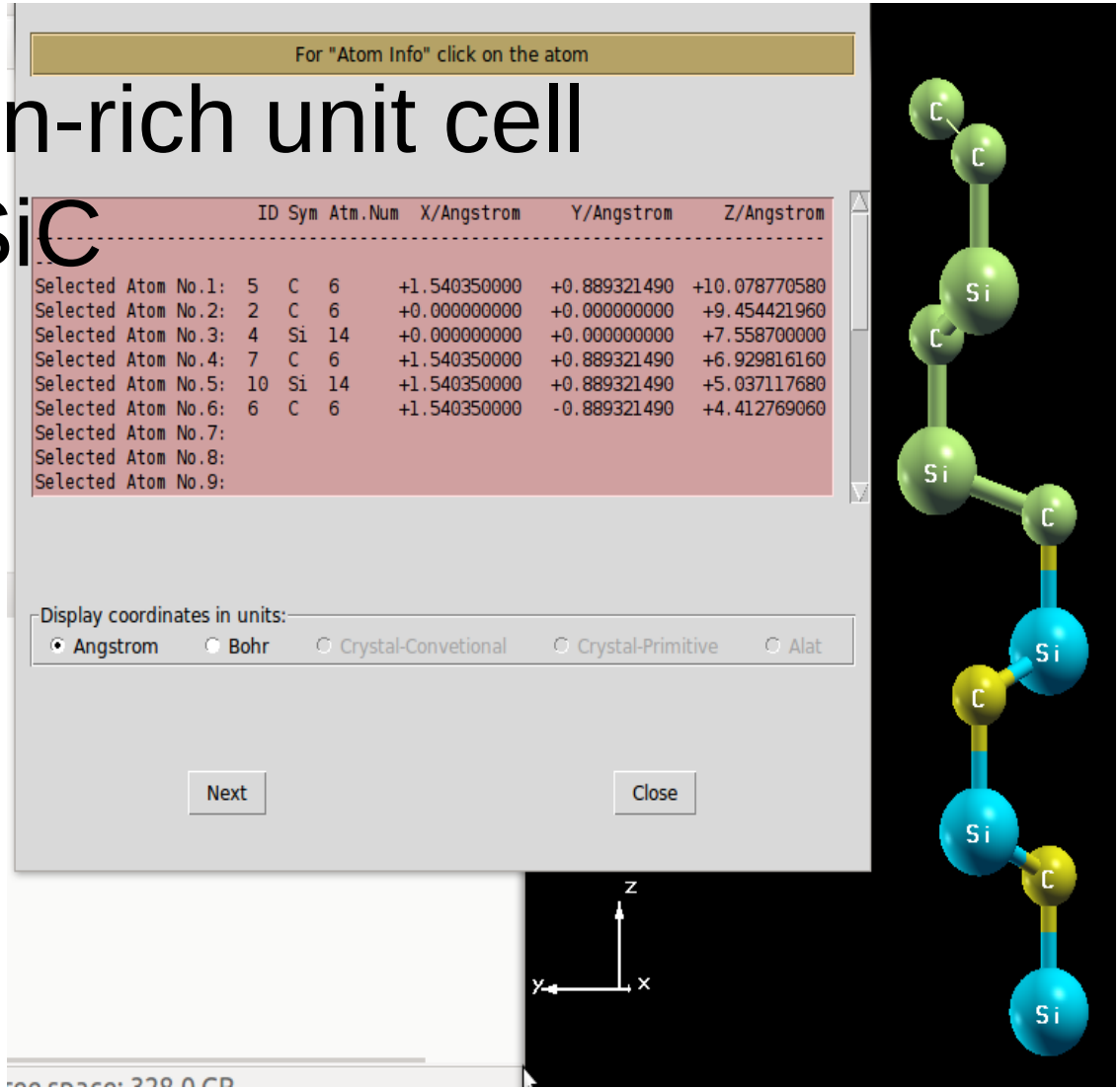


Figure 6. : Visualization of the unit cell's atomic configuration as specified in data.singlelayer.xyz. This is the carbon-rich substrate to be used for single layer graphene growth.

Generating supercell

- We then generated a supercell comprised of 12 x 12 x 1 unit cells as specified in data.singlelayer.xyz.
- This is accomplished by using the command
- replicate 12 12 1
- See the input script in.anneal (line 14 and line 15).

Periodic BC

- Periodic boundary condition is applied along the *x*-, *y*- and *z*-directions via the command (in line 8, in.anneal):
  - boundary p p p
- We created a vacuum of thickness 10 nm (along the *z*-direction) above and below the substrate.
- The 12 x 12 x 1 supercell constructed according to the above procedure is visialised in Figure 7.

Figure 7 (a)

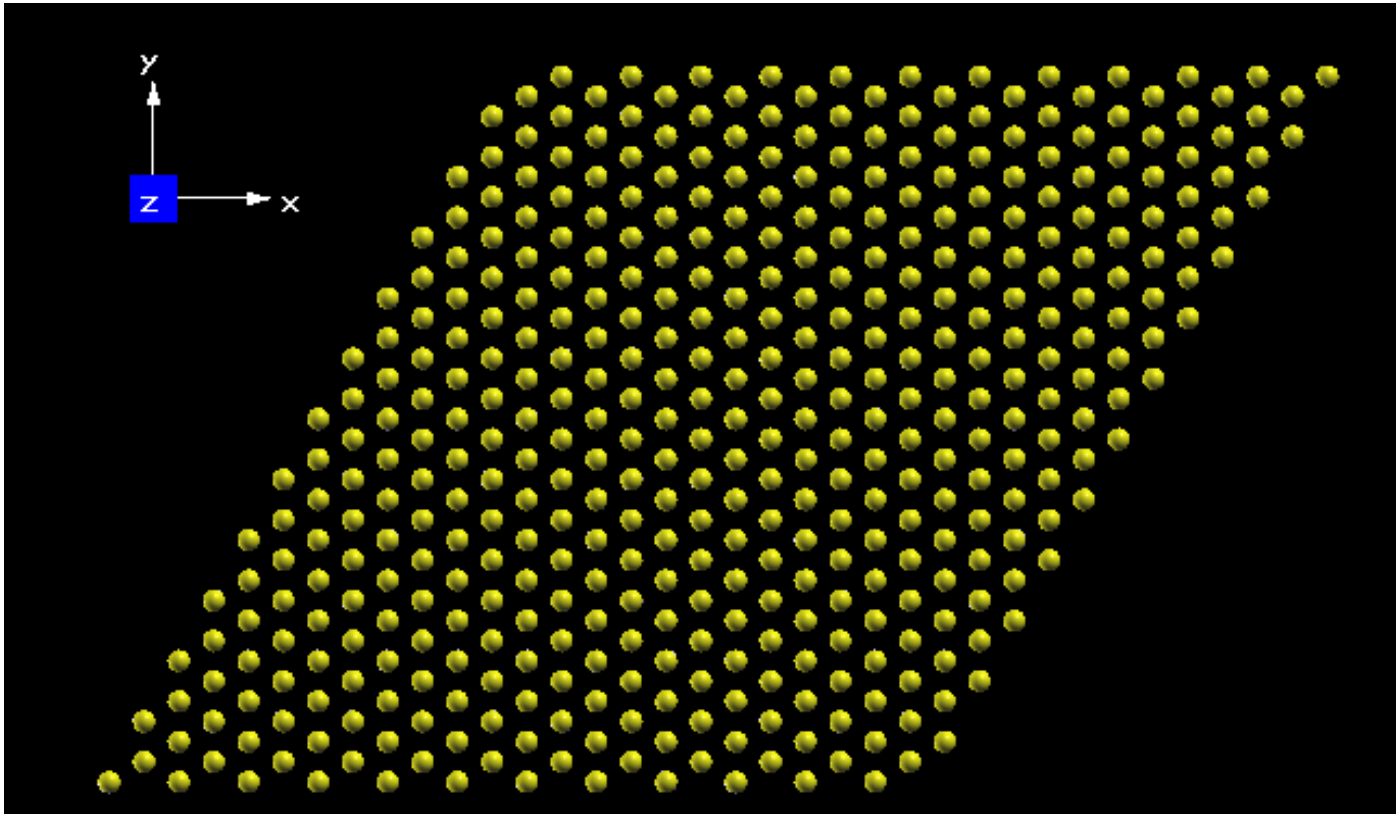


Figure 7: A 1584-atom supercell mimicking a carbon-rich SiC substrate. It is made up of 12 x 12 x 1 unit cells as depicted in Figure 6. 7(a) Top view, 7(b) side view and 7(c) a tilted perspective are presented. Yellow: Carbon; Blue: Silicon.

Figure 7 (b)

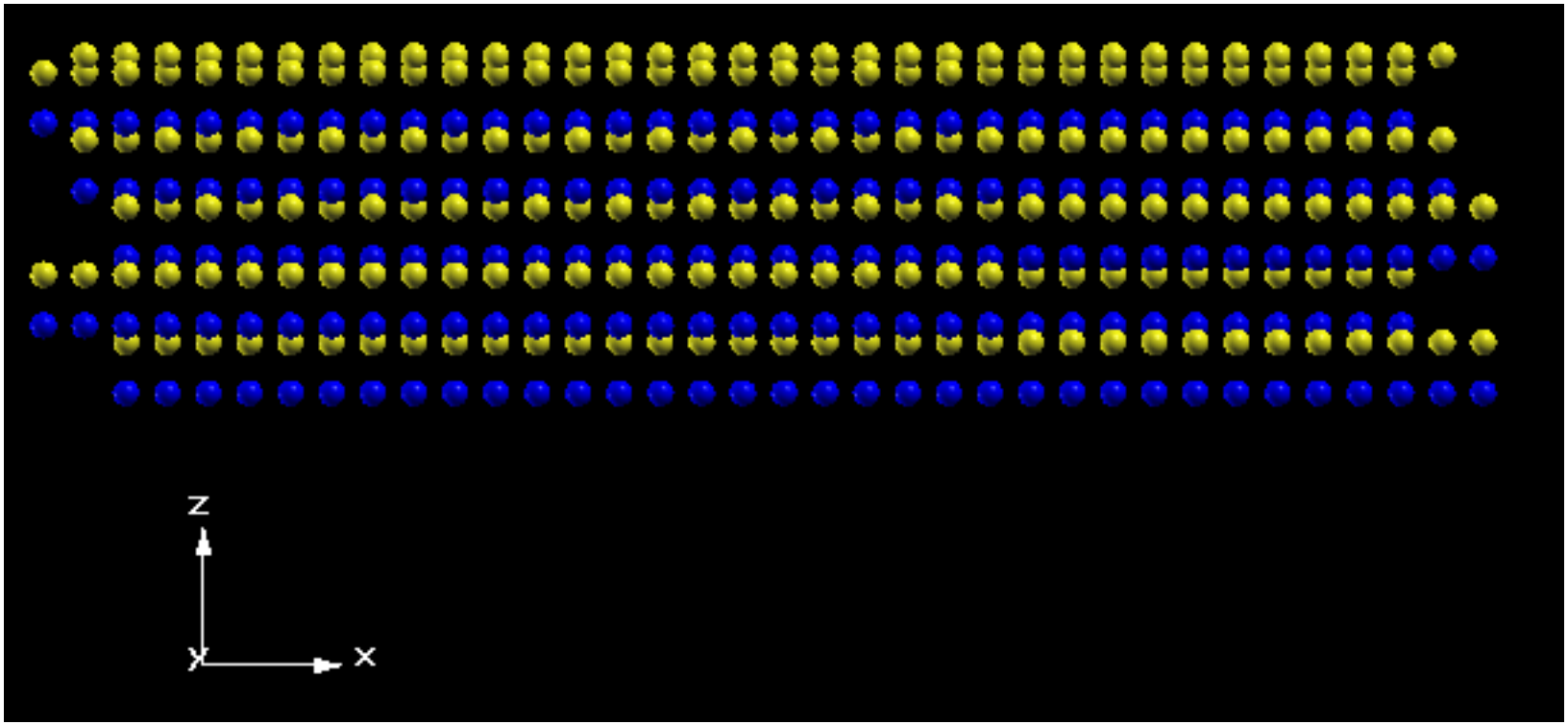
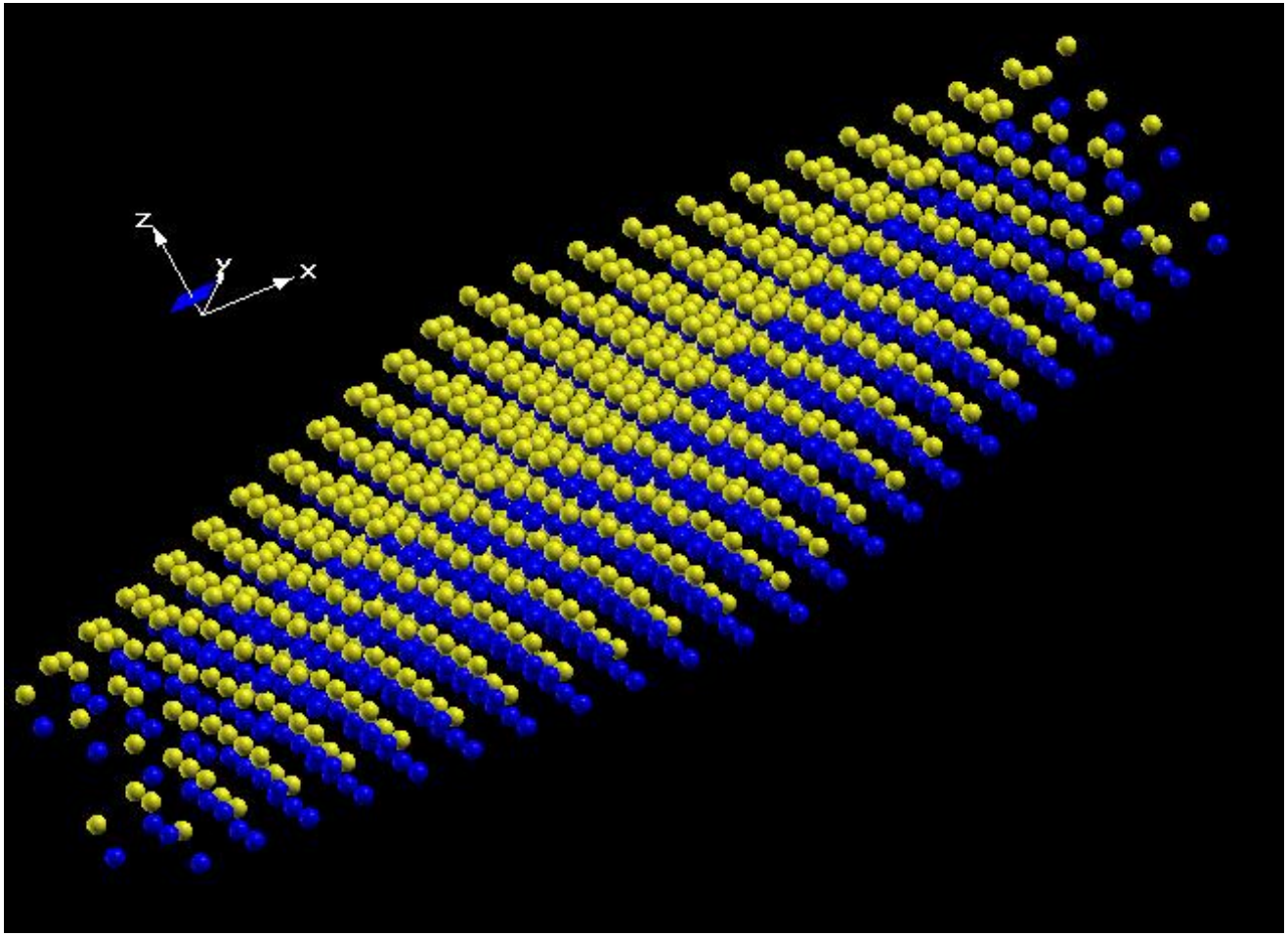


Figure 7 (c)



Visualisation of the 12 x 12 x 1 supercell

- There is a total of 1584 atoms in the simulation box.
- Coordinates of all the atoms in the supercell can be obtained from LAMMPS's trajectory file during the annealing process.
- These coordinates are simply the atomic coordinates of the first step output during the MD run.
- View the structure file 10101.xyz using VMD.
- Such a Carbon-rich substrate will be used as out input structure to LAMMPS to simulate epitaxial graphene growth.

Annealing procedure

- **Once the data file for the Carbon-rich SiC substrate is prepared, we proceed to the next step to growth a single layer graphene via the process described in Figure 8 below.**

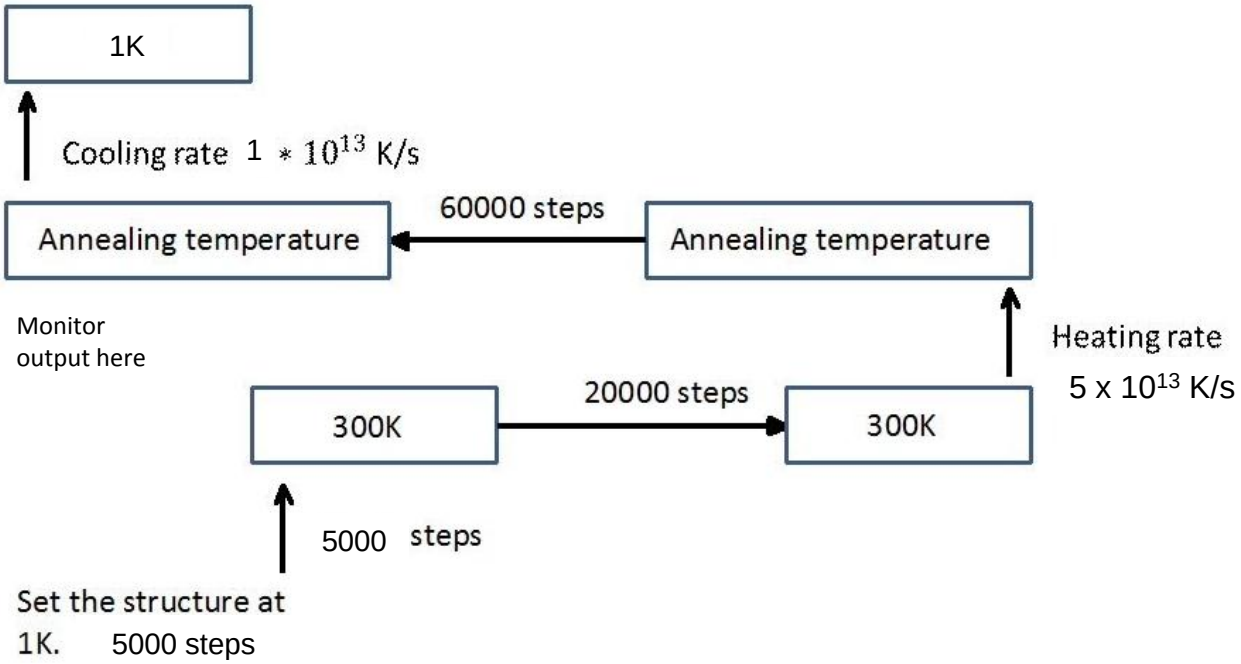


Figure 8. Annealing procedure based on suggestion by Prof. S.K. Lai.

Implementation

- To implement the above procedure, a fixed value of target annealing temperature was first chosen, e.g. Tanneal = 900 K.
- For this fixed taret Tanneal, we ran the LAMMPS input script (in.anneal) to monitor the LAMMPS output while the system undergoes equilibration at the target annealing temperature (after the temperature has been ramped up gradually from 1 K).

Figure 9
Temperature profile

- A typical temperature profile that specifies how the temperature of the system being simulated changes as a function of step is illustrated (for Tanneal = 1200 K).

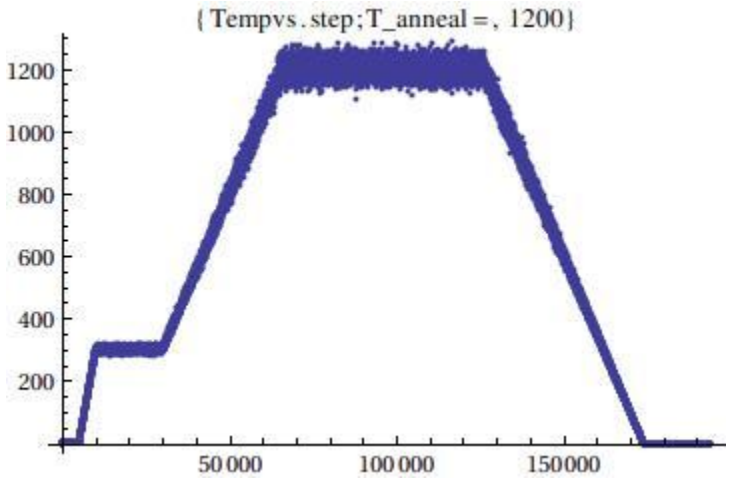


Figure 9

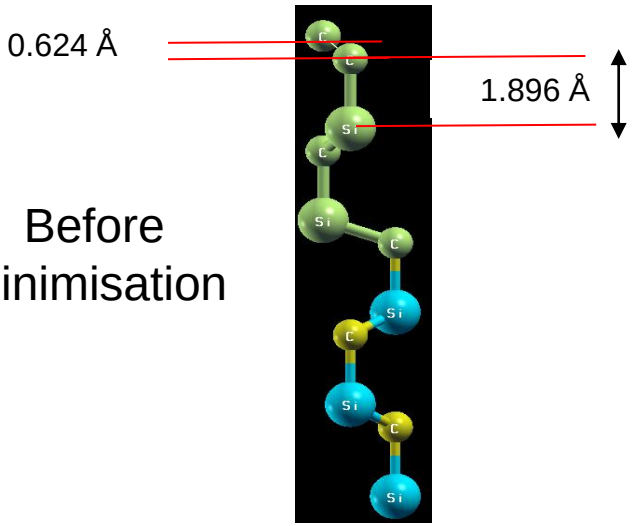
Implementation (cont.)

- Should graphene is formed at the target annealing temperature, we shall observe the following phenomena during equilibrium (at that annealing temperature):
- (i) An abrupt formation of hexagonal rings by the carbon rich layer (visualize the lammps trajectory file using VMD in video mode),
- (ii) an abrupt drop of biding energy,
- (iii) an abrupt change of pressure.
- In actual running of the LAMMPS calculation, we repeat the above procedure for a set of selected target annealing temperature one-by-one, Tanneal = 400 K, 500K, 1100K, 1200 K …, 2000 K.

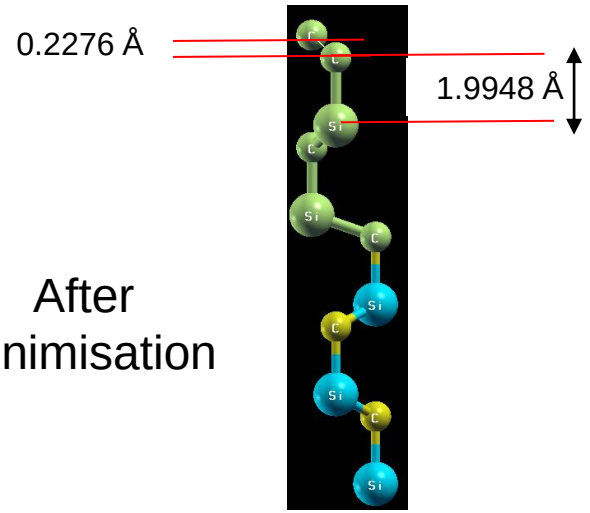
Numerical parameters

- The essential parameters used in annealing the substrate for single layered graphene growth:
- 1. damping coefficient: 0.005
- 2. Timestep: 0.5 fs.
- 3. Heating rate from 300 K -> target temperatures, 5 x 10^{13} K/s.
- 4. Cooling rate: From target temperatures -> 1 K, 1 x 10^{13} K/s.
- 5. Target temperatures: 700 K, 800 K, …, 2000 K.
- 6. Steps for equilibration: (i) At 1K, 5000 steps. (ii) At 300 K, 20,000 steps, (iii) target annealing temp -> target annealing temp, 60,000 steps.
- Essentially, all the parameters used are the same as that used by the NCU group.

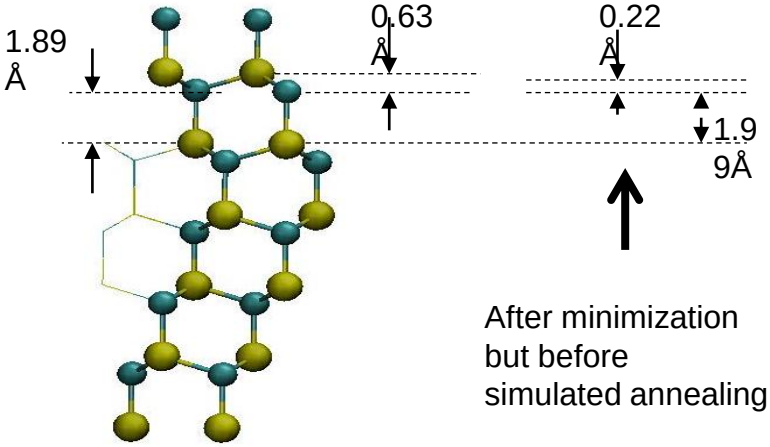
Configuration of the carbon-rich substrate before and after equilibration at T = 1.0 K for single-layered graphene formation



Before minimisation



After minimisation



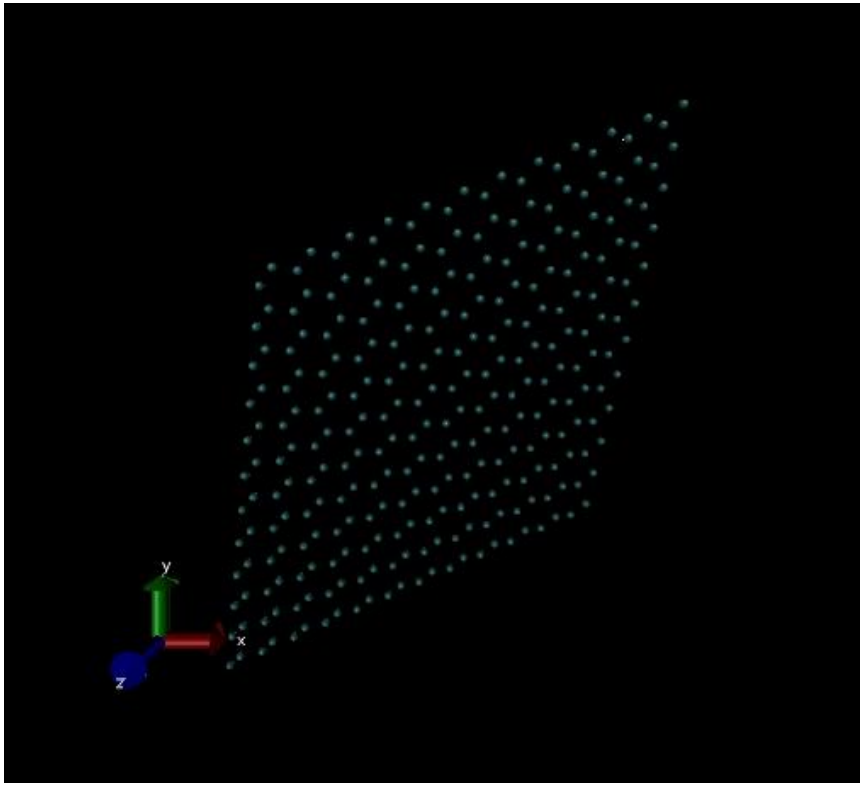
After minimization but before simulated annealing

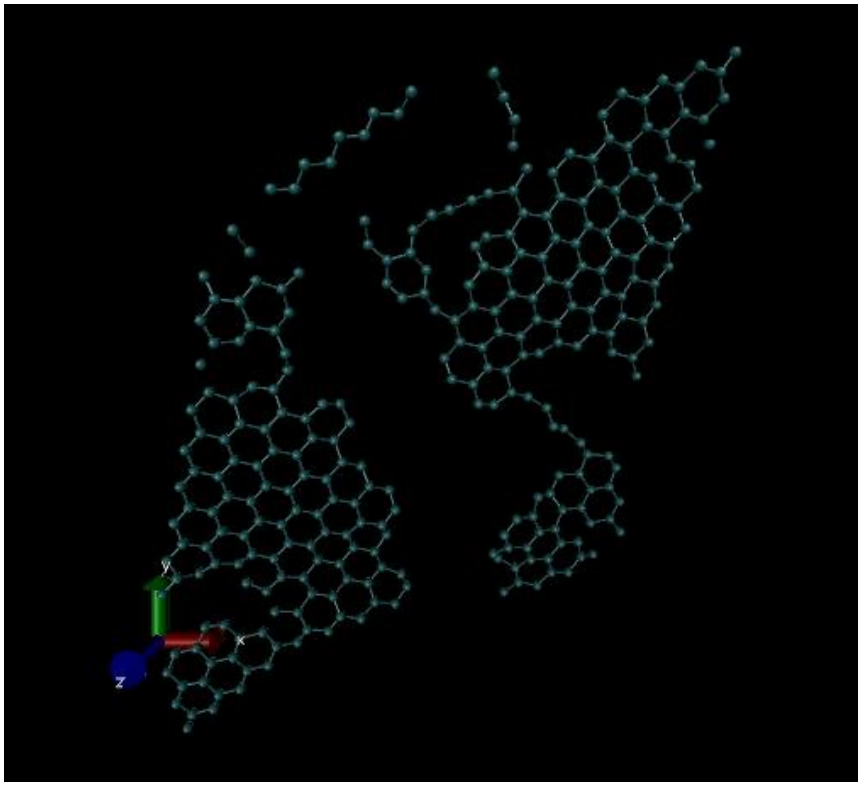
As comparison, this figure shows the geometry obtained by the NTCU group before and after minimisation

Trajectory output

- Trajectory output of the LAMMPS run with TEA force filed for all Tanneal can be found in the directory /data/single/TEA.
- For example, dynamic formation of single-layered graphene on the SiC substrate for Tanneal = 1200 K can be viewed using VMD on the file 700_dynamicbonding_graphene.vmd (use the option File -> Load Visualizatioin State). This is a processed trajectory file in which dynamic bonding is enabled, and only the graphene layer is displayed (without substrate).
- The original LAMMPS trajectory file 1200.lammpstrj can be found in the same directory.

Graphene before and after formation at Tanneal = 1200 K





Data and results for single layer graphene formation

- The output for all Tannealing = {700K, 800K, …, 2000 K} are displayed in Figures 10 for both TEA force fields.
- In these graphs the following quantities are included:
- (i) Temperature vs. step (tempvsstep.dat)
- (ii) Binding energy versus step during equilibration at target annealing temperature (bindingenergyvsstep.dat).
- (iii) Average nearest neighbour of the topmost carbon atoms versus step during equilibration at target annealing temperature (avenn_vs_step.dat).
- (iv) Average distance between the topmost carbon atoms and the Si atom lying just below these carbon atoms vs step (distance34vsstep.dat). This distance represents the “thickness” between the graphene and the substrate just below it (see next slide)
- All these data are to be found in the directory /data/single.

Definition of d34 for single layer graphene formation

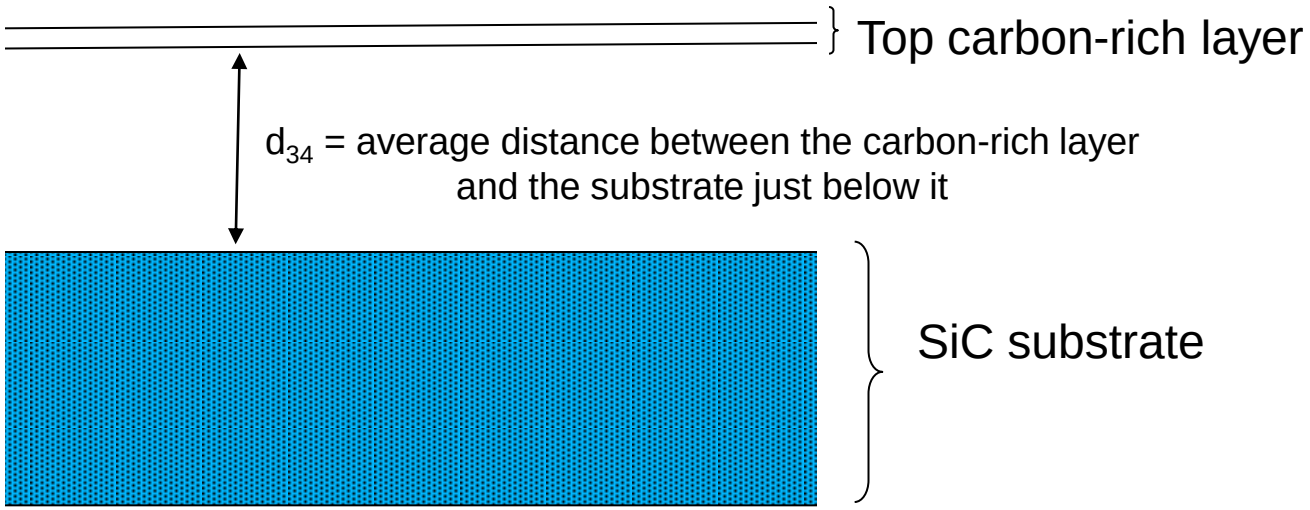
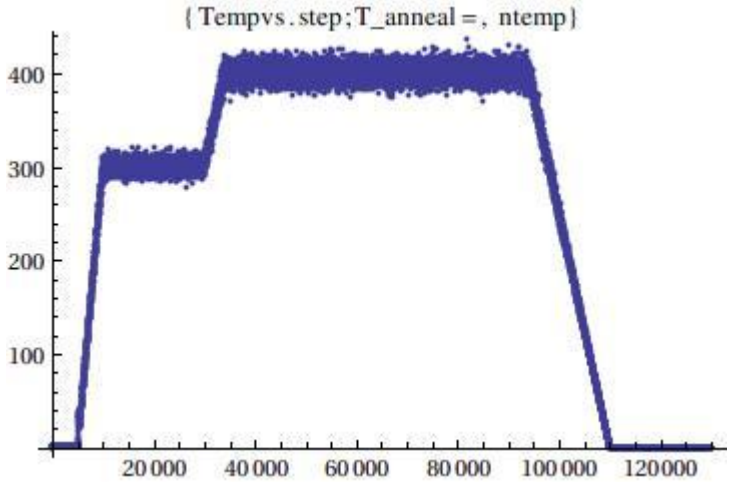
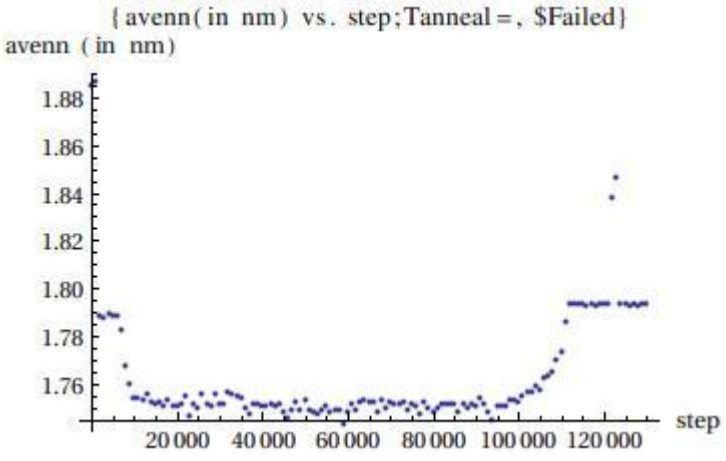
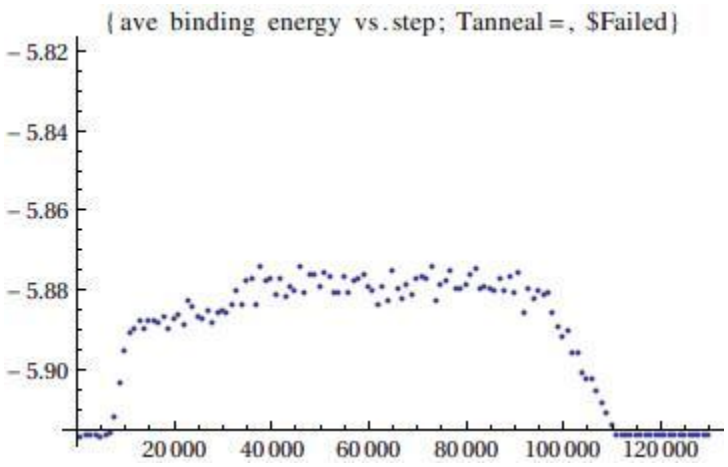


Figure 10(i): Tanneal = 400 K.







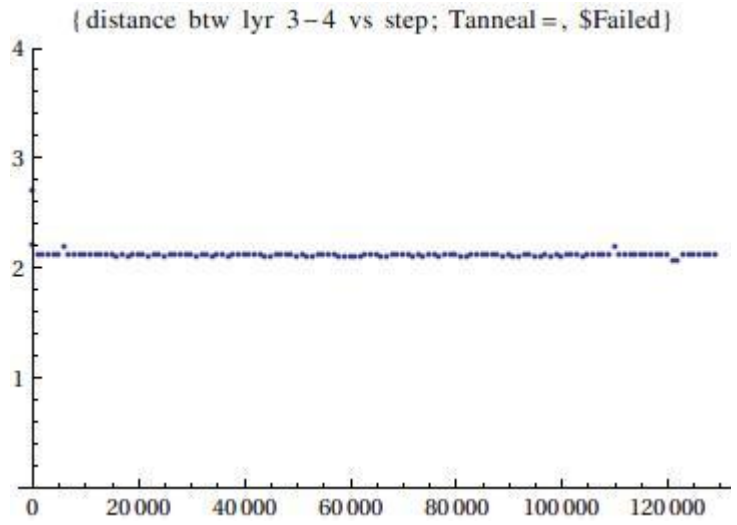
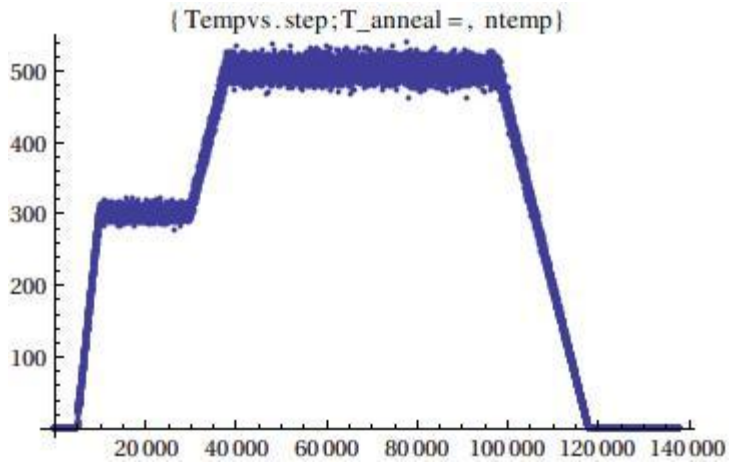
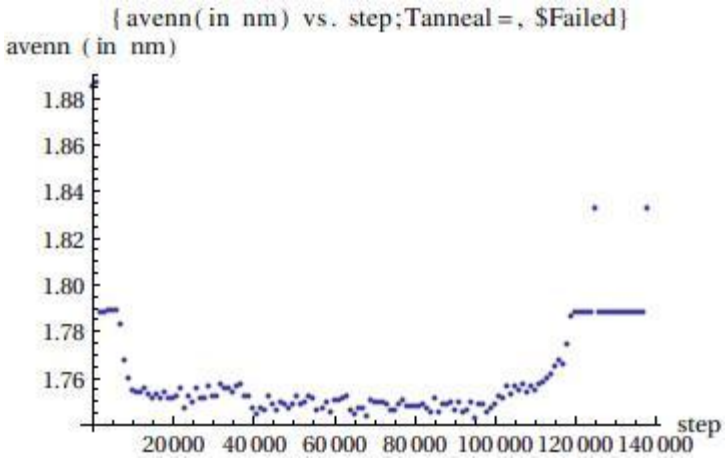
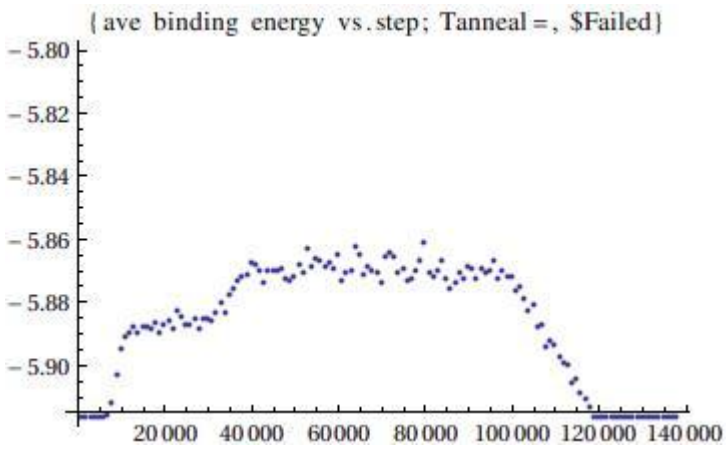


Figure 10(ii): Tanneal = 500 K.







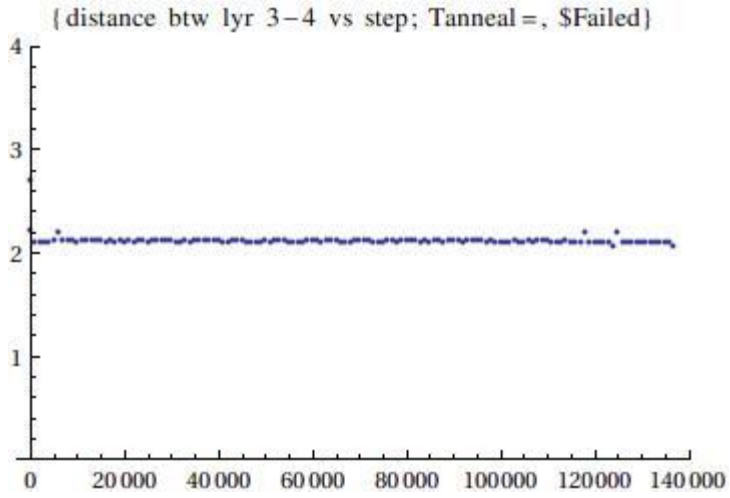
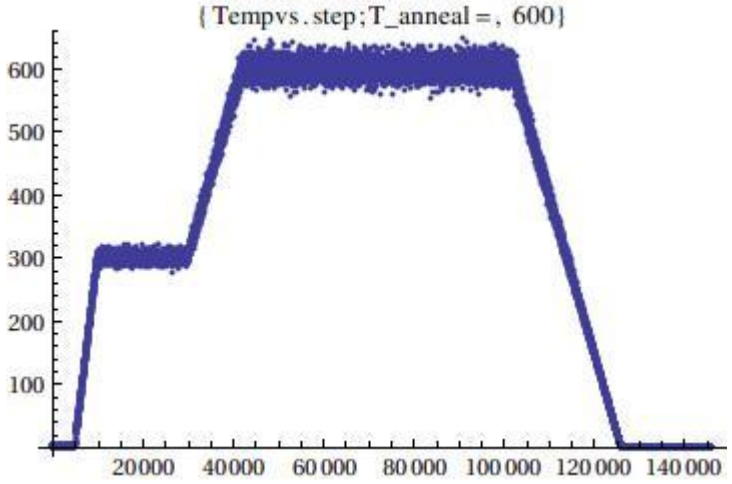
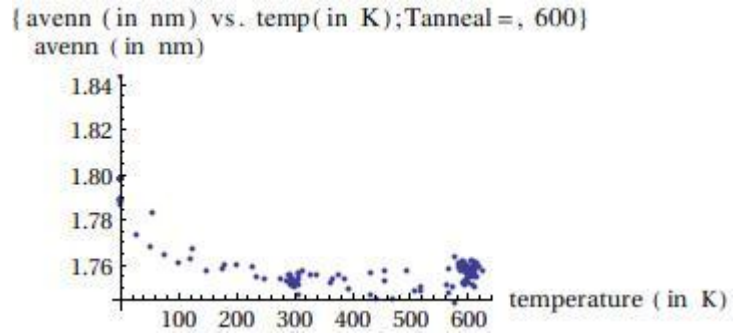
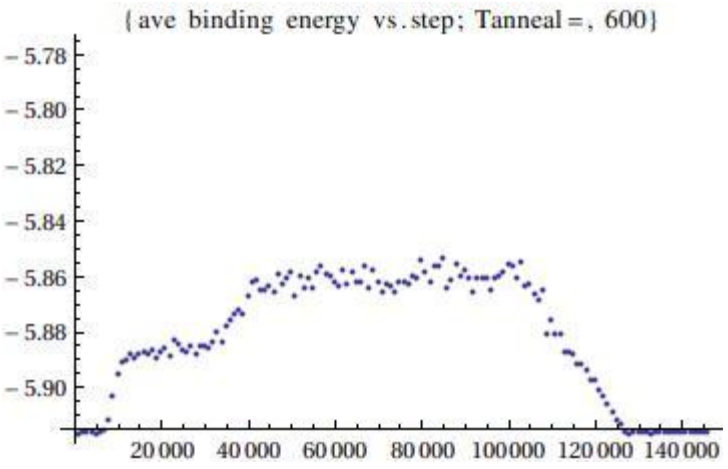


Figure 10(iii): Tanneal = 600 K.







