Department of Materials Science and Engineering

MSE-316 Materials Laboratory II

Modeling and Simulation in MSE

2021-2022

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MSE212 Materials Laboratory, which is the first department laboratory course of the IZTECH Materials Science and Engineering Department undergraduate program, aims to provide students with information about the basic operations in metallurgy and materials engineering. The experiments that are planned to be shown are laboratory-scale versions of the methods frequently used in the industry. With this course, the theoretical topics will also be visualized.

We wish success to all students.

Grading System

Quiz	30%
Report	70%

GENERAL RULES OF THE COURSE

1. The starting time of the laboratory is **08:45 on Friday**. Students are required to arrive at the laboratory on time.
2. It is of great importance to come to the laboratory prepared by reading the experiment sheet before the laboratory. Laboratory instructors will conduct a quiz about the experiment.
3. Each student has to experiment with the group specified in the list.
4. Students have to do the make-up experiment during the make-up week, complete all the experiments and submit all their reports.
5. Reports will be submitted to the TURNITIN system. Uploaded after **17.30 the next Friday** will not be accepted.
6. Experiments will be done in groups. However, the preparation of reports should be done individually. When detecting any duplicate report, it will be automatically graded with zero.

| Group	Time
1	
2	
3	
4	

1. **The objective of the course**

 – is to become familiar with simulation and modeling in MSE

 – and introduce fundamentals, basic concepts, and applications of modeling and simulation in MSE.

This practice presents the elementary methods and principles for atomistic modeling and simulating materials' structure, properties, and behavior.

2. **Theoretical Background**

   Theoretical, experimental, and computational methodologies are the three main complementary basements for scientific research. Synthesis and characterization kind laboratory works primarily are practical techniques. Modeling and simulational methods are part of computational sciences, where theoretical methods are applied to investigate and forecast systems' physical circumstances or behavior. Computational sciences are beneficial because there is not enough time or resources to examine all the experimental possibilities. The computational methodologies provide a robust alternative to practical methods and observation processes when phenomena are not observable or when measurements are impracticable or too costly. The potential of computational science is also crucial for developing and discovering promising materials. Computational modeling of materials on high-performance computer simulations is gradually becoming a reliable tool for scientific investigations in materials science. The remarkable advancements in computer science and theoretical methods have dramatically impacted design materials and indicated numerous advantageous research directions in the last century. Now, one can compute materials' phase diagrams, power spectrums, conductances, and properties.
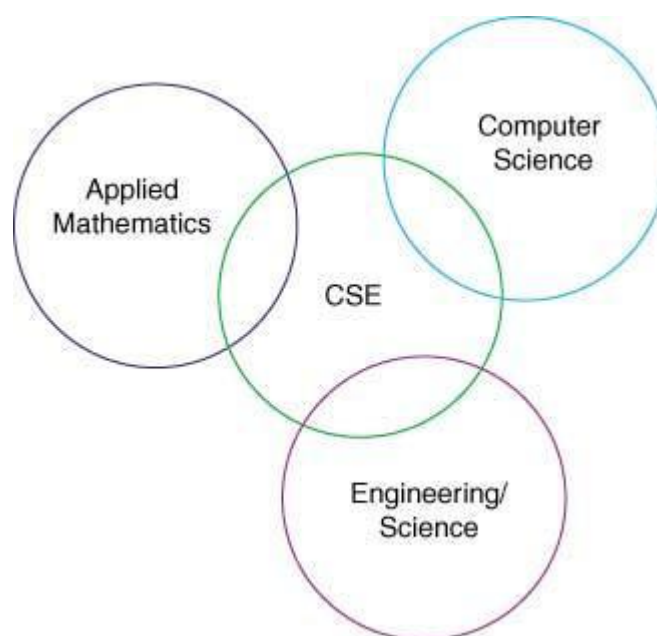
  Several modeling techniques for the simulation of materials describe systems at different length scales. Since all materials are composed of atoms, the atomic structure dictates the materials' both properties and performance. So, atomistic-level modeling provides information about deformations during various processes, fundamental properties of materials, and stability. Nevertheless, the atomistic-level simulation would require a substantial computational cost for an extensive size regime, with lengths more significant than the typical lattice constant. In this regime, materials can be regarded as a continuum.

