DFTB+ stability calculations

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1 Introduction

To confirm the stability of Fe_2N_6 doped graphene it is possible to use DFTB calculations, as noted by Meng *et. al.*[1].

2 Configuring ASE for DFTB calculations

For general overview for this refer to ASE DFTB page.

2.1 Obtaining DFTB+

First we have to obtain the DFTB+ program from it's homepage, it states that it may be benefical to employ MPI parallelism, but currently I'll test the default executables with only OpenMP parallelism (this should not be important when performing calculations on laptop).

```
$ wget https://github.com/dftbplus/dftbplus/releases/download/20.2.1/dftbplus-20.2.1.x86_64-linux.tar.xz
$ tar xf dftbplus-20.2.1.x86_64-linux.tar.xz
```

2.2 Obtaining parameters for DFTB+

The DFTB+ module of ase requires external parameters that can be obtained from DFTB homepage. For current testing I will use parameter set used for transition metals in biological systems for Me-N/C bonds and other parameters for C-C/N bonds. I am not sure how appropriate it is to mix those, but since we need potentials for each type of bond pairs, this has to do for now.

```
$ wget https://dftb.org/fileadmin/DFTB/public/slako/trans3d/trans3d-0-1.tar.xz
$ tar xf trans3d-0-1.tar.xz
$ wget https://dftb.org/fileadmin/DFTB/public/slako/mio/mio-1-1.tar.xz
$ tar xf mio-1-1.tar.xz
$ mkdir trans3d_mio # create common folder for both potentials
$ cp trans3d-0-1/* ./trans3d_mio/
$ cp mio-1-1/* ./trans3d_mio/
```

2.3 Setting environment for work with DFTB

First we define variable to locate DFTB+ executable location, and secondly we define where to look for potential files. Note, that this must be done on each new terminal launch (or lines added to .bashrc file, or prepended to bash script for each launch). Also, since we are dealing with environment variables now, we can configure how many cores we want to use for calculations. Since DFTB+ employs OpenMP, by default it uses all available cores, we can change this with OMP_NUM_THREADS variable.

```
$ export ASE_DFTB_COMMAND="/mnt/d/PhD/DFTB/dftbplus-20.2.1/bin/dftb+ > PREFIX.out"
$ export DFTB_PREFIX=/mnt/d/PhD/DFTB/Params/trans3d_mio
$ export OMP_NUM_THREADS=6
```

furthermore, there seems to be problem with binding calculator as noted in ASE mailing list. This fix involves changing the DFTB calling method in ASE files.

```
$ sed -i "s/assert len(words) == 2/assert len(words) == 1/g" \
    /home/ritum/miniforge3/lib/python3.7/site-packages/ase/calculators/dftb.py
    # remove \ and locate file to your dftb.py location, or just manually rename in the file
```

2.4 Running test

Once we have downloaded the DFTB+, parameter files, set up environment variables and corrected the ASE code, we can perform test, to make sure that everything is done properly.
To do this we use example python program that is given in ASE DFTB page. To make thinks more automatic, I'm hosting the script on my owncloud.
To run it:

```
$ wget https://owncloud.ut.ee/owncloud/index.php/s/2yYiJpyEY6HzWSL/download
$ mv download DFTB_test.py
$ python DFTB_test.py
$ ase gui geo_end_NVE.xyz geo_end_NVT.xyz # view the result of test
```

if this does not produces any errors we have successfully set up DFTB+ with ASE.

2.5 Troubleshooting

Here I will note errors I have encountered and how to fix them.

2.5.1 Calculator "dftb" failed with command ... error code 127

The environment variable to dftb+ executable is not properly set up.

2.5.2 assert len(words) == 2 failed

For newest DFTB+ version ASE bindings are incorrect and must be fixed, see section 2.3.

2.6 No such file or directory: './results.tag'

Error with DFTB+ input, for more details see simulation output file which in python is named with label tag, so for later simulation it will be *structure.out*. I encountered this when I had no proper potential files, *e.g.* for C-C bonds.

3 Stability confirmation for Fe_2N_6 doped graphene

Now that we have set up ASE for the work, let's try to reproduce results from the publication. Since, the publication does not state much details, only that the simulation was run for 10ps with time step of 1fs at 4 different temperatures (500, 900, 1000 and 1200K), let's try to use some sensible parameters for our simulation.

