EON: hands-on session II (Sunday afternoon)

This exercise illustrates how the EON software can be used to perform nudged elastic band (NEB) and adaptive kinetic Monte Carlo calculations (AKMC). The initial state of the system consists of an Al-adatom on a Al(100) surface and the NEB calculation is first used to find minimum energy paths for diffusion, both the hop and concerted exchange mechanisms. There, the final state is specified for each mechanism. Then, AKMC calculations are used to find various possible mechanisms without specifying a final state. The interaction between the atoms is described using the embedded atom method (EAM), as implemented within EON (specifically eam_al).

NEB calculations of the hopping mechanism

Start by downloading the configuration of a Al(100) slab without an adatom. The file name is cleanslab_config.con at the URL `https://notendur.hi.is//~hj/RareEventSummerSchool19.html`. A configuration file of the '.con' format includes information about cell dimensions, atom types, atom coordinates and constraints, see Fig. 1.

```
eon configuration file
0.0000 TIME
16.970563   16.970563   30.000000
90.000000   90.000000   90.000000

1 # of element types
216 # of atoms
26.9815385 atomic mass
Al Chemical symbol for element of type 1
Coordinates of Component 1
   1.41421356237309515    1.41421356237309515   10.00000000000000000 1    0
   4.24264068711928566    1.41421356237309515   10.00000000000000000 1    1
   7.07106781186547551    1.41421356237309515   10.00000000000000000 1    2
   9.89949493661166535    1.41421356237309515   10.00000000000000000 1    3
  12.72792206135785698    1.41421356237309515   10.00000000000000000 1    4
  15.55634918610404682    1.41421356237309515   10.00000000000000000 1    5
   1.41421356237309515    4.24264068711928566   10.00000000000000000 1    6
   4.24264068711928566    4.24264068711928566   10.00000000000000000 1    7
   7.07106781186547551    4.24264068711928566   10.00000000000000000 1    8
   9.89949493661166535    4.24264068711928566   10.00000000000000000 1    9
  12.72792206135785698    4.24264068711928566   10.00000000000000000 1   10
  15.55634918610404682    4.24264068711928566   10.00000000000000000 1   11
   1.41421356237309515    7.07106781186547551   10.00000000000000000 1   12
   4.24264068711928566    7.07106781186547551   10.00000000000000000 1   13
   7.07106781186547551    7.07106781186547551   10.00000000000000000 1   14
```

Cell dimensions
Constraints (1=fixed)
Cartesian coordinates (x, y, z)

Figure 1: An example of '.con' file with explanations marked with yellow color. Coordinates of only the first 14 atoms in the file are shown.

The graphical user interface (GUI) of the Atomistic Simulation Environment (ASE) can be used to visualize '.con' files directly. If you have installed ASE, execute the command: $ase-gui initial_config.con to visualize the Al(100) surface. (**Note:** If you are working on a remote host you will need to have X-forwarding enabled on both server and client side.)

The system described by the initial_config.con file contains 216 Al atoms in a slab with 6 layers, where each layer contains 6x6 atoms. In the bottom two layers the atoms are fixed in place.

A second file describing what should be calculated is also required by EON. This is the 'config.ini' file. It contains information about the way the energy of the system should be calculated and thereby the interaction between the atoms, as well as the way the atoms will be moved during the calculation. Information about the input parameters of the 'config.ini' file are easily accessible on the website: `https://theory.cm.utexas.edu/eon/documentation.html` (**Note: there is one mistake in the documentation - use 'job' instead of 'job_type'**).

When an NEB calculation is performed, a product (final) state configuration also needs to be specified. This should preferably correspond to an energy minimum and hence already be on a minimum energy path (MEP). To do this you need to displace atoms roughly in the way you want the final state to look, and then perform a structural optimization where the potential energy of the system is minimized with respect to to all Cartesian coordinates of the unconstrained atoms. The calculation should at least reach the same numerical accuracy as the convergence criterion of the NEB calculation.

The 'config.ini' file for a structural optimization could look like this:

```
[Main]
job = minimization

[potential]
potential = eam_al

[debug]
write_movies = True
```

To generate the reactant and product state configurations for an adatom hop, do the following:

1. create a directory for the calculation
2. copy the 'cleanslab_config.con' file to the directory and rename it as 'pos.con'
3. edit this file and add an Al-adatom to a fourfold binding site
4. create and set-up a proper 'config.ini' file
5. type 'eonclient' and hit enter

A file called 'min.con' should have been generated containing the optimized structure for an Al adatom on the Al(100) surface.