As a consequence, continuum mechanics governs the simulation models. Figure 1. shows the relation between length scales and models. Besides, we categorize simulation models according to parameters that are the simulation's inputs. If input parameters are only derived from fundamental constants such as speed of light, and Planck constant, then the simulation is categorized as ab-initio or first-principles method.

On the other hand, empirical models include parameters from experiments or other first-principle calculations. Applying first-principles methods to realistic materials is limited because ab-initio simulations need considerable memory when materials are formed of more than one hundred atoms. So, empirical techniques help overcome this size issue.
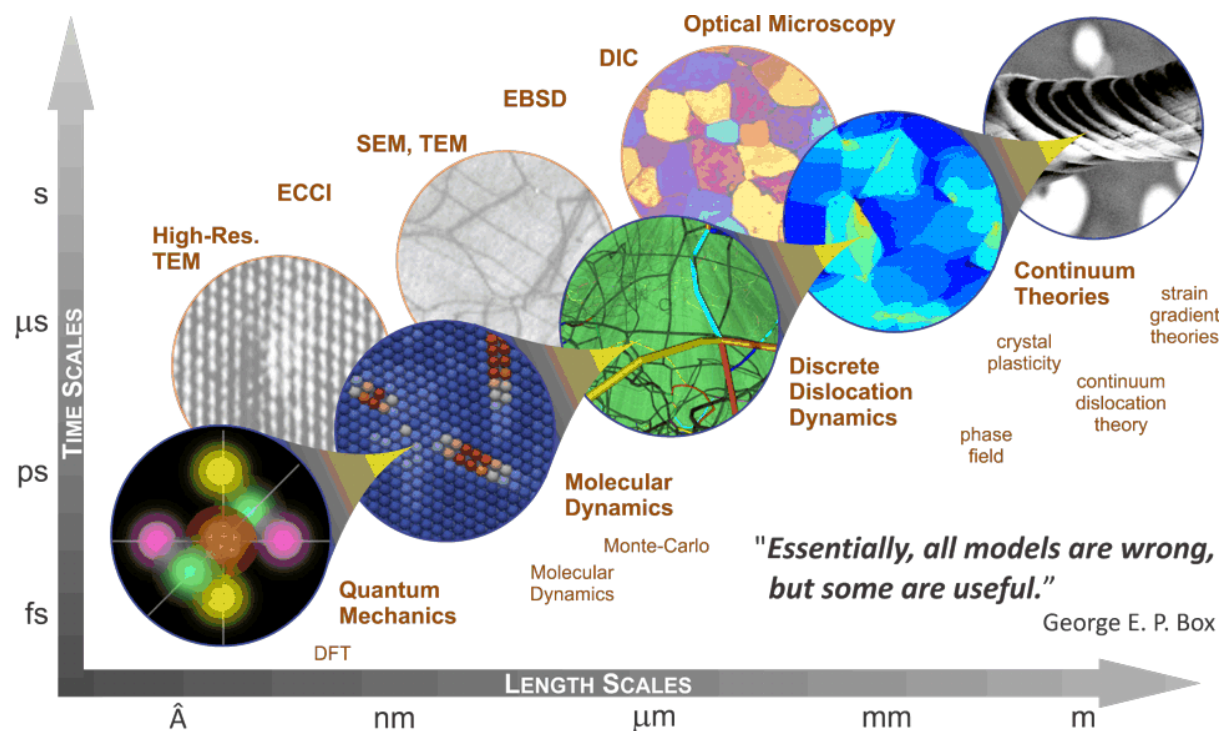

Figure 1. Computational and experimental techniques for a variety of length and time scales. [1]

This week, we demonstrate how to determine perfect and defected graphene's internal structure and spatial properties with two distinct methods: Molecular Dynamics(MD) and Density Functional Theory(DFT). Besides, we show how to calculate the electronic band structure of graphene and the phonon density of states of the monoatomic chain with DFT. To imply MD, Lammps (Large-Scale Atomistic/Molecular Massively Parallel Simulator). For DFT, we will use VASP (Vienna ab-inito Simulation Package). Besides VASP, we take advantage of the Phonopy package for phonon density of states.