3.1 MD parameters

For simulation we use NVT ensemble with 2x2x1 k-point sampling, with 1fs time step for overall 10ps, for thermostat we us Nose-Hoover thermostat with coupling strength of 3200 cm^{-1}. Overall the calculator in ASE is:

```
calculator_NVT = Dftb(atoms=atoms,
                      kpts=(2,2,1),
                      label='structure',
                      Hamiltonian_MaxAngularMomentum_='',
```

```
Hamiltonian_MaxAngularMomentum_Fe='d',
Hamiltonian_MaxAngularMomentum_C='p',
Hamiltonian_MaxAngularMomentum_N='p',
Hamiltonian_MaxAngularMomentum_H='s',
Driver_='VelocityVerlet',
Driver_MDRestartFrequency=5,
Driver_Velocities_='',
Driver_Velocities_empty='<<+ "velocities.txt"',
Driver_Steps=time, # for testing - 1000 steps = 1 ps
Driver_KeepStationary='Yes',
Driver_TimeStep=4.13, # time step 1 fs
Driver_Thermostat_='NoseHoover',
Driver_Thermostat_Temperature=temperature,
Driver_Thermostat_CouplingStrength=0.00232284721 # 3200 cm-1
)
```

3.2 Running calculation

To deal with setting environment variables, we create shell script to handle that for us, further adding a line to extract our desired results (energy versus timestep).

```
# use: $ sh run_script.sh fname time_in_fs temperature_in_K

# exports for DFTB+ calculations
export ASE_DFTB_COMMAND="/mnt/d/PhD/DFTB/dftbplus-20.2.1/bin/dftb+ > PREFIX.out"
export DFTB_PREFIX=/mnt/d/PhD/DFTB/Params/trans3d_mio
export OMP_NUM_THREADS=6

# main code
python md_script_bimet.py $1 $2 $3

# extract energies for display
grep 'Total Energy' structure.out | awk '{print $3}' > ${1}_t${2}_T${3}_energies.dat
```

now we run this for each of the 4 temperatures as in publication (each temperature run takes about 5 minutes on my machine using 6 cores), and obtain following results in Figure 1:

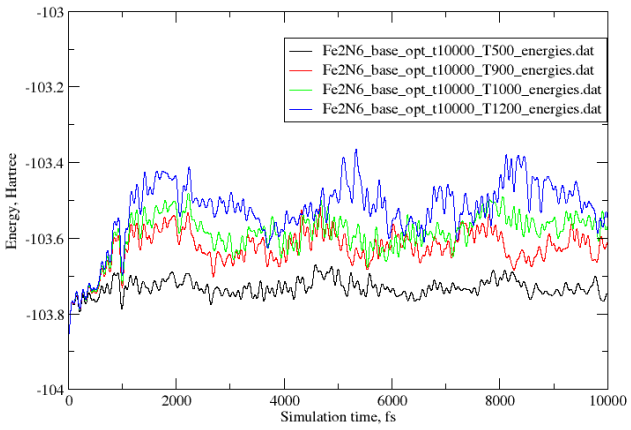

Figure 1: Obtained MD simulation results

compare to reference publication's data in Figure 2

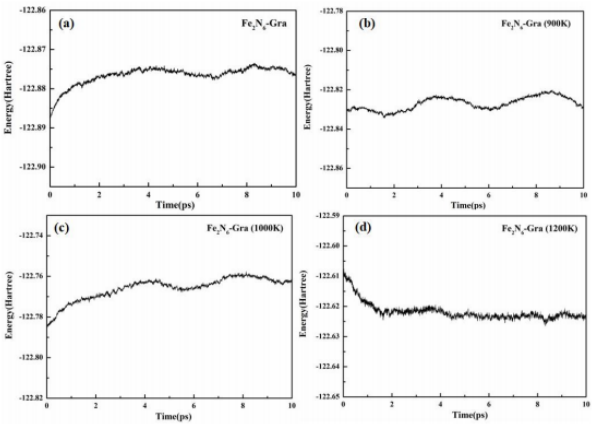

Figure S2. Total energy change of Fe_2N_6-Gra at 10 ps by MD simulations at (a) 500, (b) 900, (c) 1000 and (d) 1200 K, respectively.

Figure 2: Reference publication MD simulation results

Hence overall we observe that in our case the energy fluctuations also are stable, which is good, but we probably could consider more appropriate MD simulation conditions, and prequilibration, since if we consider temperature fluctuations in T=1200K run as shown in Figure 3, we observe that early in the simulation the temperature significantly differs from required.

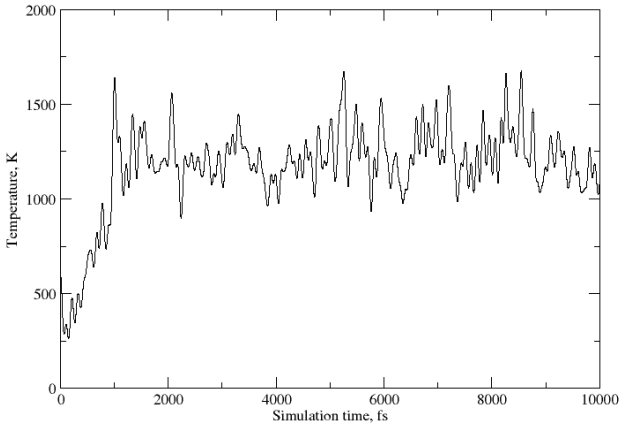

Figure 3: Temperature fluctuations in T=1200K MD simulation

References

(1) Meng, Y.; Yin, C.; Li, K.; Tang, H.; Wang, Y.; Wu, Z. *ACS Sustainable Chemistry & Engineering* **2019**, *7*, 17273–17281.