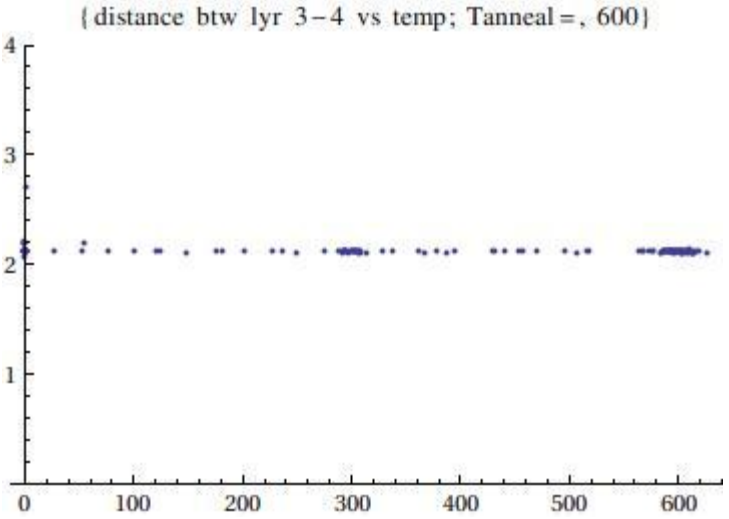
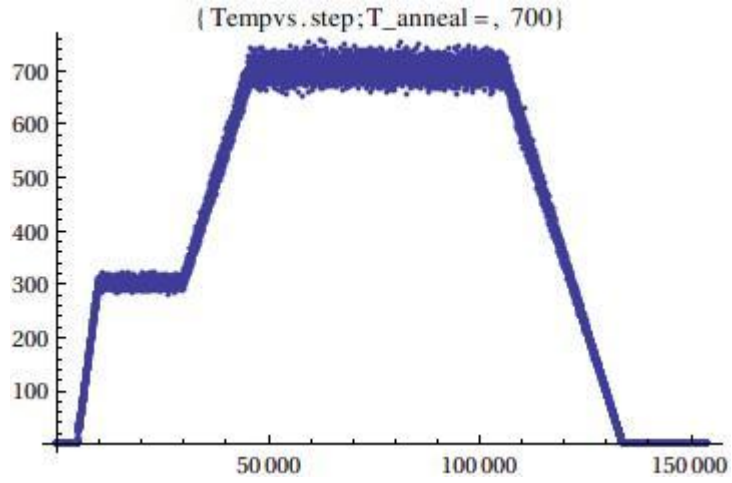
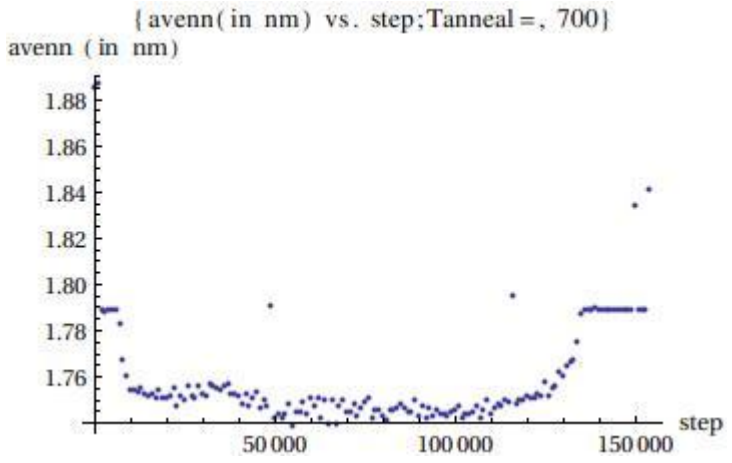
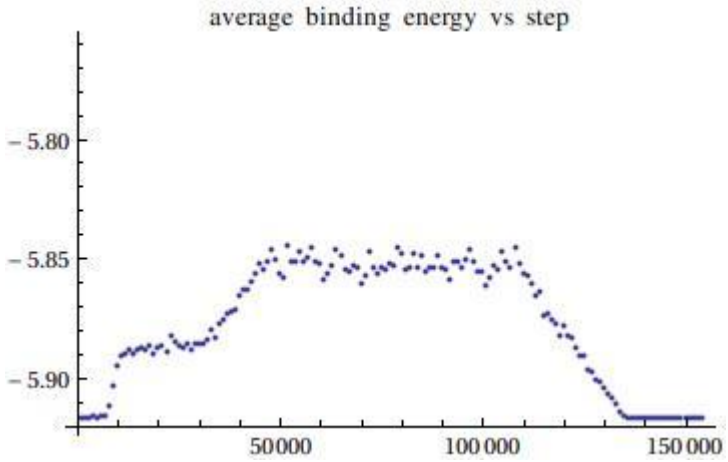


Figure 10(iv): Tanneal = 700 K.







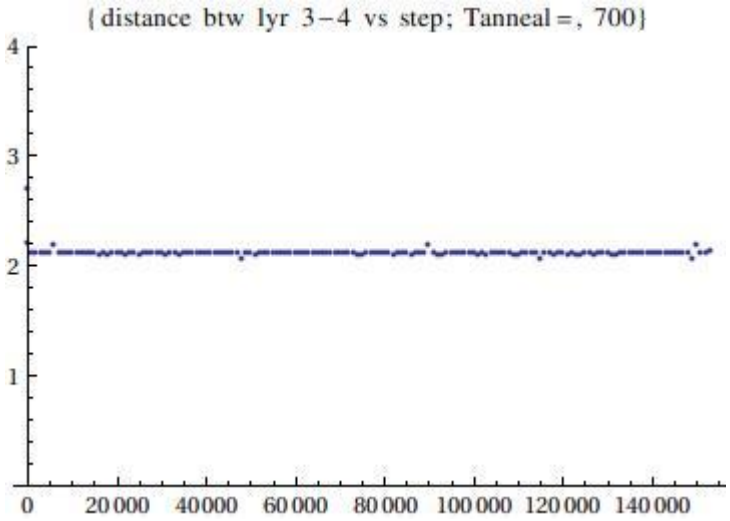
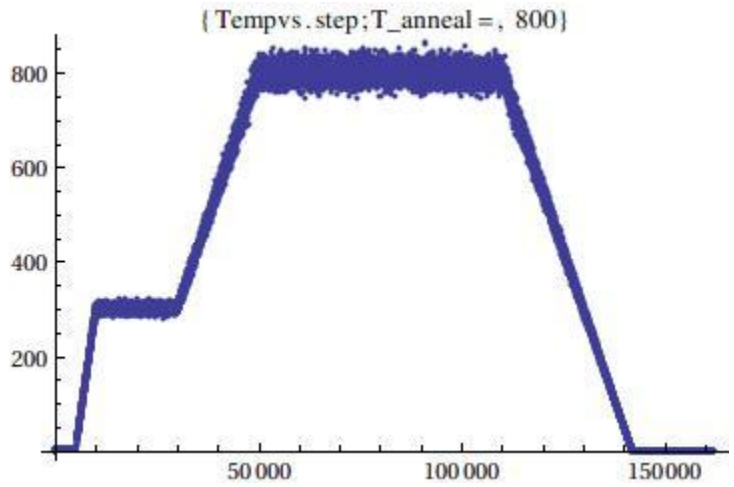
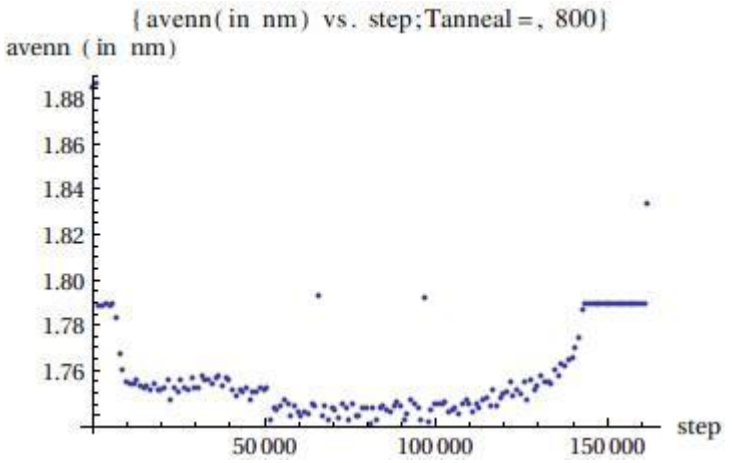
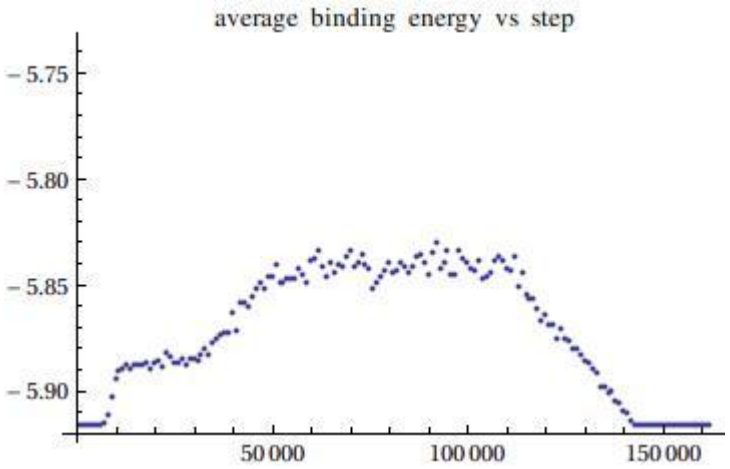


Figure 10(v): Tanneal = 800 K.







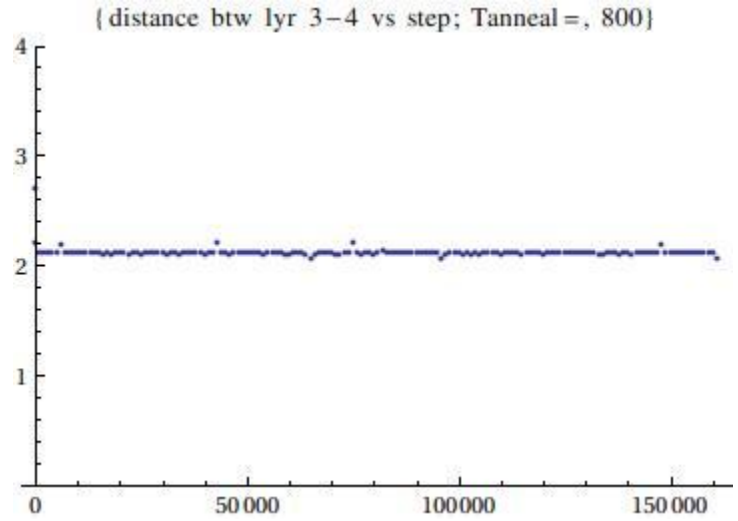
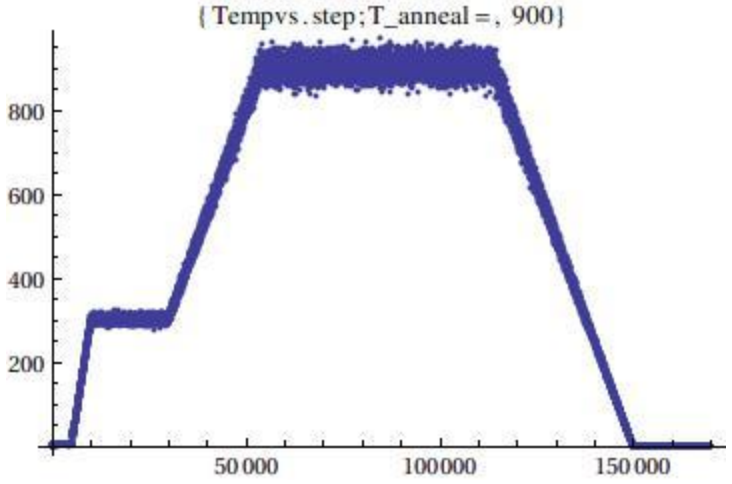
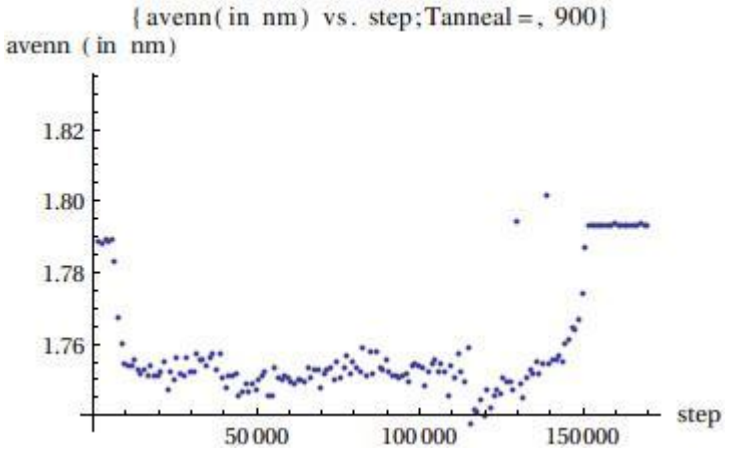
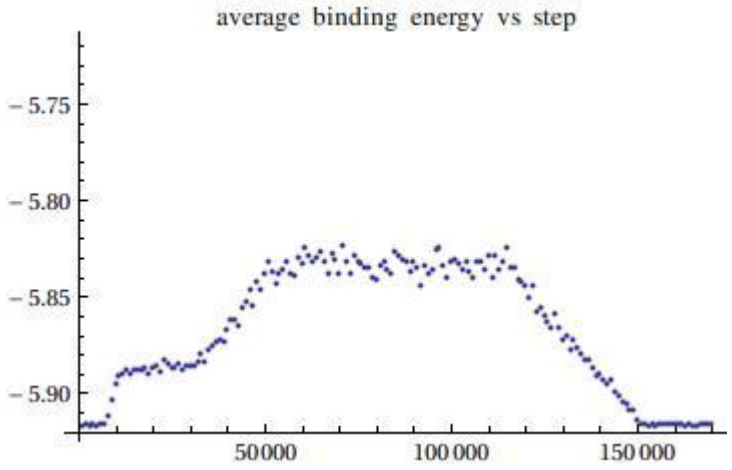


Figure 10(vi): Tanneal = 900 K.







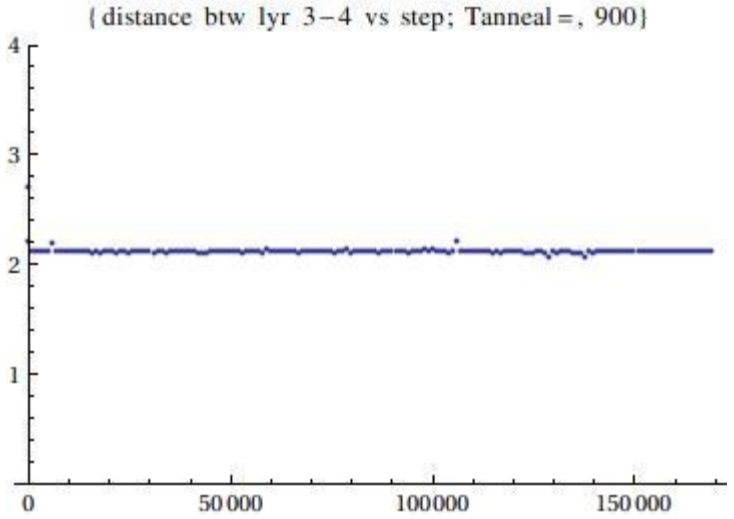
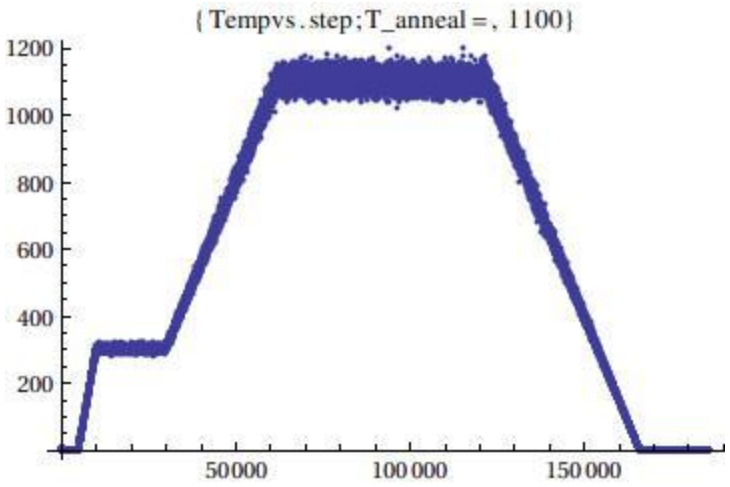
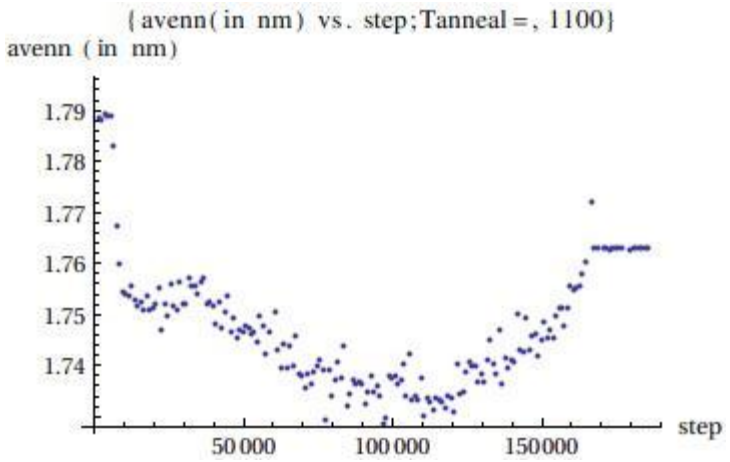
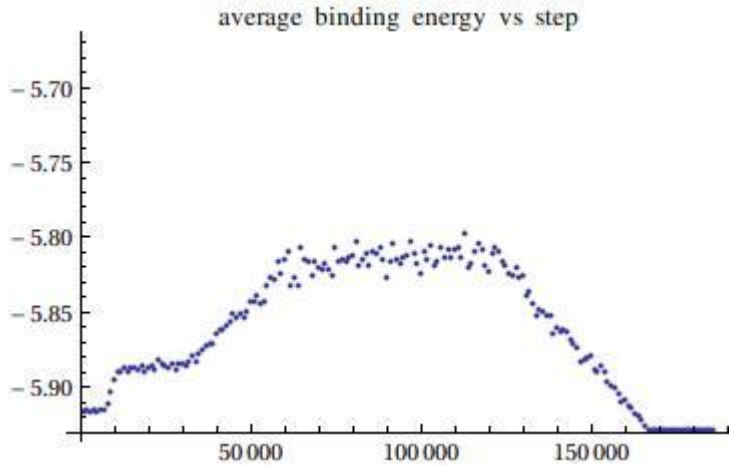


Figure 10(vii): Tanneal = 1000 K.

Figure 10(viii): Tanneal = 1100 K.







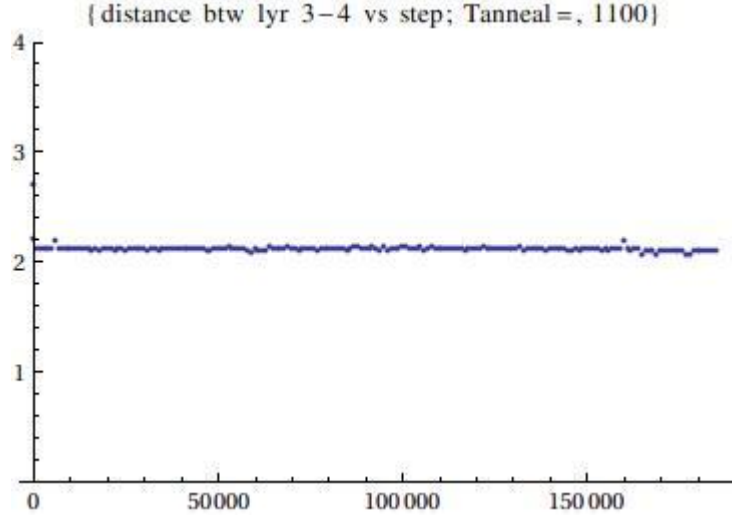
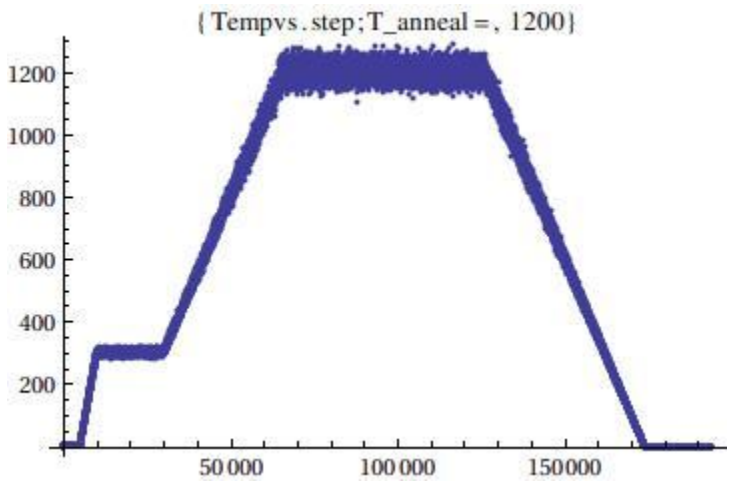
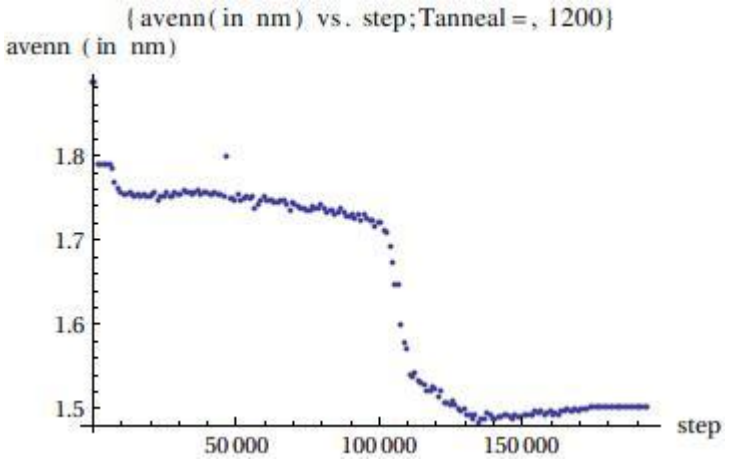
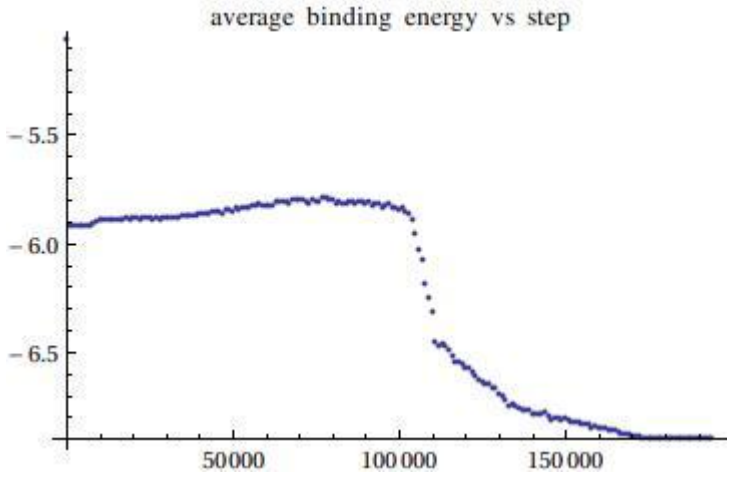


Figure 10(ix): Tanneal = 1200 K.







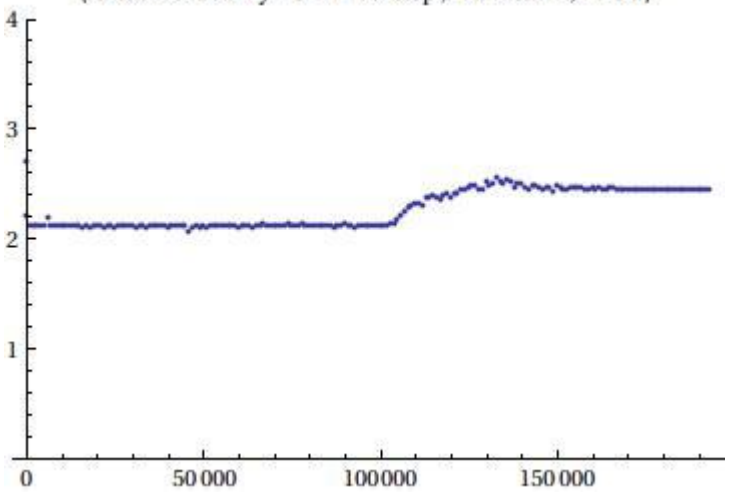
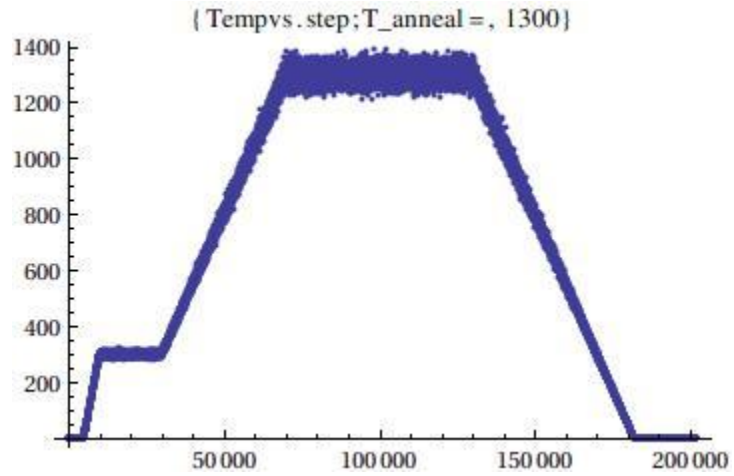
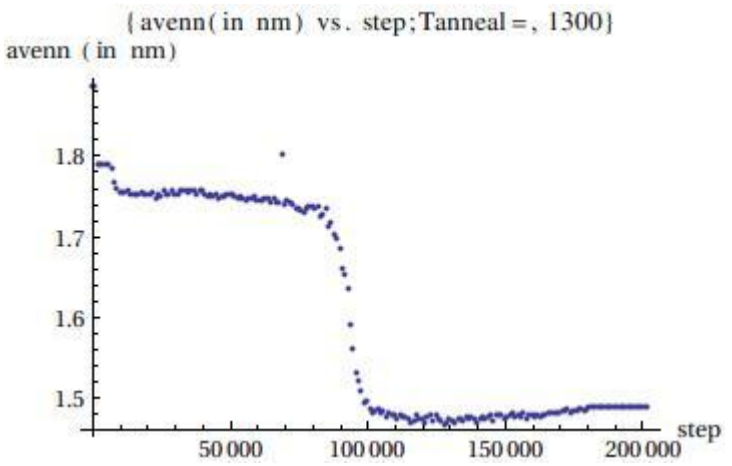
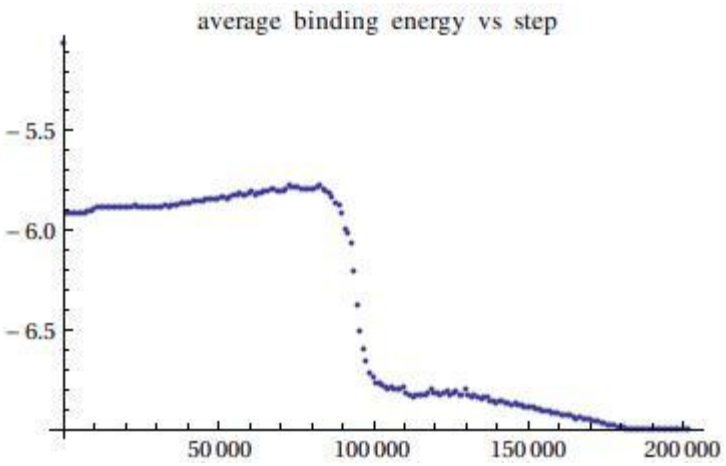


Figure 10(x): Tanneal = 1300 K.







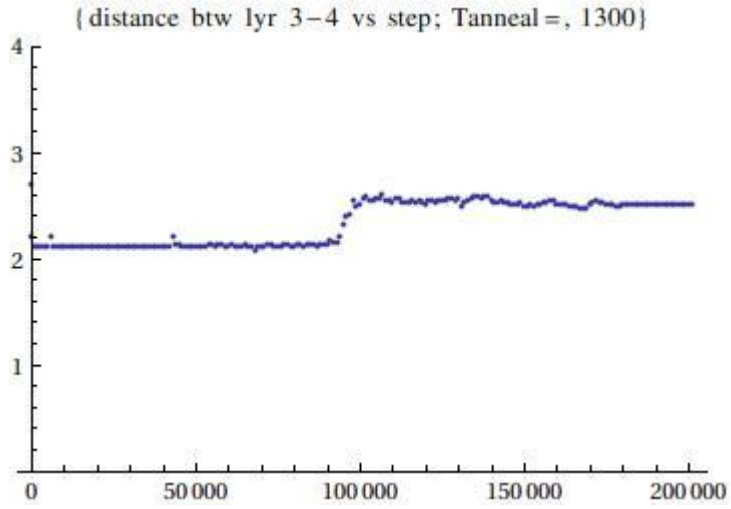
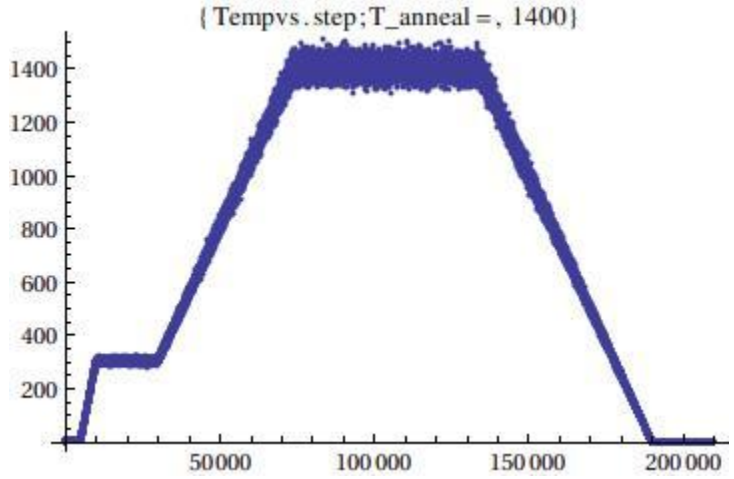
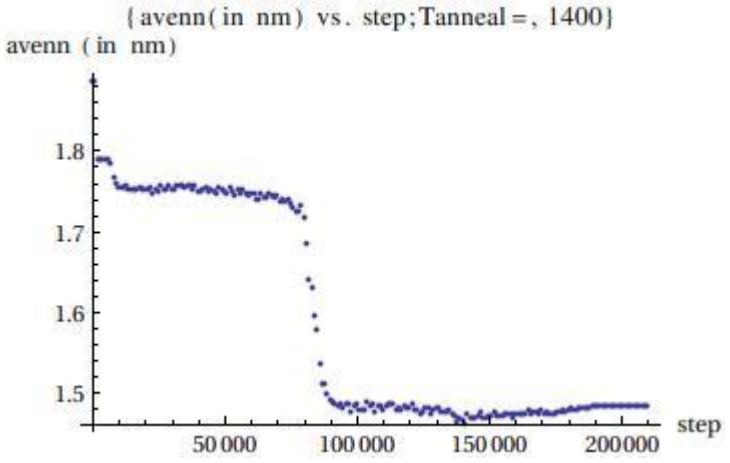
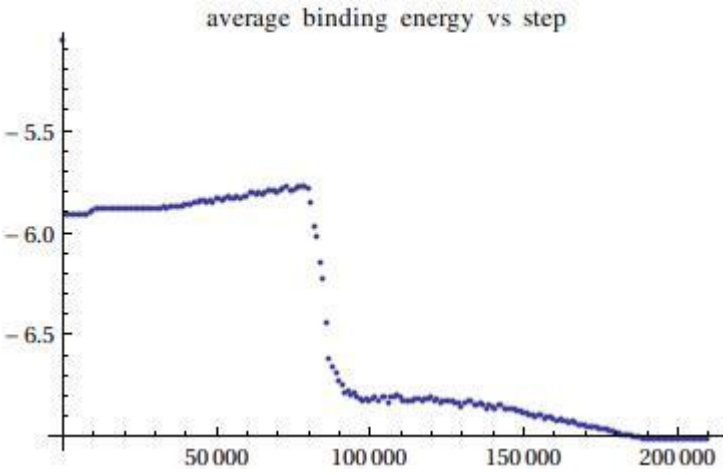


Figure 10(xi): Tanneal = 1400 K.







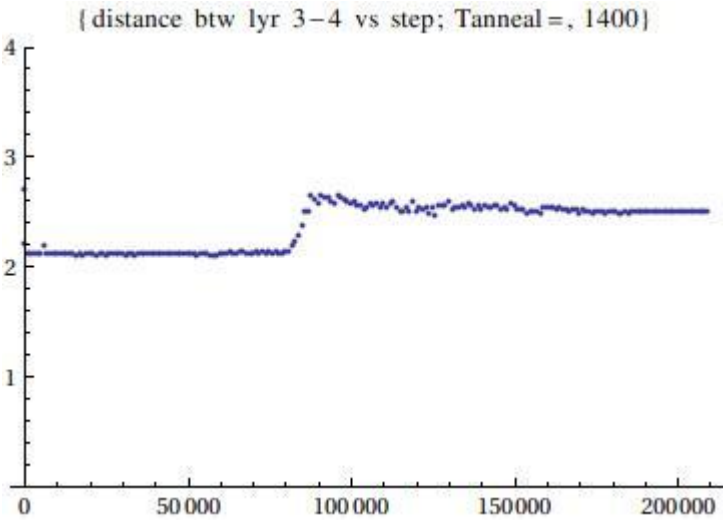
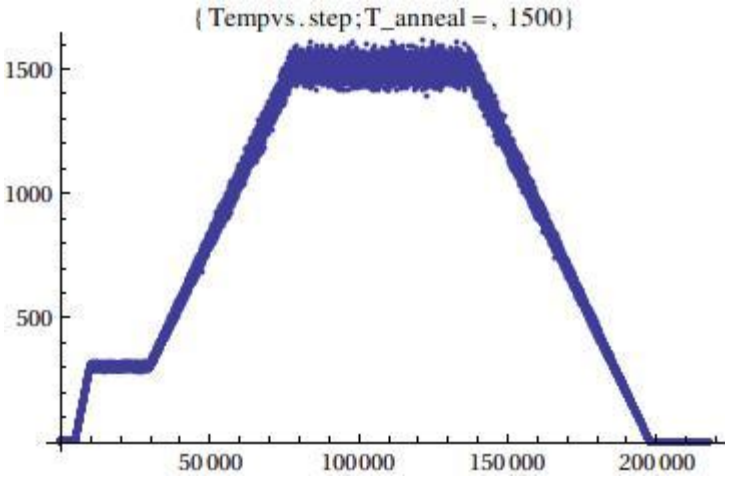
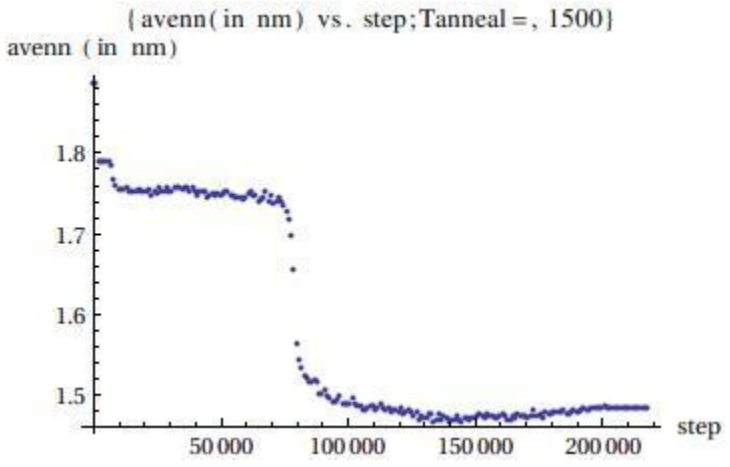
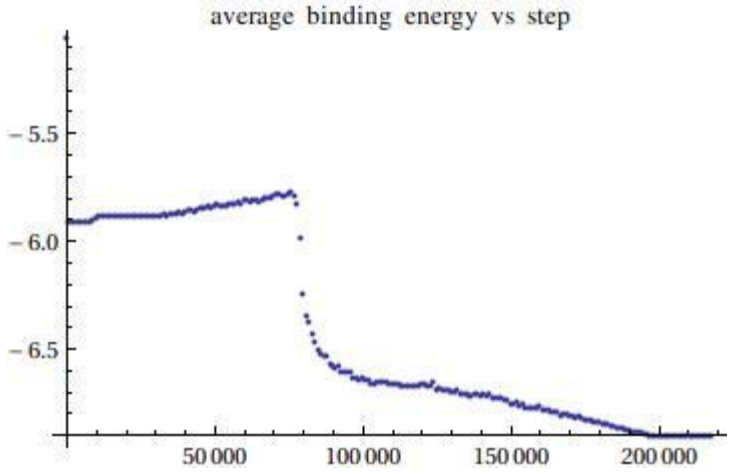


Figure 10(xii): Tanneal = 1500 K.







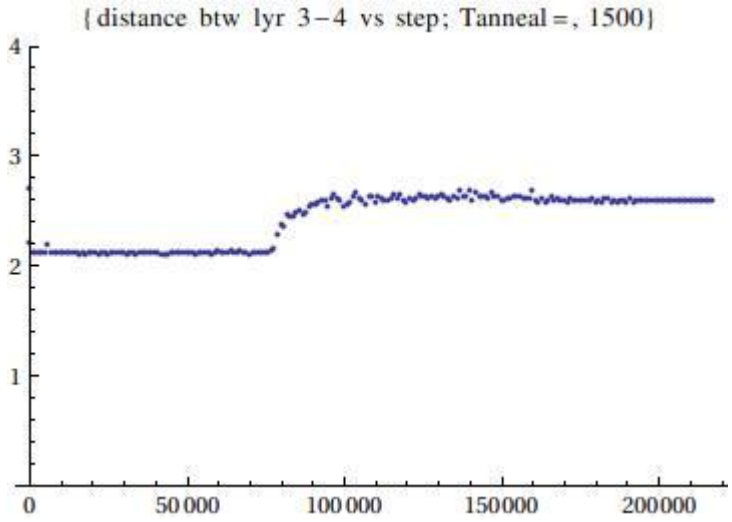
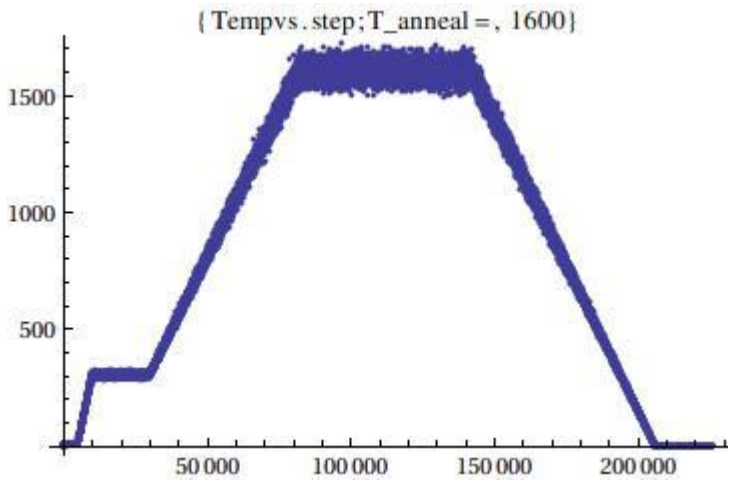
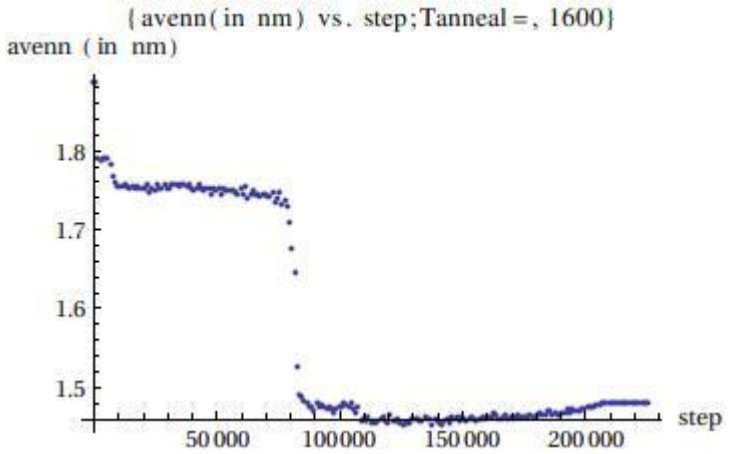
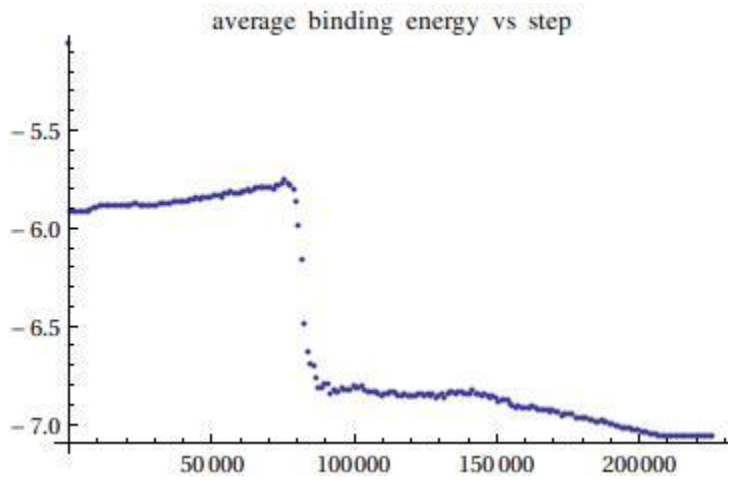


Figure 10(xiii): Tanneal = 1600 K.