This handout describes the MD and DFT methods, then the usage of VASP, Lammps, and Phonopy packages. Next, the installation and usage of the VESTA package, used for measuring bond length and angles, are presented. Ultimately, the details of simulations and receipts of processes are given. You can find all input files on the https://github.com/psiFender/MSE316-Iztech .

3. Modeling Methods

3.1 Molecular Dynamics

MD is a computational simulation method for investigating the physical activities of atoms and molecules. The atoms and molecules are permitted to interact for a settled period, giving a perspective of the dynamic "evolution" of the system. In the most familiar version, the trajectories of atoms and molecules are defined by numerically solving Newton's equations of motion for a system of interacting particles. Forces between the particles and their potential energies are often calculated using interatomic potentials or molecular mechanics force fields. First used in theoretical physics, the MD method soon earned material science popularity, and since the 1970s, it is also common in biochemistry and biophysics. One can test the results of MD simulations through comparison to experiments.
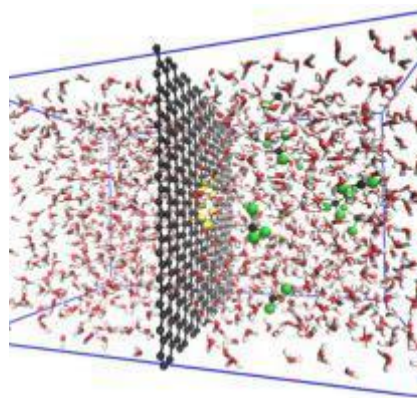
3.2. Density Functional Theory

Most science and engineering problems are relevant to the systems' ground-state solution to the famous Schrödinger's equation. DFT is a powerful and affordable ab-initio method to discover approximately the ground-state configuration. The application of DFT computations is rapidly evolving into a "standard tool" for various system modeling concerns in materials science, physics, chemistry, and numerous branches of engineering.

The Nobel Prize in Chemistry 1998

Photo from the Nobel Foundation archive.
Walter Kohn
Prize share: 1/2
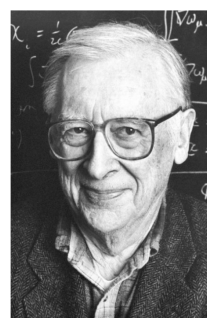
Photo from the Nobel Foundation archive.
John A. Pople
Prize share: 1/2

DFT is based on two theorems provided by Hohenberg-Kohn and a scheme work established by Kohn-Sham. Discovering such a tool brought a Nobel prize to Kohn. Before starting the fundamentals of DFT, the meaning of the term functional should be explained. Functional is a type of function which takes a function as an argument. The first Hohenberg-Kohn theorem states that "The ground-state energy from Schrödinger's equation is a unique functional of the electron density."[3] In this way, the ground state energy can be expressed as E[n(r)], where n(r) indicates electron density and [] stands for functional. This result is essential because now we must deal with three spatial variables instead of 3N variables, where N is the total number of electrons the
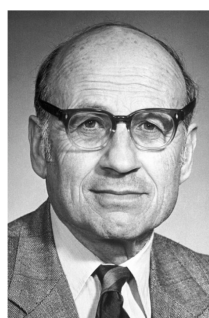
system has. The second Hohenberg-Kohn theorem remarks, "The electron density that minimizes the energy of the overall functional is the actual electron density corresponding to the complete solution of the Schrödinger equation." [3] However, these theorems do not give any idea of the solution process that Kohn and Sham provide. DFT calculations are not exact solutions to the complete Schrödinger equation. Comparing DFT results with careful experimental measurements can estimate the uncertainty between accurate and approximate solutions. A curious reader can find a detailed description of DFT in the ref.[3].
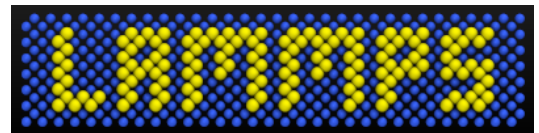
4. Programs