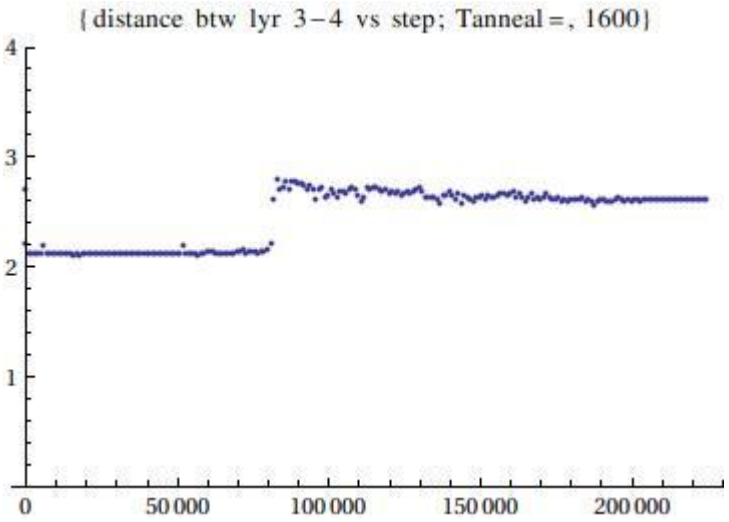
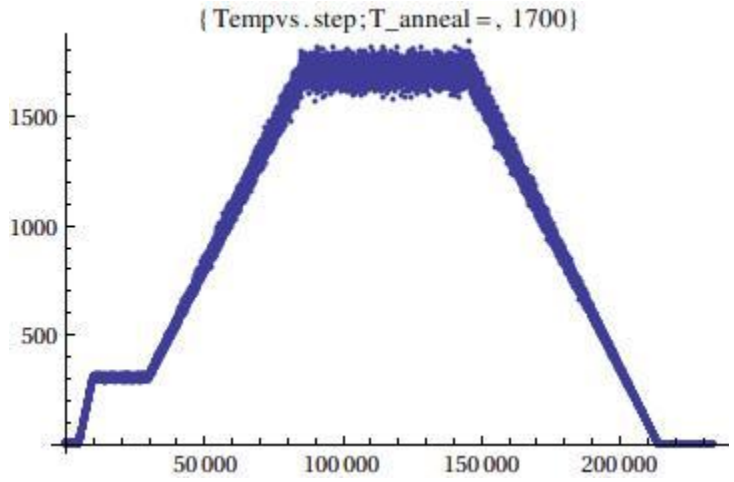
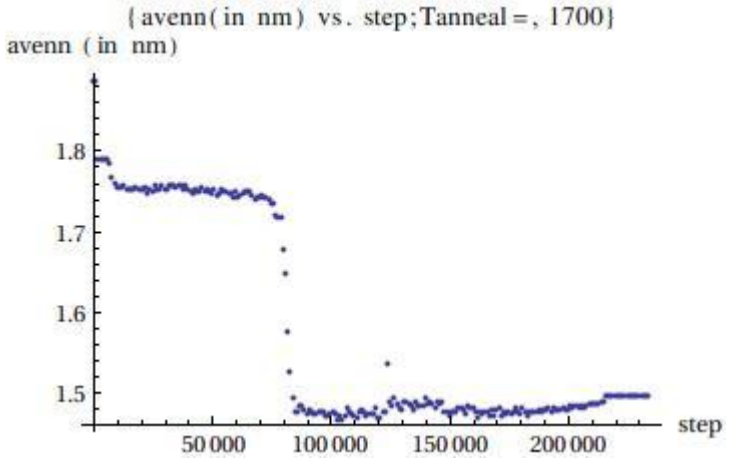
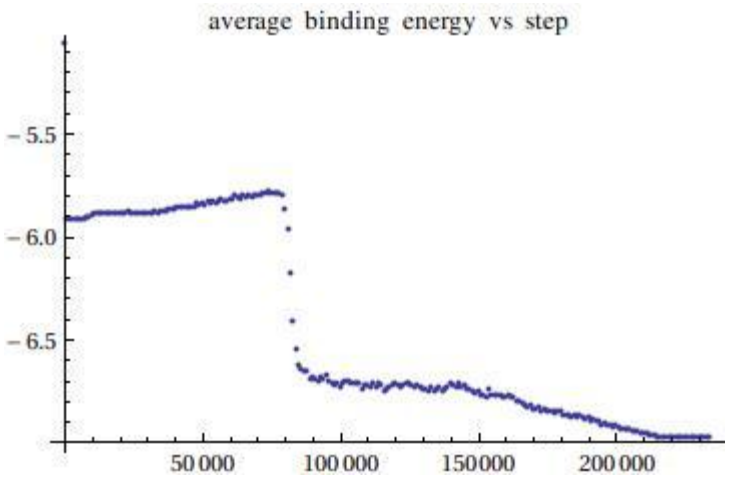


Figure 10(xiv): Tanneal = 1700 K.







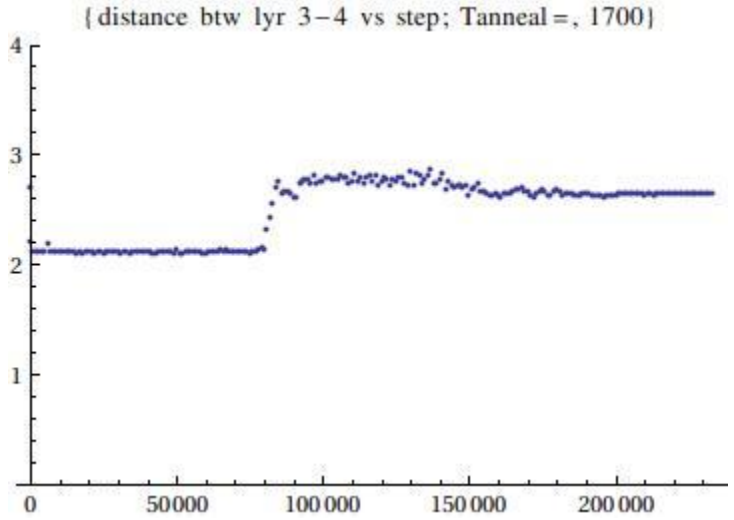
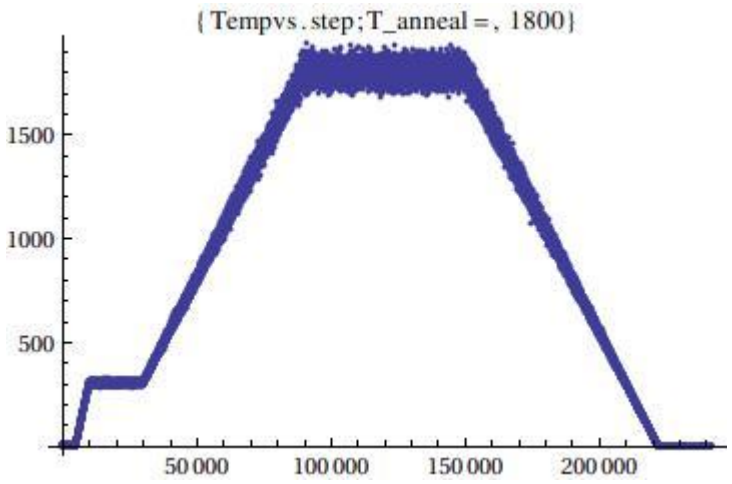
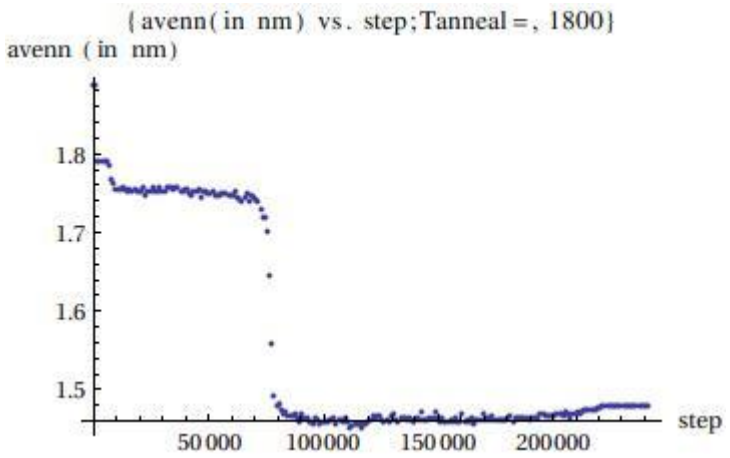
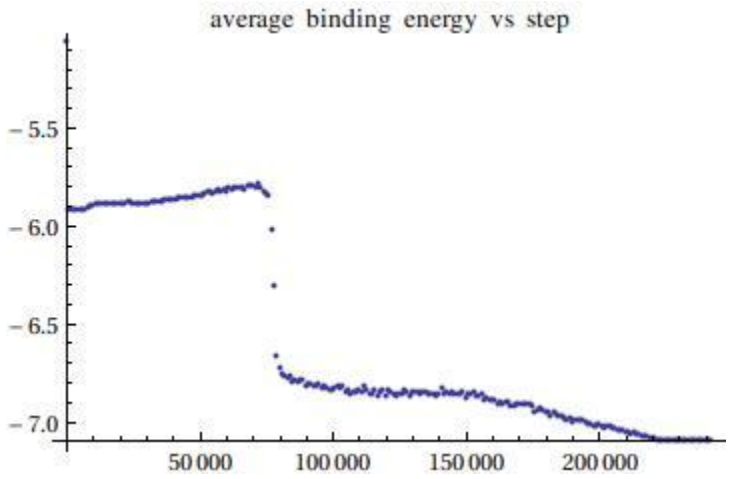


Figure 10(xv): Tanneal = 1800 K.







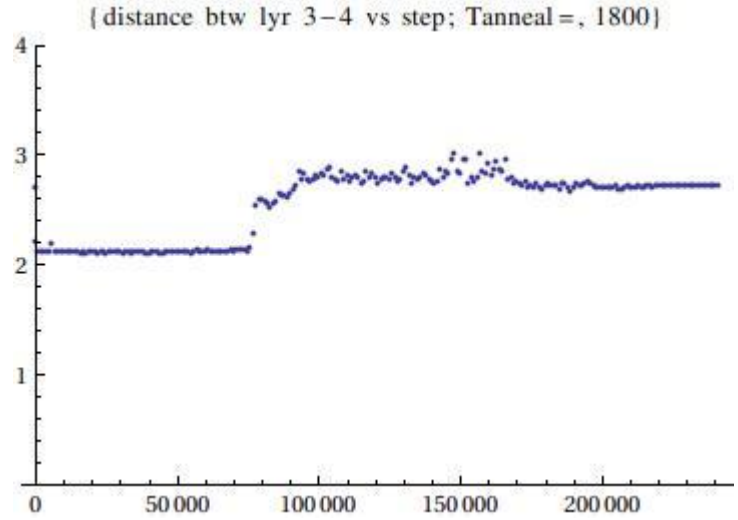
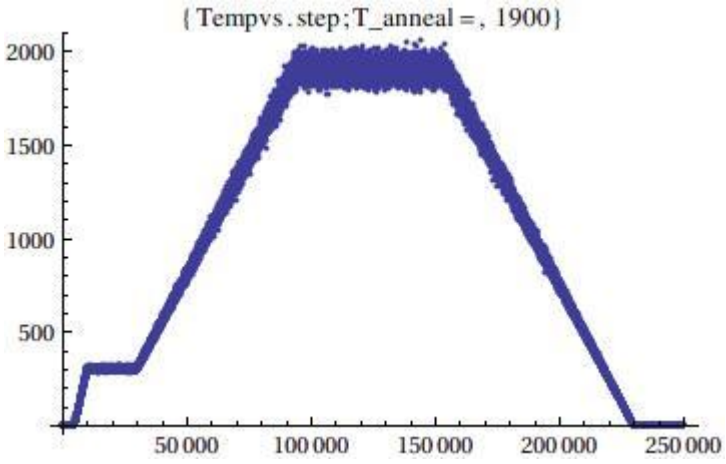
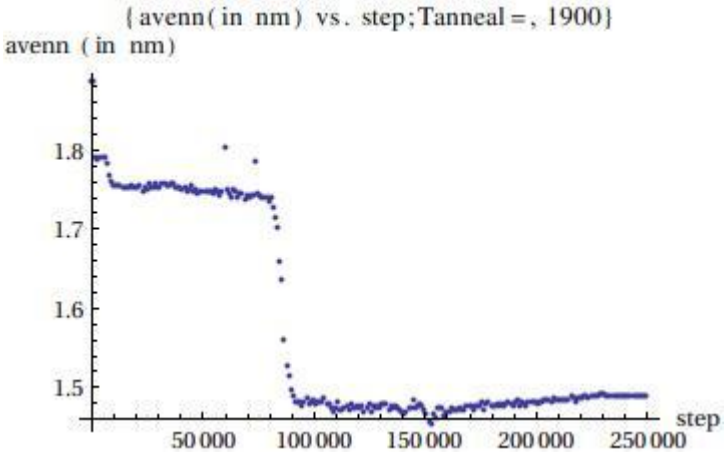
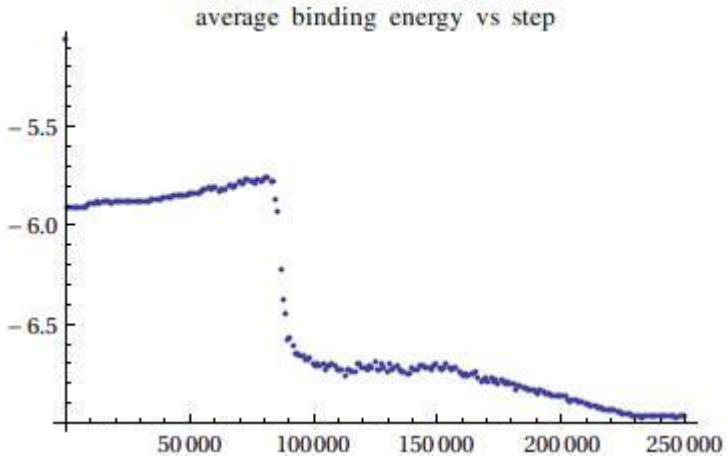
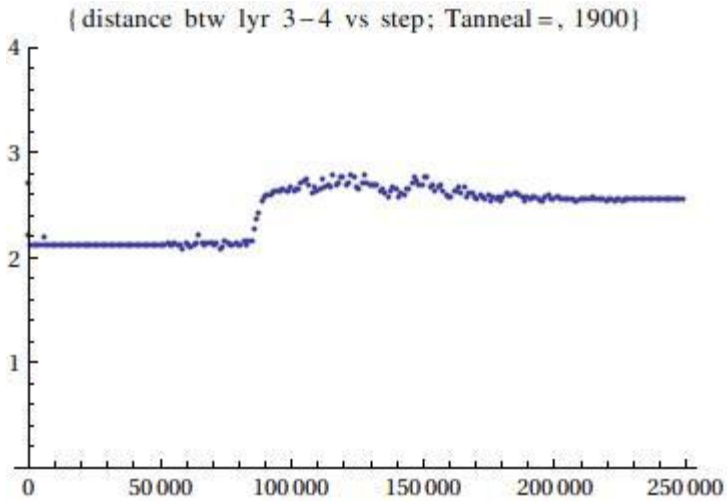


Figure 10(xvi): Tanneal = 1900 K.



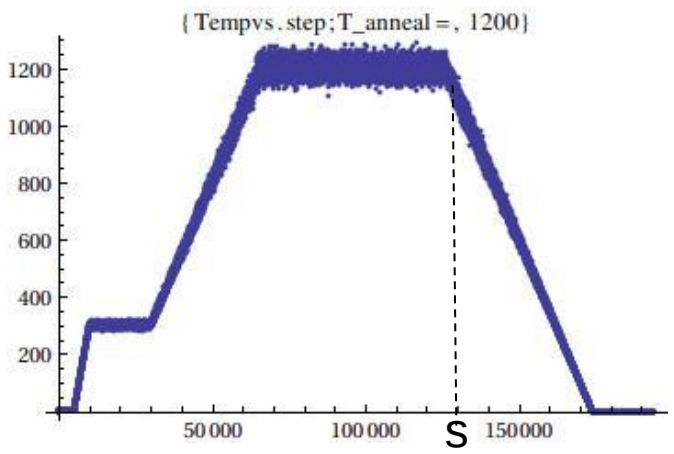


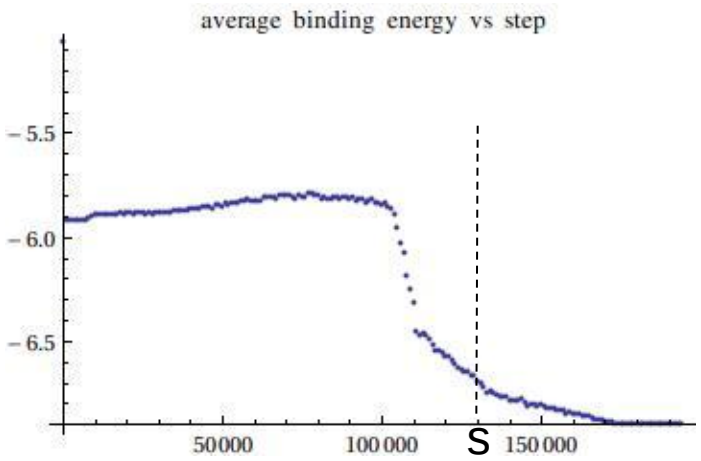




Determination of binding energy (BE)

- Should an abrupt change in binding energy occurs at a given Tanneal during equilibration, such as that illustrated below (for Tanneal = 1200 K), how do we decide the value of the binding energy (which is step-dependent) for this annealing temperature?
- Suggest to choose the value of the BE at the end of equilibration, denoted as *s*. *s* is Tanneal-dependent:
- *s* = 90000+(2/3)(Tanneal-300)





BE vs. Tanneal

- Based on the data shown in Figures 10, we abstract the value of BE at step = *s* from annealing temperature to plot the graph of BE vs Tanneal.
- The values of BE (at step *s*) vs Tanneal is tabled in bdvstemp.dat.
- The resultant curve is shown in Figure 11.

Binding energy vs anneal temperature

data\single\TEA\bdvstemp.dat

Anneal temp	binding energy
400	-5.880829270833332
500	-5.868849618055552
600	-5.858356840277779
700	-5.853619340277778
800	-5.846055347222225
900	-5.831880138888886
1100	-5.817465729166667
1200	-5.808956701388889
1300	-5.99745027777778
1400	-6.751486666666667
1500	-6.5904123611111105
1600	-6.798648229166668
1700	-6.697513090277775
1800	-6.814728368055552
1900	-6.576965069444443
2000	-6.614329895833334

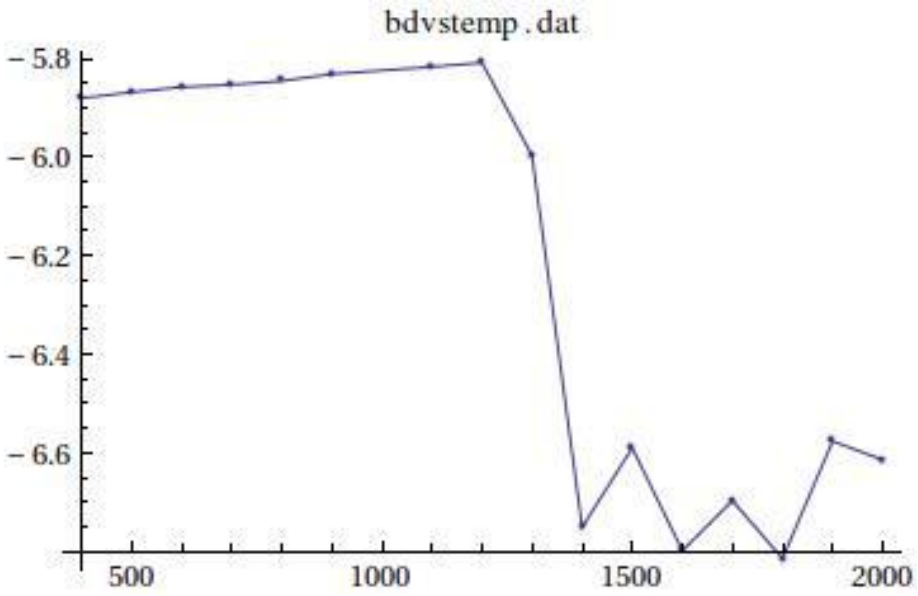


Figure 11

Average nearest neighbour (nn) vs anneal temperature

- Based on the data shown in Figures 10, we abstract the value of average nn at step = *s* from each annealing temperature to plot the graph of ave nn vs Tanneal.
- The resultant curve is shown in Figure 12.

Average nearest neighbour (nn) vs anneal temperature

data\single\TEA\avennvstemp.dat

Anneal temp	average nn
400	1.7506521837666498
500	1.7463308848628443
600	1.7535358998528505
700	1.7428323576363118
800	1.7434199844705522
900	1.755339645172511
1100	1.7324194569702076
1200	1.7287109331017865
1300	1.658732172065723
1400	1.4872606748045474
1500	1.5048100430386822
1600	1.4789575688624732
1700	1.4770801292840978
1800	1.469249503109946
1900	1.4879246326794398
2000	1.4953312960924399

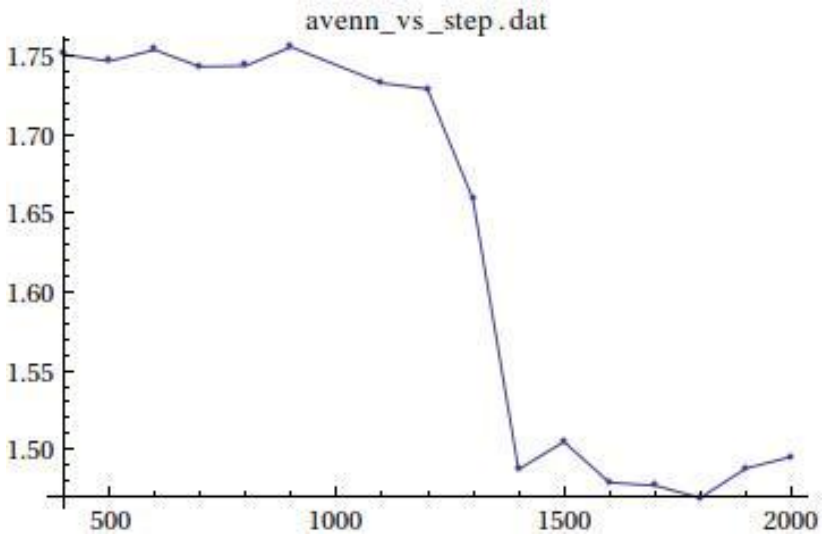


Figure 12

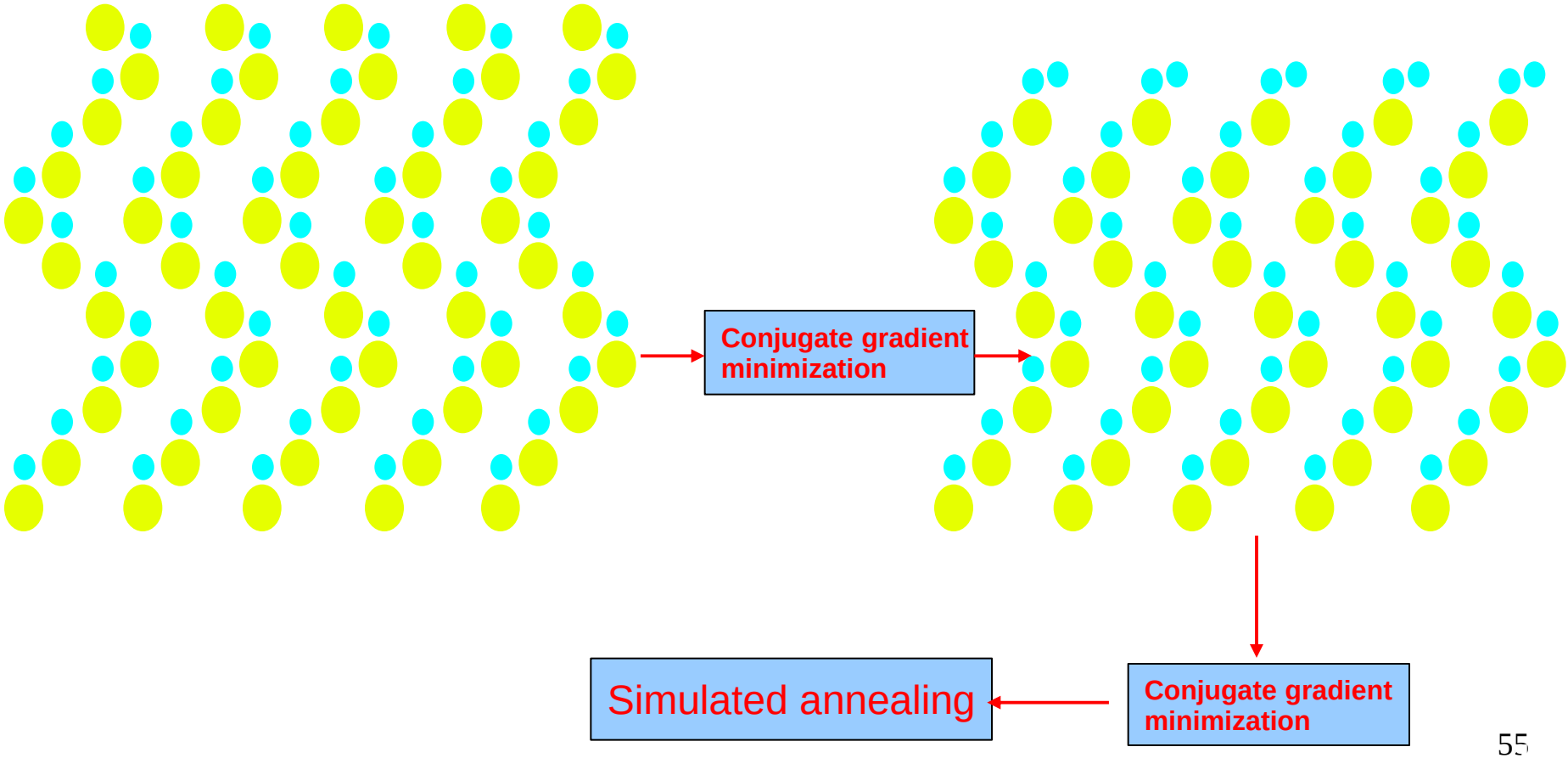
Data and results for single layer graphene formation

- From the data generated, we conclude that:
  - Graphene formation is observed only when Tanneal= T_f (transition temperature) = 1200 K or above for TEA potential.

Double-layered graphene formation

Figure 13

•We follow the procedure of the NTCU group to prepare a two-layered carbon-rich substrate. Thickness of the substrate is *z*=1.



Two-layered carbon-rich substrate with thickness $z = 1$ for double-layered graphene formation

Figure 14: After minimising the two-layered carbon-rich substrate with thickness, *z* = 1

- Shown here is the 15 x 15 x 1 supercell after energy minimisation
- The values of the *z*-coordinates allow us to estimate the distances between the atomic layers.

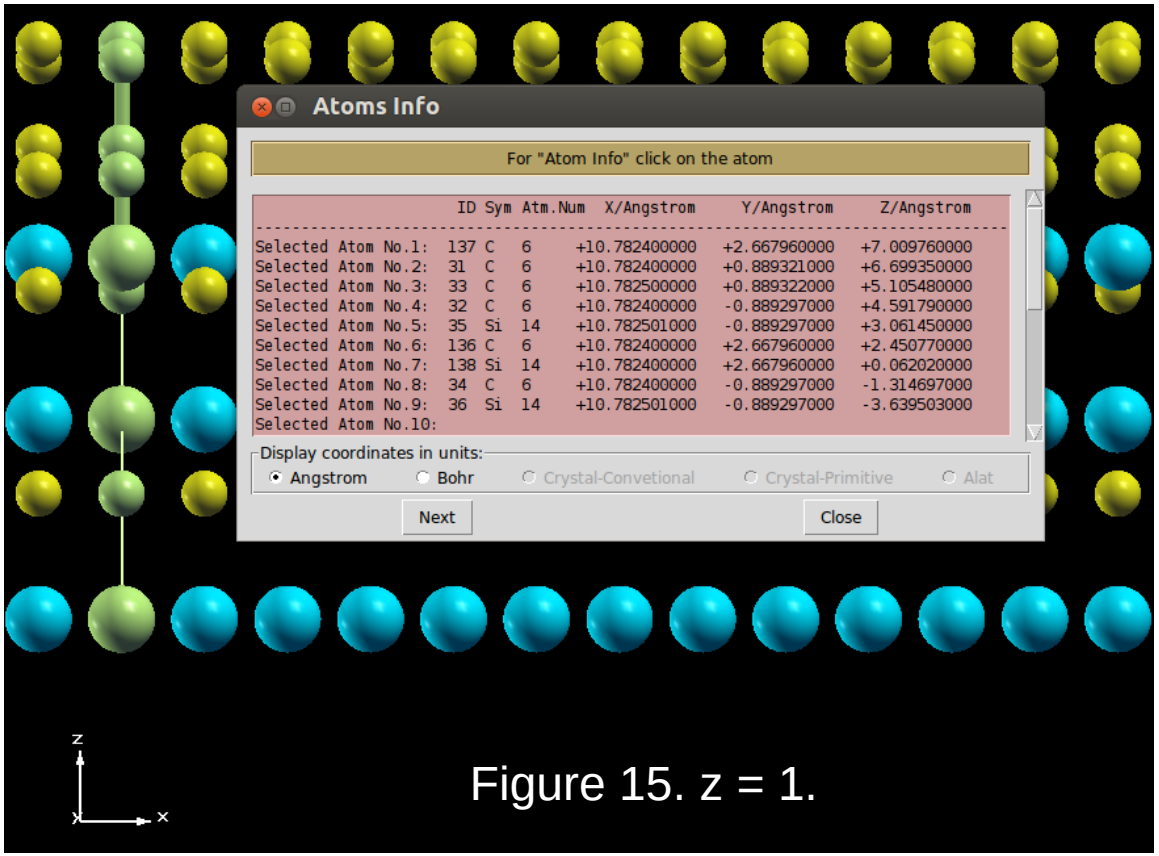
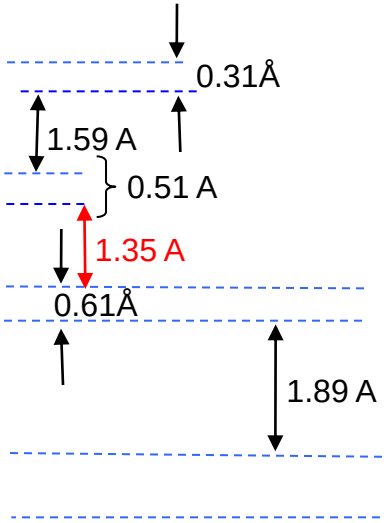


Figure 15. z = 1.



Note: we note that the substrate get distorted significantly.

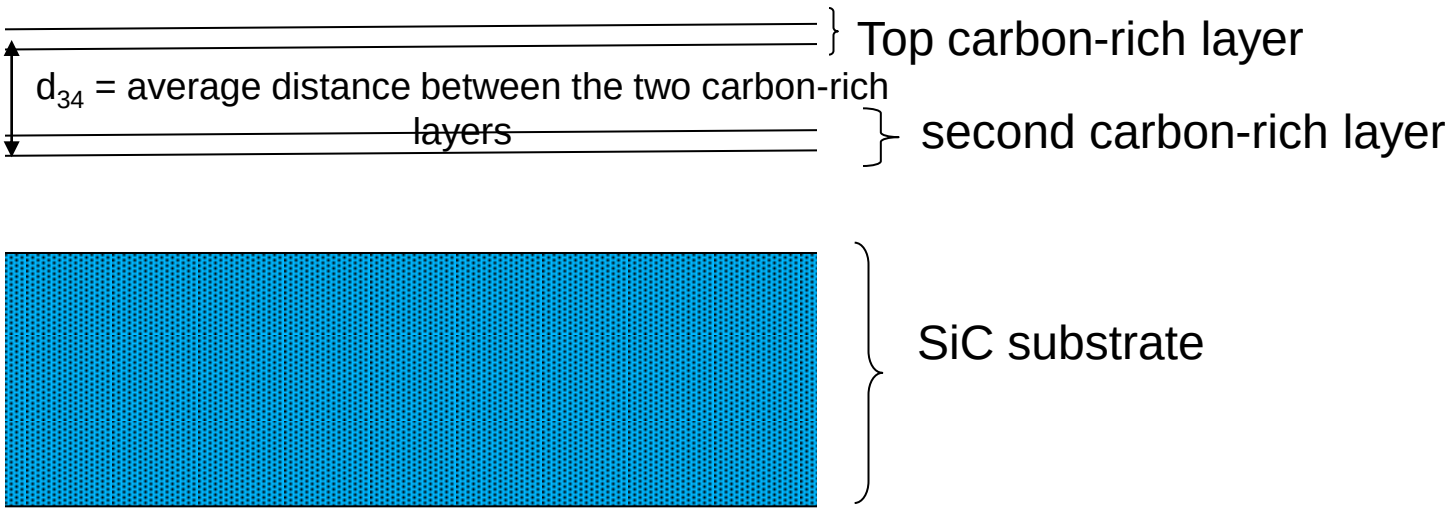
Visualising graphene formation for 15 x 15 x 1 supercell at Tanneal = 700 K, *z* = 1

- We found that for substrate thickness *z* = 1, double-layered graphene is formed at as low as Tanneal = 600K.
- The dynamical formation for Tanneal = 700 K can be visualised by viewing the following files with VMD, using option File -> ‘Load Visualization State’. These are processed trajectory files where dynamic bonding option was enabled, with Distance Cutoff set to 1.7.
- 700_dynamicbonding_graphene.vmd
- 700_dynamicbonding_bulk.vmd
- The original trajectory file 700.lammpstrj can be found in the same directory.

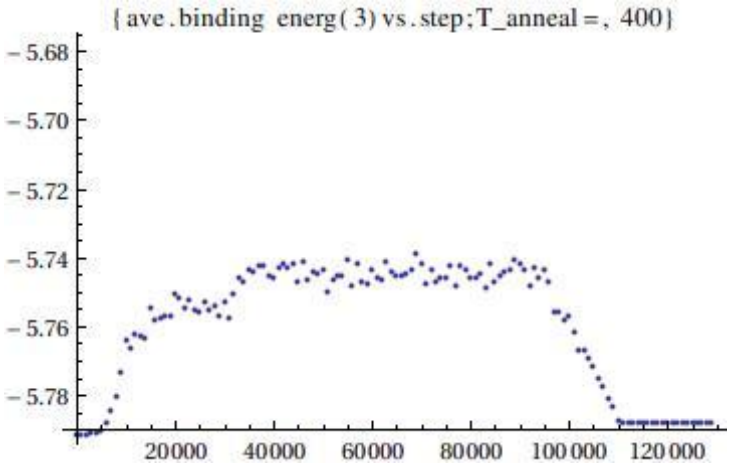
Output for double-layered graphene formation

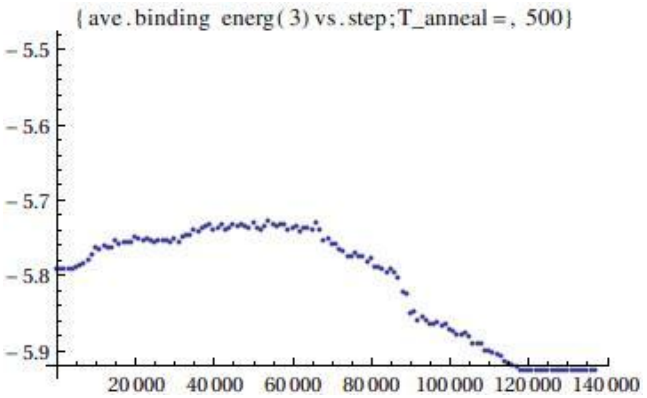
- The output for the simulation (for only TEA) will be presented

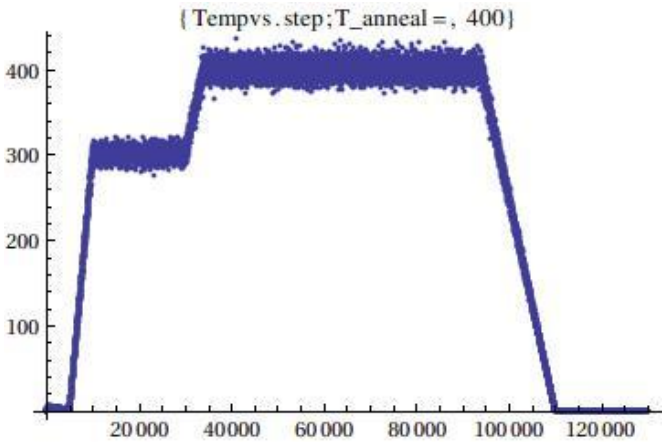
1. Average binding energies (BE) for the top and the second graphene layer vs. step at a fixed target annealing temperature.
2. Average nearest neighbours (bound length) for the top and the second graphene layer vs. step at a fixed target annealing temperature.
3. Average distances between the carbons in top carbon-rich layer and the carbon-rich layer below it vs. step at a fixed target annealing temperature (see figure below).

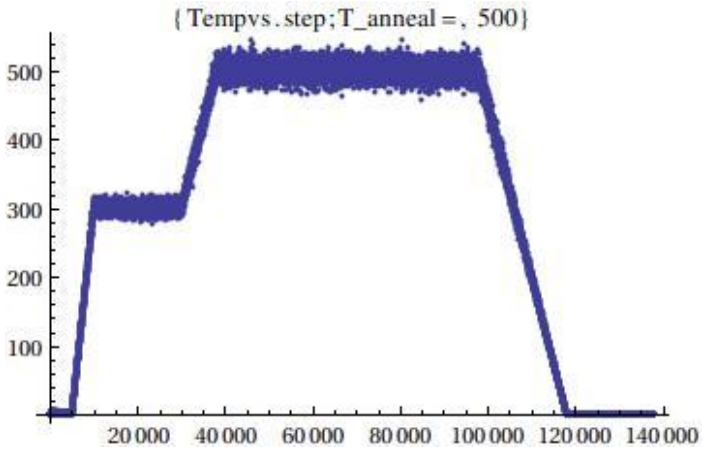


Average BE (top carbon-rich layer) vs. step, substrate thickness z = 1

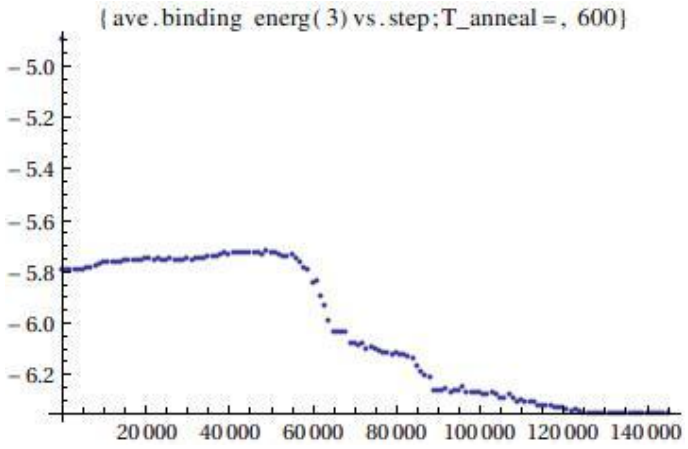


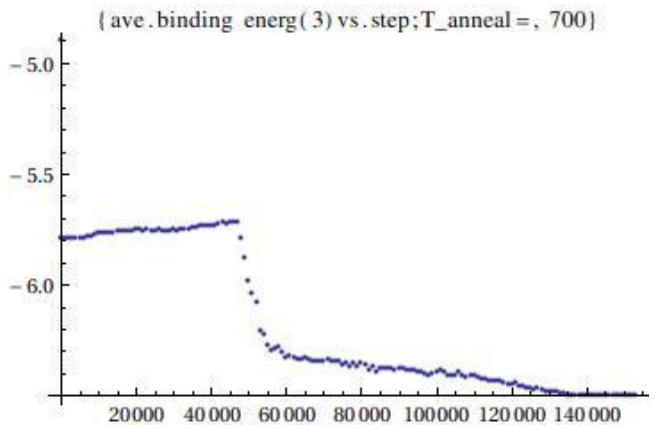


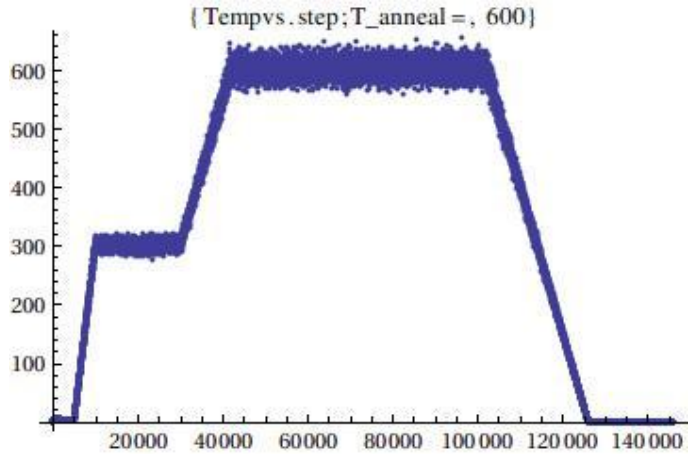


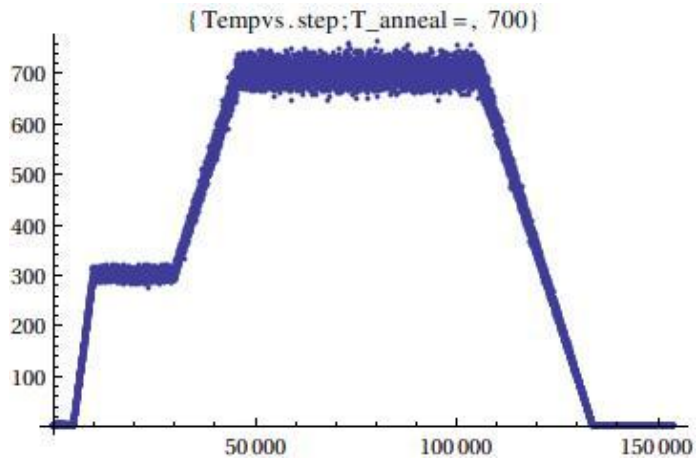


Average BE (top carbon-rich layer) vs. step, substrate thickness z = 1

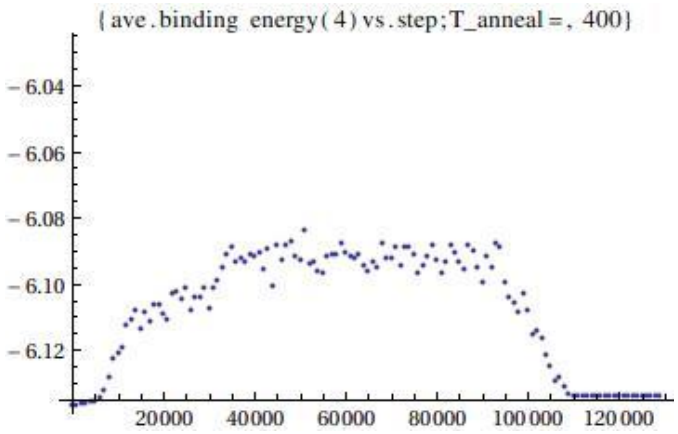


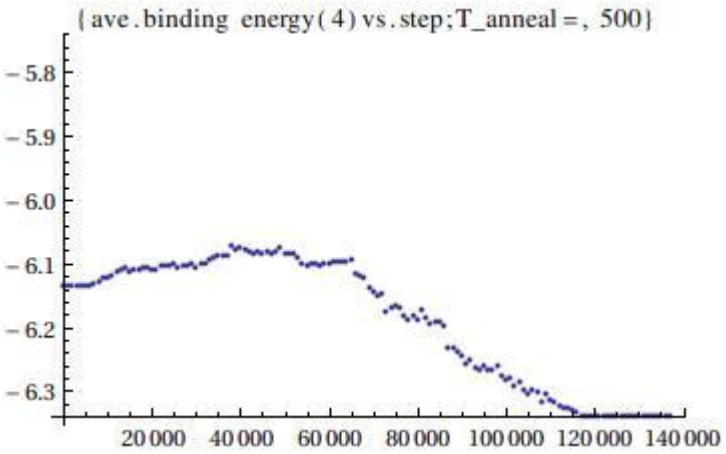


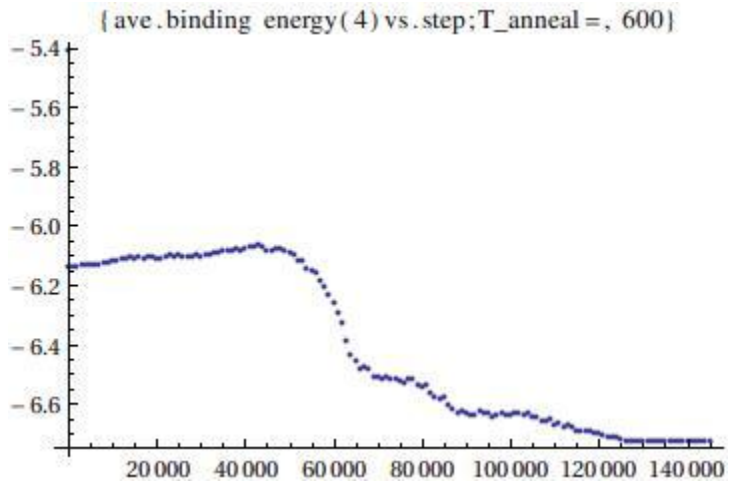


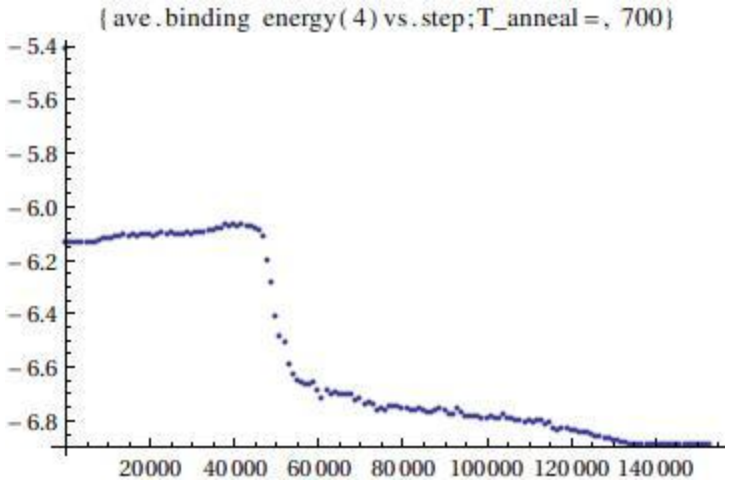


Average BE (second carbon-rich layer) vs. step, substrate thickness z = 1

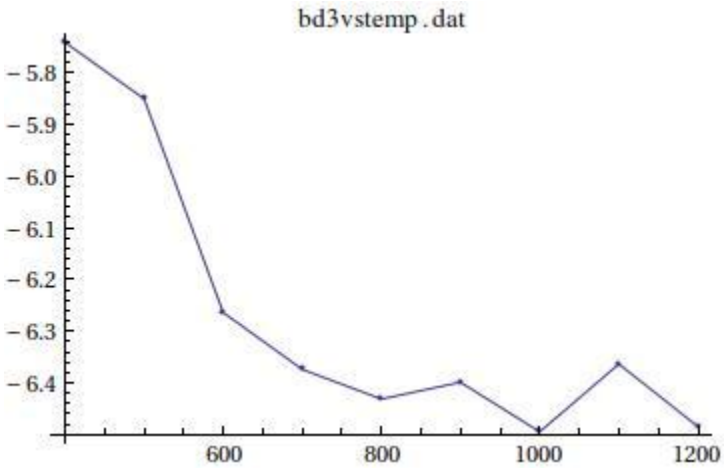




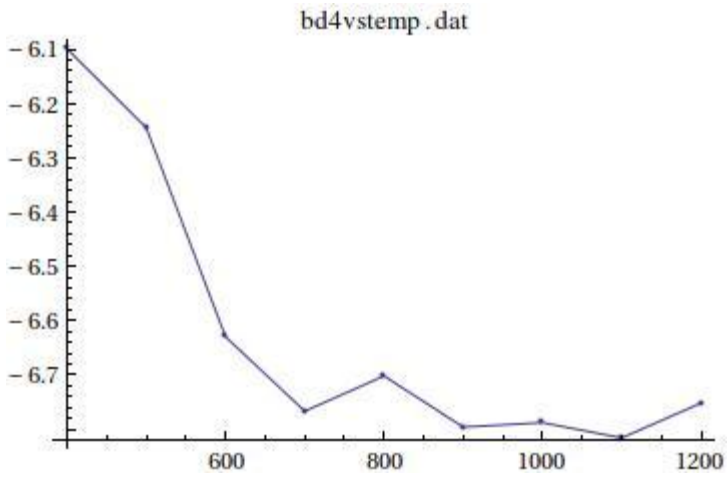




Binding energies vs. Tanneal, z = 1

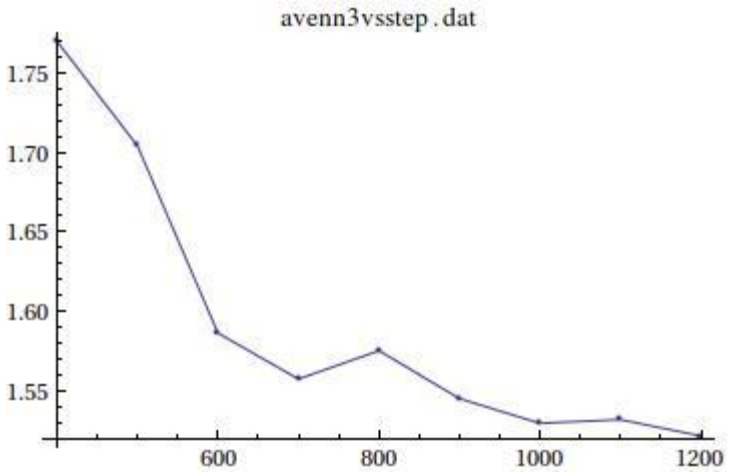


Top carbon-rich layer

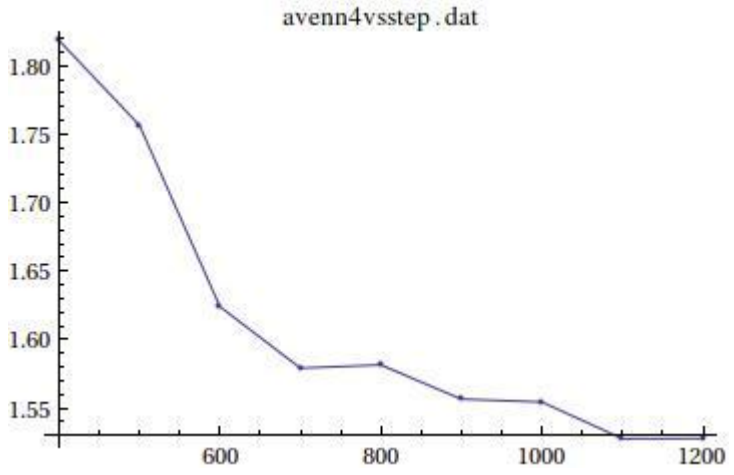


second carbon-rich layer

Average nearest neighbour (nn) vs. Tanneal, $z = 1$

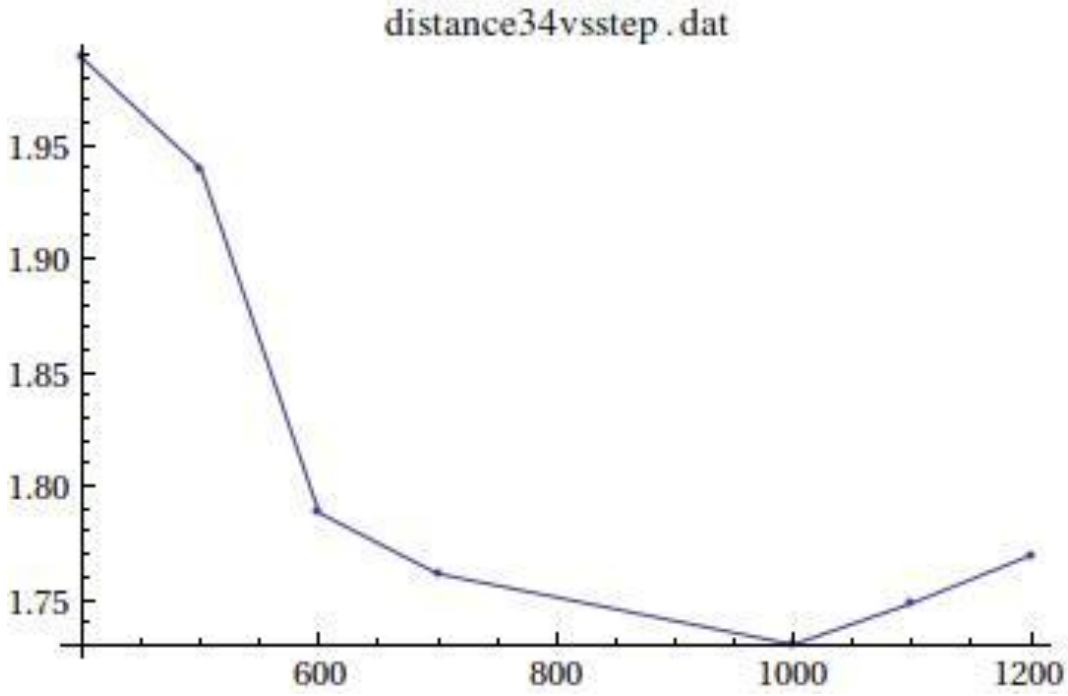


Top carbon-rich layer



Second carbon-rich layer

Average distance between the two carbon-rich layers vs. Tanneal, z = 1



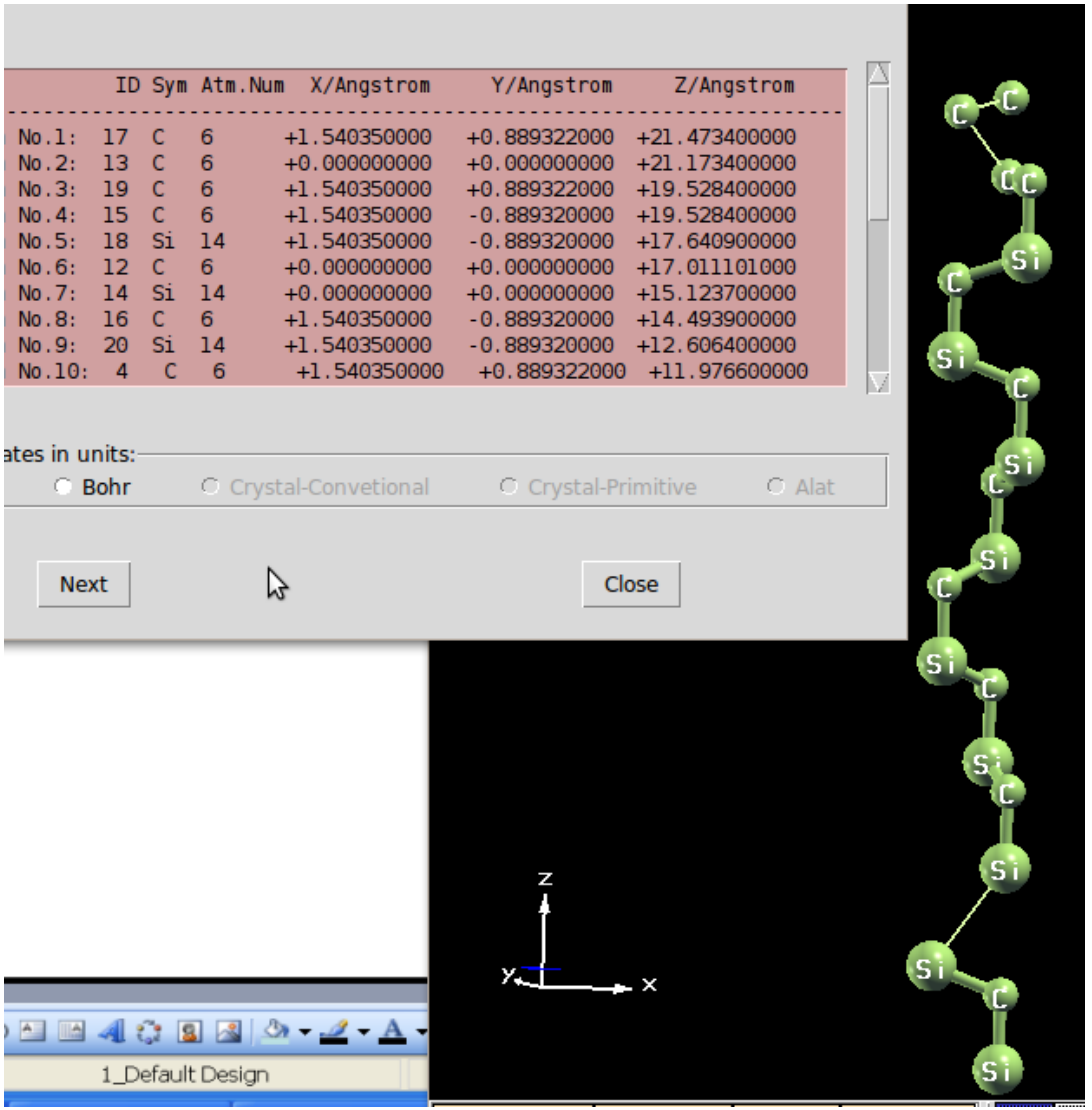
Location of data for $z = 1$

- The data for substrate thickness $z = 1$ double layered graphene formation can be found in the folder \data\doublelayer\z1

Two-layered carbon-rich substrate with thickness $z = 2$ for double-layered graphene formation

Figure 15: Substrate with thickness *z*=2

- A 6H-SiC unit cell with a thickness *z* = 2 substrate unit cell is shown.
- This is a original unit cell without any atoms removed nor displaced.
- We shall subject this unit cell to the energy minimization and modification procedure as depicted in Figure 13.
- The results of the minimised structure is displayed in Figure 16.

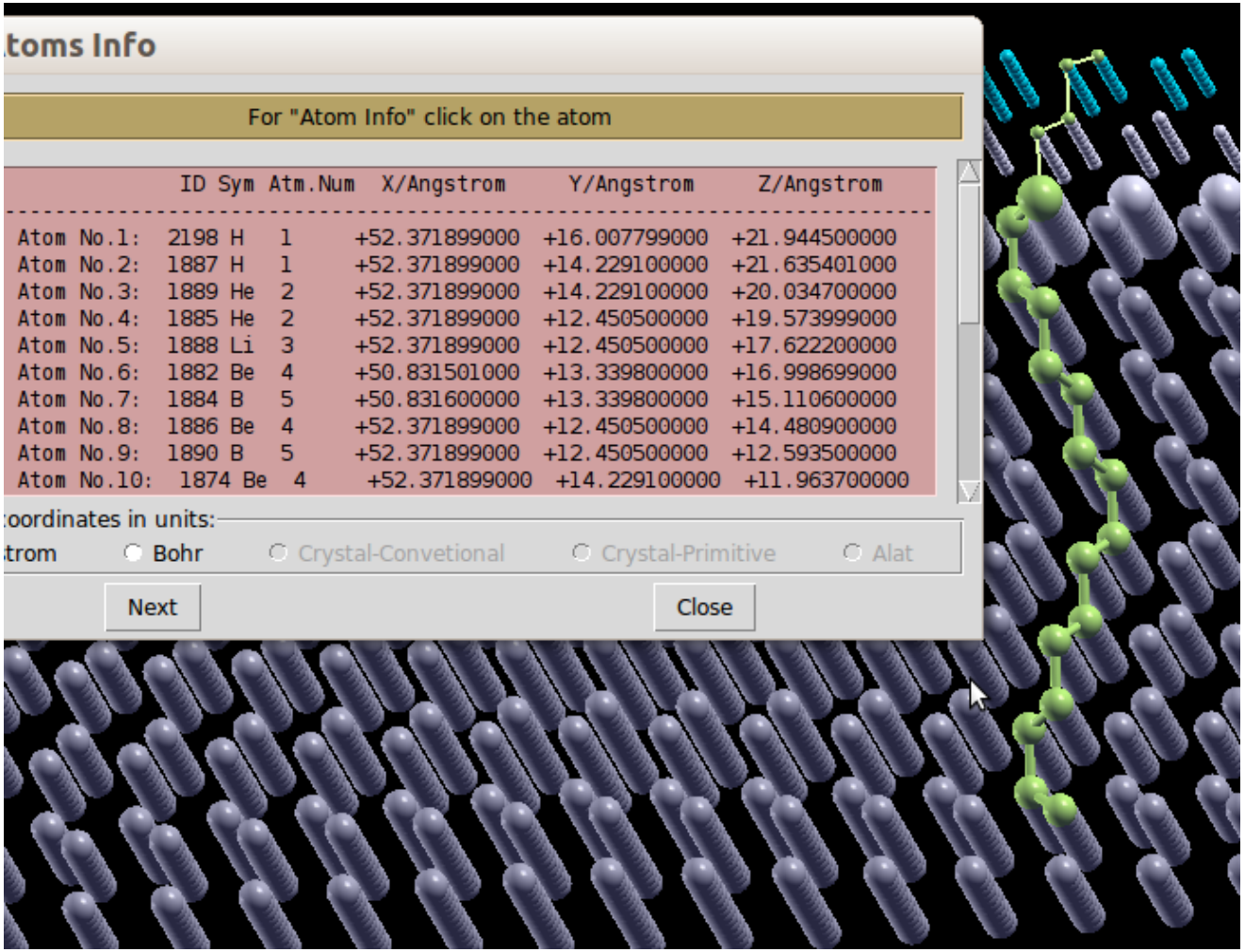


.xyz file for the coordinates for substrate with thickness *z*=2

- 20
- Carbon rich 6H-SiC with thickness z = 2
- C 0 0 9.45939
- Si 0 0 0.020741
- Si 0 0 7.57191
- C 1.54035 0.889322 11.9766
- C 1.54035 -0.88932 4.42492
- C 1.54035 0.889322 6.94215
- C 1.54035 -0.88932 -0.614502
- Si 1.54035 0.889322 10.0892
- Si 1.54035 -0.88932 2.53745
- Si 1.54035 0.889322 5.05468
- Si 1.54035 -0.88932 -2.450897
- C 0 0 17.011101
- C 0 0 21.1734
- Si 0 0 15.1237
- C 1.54035 -0.88932 19.5284
- C 1.54035 -0.88932 14.4939
- C 1.54035 0.889322 21.4734
- Si 1.54035 -0.88932 17.6409
- C 1.54035 0.889322 19.5284
- Si 1.54035 -0.88932 12.6064

Figure 16:

Shown here is the structure of the energy-minimised 15 x 15 x 1 supercell of two-layered carbon-rich substrate with thickness $z = 2$



The values of the gaps between atomic layers are measured in Figure 17.

To check this with JJ

Figure 17:
Distances between the atomic layers after energy-minimization, with z = 2.

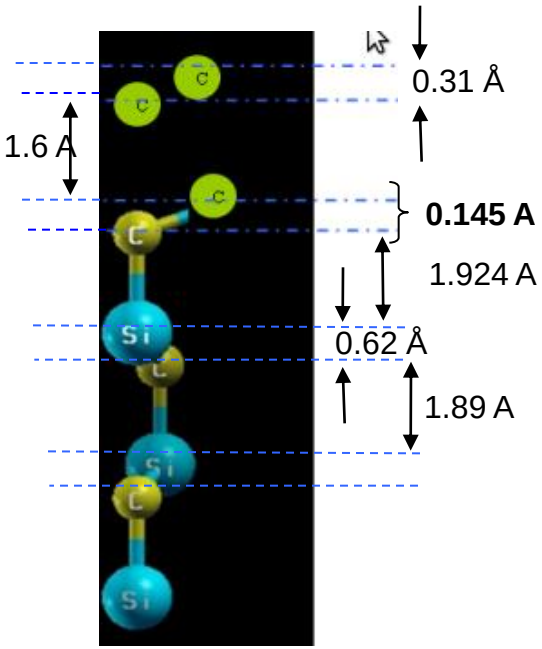
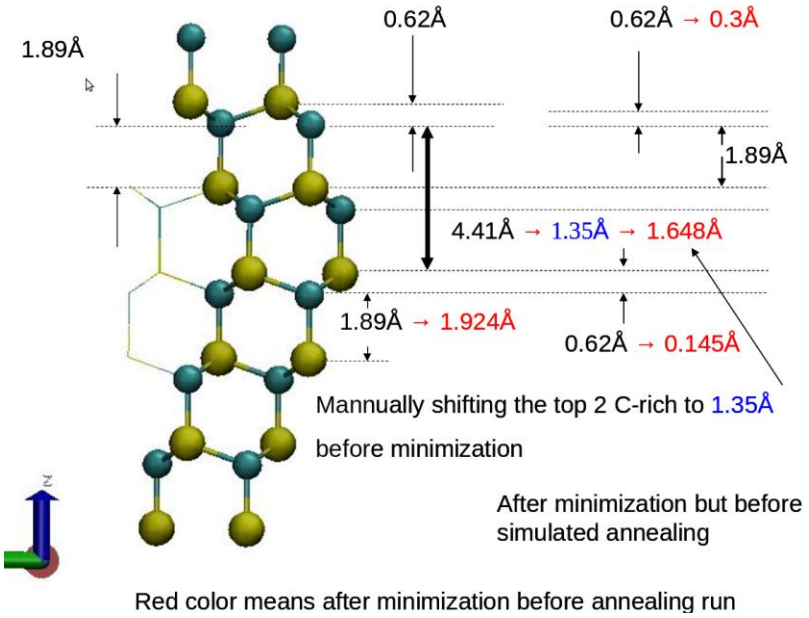


Figure 17

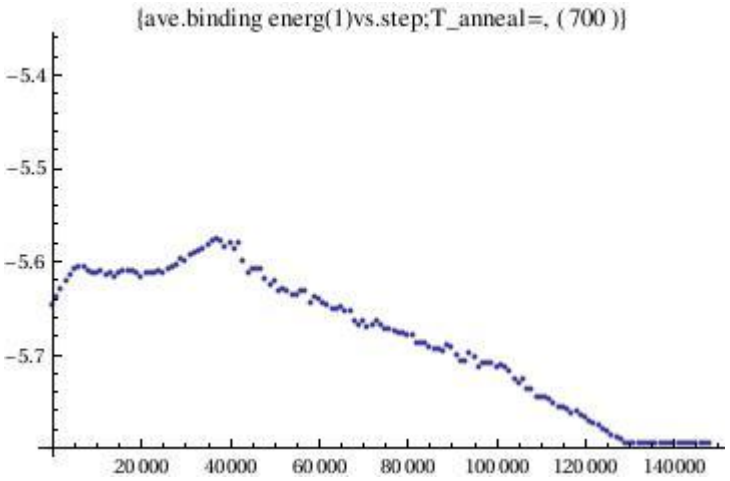


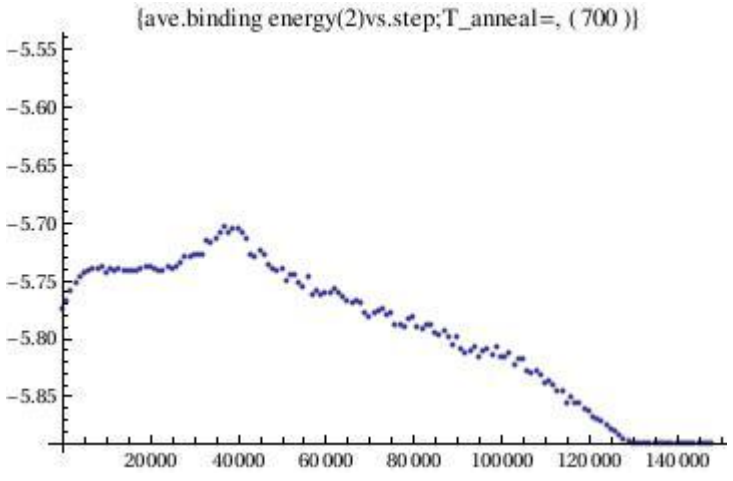
As a comparison, this figure shows the configuration obtained by the NTCU group.

Visualising graphene formation for 15 x 15 x 1 supercell at Tanneal = XXX K, *z* = 2

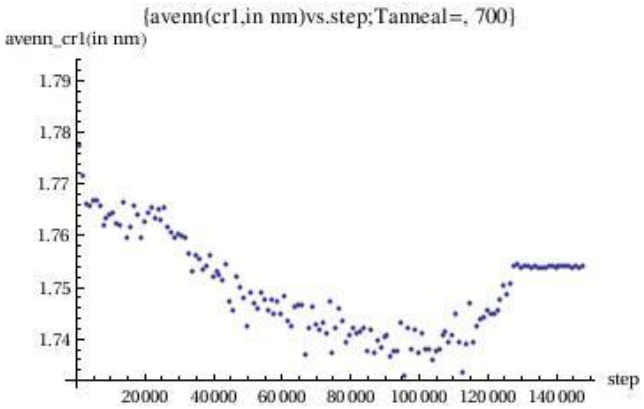
- We found that for substrate thickness *z* = 2, double-layered graphene is formed at as low as Tanneal = xxx K.
- The dynamical formation for Tanneal = xxx K can be visualised by viewing the following files with VMD, using option File -> ‘Load Visualization State’. These are processed trajectory files where dynamic bonding option was enabled, with Distance Cutoff set to xx.
- xxx_dynamicbonding_graphene.vmd
- xxx_dynamicbonding_bulk.vmd

Tanneal = 700 K for substrate thickness z = 2 (binding energy)

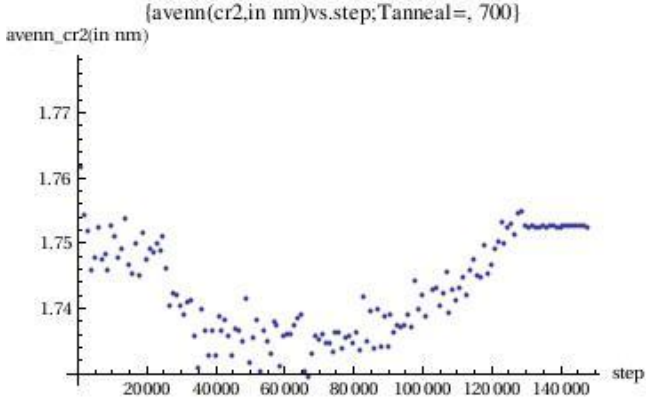




Tanneal = 700 K for substrate thickness z = 2 (nearest neighbour)

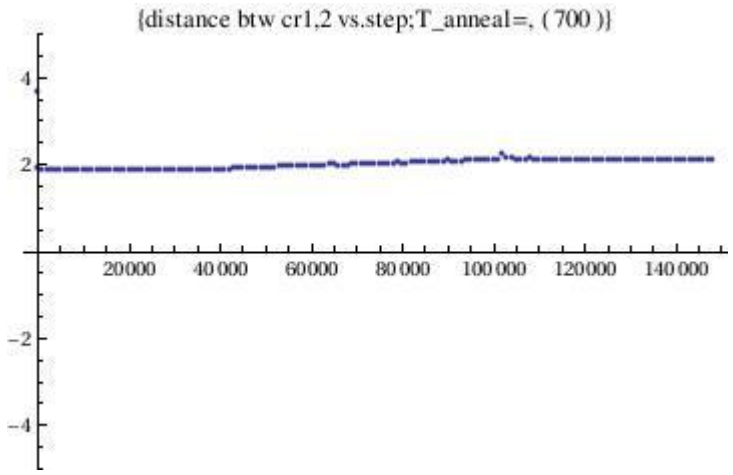


Top carbon rich layer

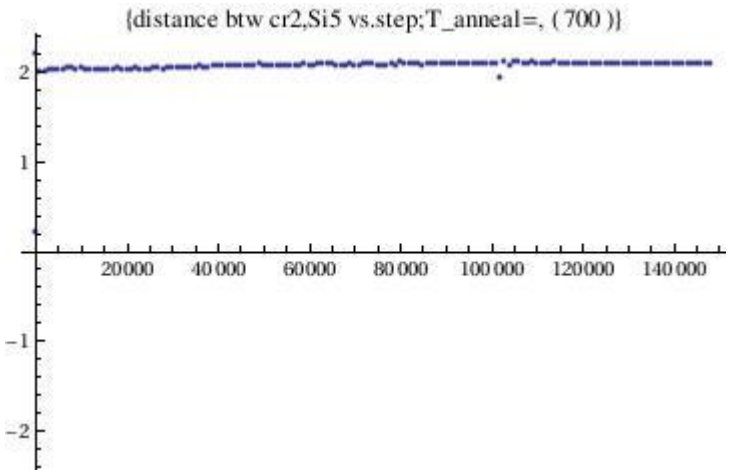


Second carbon rich layer

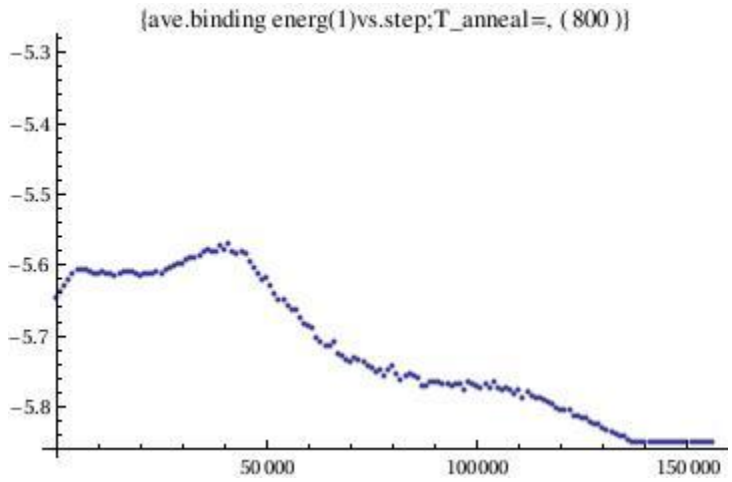
Tanneal = 700 K for substrate thickness *z* = 2 (distance between two graphene layer)

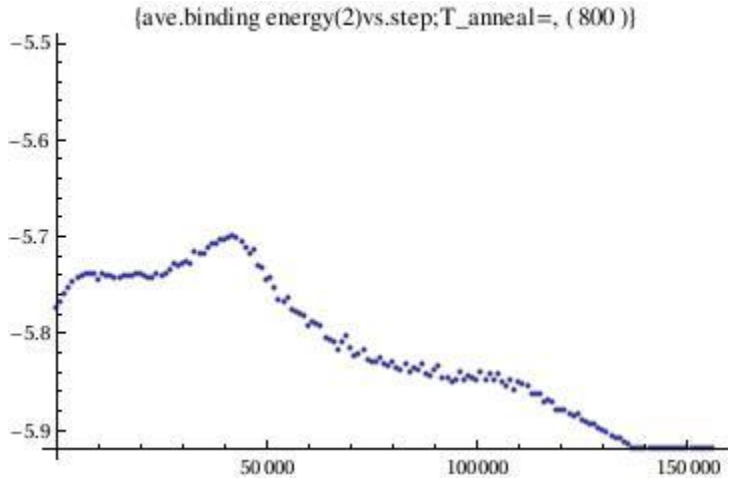


Tanneal = 700 K for substrate thickness z = 2 (distace between graphene and buffer layer)

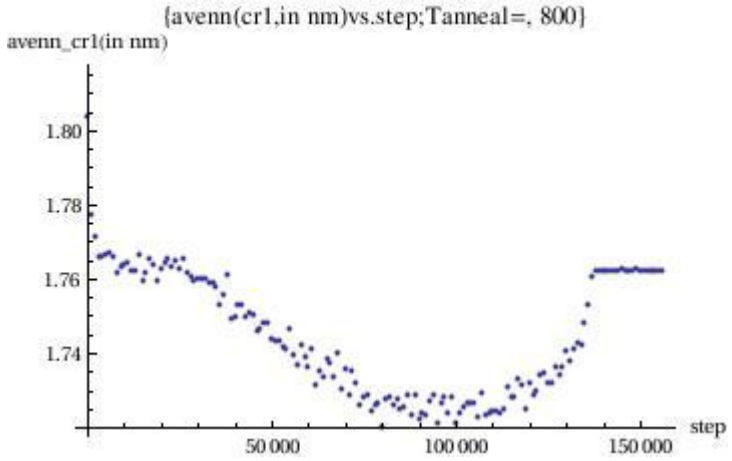


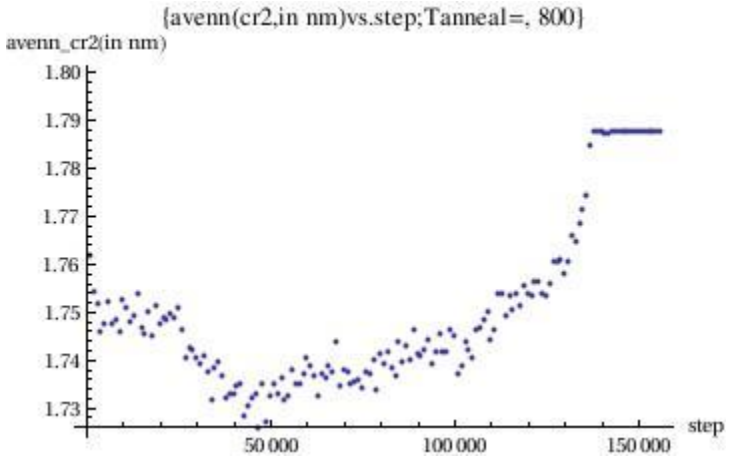
Tanneal = 800 K for substrate thickness *z* = 2 (binding energy)



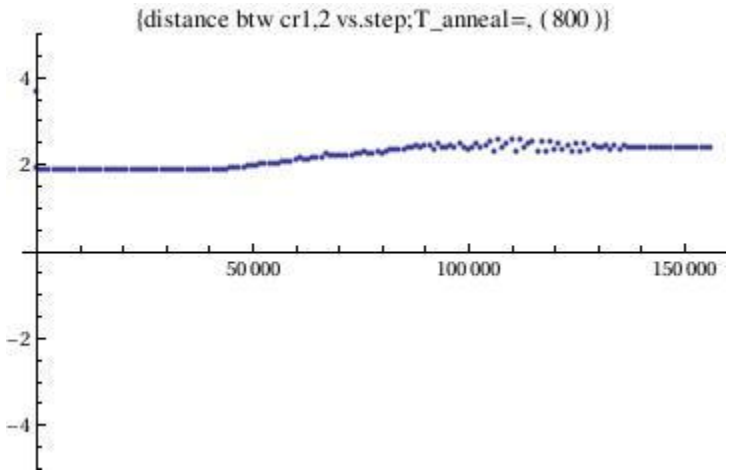


Tanneal = 800 K for substrate thickness z = 2 (nearest neighbour)

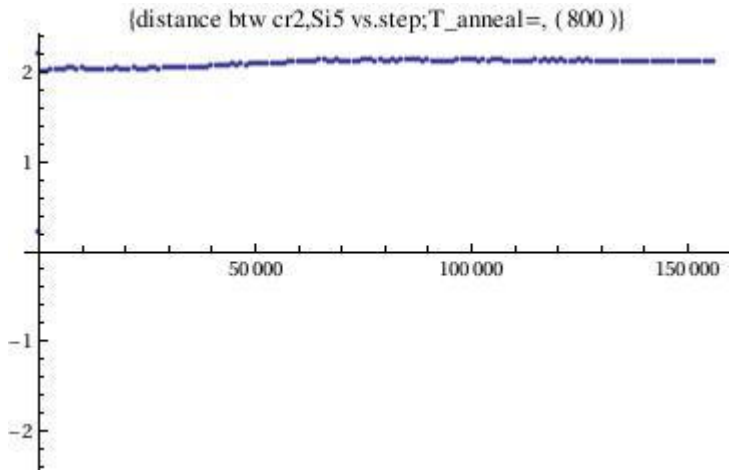




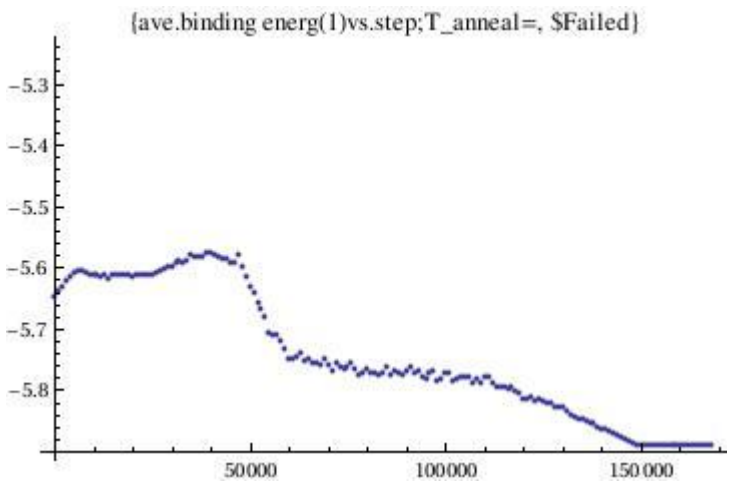
Tanneal = 800 K for substrate thickness z = 2 (distance between two graphene layer)

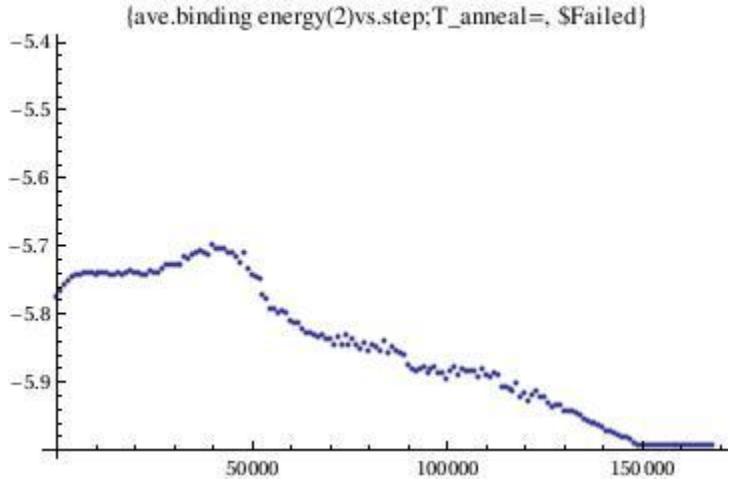


Tanneal = 800 K for substrate thickness z = 2 (distace between graphene and buffer layer)

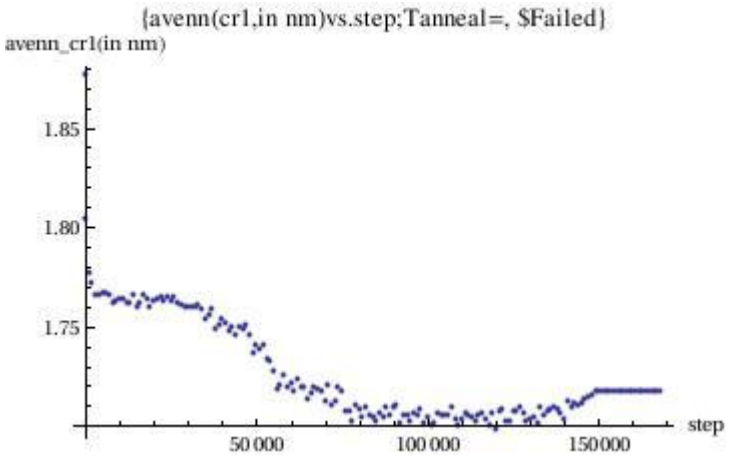


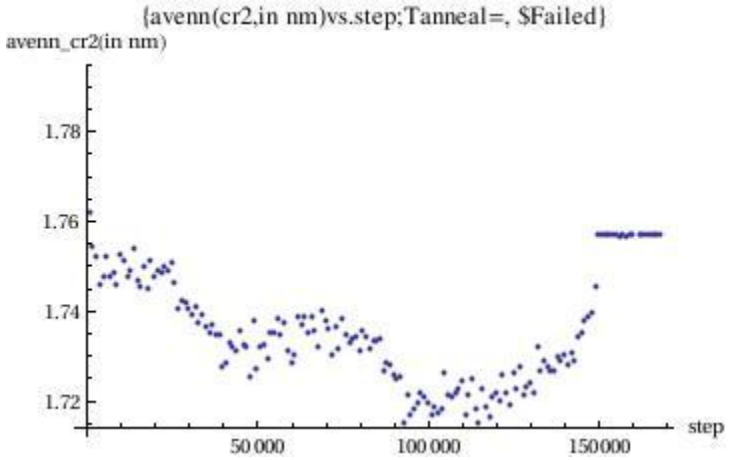
Tanneal = 900 K for substrate thickness z = 2 (binding energy)



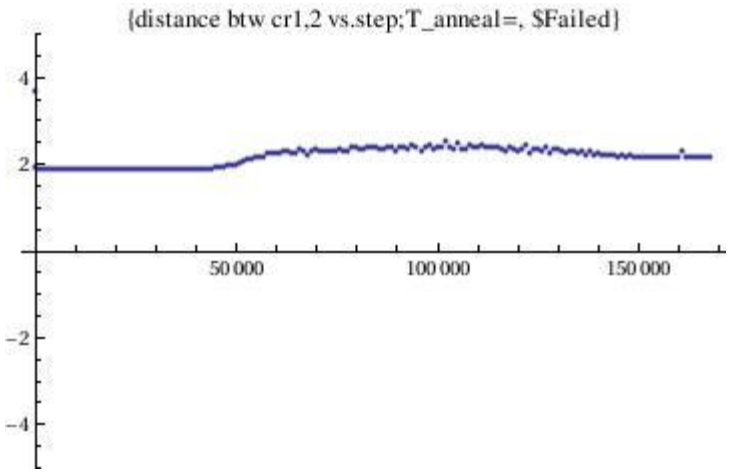


Tanneal = 900 K for substrate thickness z = 2 (nearest neighbour)