4.1. VASP

Vasp is a computer program for atomic scale materials modeling, e.g., density functional theory and quantum-mechanical molecular dynamics, from first principles. VASP computes an approximate solution to the many-body Schrödinger equation, either within density functional theory (DFT), solving the Kohn-Sham equations, or within the Hartree-Fock (HF) approximation.

4.2. Lammps

LAMMPS is a classical molecular dynamics simulation code focusing on materials modeling. It is an accelerated code since the program was designed to run efficiently on parallel computers. The program was initially invented at Sandia National Laboratories. Lammps is a freely-distributed program.

4.3. Phonopy

Phonopy is an open-source program for phonon calculations at harmonic and quasi-harmonic levels. It performs with numerous DFT programs (we are interested in using VASP for this work) as sources of inter-atomic forces. It uses the finite displacement method and symmetry relations for calculating elements of the dynamical matrix. It works for all crystal symmetries and supplies phonon band structure, phonon DOS and partial-DOS, phonon thermal properties (free energy, heat capacity, and entropy), phonon group velocity, mean square displacements, irreducible representations of normal modes, quasi-harmonic approximation (thermal expansion, heat capacity at constant pressure), mode Grüneisen parameters, non-analytical-term correction (LO-TO splitting).

4.4. VESTA

VESTA is a 3D visualization program for structural models. This software is freely distributed to academic, scientific, educational, and noncommercial users; and is available for all operating systems. One can download and install the VESTA program via the link:

https://jp-minerals.org/vesta/en/download.html
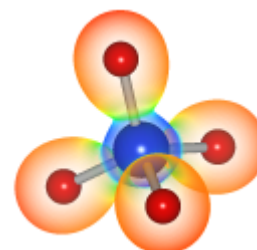
Download the suitable version according to the operating system and extract the entire contents of the archive file to a directory. Then, execute VESTA in that directory by double-clicking the "VESTA" file on a file manager.

5. Prescriptions

Process 1. The Structural Properties of Pure and Defected Graphene with MD and DFT

The energy minimization, or determining the ground-state configuration, is much-performed work concerning other simulations since the ground state remarkably determines the material's properties. This tutorial will demonstrate finding the ground-state structure with two distinct methods. The first method, density functional theory, is a quantum mechanical method that approximately solves Schrödinger's equation. For this method, the VASP package will be used. For this task, the Vasp package will require the following input files: POSCAR, POTCAR, INCAR, and KPOINTS.

The POSCAR file contains the structural details such as the number and types of atoms inside the cell, the lattice vectors, and each atomic coordinate. Graphene's unit cell is composed of two atoms. The POSCAR file for graphene is following:

Graphene

2.4606 # lattice constant

+0.5000000000000000 +0.8660254037844 0.0000000 #first lattice vector

-0.5000000000000000   0.8660254037844 0.0000000 #second lattice vector

 0.0000000000000000   0.00000000000 12.000000 #third lattice vector

  C   #type(s) of atom(s)