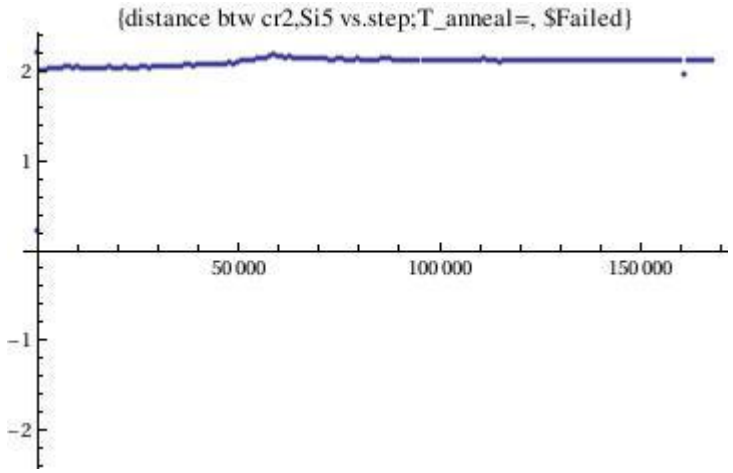




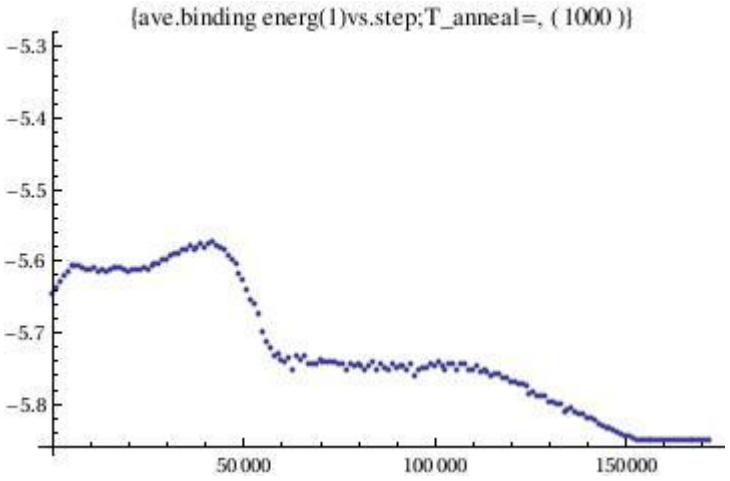
Tanneal = 900 K for substrate thickness *z* = 2 (distance between two graphene layer)

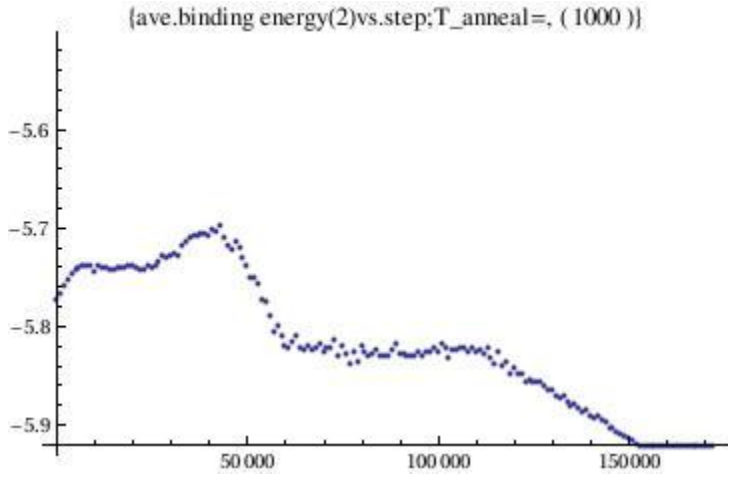


Tanneal = 900 K for substrate thickness *z* = 2 (distace between graphene and buffer layer)

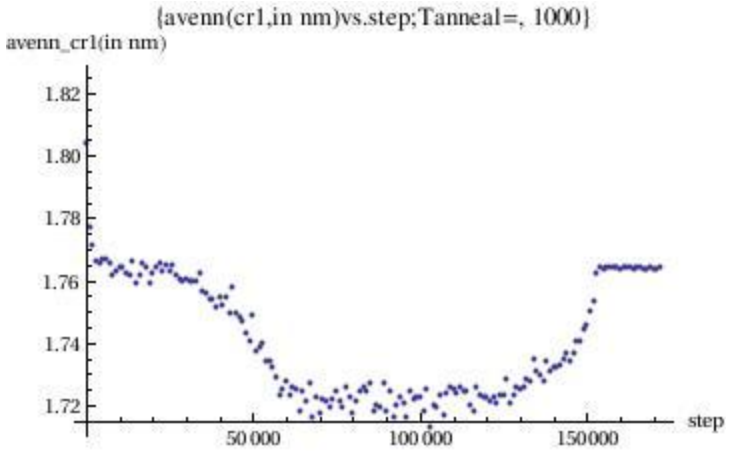


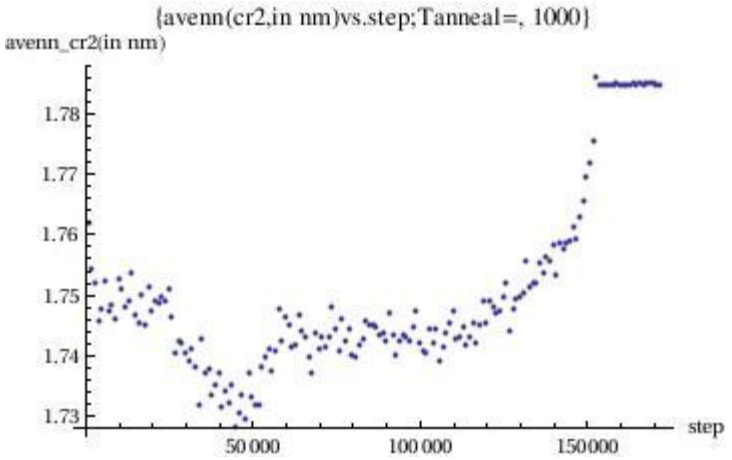
Tanneal = 1000 K for substrate thickness *z* = 2 (binding energy)



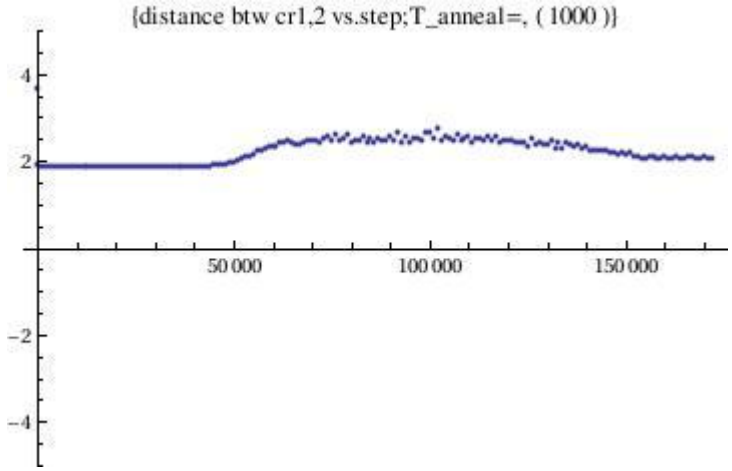


Tanneal = 1000 K for substrate thickness *z* = 2 (nearest neighbour)

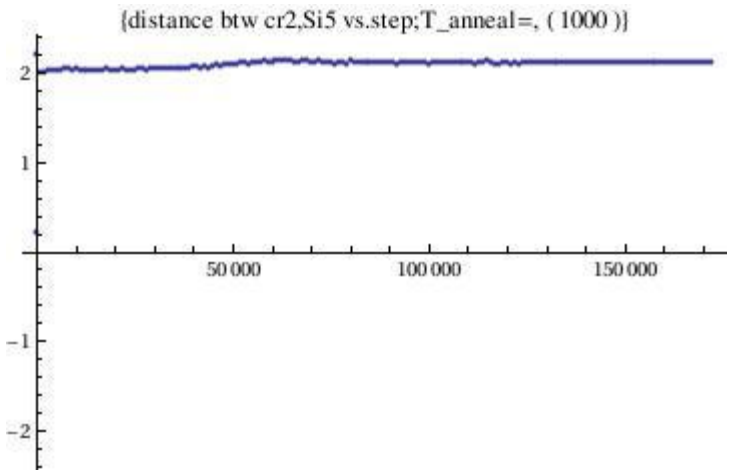




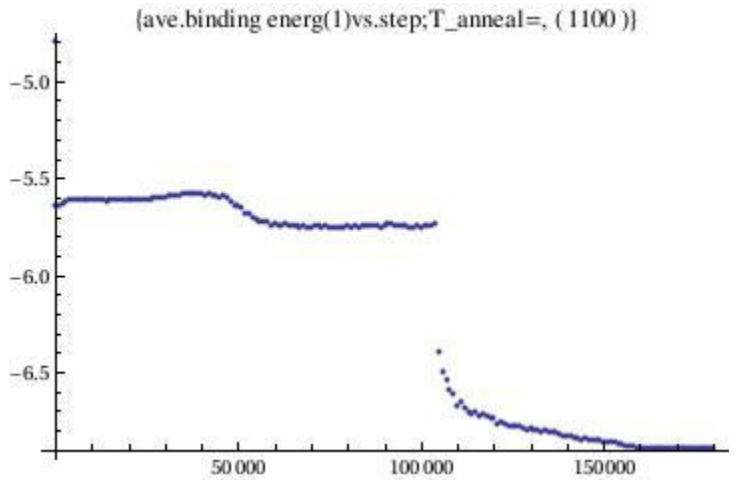
Tanneal = 1000 K for substrate thickness *z* = 2 (distance between two graphene layer)

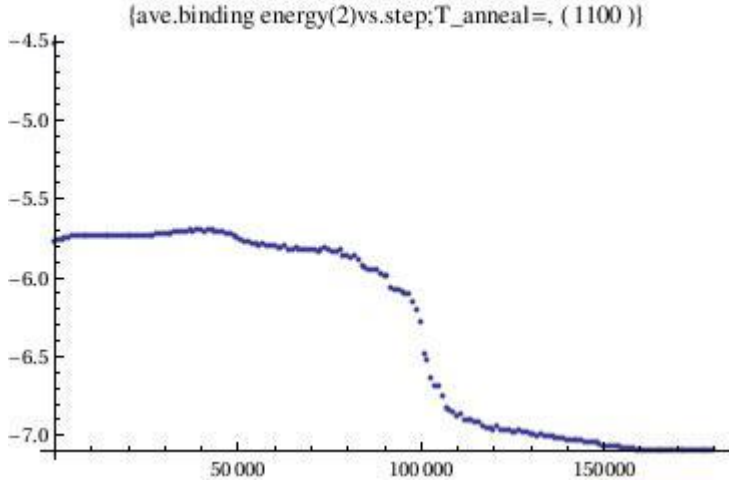


Tanneal = 1000 K for substrate thickness *z* = 2 (distace between graphene and buffer layer)

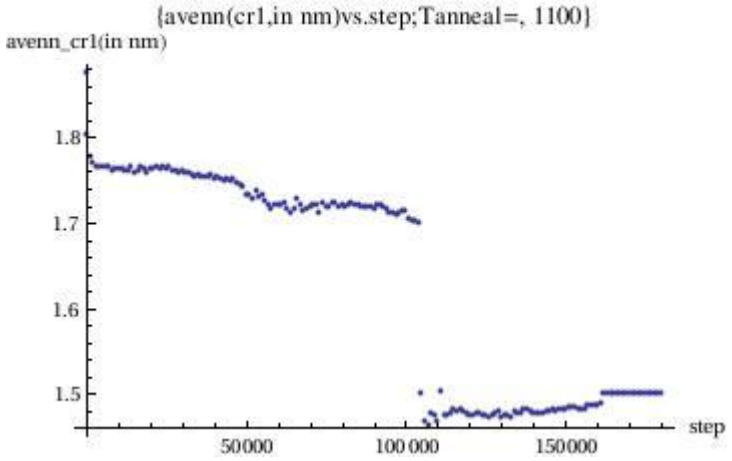


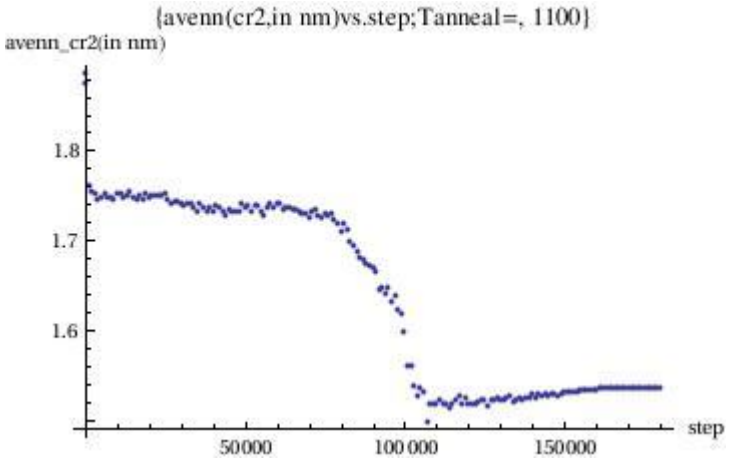
Tanneal = 1100 K for substrate thickness *z* = 2 (binding energy)



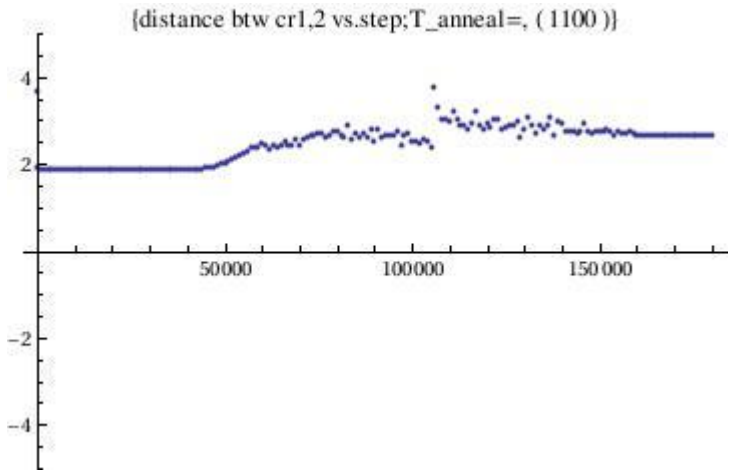


Tanneal = 1100 K for substrate thickness *z* = 2 (nearest neighbour)

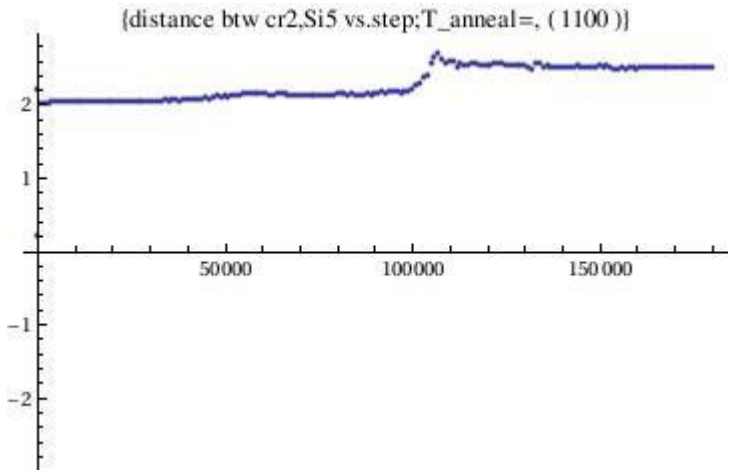




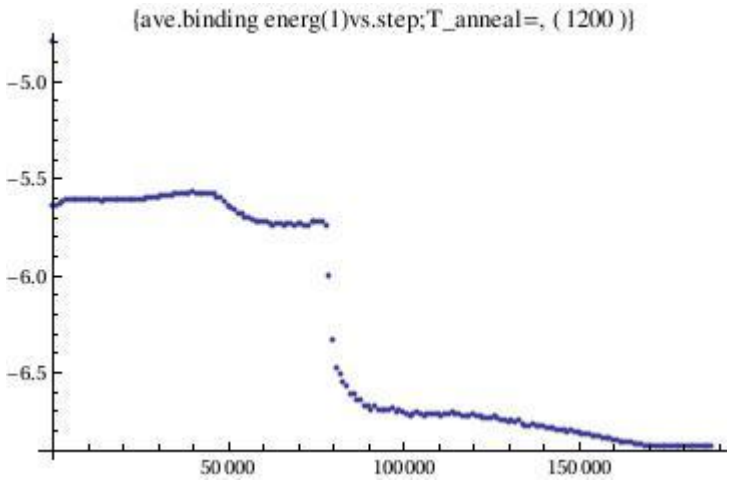
Tanneal = 1100 K for substrate thickness *z* = 2 (distance between two graphene layer)

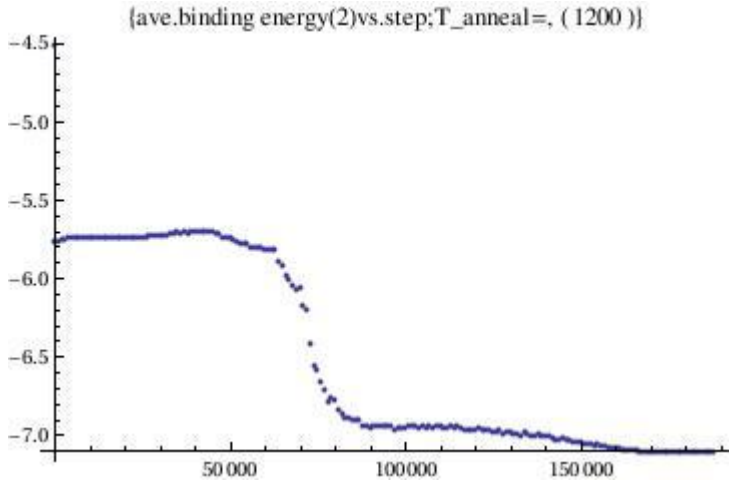


Tanneal = 1100 K for substrate thickness *z* = 2 (distace between graphene and buffer layer)

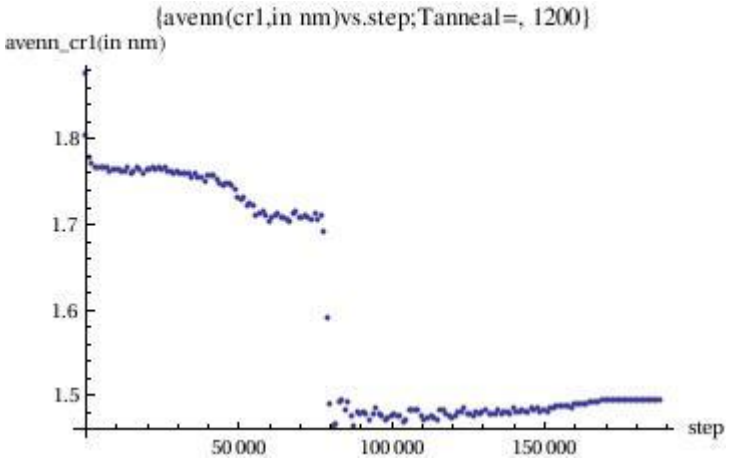


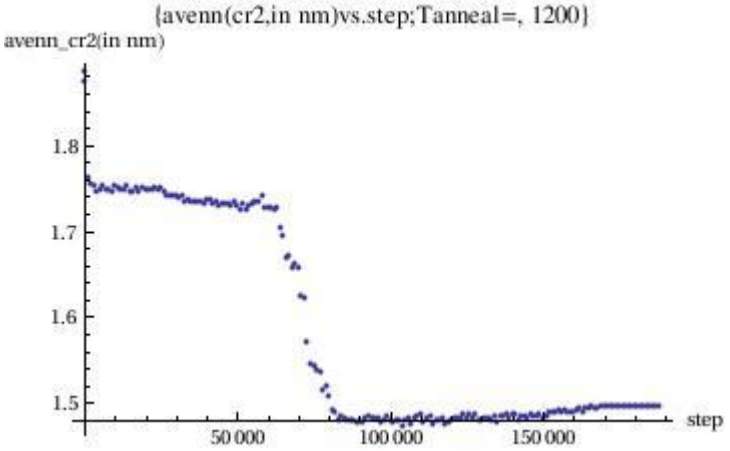
Tanneal = 1200 K for substrate thickness *z* = 2 (binding energy)



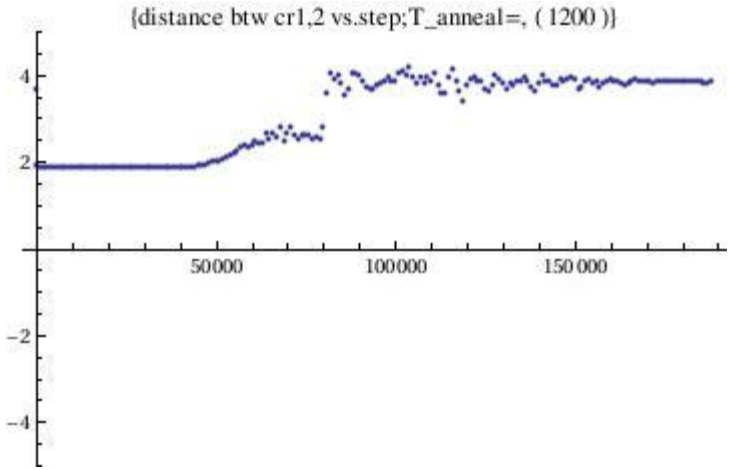


Tanneal = 1200 K for substrate thickness *z* = 2 (nearest neighbour)

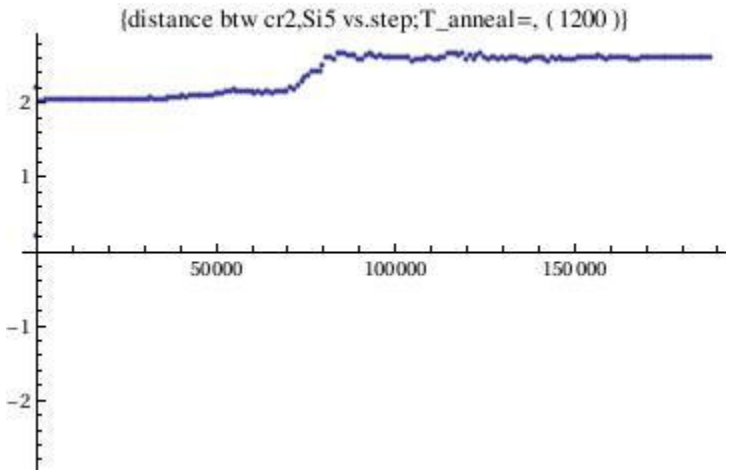




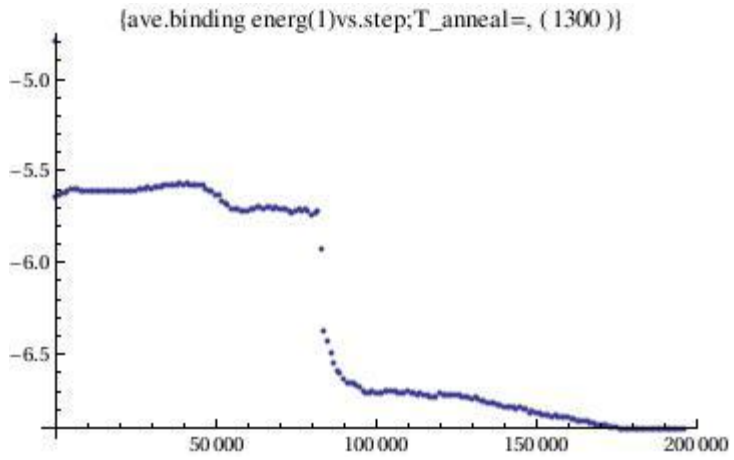
Tanneal = 1200 K for substrate thickness *z* = 2 (distance between two graphene layer)

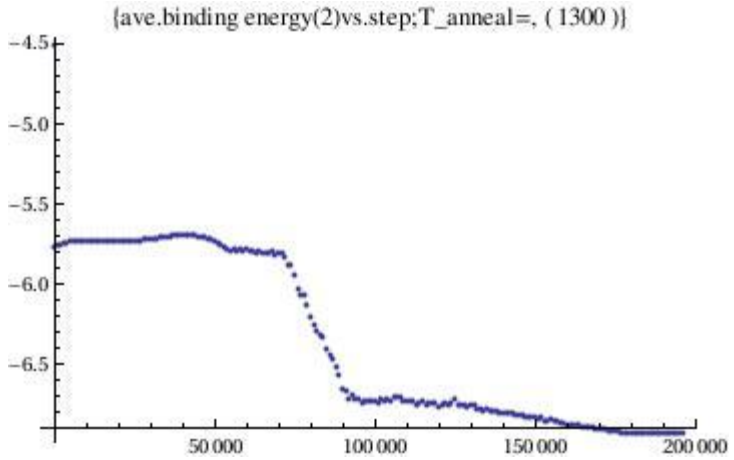


Tanneal = 1200 K for substrate thickness *z* = 2 (distace between graphene and buffer layer)

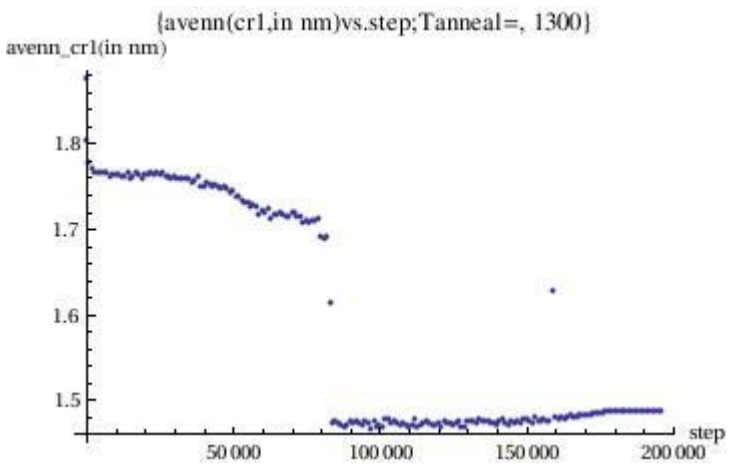


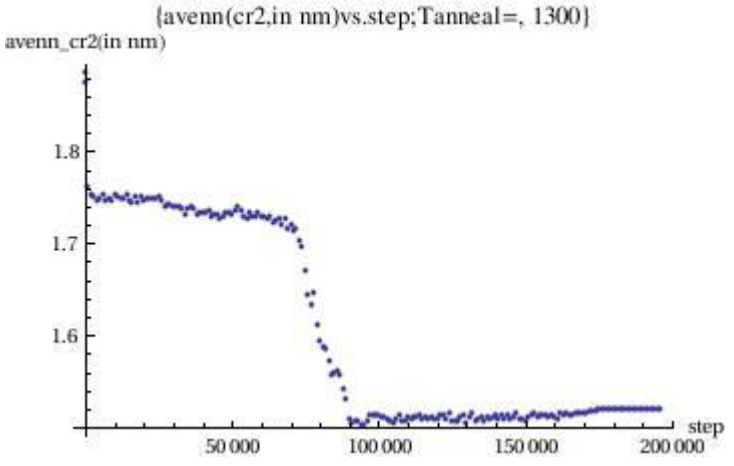
Tanneal = 1300 K for substrate thickness *z* = 2 (binding energy)



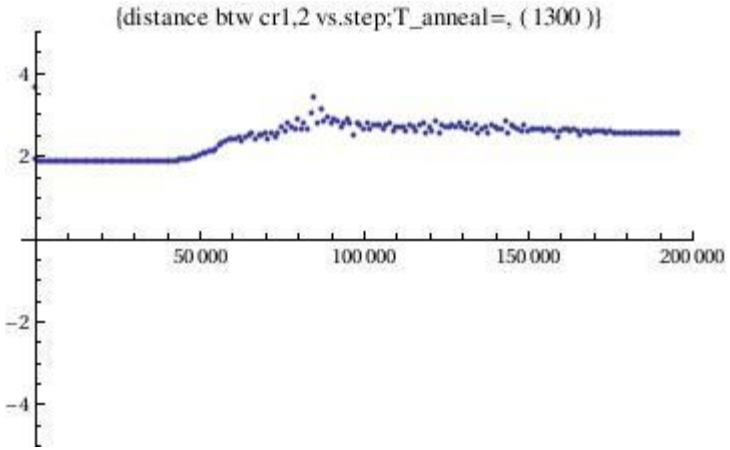


Tanneal = 1300 K for substrate thickness *z* = 2 (nearest neighbour)

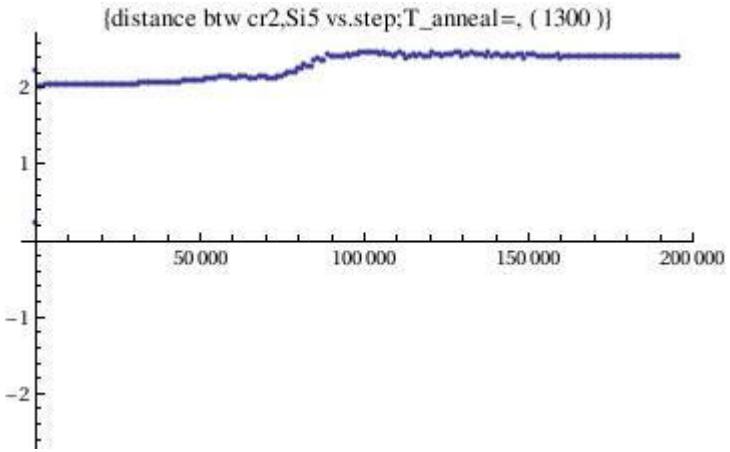




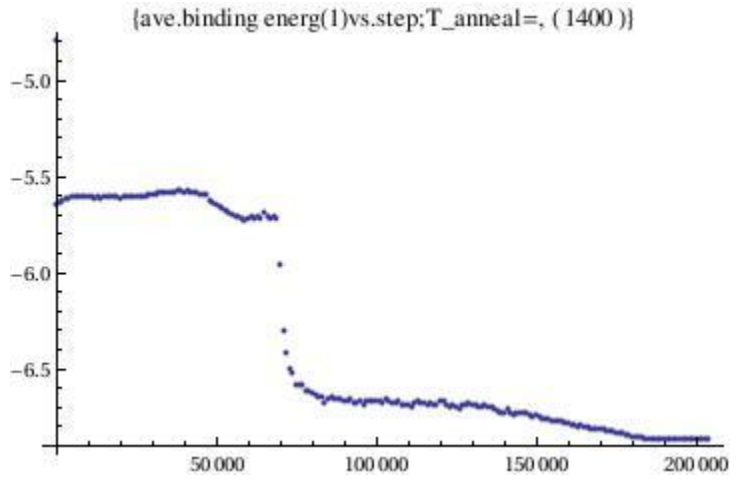
Tanneal = 1300 K for substrate thickness *z* = 2 (distance between two graphene layer)

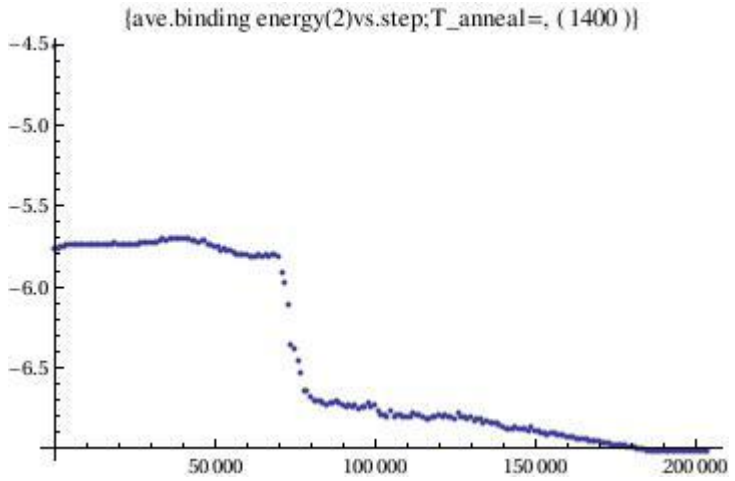


Tanneal = 1300 K for substrate thickness *z* = 2 (distace between graphene and buffer layer)

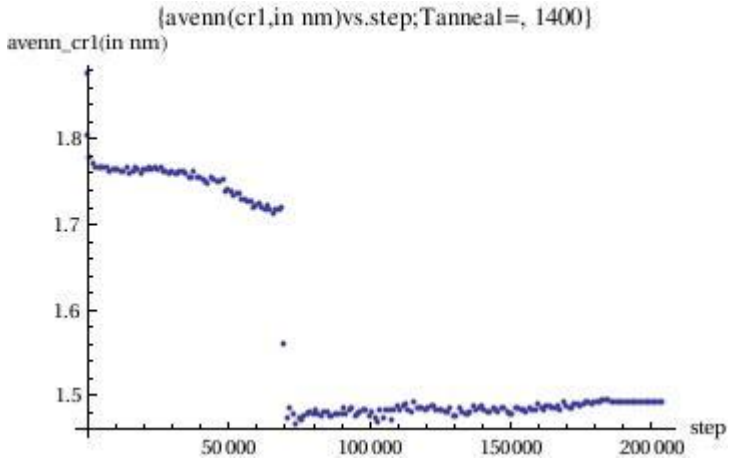


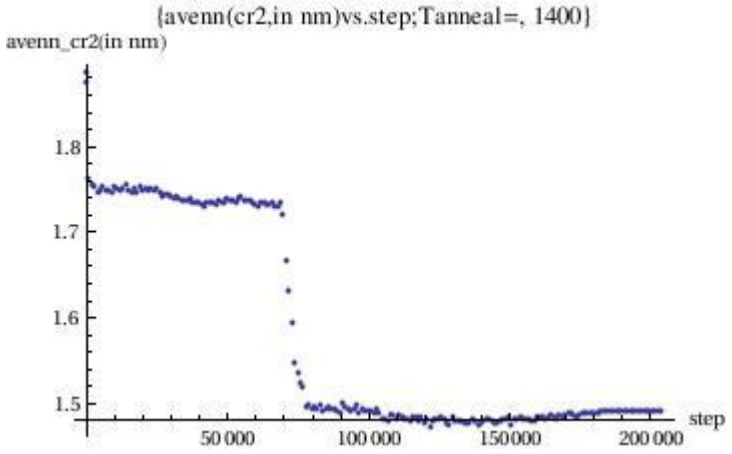
Tanneal = 1400 K for substrate thickness *z* = 2 (binding energy)



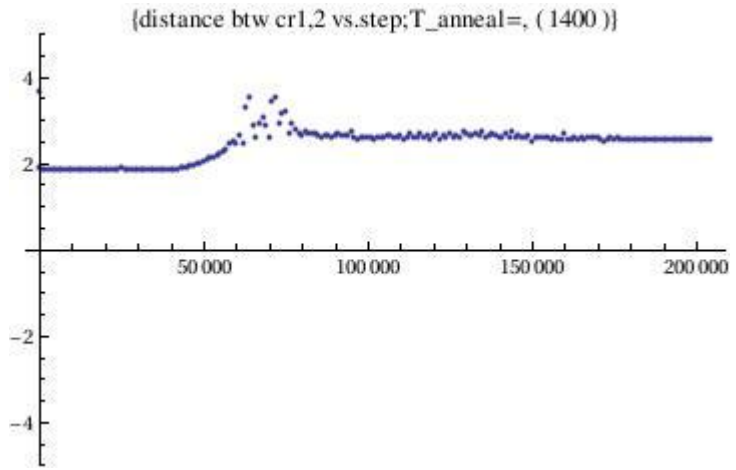


Tanneal = 1400 K for substrate thickness *z* = 2 (nearest neighbour)

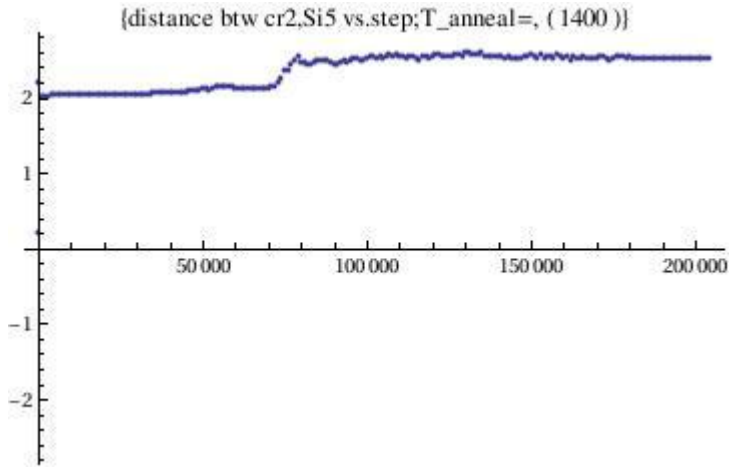




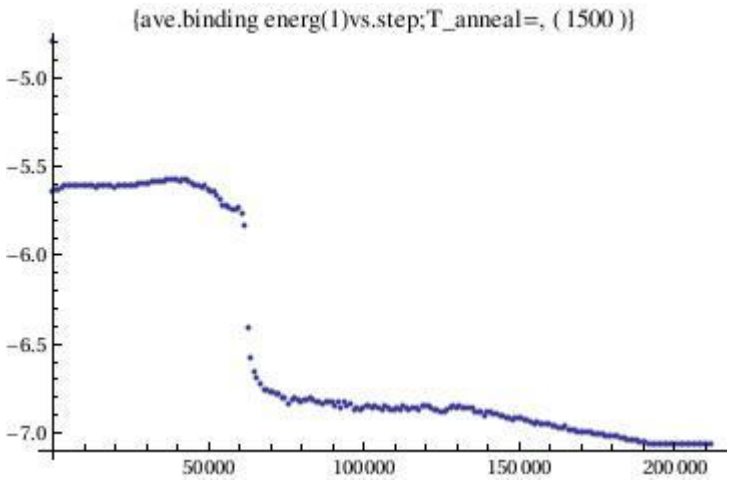
Tanneal = 1400 K for substrate thickness *z* = 2 (distance between two graphene layer)

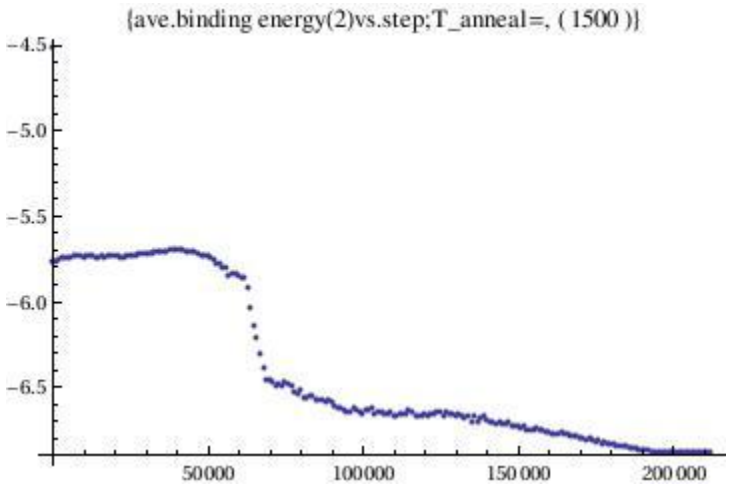


Tanneal = 1400 K for substrate thickness *z* = 2 (distace between graphene and buffer layer)

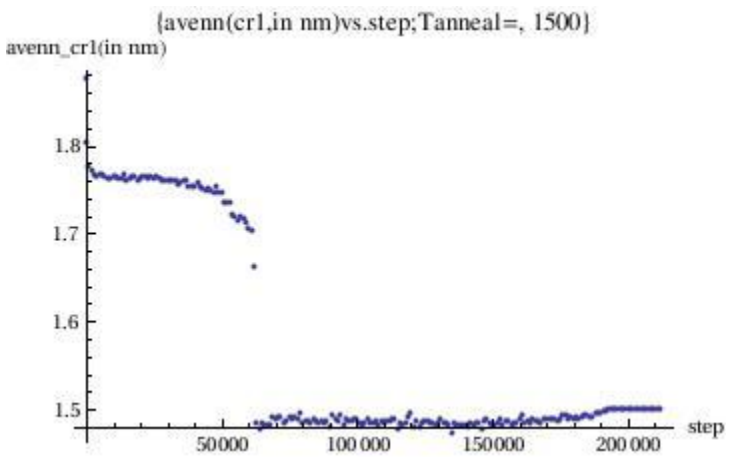


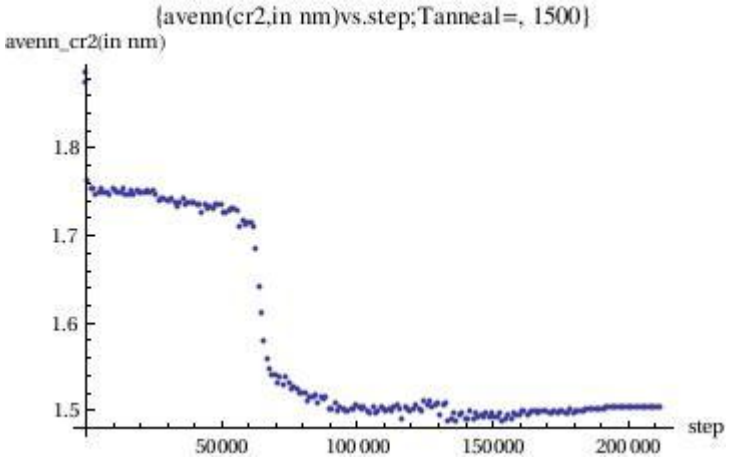
Tanneal = 1500 K for substrate thickness *z* = 2 (binding energy)



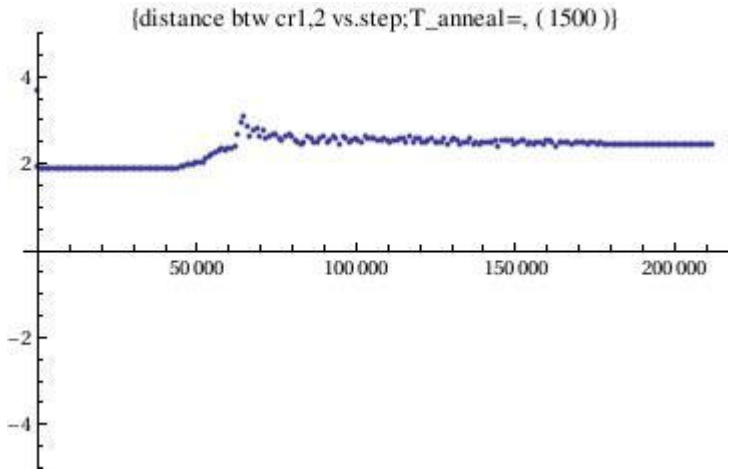


Tanneal = 1500 K for substrate thickness *z* = 2 (nearest neighbour)

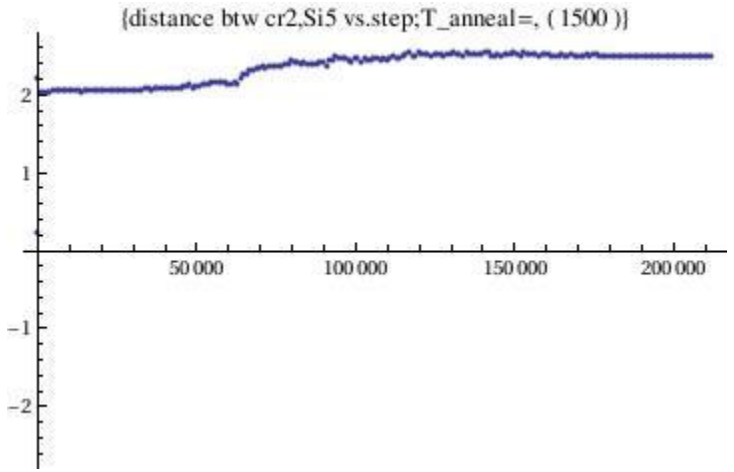




Tanneal = 1500 K for substrate thickness *z* = 2 (distance between two graphene layer)

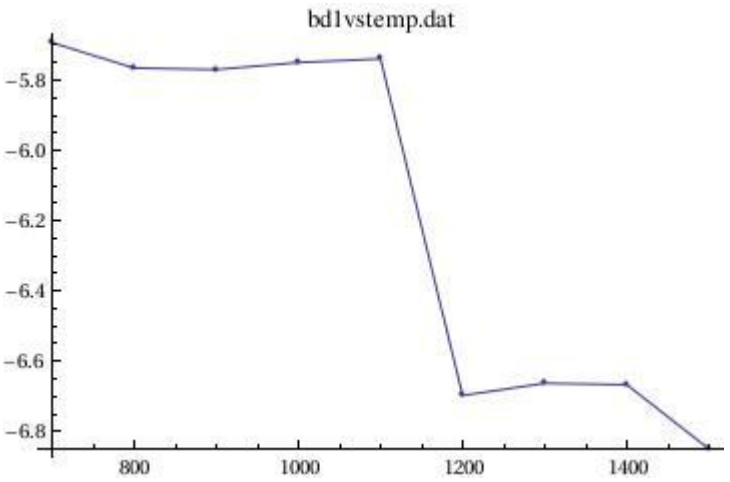


Tanneal = 1500 K for substrate thickness *z* = 2 (distace between graphene and buffer layer)

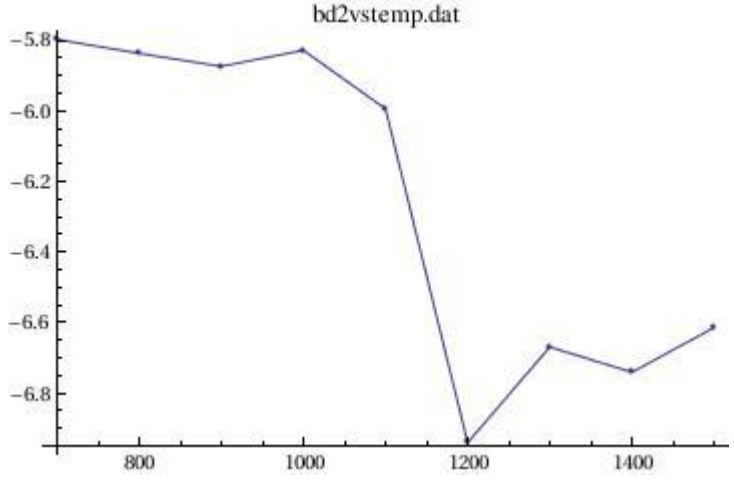


Summary of Annealing of 2 Layers Greaphene

Binding Energy

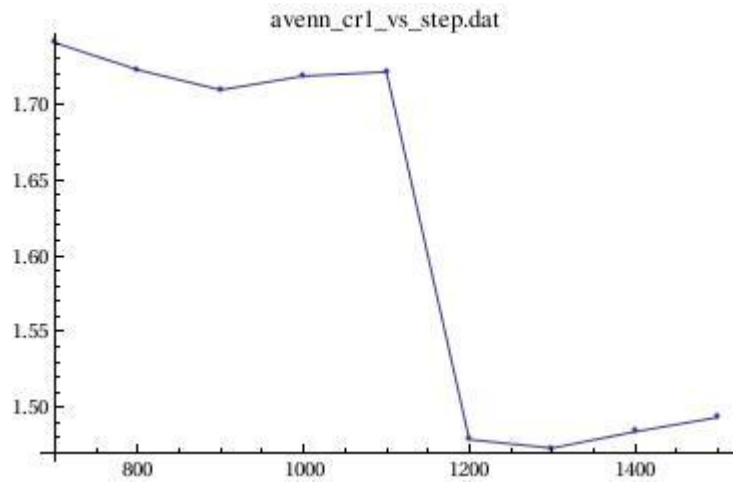


Top carbon-rich layer

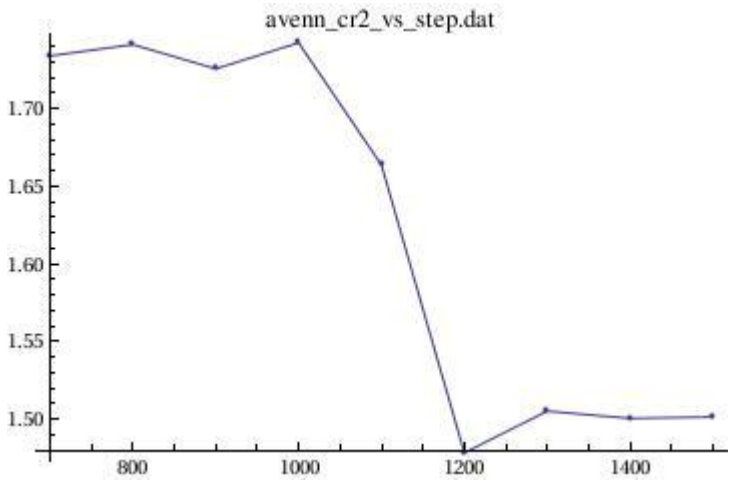


second carbon-rich layer

Average Nearest Neighbour

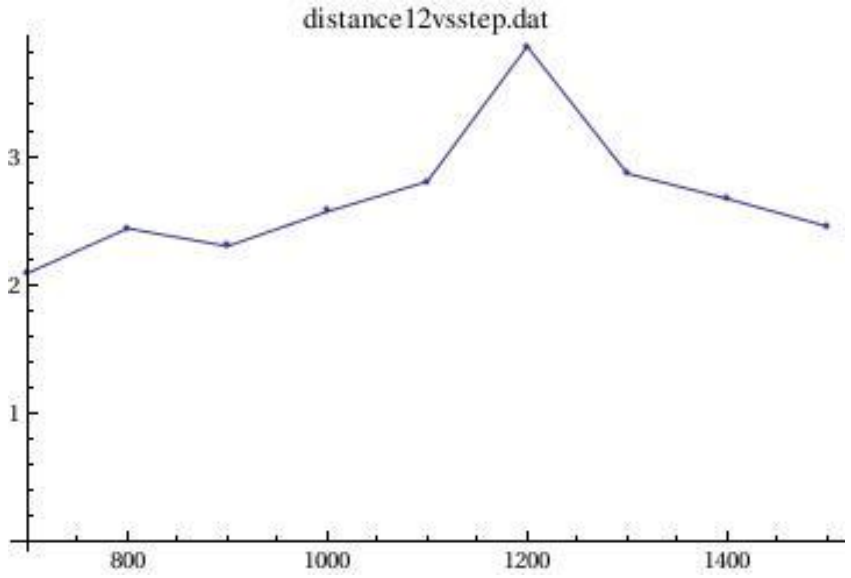


Top carbon-rich layer

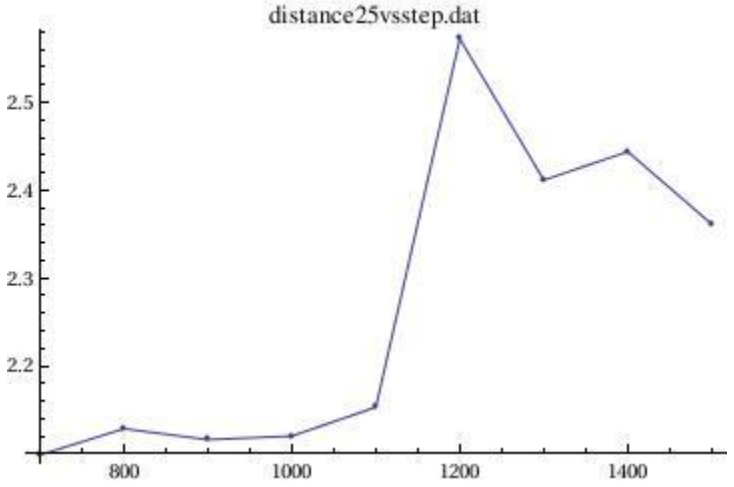


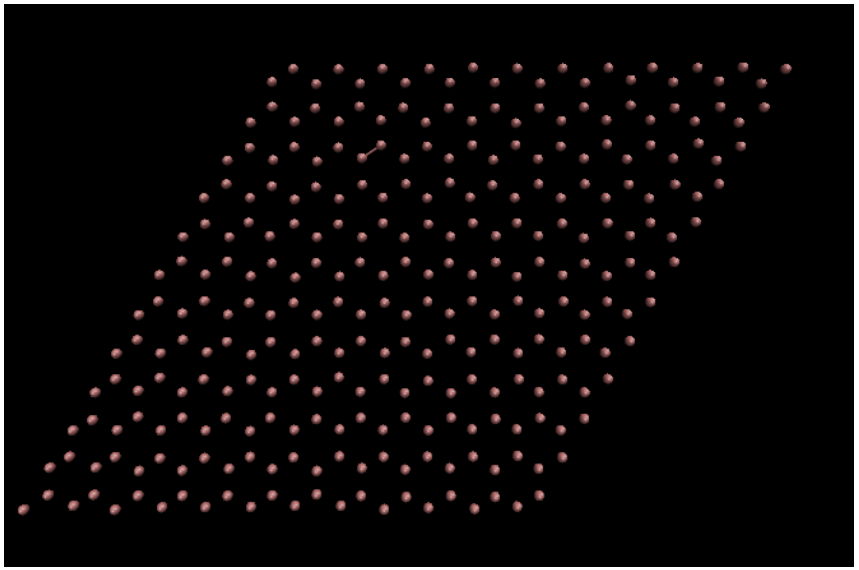
second carbon-rich layer

Average Distance of Two Graphene Layers

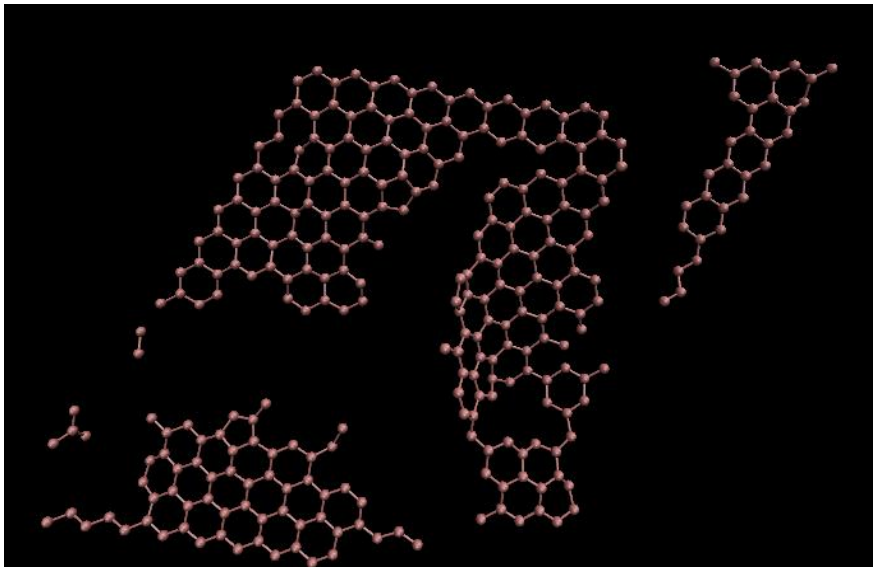


Distance Between Graphene and Buffer Layer

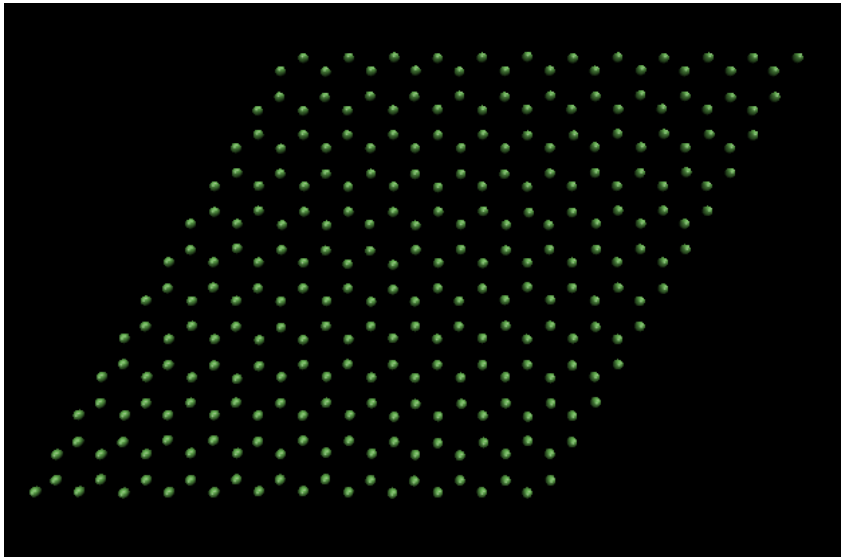




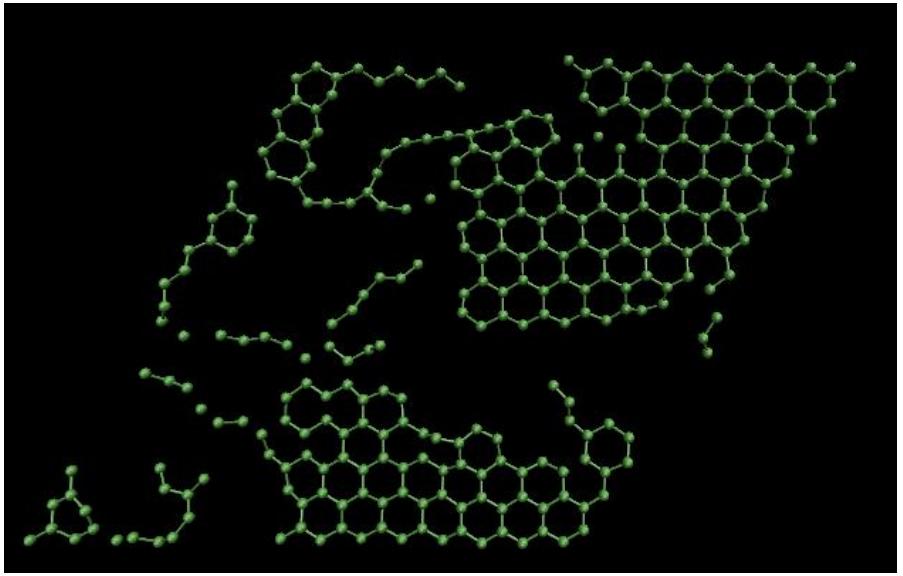
Top layer carbon at 300 K



Top layer graphene formation at 1200 K



Bottom layer carbon at 300 K

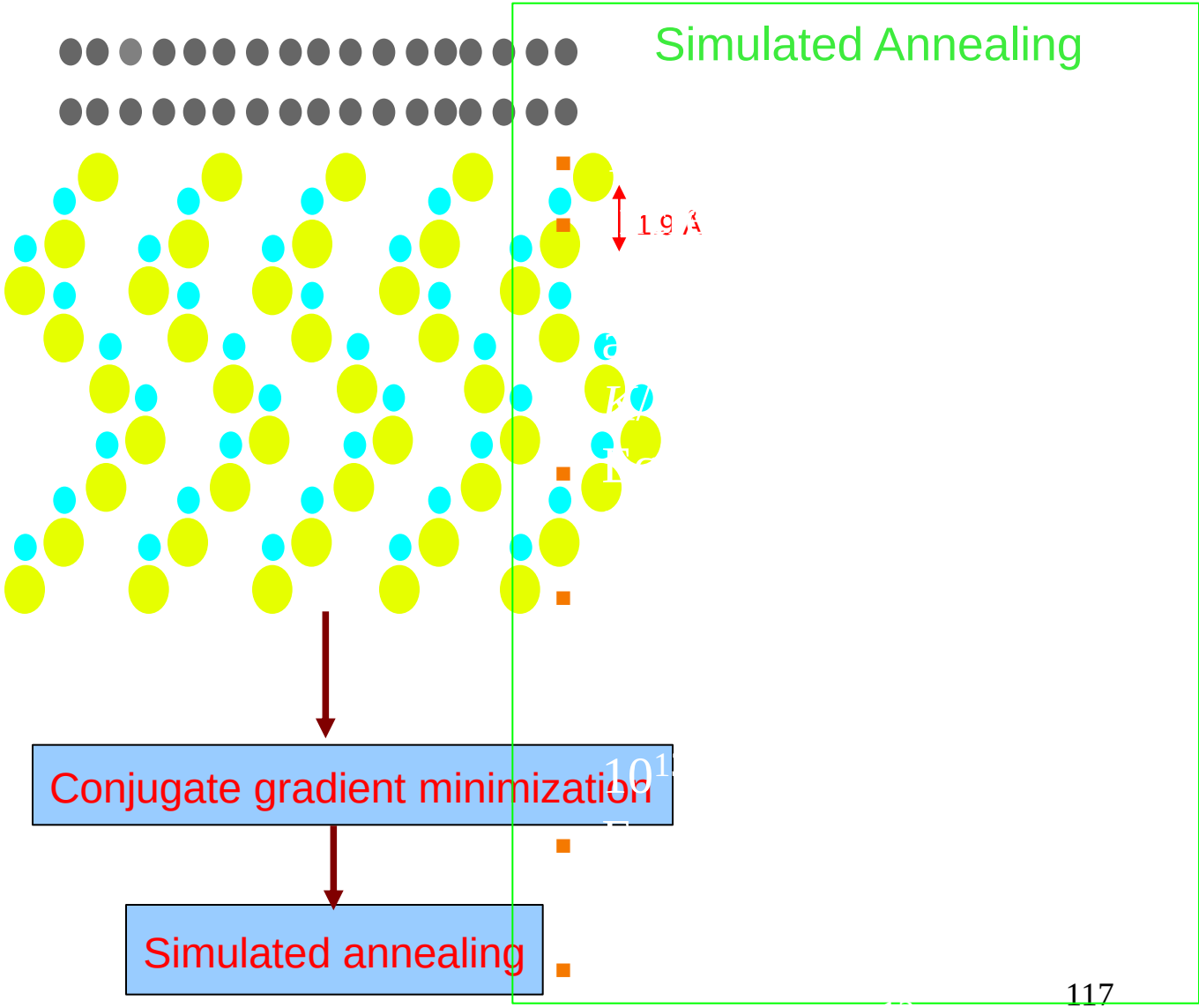


Bottom layer graphene formation at 1200 K

We have the identical results with the thickness of substrate z=3

Three-layered carbon-rich substrate with thickness $z = 2$ for trilayered graphene formation

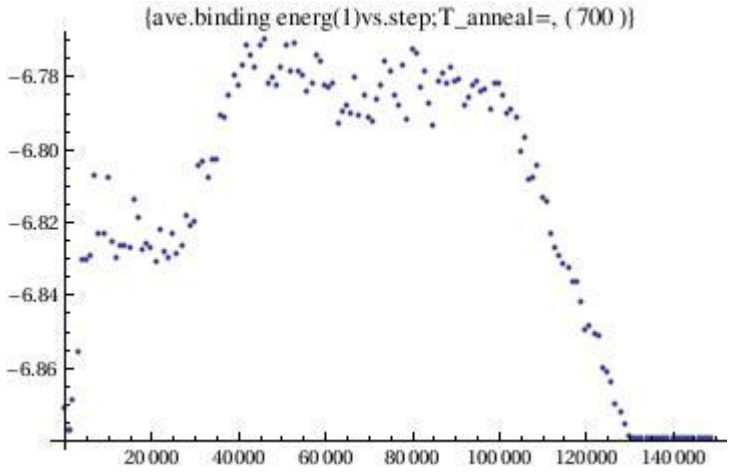
Simulation method of graphene growth (three layers)

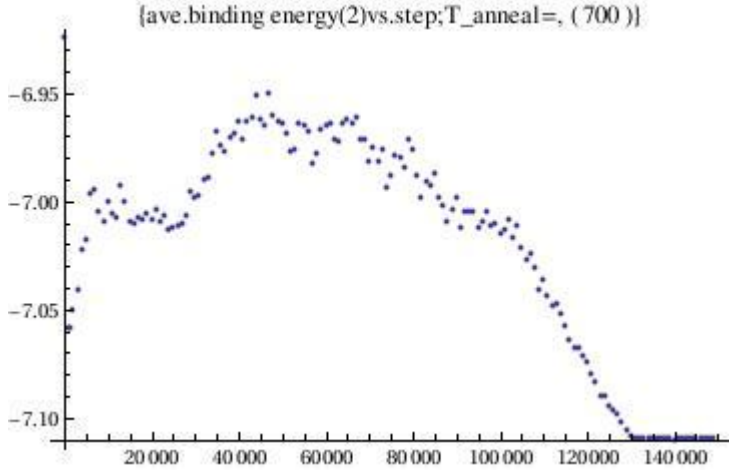


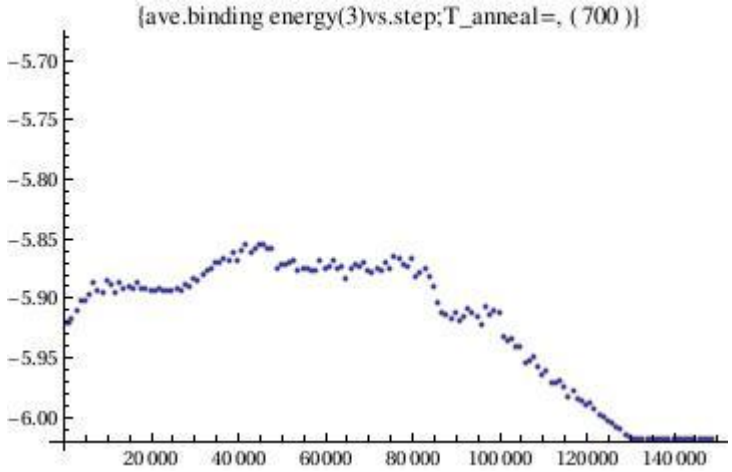
Simulated Annealing

- Timestep = 0.5 fs
- Increase the temperature slowly until it attains 300 *K* at approximately $5^{\times}10^{13}$ *K*/*s*.
- Equilibrating the system at 300 *K* for 20000 MD steps.
- Raise the temperature of the system slowly to the desired T at approximately 10^{13} *K*/*s*.
- Equilibrating the system at T for 30000 MD steps.
- Cool down the system until 0.1 *K* at $5x10^{12}$ *K*/*s*
- Extracting the result.

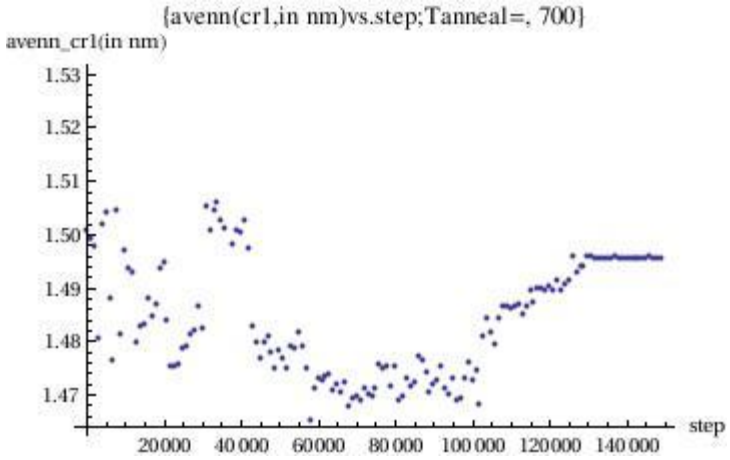
Tanneal = 700 K for substrate (binding energy)

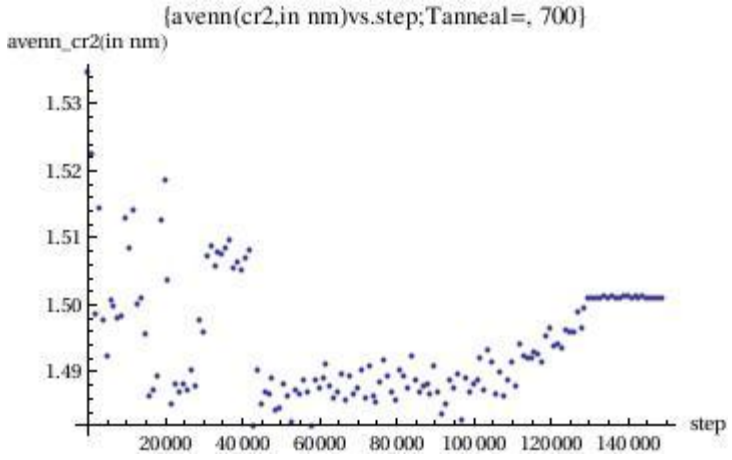


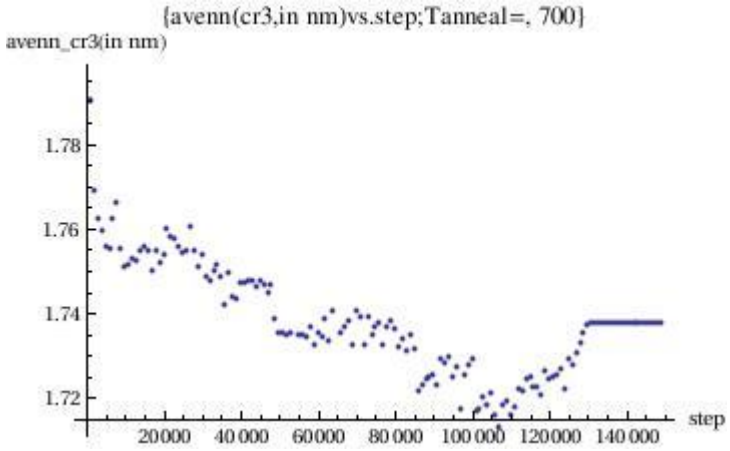




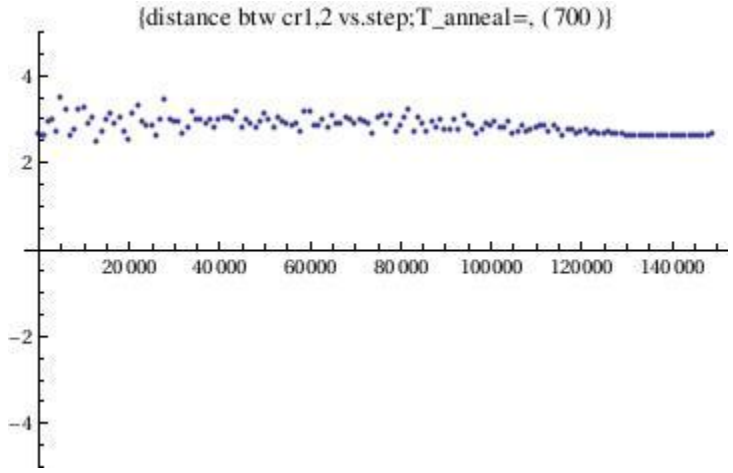
Tanneal = 700 K for substrate (nearest neighbour)

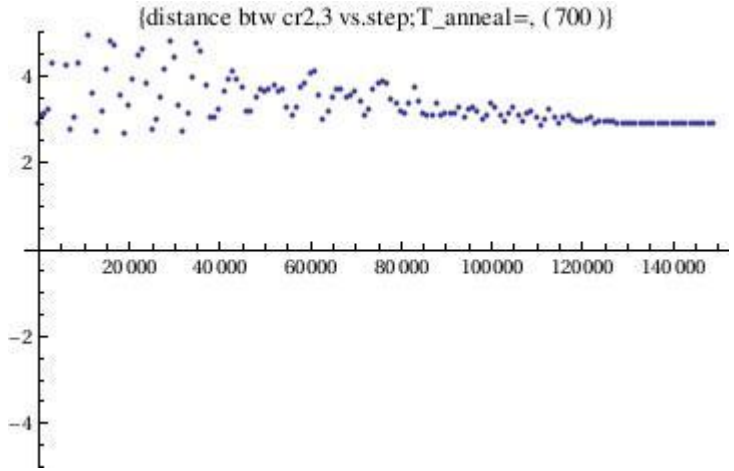




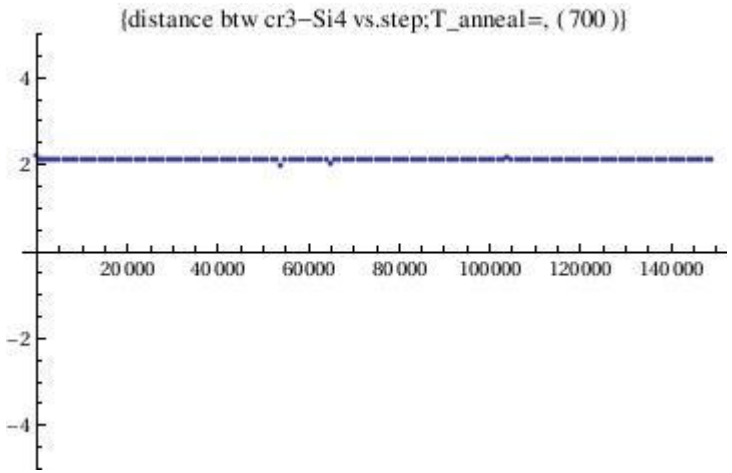


Tanneal = 700 K for substrate (distance between graphene layers)

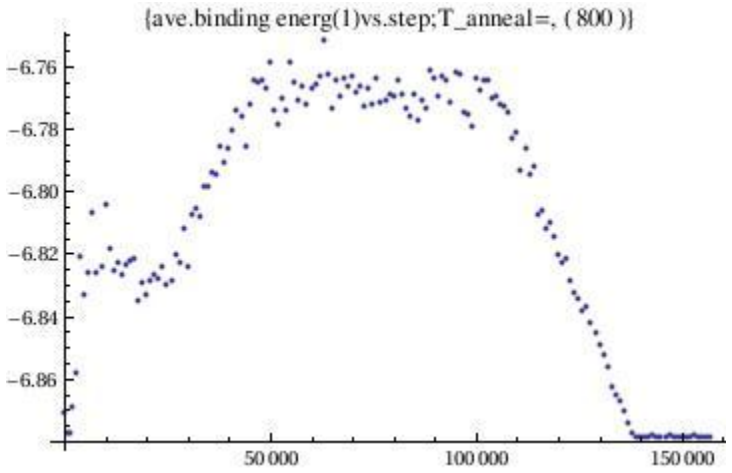


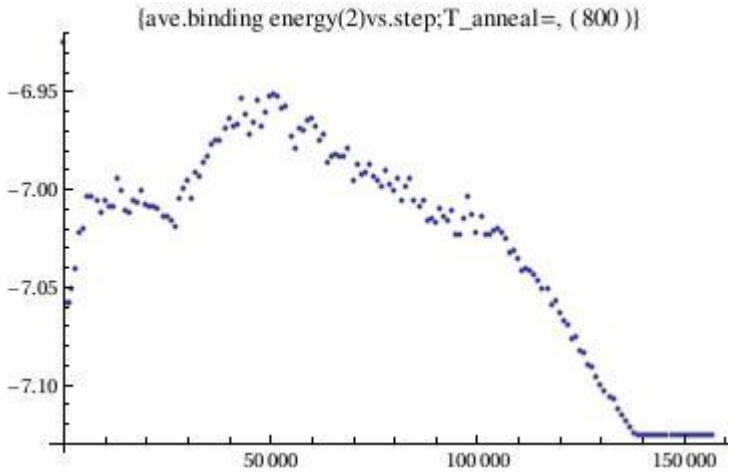


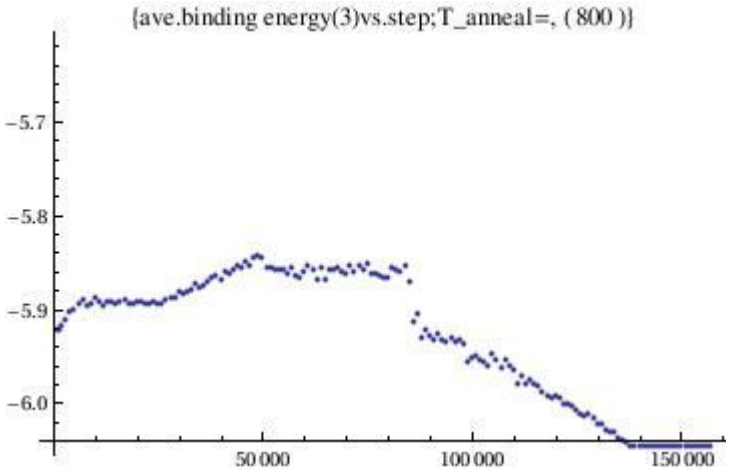
Tanneal = 700 K for substrate (distace between graphene and buffer layer)



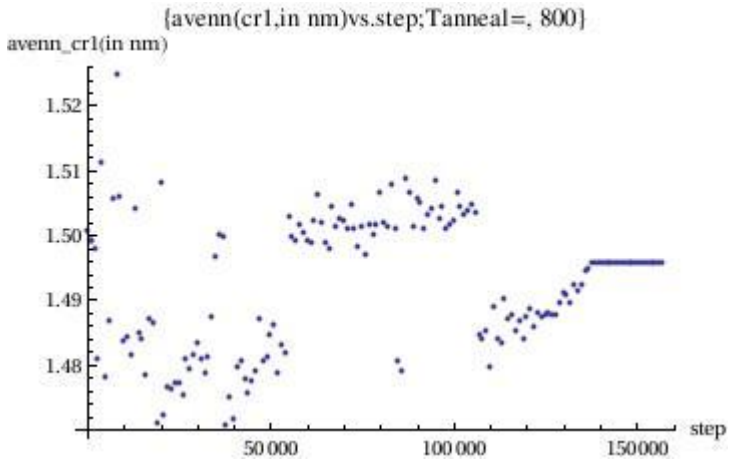
Tanneal = 800 K for substrate (binding energy)

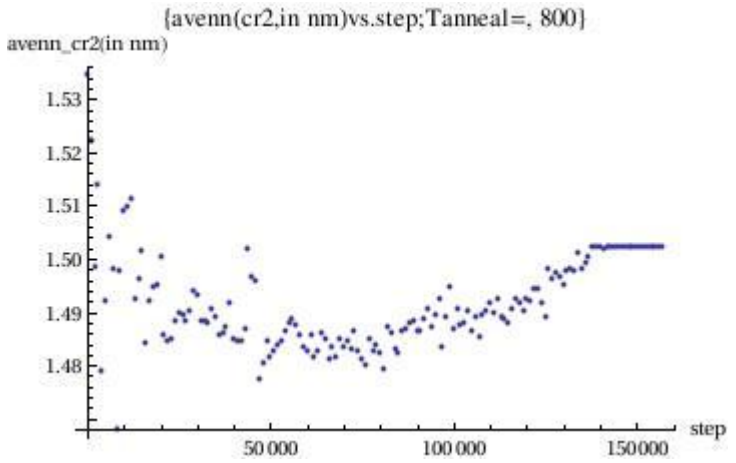


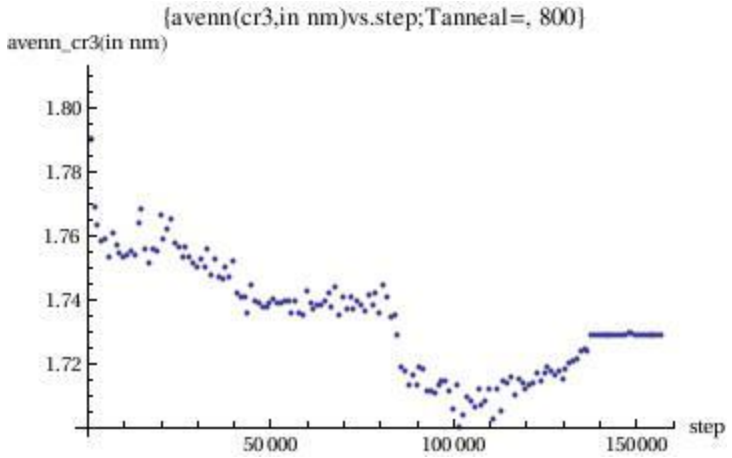




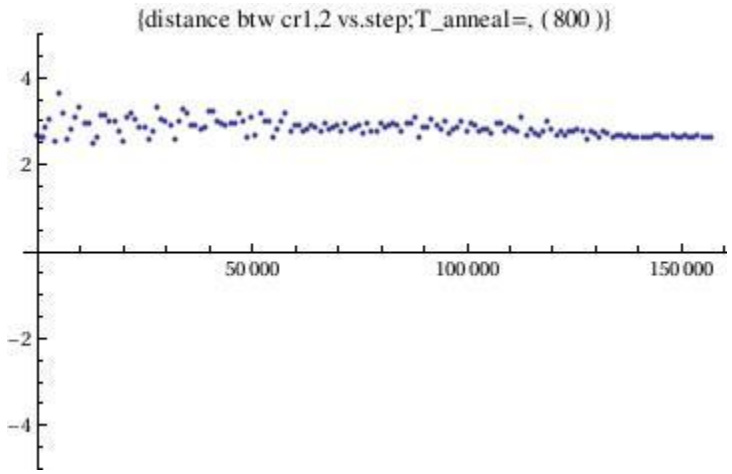
Tanneal = 700 K for substrate (nearest neighbour)

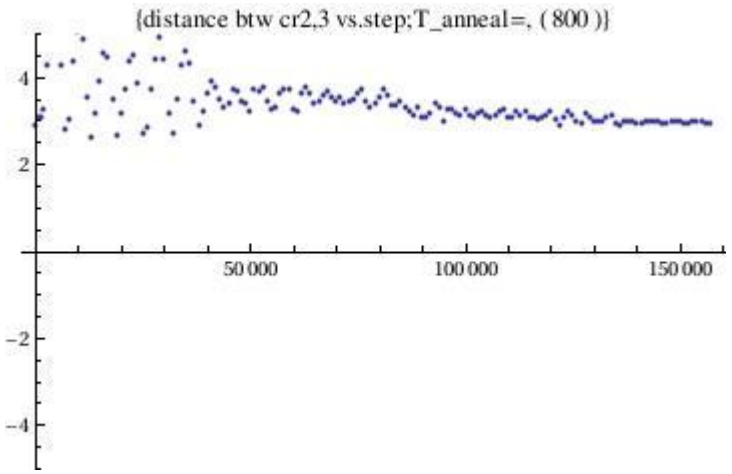




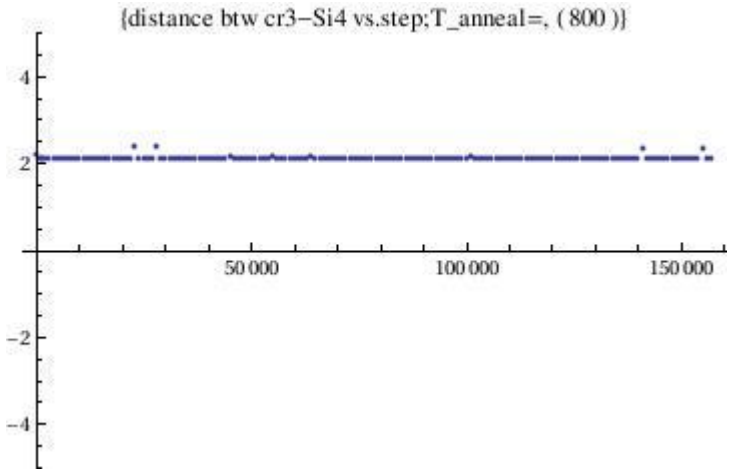


Tanneal = 800 K for substrate (distance between graphene layers)

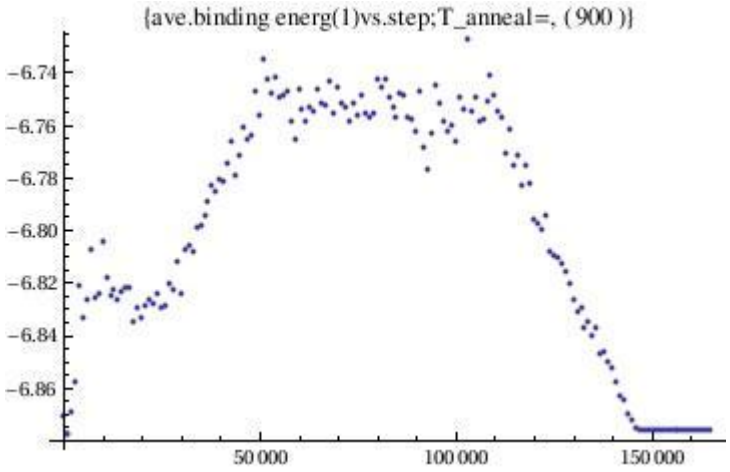


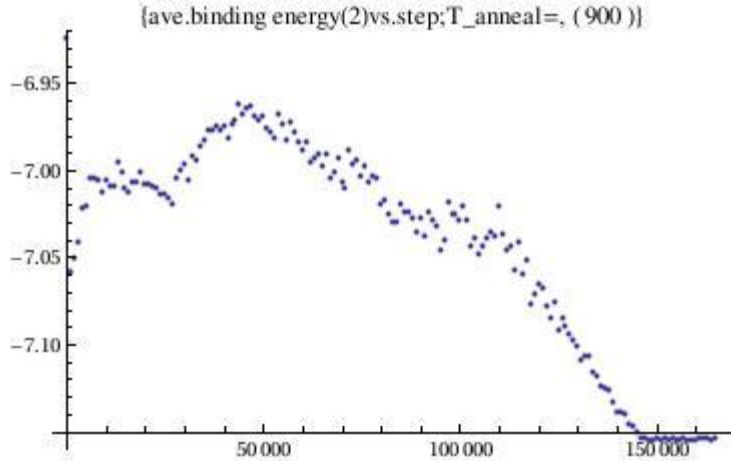


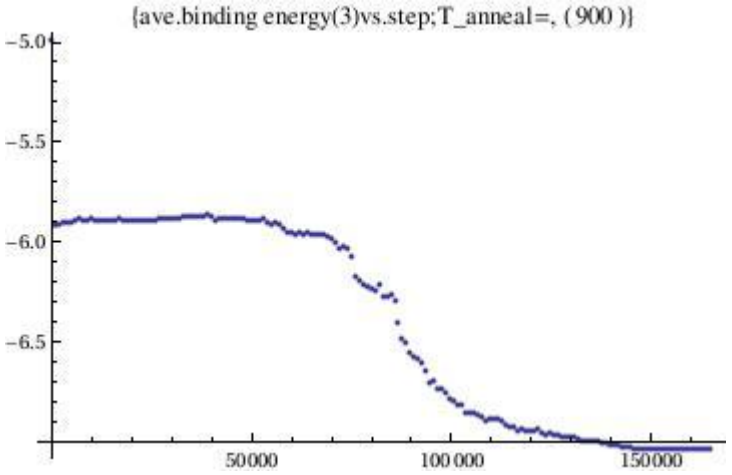
Tanneal = 800 K for substrate (distace between graphene and buffer layer)



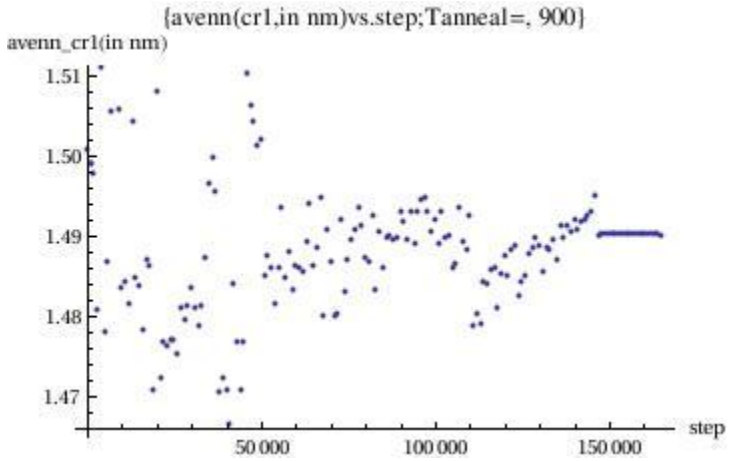
Tanneal = 900 K for substrate (binding energy)