  2 #number of atoms

Direct   #coorinates will be given in direct coordinates

0.333333330 0.33333333 0.5000000000

0.666666666 0.66666666 0.50000000000

The first line is a comment line, one can write whatever he/she wants, but it is generally for the system's name. The second line is for the lattice constant. The following three lines contain the lattice vectors; the first line corresponds to the first lattice vector, the second to the second, and the third to the third. The type(s) of atoms is written in the sixth line. The number of atoms for each type is written in the seventh line; the ordering must be the same as the previous line. The following line specifies whether the atomic positions are provided in cartesian coordinates or direct coordinates. The remaining lines provide atomic coordinates, and the ordering of these lines must be correct and consistent with the number of atoms per species. The POTCAR file is a pseudopotential file for each atomic species used in the calculation. If the cell contains more than one type of atom, the POTCAR files need to be concentrated in the same order as the sixth line of the POSCAR file. The INCAR file is the central input file, determining *what and how to do it*. A curious reader can find a detailed description of the preparation of an INCAR file on the Vasp official website. Here is our INCAR file.

SYSTEM = Graphene

ICHARGE = 2   #charge from atoms

PREC   = High   #High precision

EDIFF   = 1e-5 #accuracy for electronic minimization

NELM   = 100 #max 100 electronic steps

IBRION = 2   #Use conjugate gradient algorithm

ISIF   = 3   # relax both cell and ions

NSW = 100   # 100 ionic steps

EDIFFG = -0.02 #forces smaller 0.02 A/eV

ENCUT   = 500   #cut off

Furthermore, the last file, the KPOINTS file, contains the k-point coordinates and mesh size for generating the k-point grid.

Monkhorst Pack # Comment line

0   # Automatic mesh generation

Monkhorst Pack   # Monkhorst-Pack setting

21 21 1

0 0 0

When the input files are ready, some tests on parameters should be performed to tune input parameters such as ENCUT, KPOINTS, and lattice constant. Then, the ground state configuration can be obtained by energy minimization with optimized parameters. The CONTCAR file, which is produced with optimized parameters, contains the low-energetic configuration of the system. So far, we have given the details of how to do it with density functional theory. Besides Vasp, Lammps will also be used to compare two distinct modeling methods for the same task. The Lammps package also requires input files. The central input file is generally named "input.lammps" and executes calculations by reading commands from an input script (text file), one line at a time.

```
#input file for graphene first energy minimization trial

units metal   # determines physical units

dimension 2   #graphene is a 2D material

processors * * *  #Specify how processors are mapped as a regular 3d grid to the global simulation box

boundary p p p

# read data

atom_style charge            #type of atomic coordinates

read_data grap.data         # the name of the file which contains atomic details

pair_style tersoff            #pair potential type

pair_coeff * * opt_SiC.tersoff  C      #interatomic potential


#initial minimization

dump    mydmp all atom 1 dump.lammpstrj

neigh_modify    every 1 delay 5 check yes


thermo        10

minimize      0.0 1.0e-10 100000 1000000

write_data outgeo.data
```

This input file just minimizes the energy to determine the ground state configuration and does not perform any ensemble runs. The output geometry will be saved as outgeo.data since we defined this name with the write_data command. The command, read_data, specifies the geometry file's name, which can be arbitrary. Our grap.data file:

#initial configuration of graphene

4 atoms #number of atoms

1 atom types

0.0 4.19 xlo xhi

0.0 2.42 ylo yhi

0.0 50.00 zlo zhi

 Masses

 1 12.0107 #CA

Atoms

 1   1 0.0 0.3494 0.6052 6.0000

 2   1 0.0 1.7471 0.6052 6.0000

 3   1 0.0 2.4460 1.8157 6.0000

 4   1 0.0 3.8437 1.8157 6.0000

The first line is a comment line. The second line provides the number of atoms in the cell. The third line gives the number of atom types. The following three lines specify the cell. Masses of atoms are also presented in this file. The remaining lines provide coordinates of each atom. For graphene, optimized Tersoff potential parameters give the best results. So, in this tutorial, we also choose to use them.

Process 2. The Electronic Band Structure of Graphene with DFT

The electronic band structure is obtained with Vasp within four steps: cell relaxation, the self-consistent calculation for obtaining charge density(or the CHCGAR file), the non-self-consistent analysis for bands, and plot bands with an appropriate program or script.