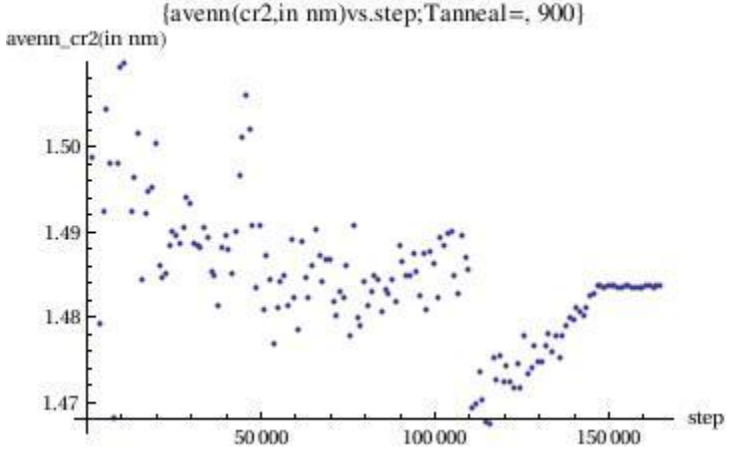


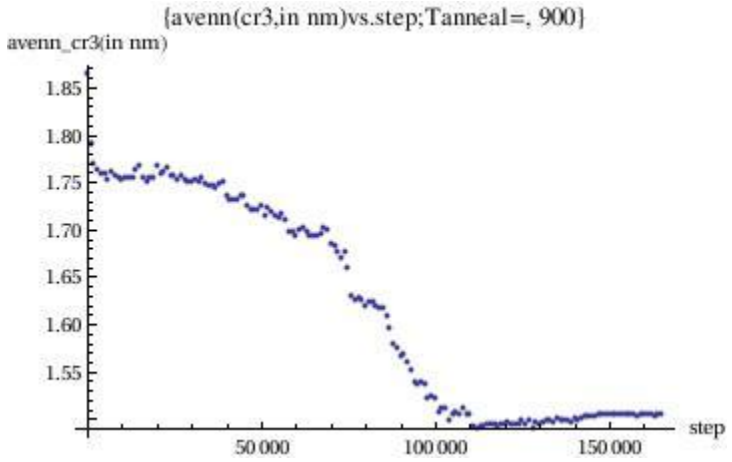




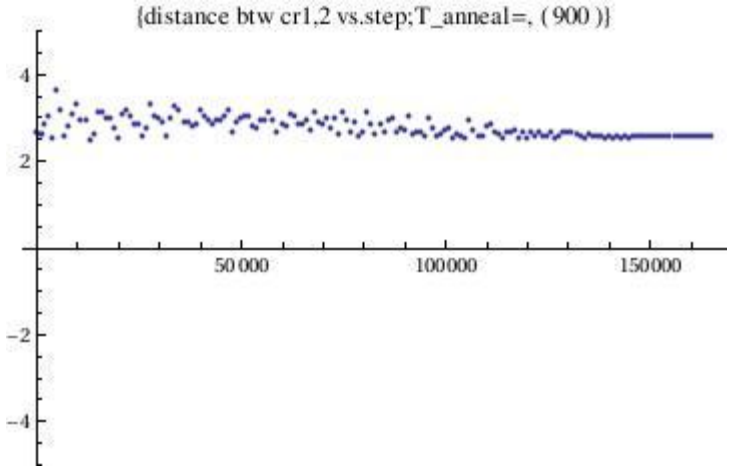
Tanneal = 900 K for substrate (nearest neighbour)

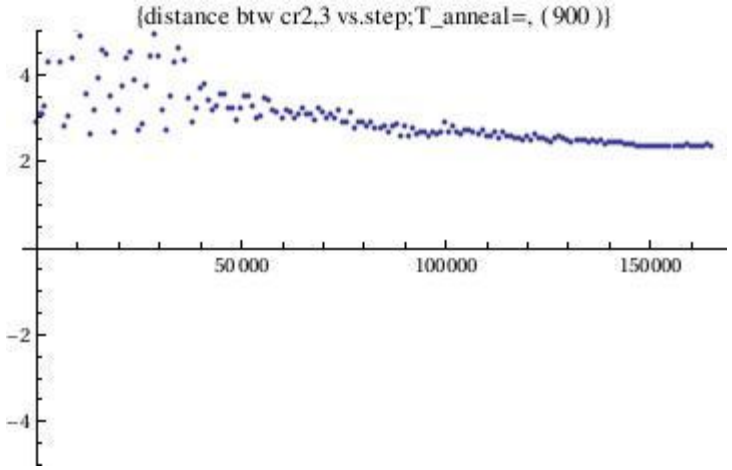




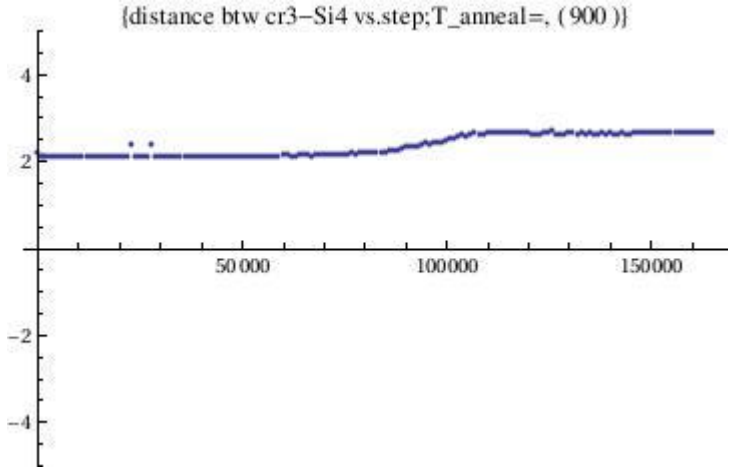


Tanneal = 900 K for substrate (distance between graphene layers)

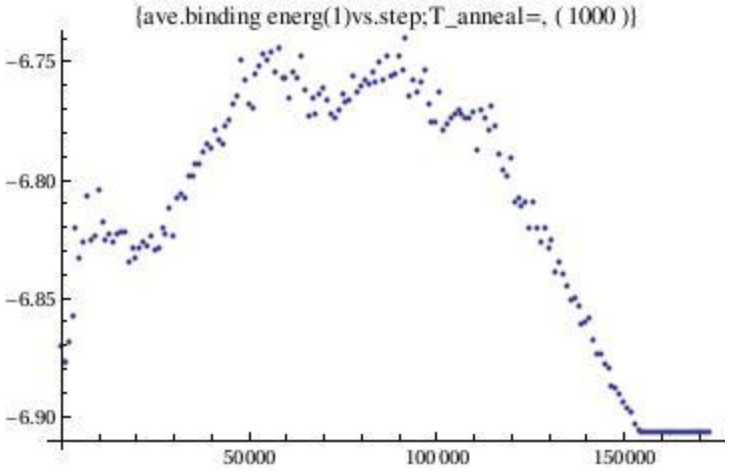


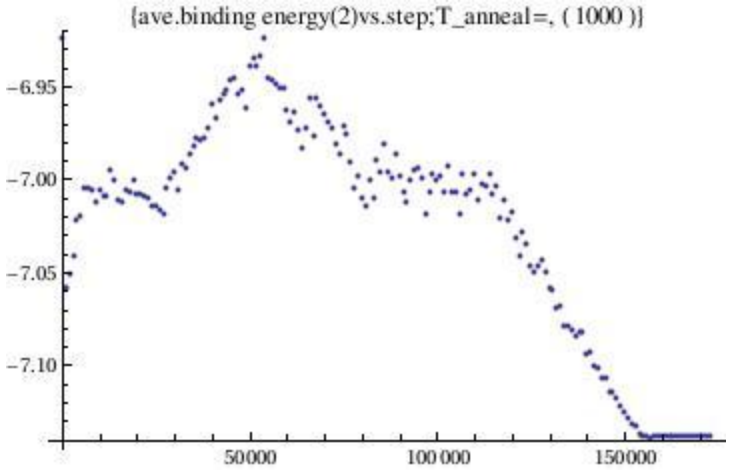


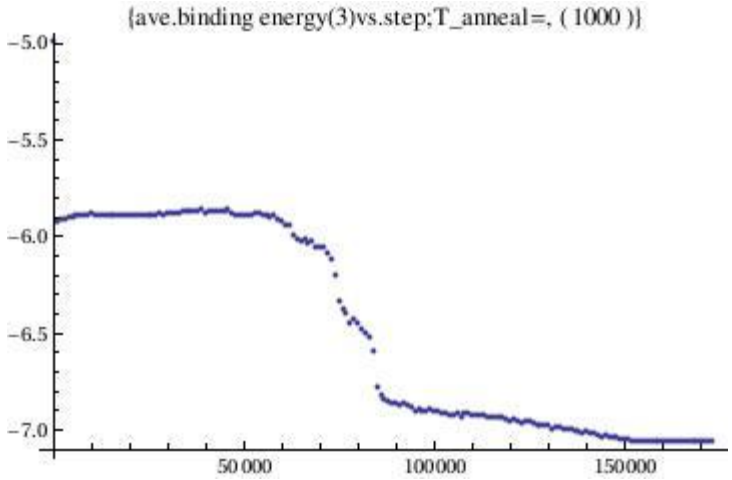
Tanneal = 900 K for substrate (distace between graphene and buffer layer)



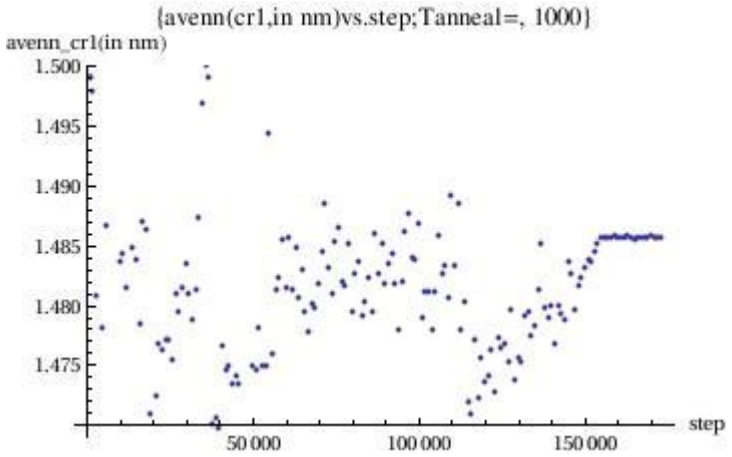
Tanneal = 1000 K for substrate (binding energy)

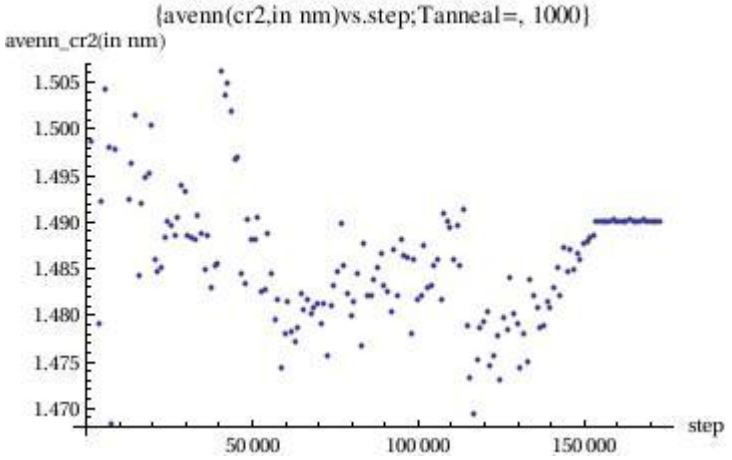


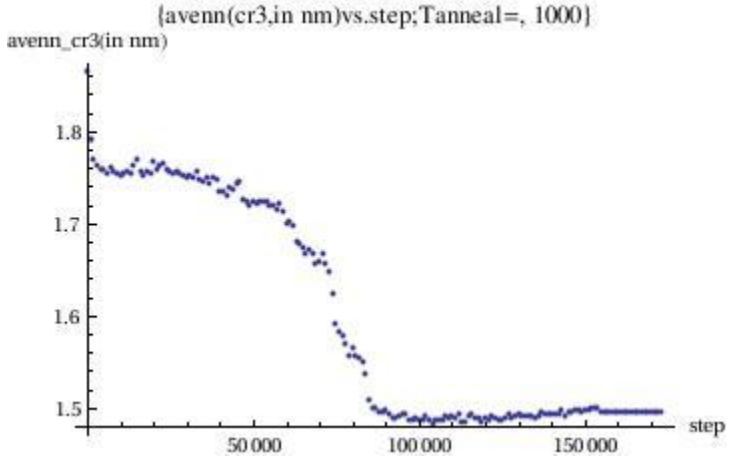




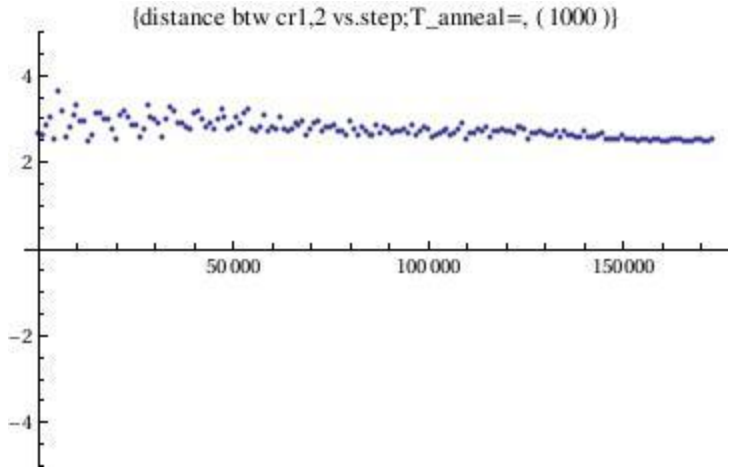
Tanneal = 1000 K for substrate (nearest neighbour)

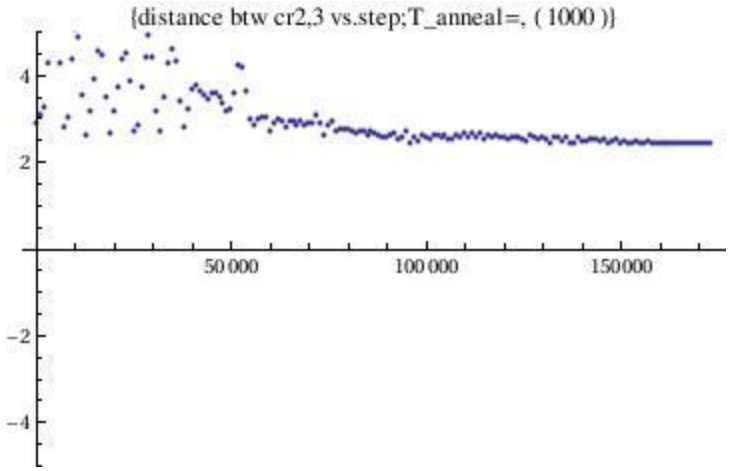




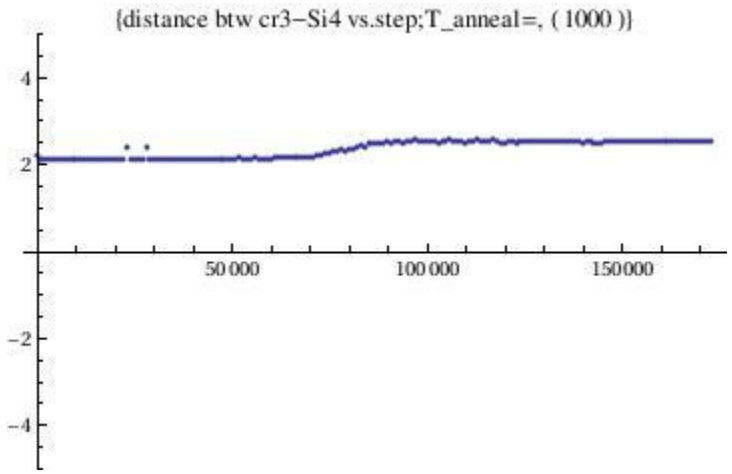


Tanneal = 1000 K for substrate (distance between graphene layers)

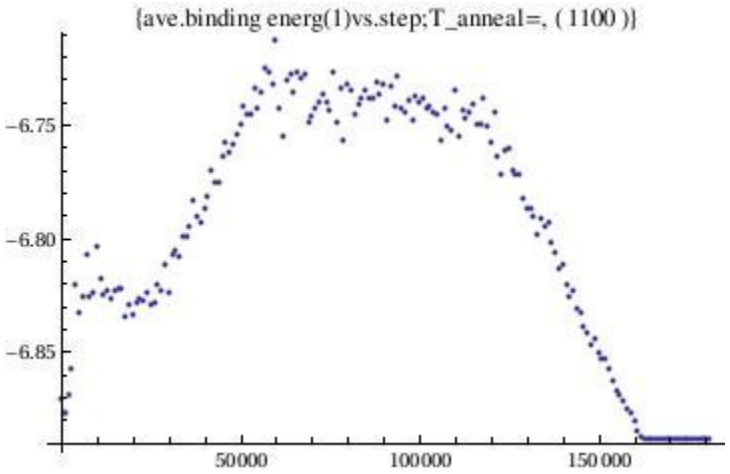


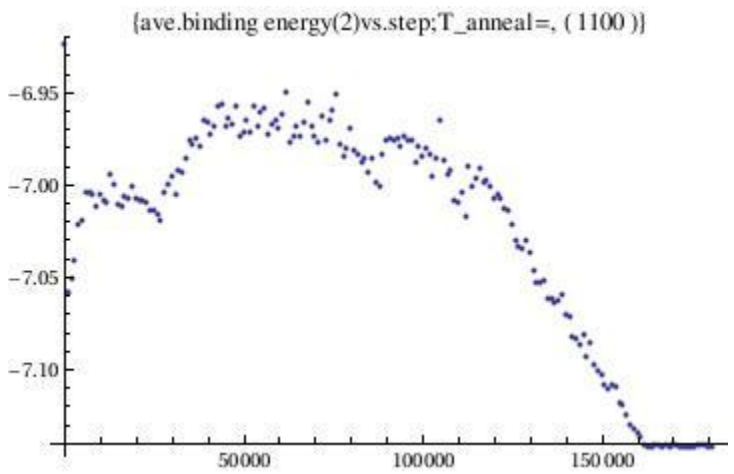


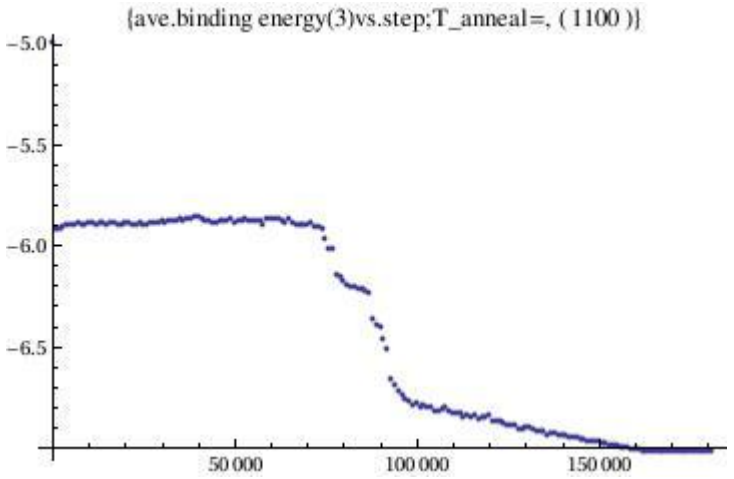
Tanneal = 1000 K for substrate (distace between graphene and buffer layer)



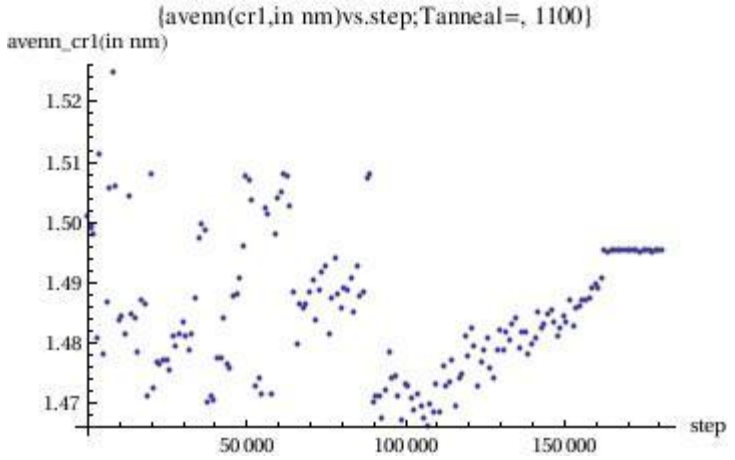
Tanneal = 1100 K for substrate (binding energy)

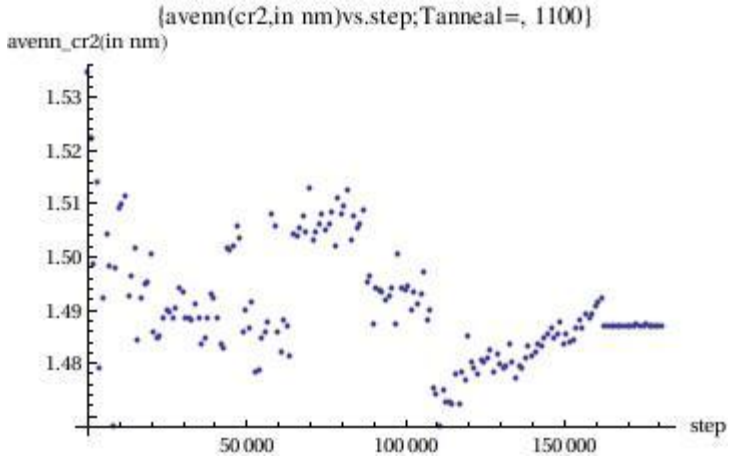


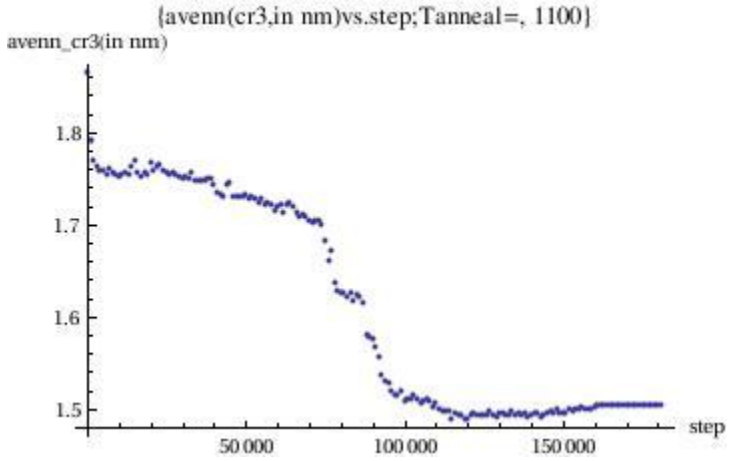




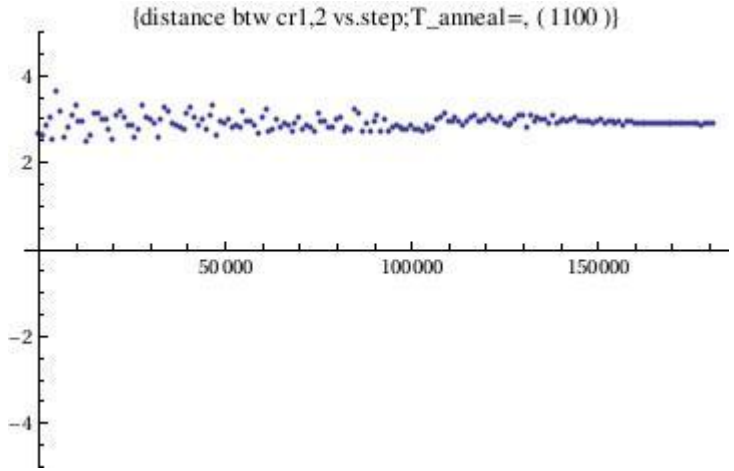
Tanneal = 1100 K for substrate (nearest neighbour)

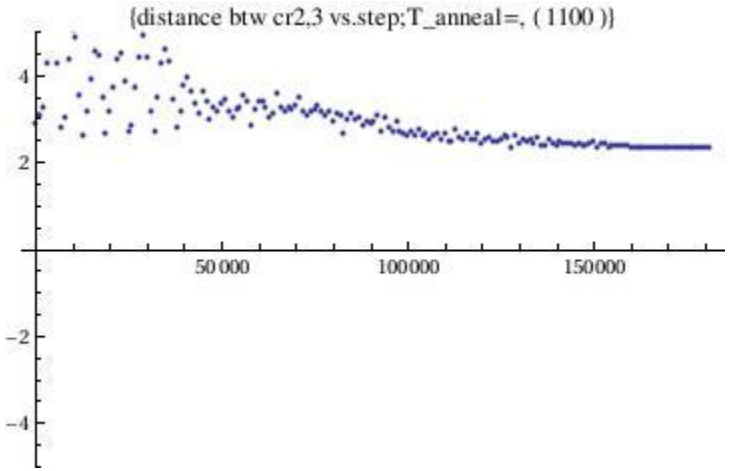




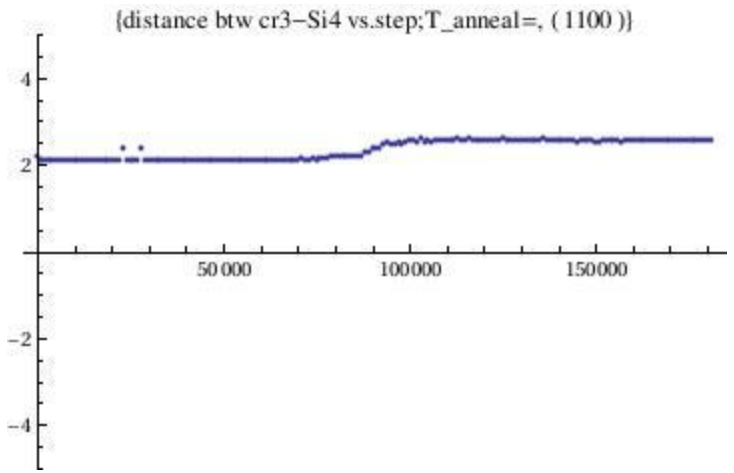


Tanneal = 1100 K for substrate (distance between graphene layers)

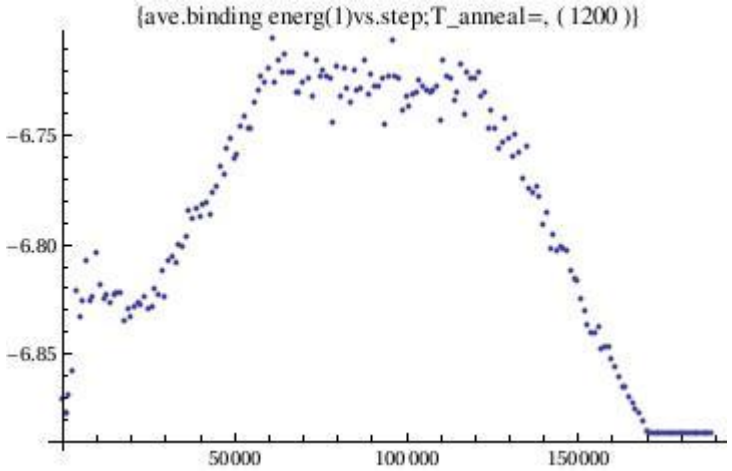


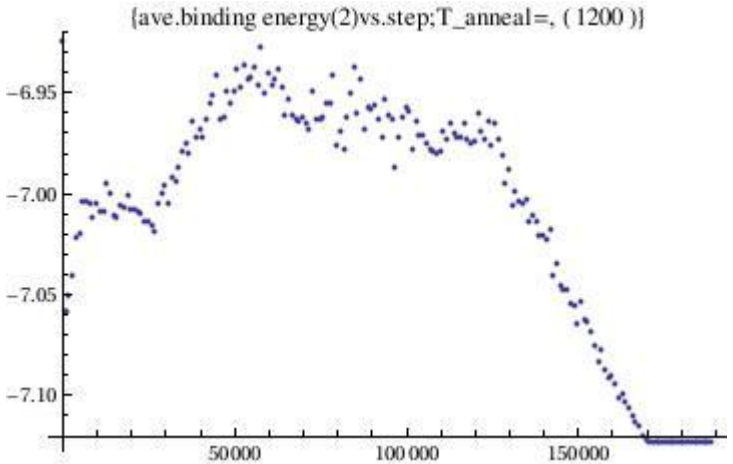


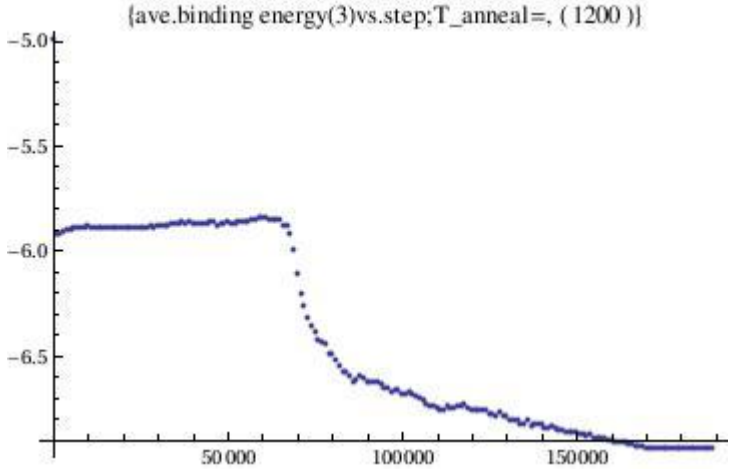
Tanneal = 1100 K for substrate (distace between graphene and buffer layer)



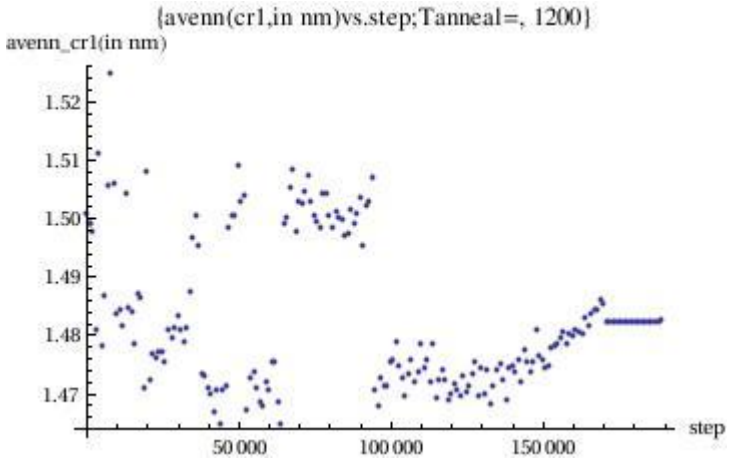
Tanneal = 1200 K for substrate (binding energy)

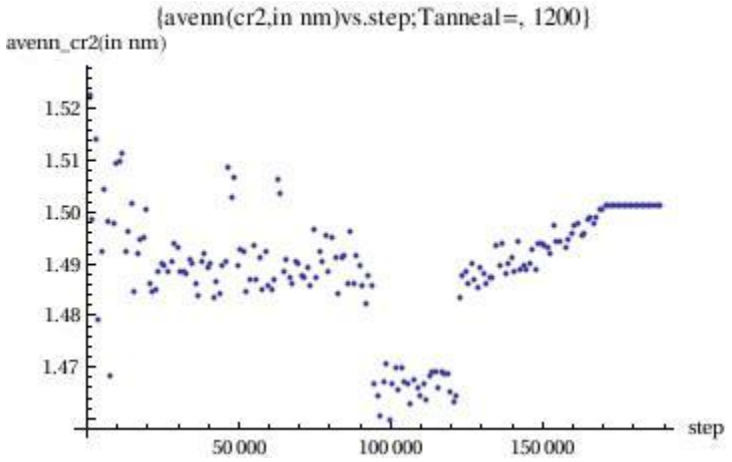


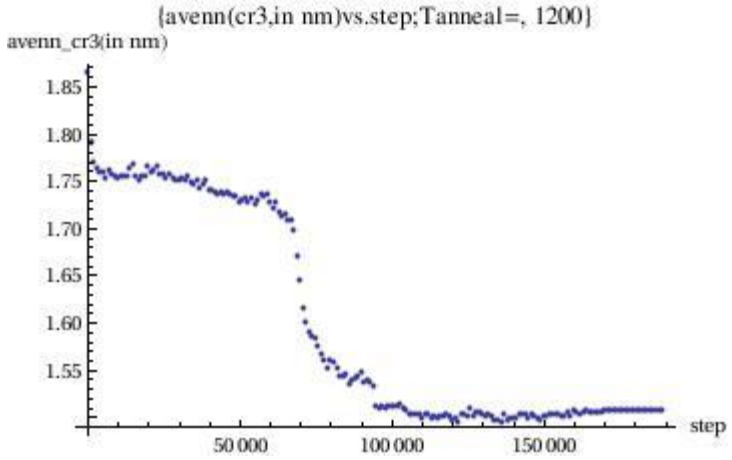




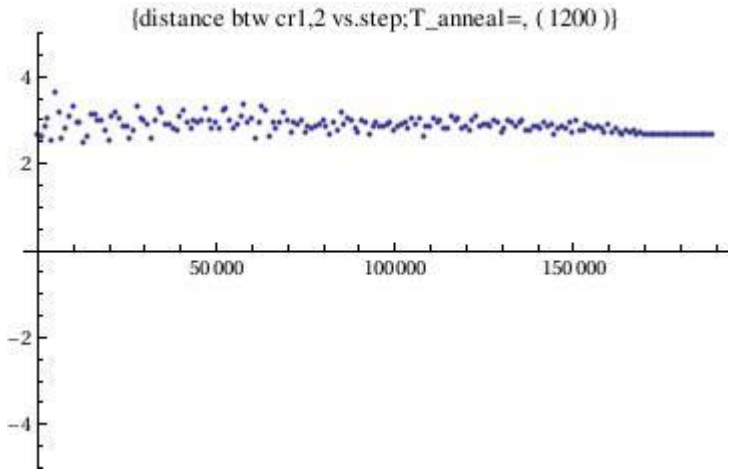
Tanneal = 1200 K for substrate (nearest neighbour)

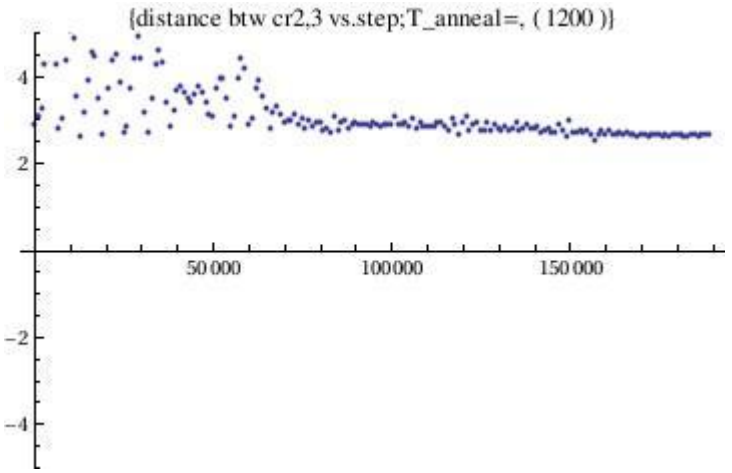




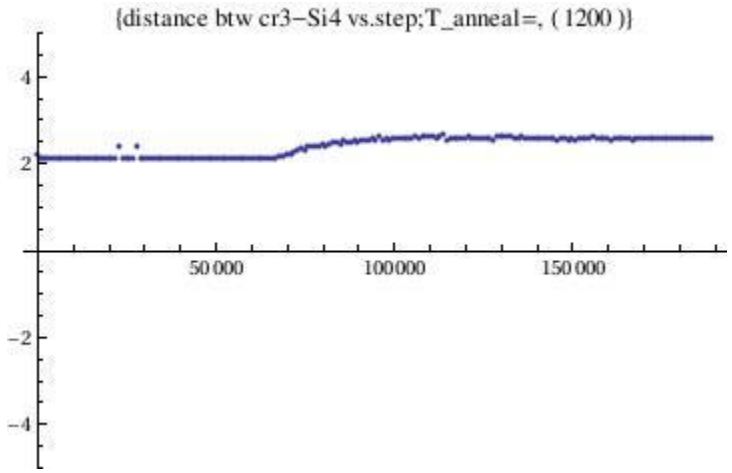


Tanneal = 1200 K for substrate (distance between graphene layers)

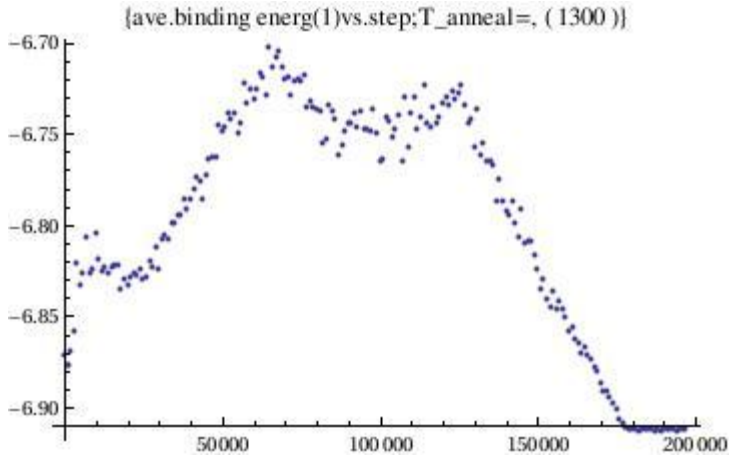


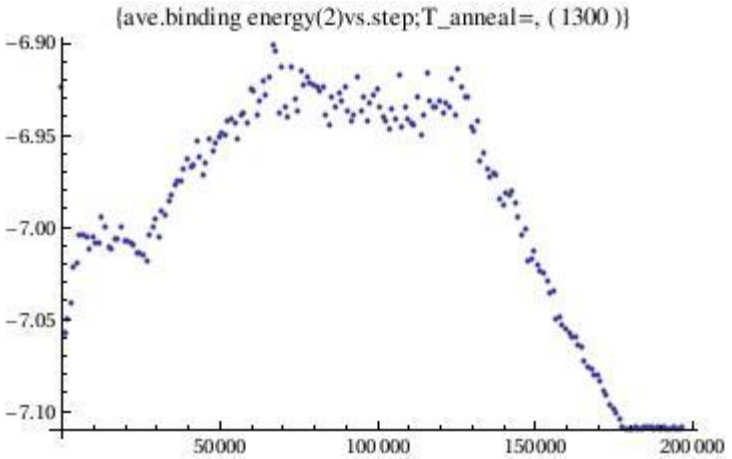


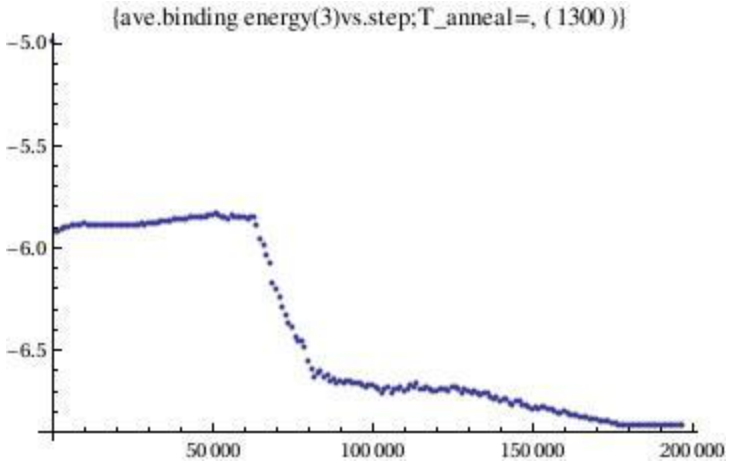
Tanneal = 1200 K for substrate (distace between graphene and buffer layer)



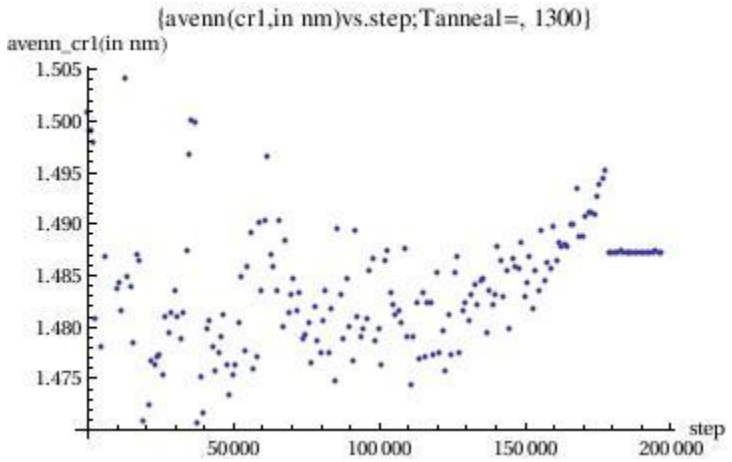
Tanneal = 1300 K for substrate (binding energy)

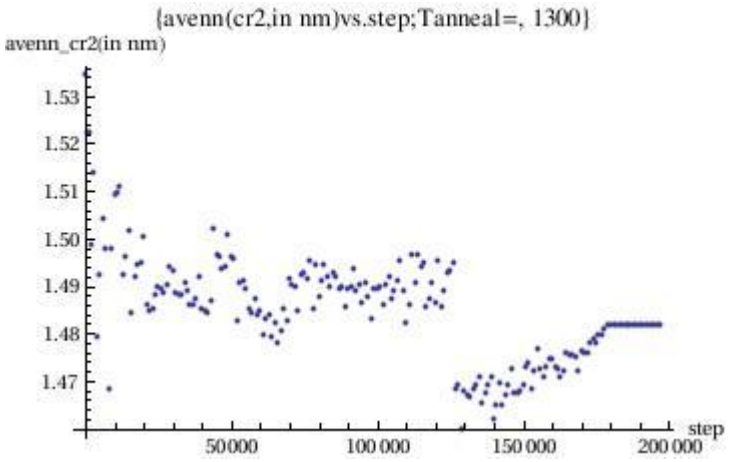


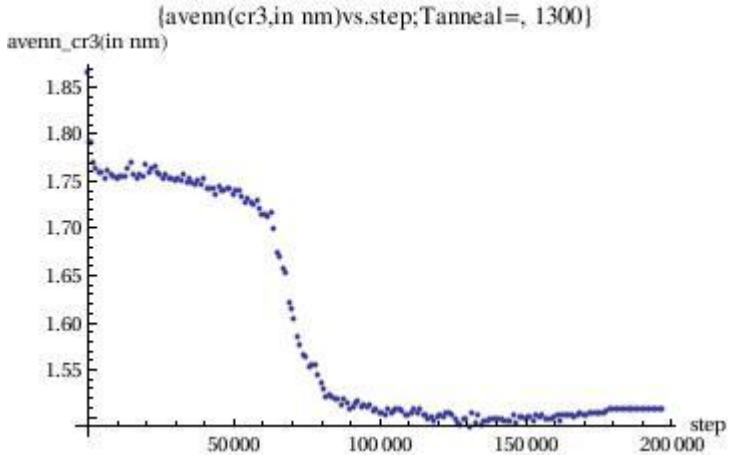




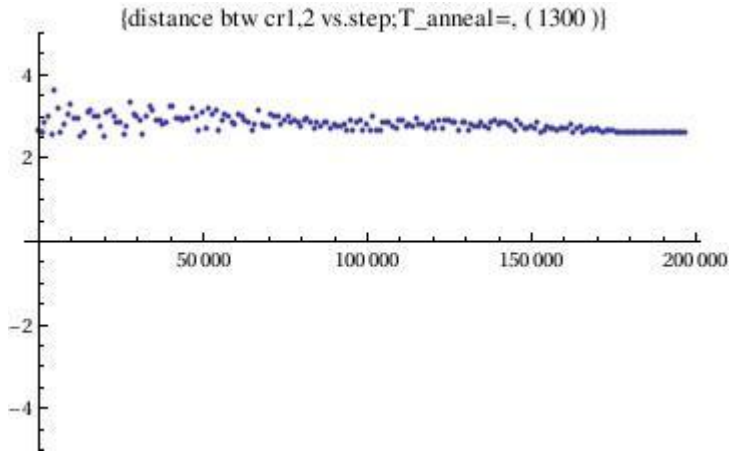
Tanneal = 1300 K for substrate (nearest neighbour)