 The first step is already performed in the previous demonstration. The POSCAR file is the result configuration of the previous one, the CONTCAR file. Now, from step one to step three, just some commands in the INCAR file are changed. For step two, IBRION should be -1, and NSW should be zero because no ionic movement is allowed in this step.

2D Graphite (Graphene) Unit Cells

(a) Direct Lattice   (b) Reciprocal Lattice & BZ

$$\Gamma = \frac{2\pi}{3a}(0,0)$$

$$M = \frac{2\pi}{3a}(1,0)$$

$$K = \frac{2\pi}{3a}\left(1,\frac{1}{\sqrt{3}}\right)$$

$$K' = \frac{2\pi}{3a}\left(1,-\frac{1}{\sqrt{3}}\right)$$

lattice sites → K, and K′ in k-space

$$a = 0.142 \text{ nm}$$

$$\vec{a}_1 = \frac{a}{2}(3,\sqrt{3}) \quad \vec{G} = k_1\vec{b}_1 + k_2\vec{b}_2 + k_3\vec{b}_3 \quad \vec{b}_1 = \frac{2\pi}{3a}(1,\sqrt{3})$$

$$\vec{a}_2 = \frac{a}{2}(3,-\sqrt{3}) \quad \vec{b}_i = 2\pi\frac{\vec{a}_j \times \vec{a}_k}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad \vec{b}_2 = \frac{2\pi}{3a}(1,-\sqrt{3}))$$
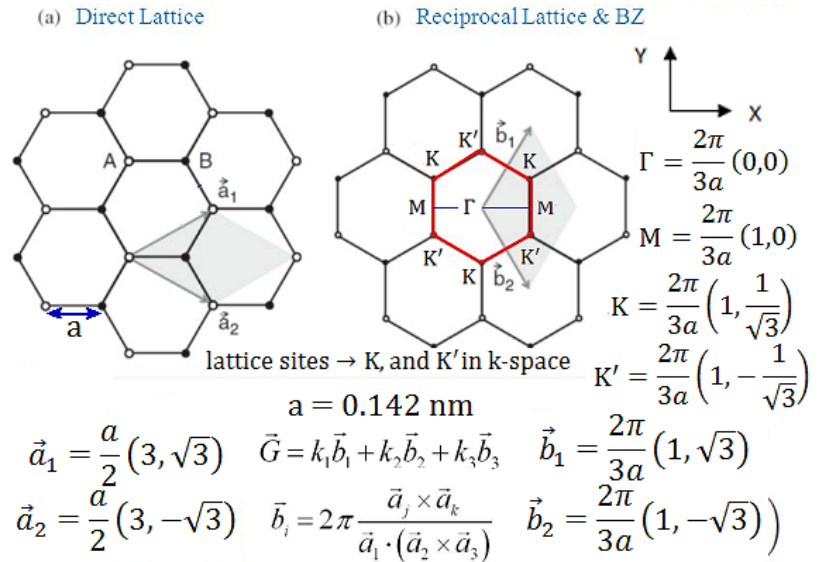
Figure 2. Direct and reciprocal lattice vectors of graphene[15]

SYSTEM = Graphene

ICHARGE = 2

PREC   = Accurate

EDIFF   = 1e-6

IBRION = -1   # no ionic movement !

NSW = 0   # no ionic movement !

ENCUT   = 500

For the non-self-calculation step, ICHARG must be 11, which means charge density read from CHGCAR. Besides, the KPOINTS file must consist of high symmetry k-points.

Here is our INCAR file for the non-self-consistent analysis:

SYSTEM = Graphene

ISTART = 0

ICHARGE = 11

PREC   = High

EDIFF = 1e-5

NELM   = 100

IBRION = -1

ENCUT = 500

And kpoints file:

k-points along high symmetry lines

 100 # 100 intersections

Line-mode

rec

 0.500000000 0.50000000 0.0000 ! M

 0.000000000 0.00000000 0.0000 ! gamma

 0.000000000 0.00000000 0.0000 ! gamma

 0.333333333 0.66666667 0.0000 ! K

 0.333333333 0.66666667 0.0000 ! K

 0.500000000 0.50000000 0.0000 ! M

This file shall provide the band structure from M to gamma, gamma to M, and K to M high symmetry point. With an appropriate plotting script or app, One can also visualize band structures. The result should be compatible with existing literature.