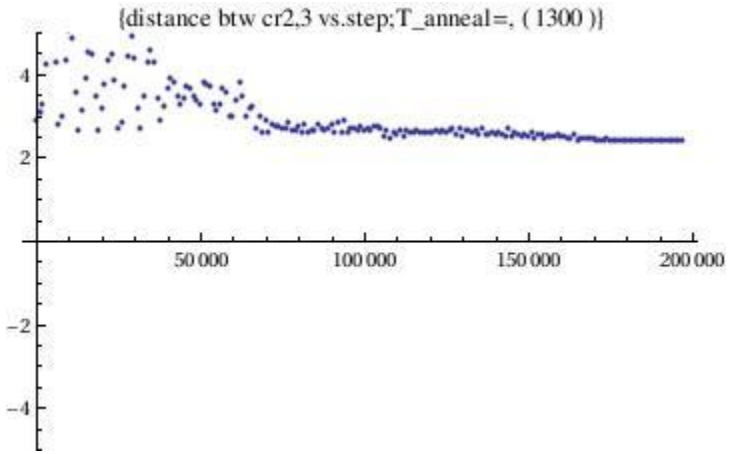




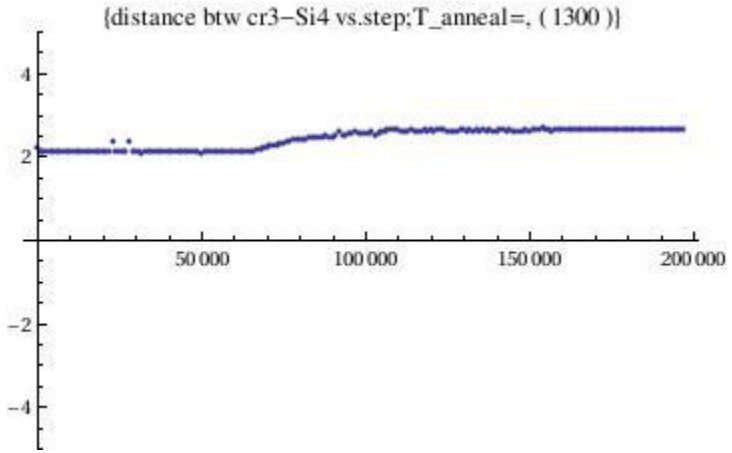


Tanneal = 1300 K for substrate (distance between graphene layers)

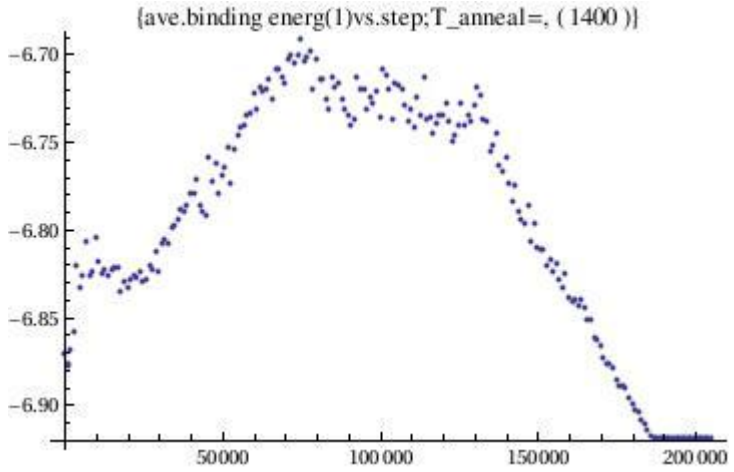


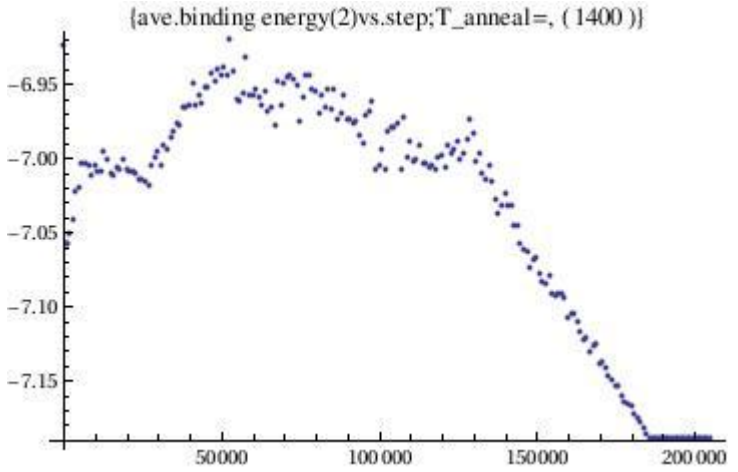


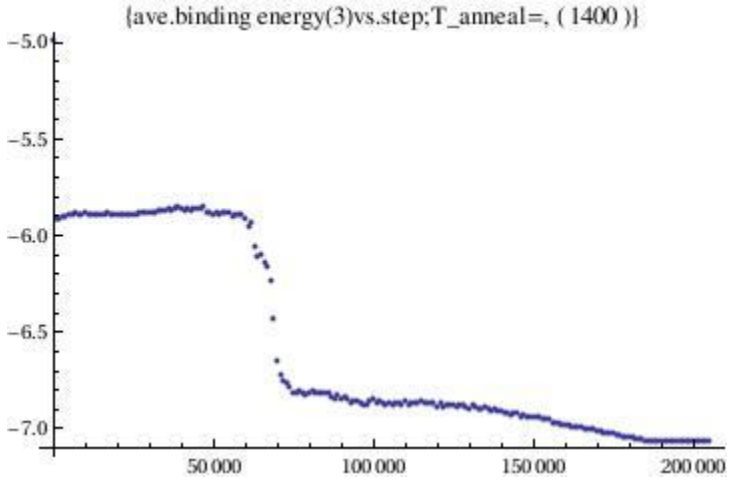
Tanneal = 1300 K for substrate (distace between graphene and buffer layer)



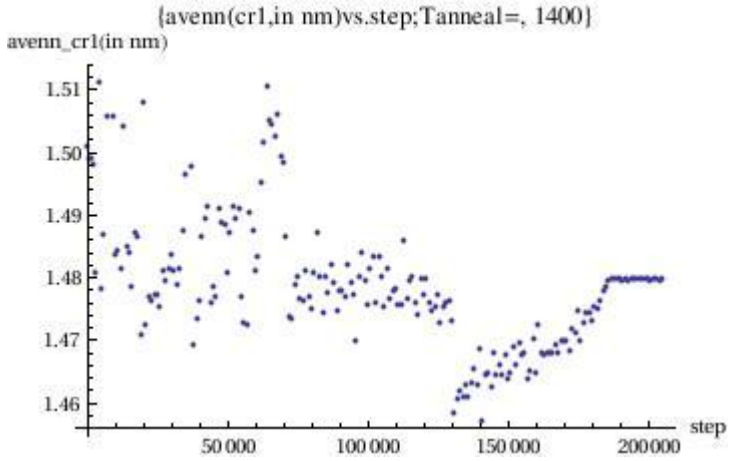
Tanneal = 1400 K for substrate (binding energy)

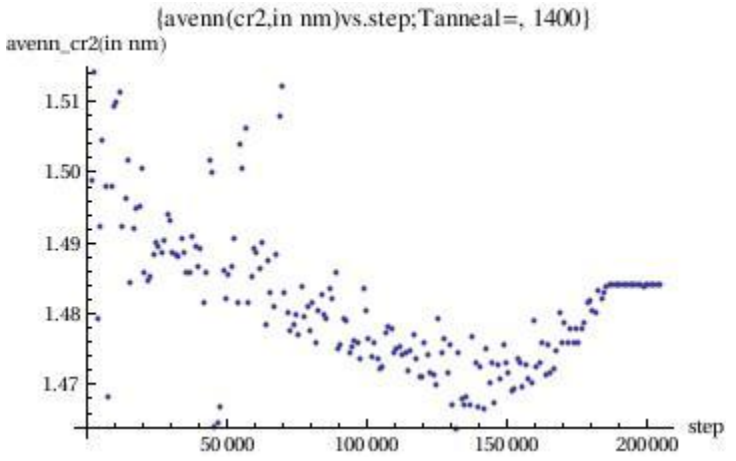


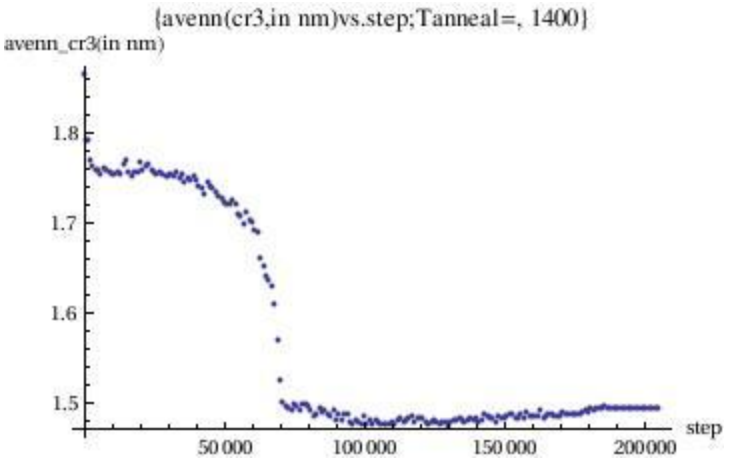




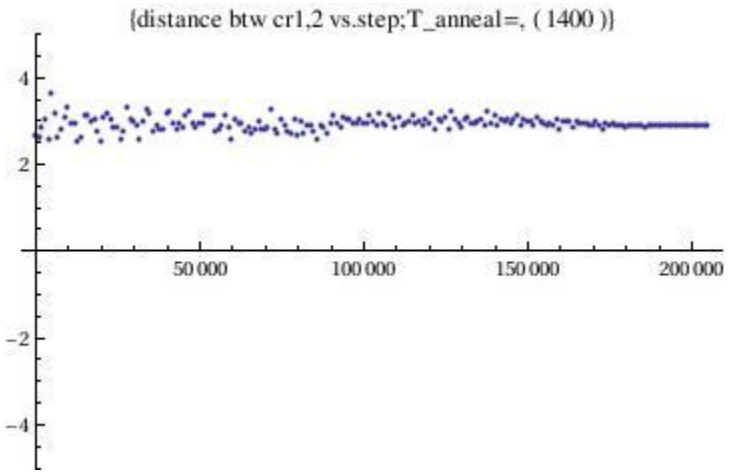
Tanneal = 1400 K for substrate (nearest neighbour)

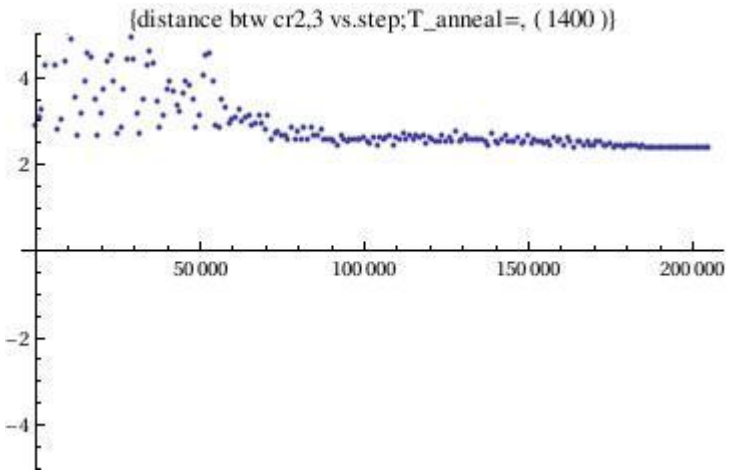




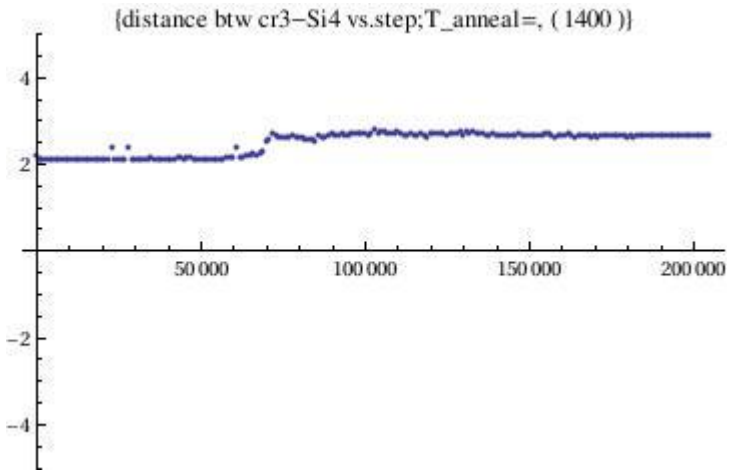


Tanneal = 1400 K for substrate (distance between graphene layers)

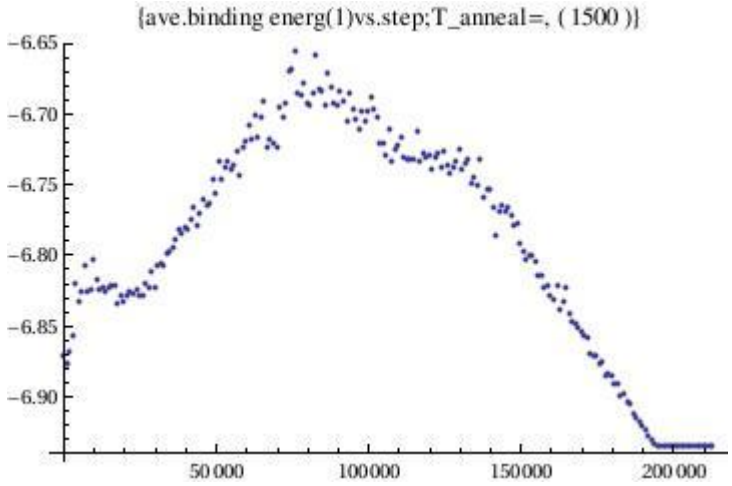


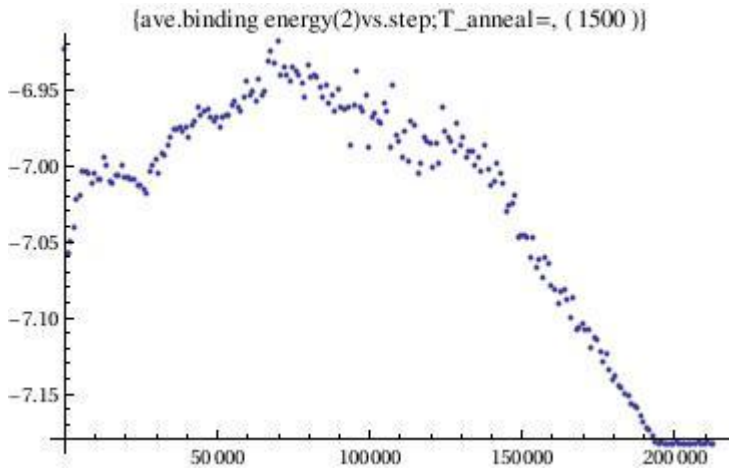


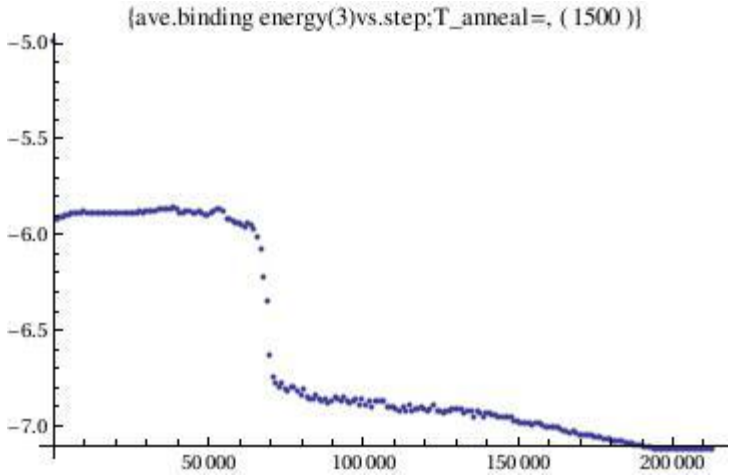
Tanneal = 1400 K for substrate (distace between graphene and buffer layer)



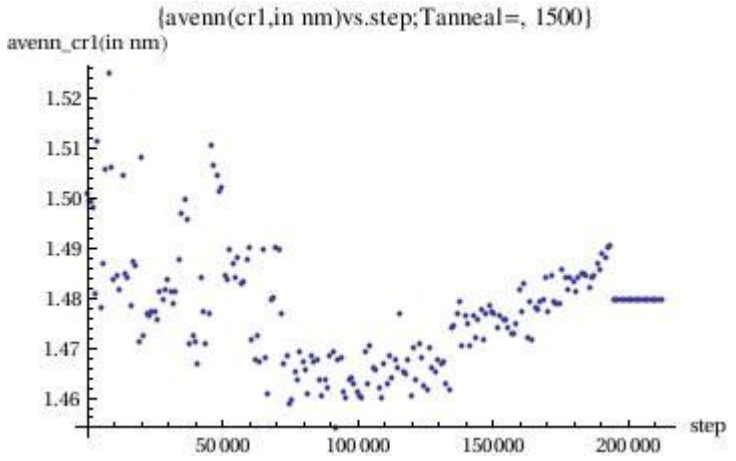
Tanneal = 1500 K for substrate (binding energy)

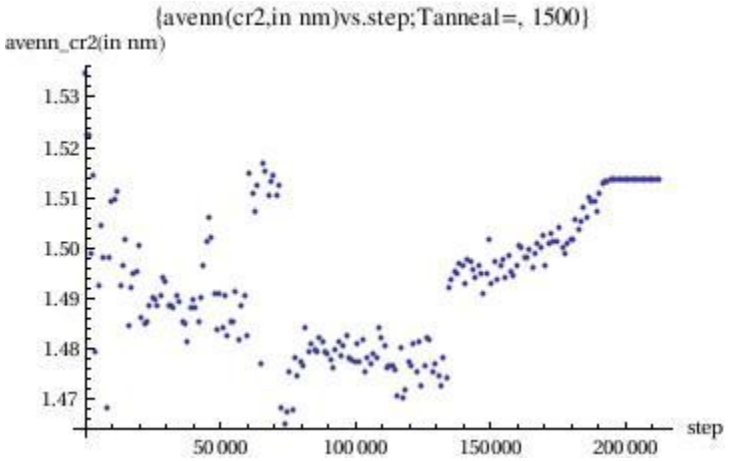


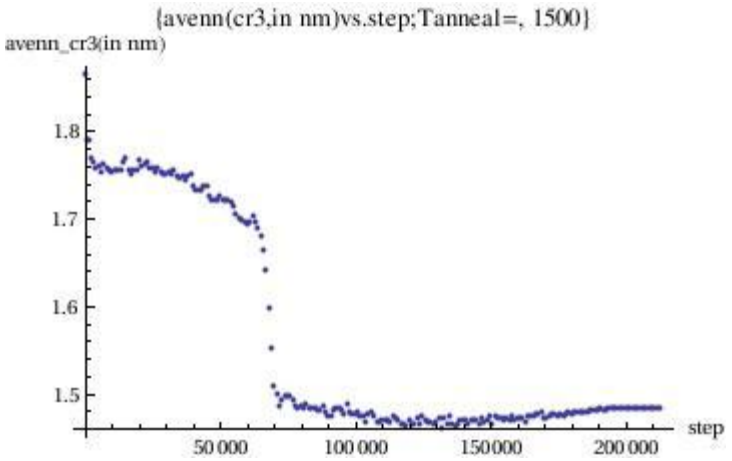




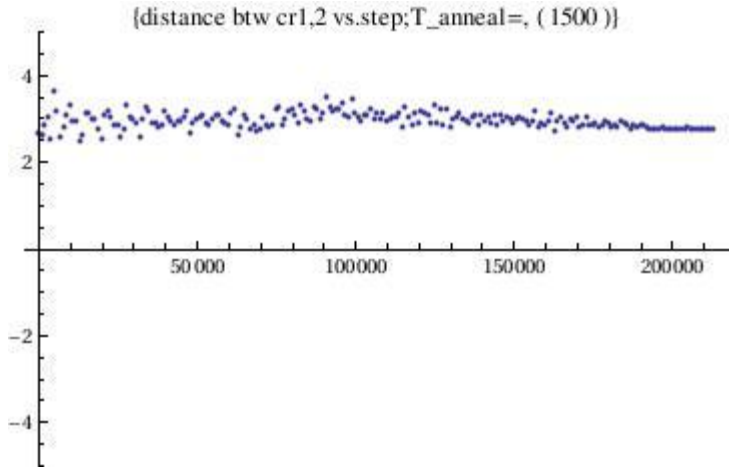
Tanneal = 1500 K for substrate (nearest neighbour)

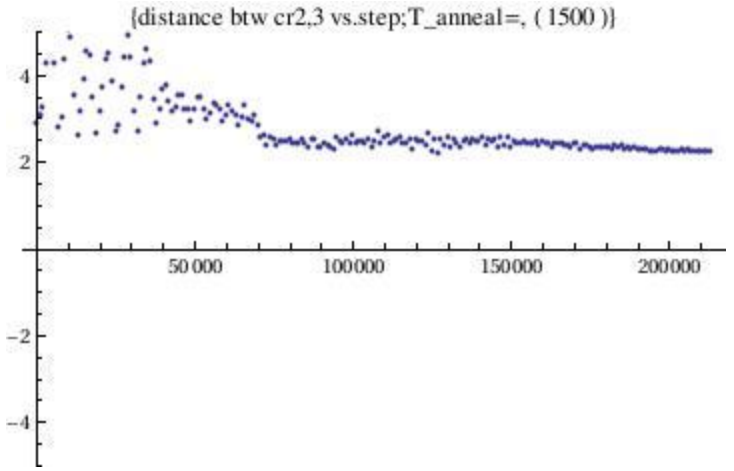




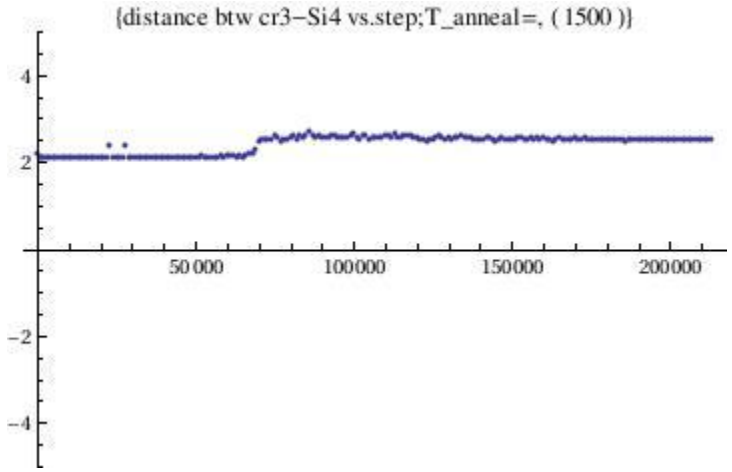


Tanneal = 1500 K for substrate (distance between graphene layers)



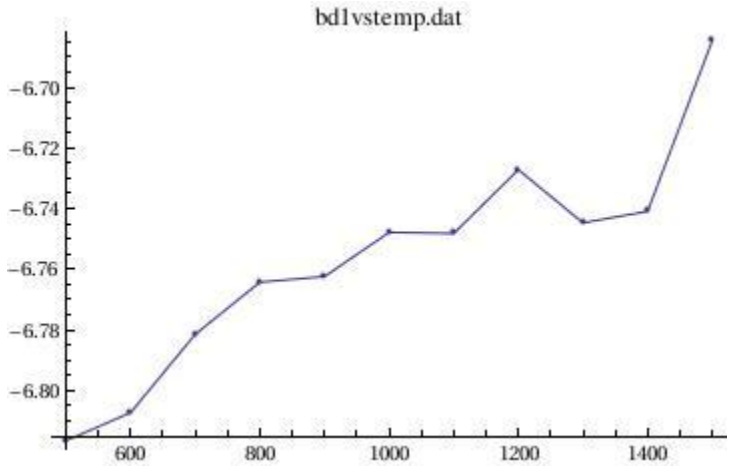


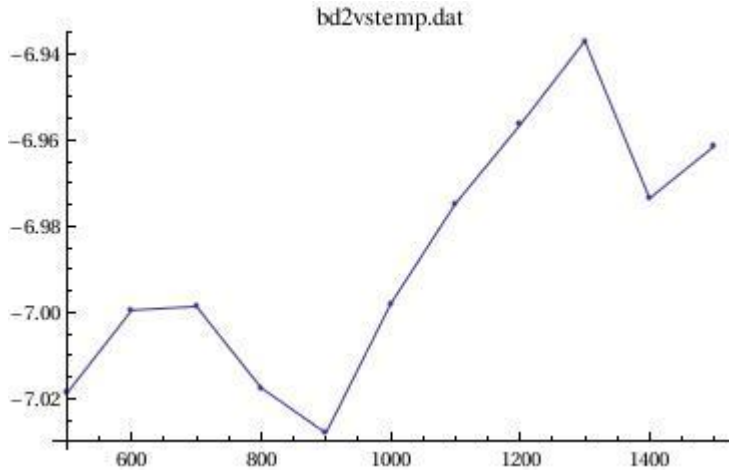
Tanneal = 1500 K for substrate (distace between graphene and buffer layer)

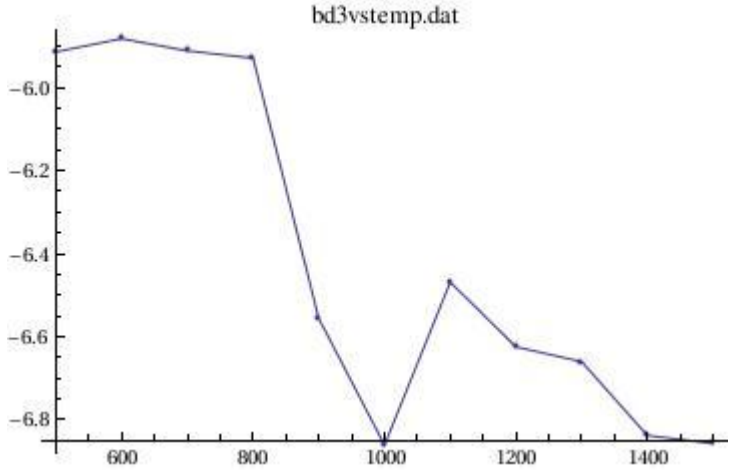


Summary

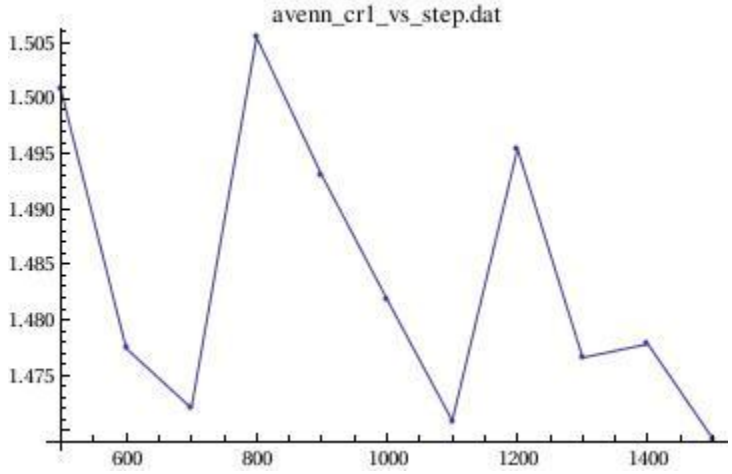
Binding Energy

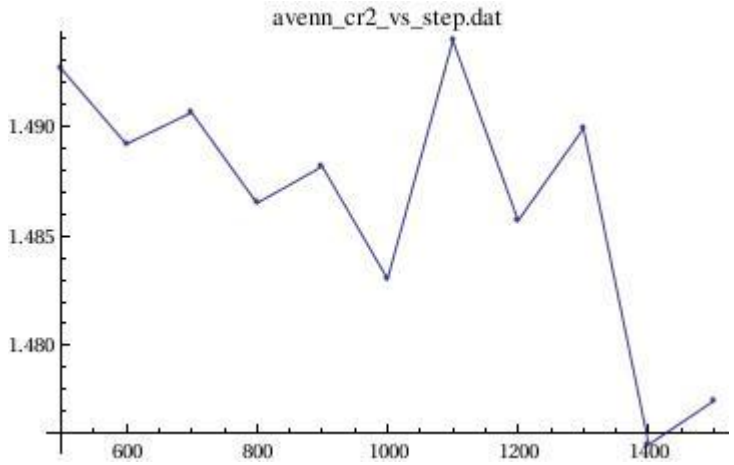


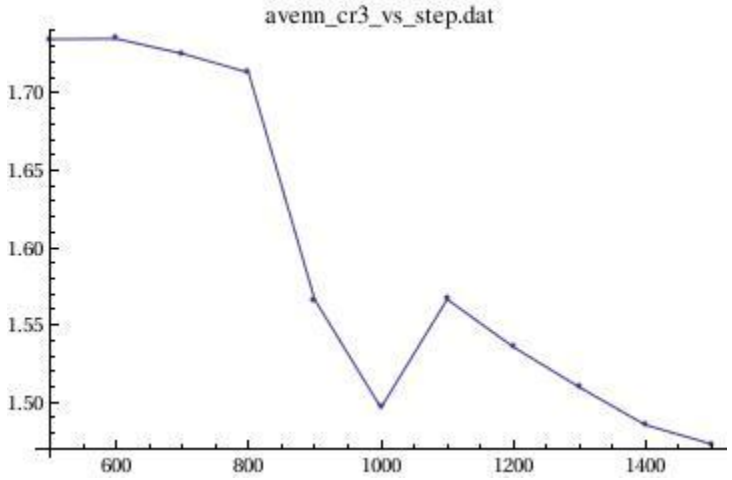




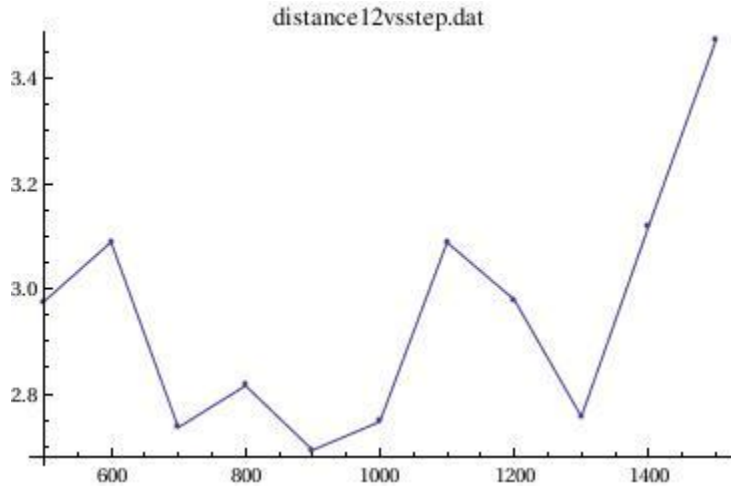
Average Nearest Neighbour



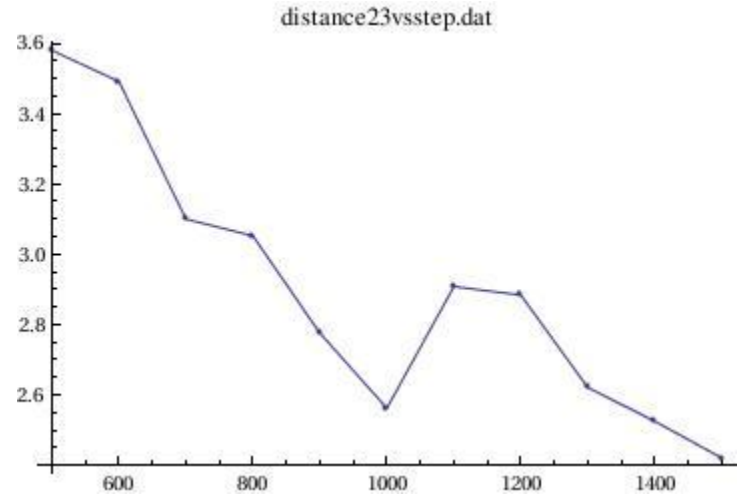




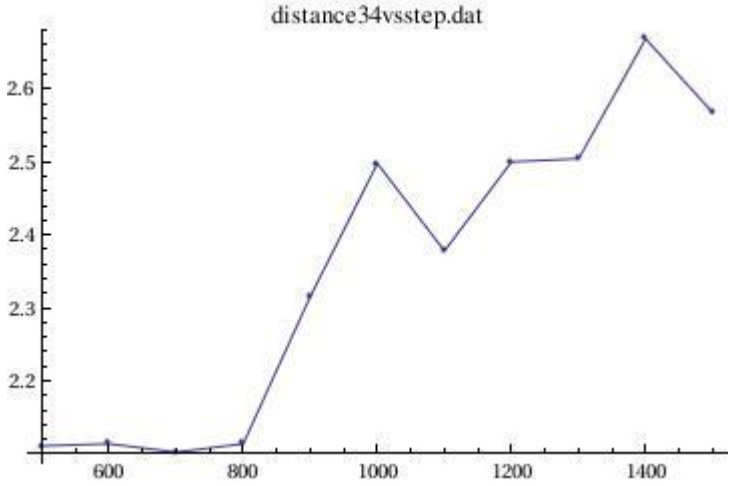
Average Distance



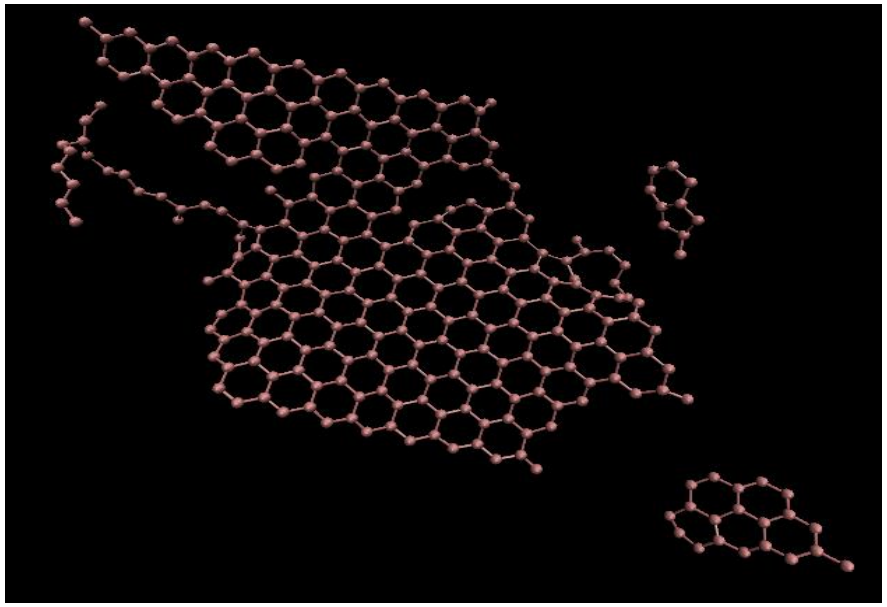
Average distance between top layer graphene and middle layer graphene



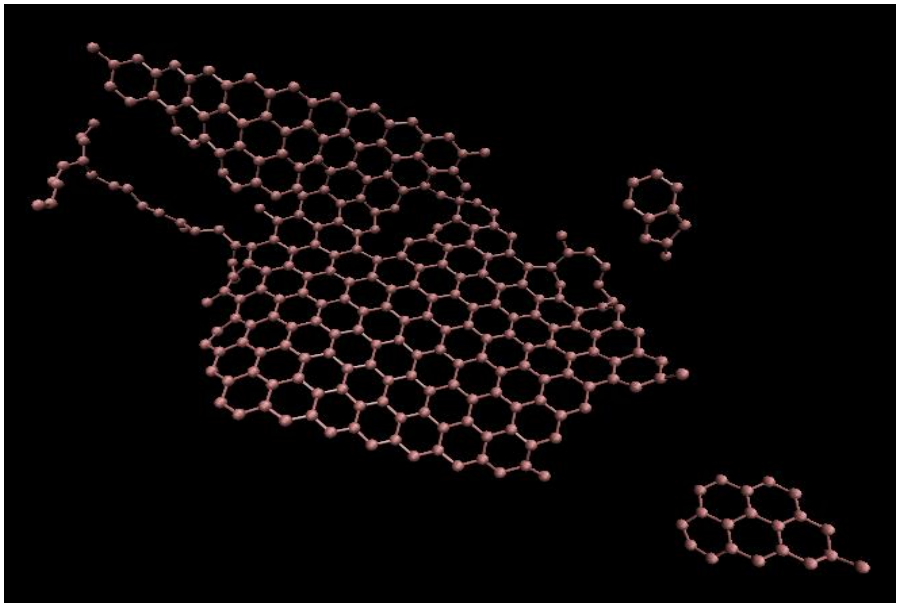
Average distance between middle layer graphene and bottom layer graphene



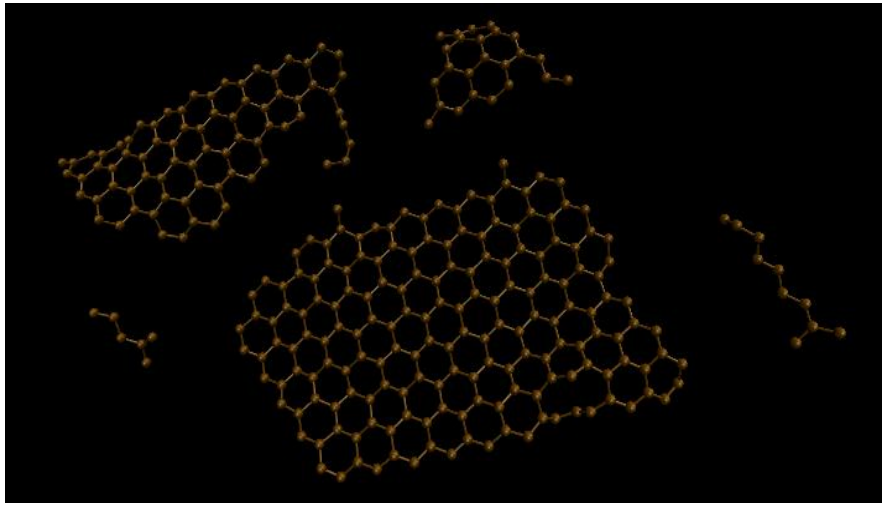
Average distance between bottom layer graphene and buffer layer



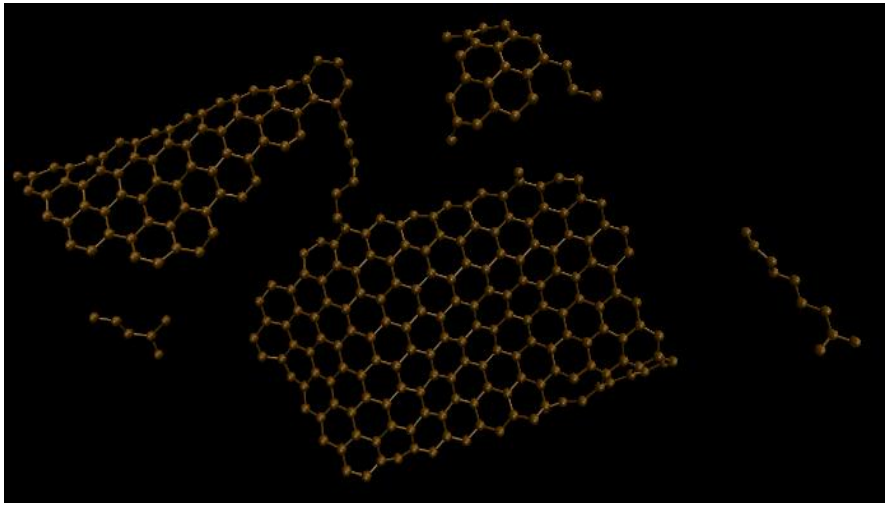
First layer graphene layer at 300K



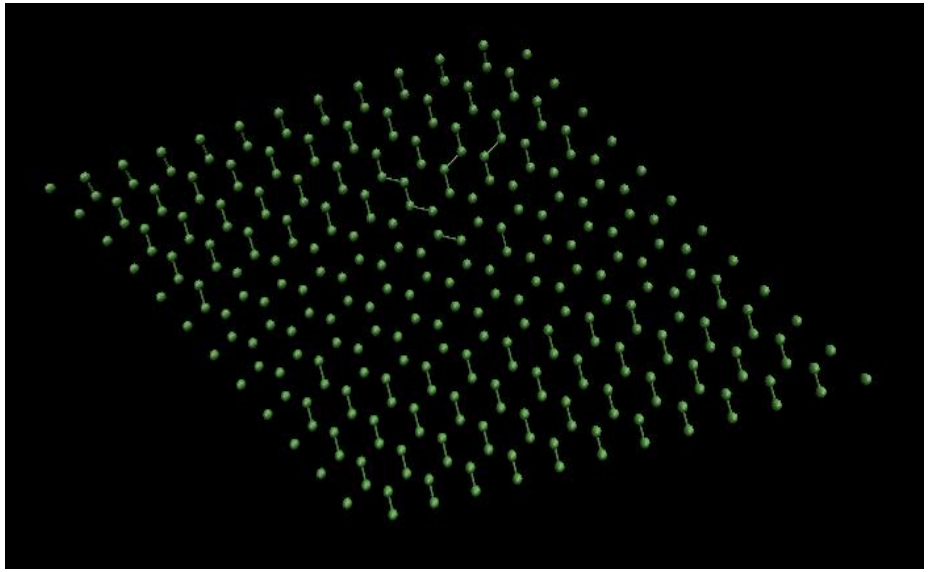
First layer graphenelayer at 1200K



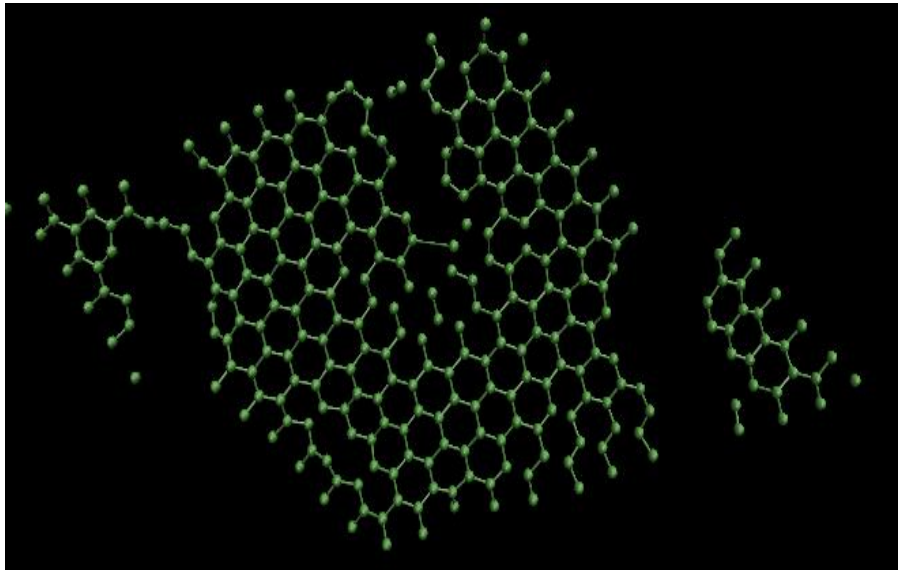
Second layer graphene layer at 300K



Second layer graphene layer at 1200K



Third layer graphene layer at 300K



Third layer graphene layer at 1200K