Process 3. The Phonon Density States of the Monoatomic Chain with DFT

The phononic density of states (DOS) is computed with density functional theory and finite difference method(Supercell method). For this tutorial, the monoatomic carbon chain is simulated with Vasp, and the density of states is calculated with Phonopy. For this purpose, the system under interest is relaxed with the Vasp package. The POSCAR file for the monoatomic carbon chain is following:

monoatomic chain   #comment line

1   #lattice constant

 1.42 0.00000 0.0000000   # first lattice vector

 0.0000 12.00 0.0000000   #second lattice vector

0.0000 0.000 12.000000 # third lattice vector

 C   # type of atom(s)

 1   #number of atoms

Cartesian   #corrdinates will be given in cartesian coordinates.

0.7 6 6   # coordinates of the atom

The INCAR file for the minimization of energy:

ICHARGE = 2

PREC   = Accurate

ISIF = 3   #relax both ions and cell

IBRION = 2Band structures can also be visualized withse conjugate-gradient algorithm

EDIFF ller 0.02 A/eV

NSW = 200   # 100 ionic steps

NELM   = 100   #100 electronic step

ENCUT   = 500

ISMEAR = 1

SIGMA = 0.1

ISYM = 1

LWAVE = .FALSE.

LCHARG = .FALSE.

NCORE = 4

LMAXMIX = 4

the KPOINTS file:

Automatic Mesh

0

G

11 6 6

0. 0. 0.

The POTCAR file is again for carbon atoms. When operating the Vasp program with these input files, the output geometry will be saved as the CONTCAR file. This CONTCAR file shall be input for the Phonopy program and be renamed POSCAR.

phonopy POSCAR -d –dim='21 1 1'

With the above command, the Phonopy program will create output files such as phonpy_disp.yaml, SPOCAR, POSCAR-001, POSCAR-002, ..
SPOSCAR is the perfect supercell structure, phonopy_disp.yaml contains the information on displacements, and POSCAR-{number} are the supercells with atomic displacements. POSCAR-{number} corresponds to the different atomic displacements written in phonopy_disp.yaml. The monoatomic chain will contain just a POSCAR-001 file since the unit cell contains one atom.

Forces on atoms are computed using the geometry files POSCAR-{number} and SPOSCAR. When Vasp is the force calculator, the computations for the finite displacement method can be proceeded just using the POSCAR-{number} files as POSCAR of VASP calculations. For each computation, there will be a vasprun.xml file.

phonopy -f dis-001/vasprun.xml dis-002/vasprun.xml …

The forces are calculated and written in the FORCE_SETS file with the above command. I assume for each force calculation; the corresponding file is named as dis-{number}.

For the last stage of the calculation, create a file, let's say DOS, and copy FORCE_SETS, POSCAR, and phonopy_disp.yaml files into the file. Then, go into the file, and create a configuration file to calculate the density of states. I name this file mesh.conf which contains the following lines:

ATOM_NAME = C

DIM = 21 1 1

MP = 240 480 480

DIM must be consistent with the supercell size.

phonopy -p -s mesh.conf

This command plots and saves the density of states.

6. Lab Report Requirements

- Geometry files will be given at the end of the section. Install the Vesta program, simulate the structure and measure the bond length and angles.

- Compare the results such as bond length and angles of low-energy configurations with existing literature, especially structures with the TEM images of synthesized graphene.
- Compare the resultant electronic band structure of graphene with existing literature.

7. Include your report:
- The references for all information you get from the literature. (Citation is important.)
- The screenshots of the structures.

References
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