To generate the product state configuration, repeat this process but choose a binding site for the adatom that is adjacent to the site previously selected for the reactant state.

You will then be in a position to find the MEP connecting the reactant and product states using the CI-NEB method:

1. create a new folder for the NEB calculation
2. copy 'min.con' from the reactant state folder to the NEB folder and rename it to 'reactant.con'
3. copy 'min.con' from the product state folder to the NEB folder and rename it to 'product.con'
4. set-up a 'config.ini' file for NEB calculations (see at end of document, if you are stuck). You should use the climbing image variant of NEB to converge rigorously on the saddle point and get a better estimate of the energy barrier.
5. type 'eonclient' and hit enter

EON summarizes the calculated results in the file 'neb.dat'. Each line corresponds to a system image along the path. The second column is the sum of straight-line distances from the reactant state to a particular image and the third column gives the energy difference of each image from the energy of the reactant state. The configuration of all images are stored in file 'neb.con'. You can find a simple python script on `https://notendur.hi.is//~hj/RareEventSummerSchool19.html` to plot (using matplotlib) the results from the 'neb.dat' file and extract the configuration of each system image from the 'neb.con' file. If the ase-gui is working properly, you can visualize the converged path as a 'movie' by typing: $ase-gui image_*

Q1: *Plot the relative energy as a function of distance from the reactant state.*

Q2: *How large is the potential energy barrier for hopping?*

NEB calculations of the exchange mechanism

For the calculation of the exchange mechanism, use the same reactant state as for the hopping mechanism, but a new product state needs to be defined and optimized.

In the exchange mechanism, the Al-adatom moves into the surface and pushes a surface Al atom out to a fourfold binding site on the surface. This binding site is in a diagonal line from the position of the adatom in the reactant state, see **Fig. 2** for visualization.

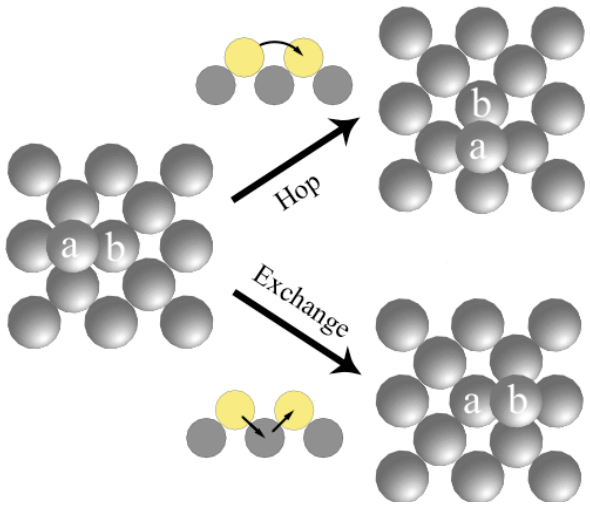

Figure 2: Illustration of the hop and exchange mechanisms of an Al-adatom diffusion event.

To generate the product state, start with a copy of the reactant state, edit the file in such a way that the Al-adatom is assigned the same coordinates as the surface atom it will push out of the way. The surface atom is then given the coordinates of an adatom in the relevant site, as shown in **Fig. 2**. Optimize the product state and perform a CI-NEB calculation.

Q3: *Plot the relative energy as a function of distance from the reactant state for the exchange process.*

Q4: *How large is the potential energy barrier for the exchange process?*

Minimum mode following calculations for Al adatom on Al(100)

While there is not time to perform a proper AKMC simulation, it is interesting to carry out a calculation that represents a first step in such a simulation, namely start with the adatom sitting on the Al(100) surface and use the minimum mode following (MMF) method to search for possible transition mechanisms and final states. The MMF method is used to map out several saddle points on the energy rim surrounding the reactant state minimum. In an AKMC simulation, this would be followed by picking a random number to select which transition occurs next and advance the system to the corresponding final state.

Copy the reactant state (Al-adatom + Al(100)) to a new folder. Setup the following config.ini file:

```
[Main]
job = akmc
temperature = 500
```

```
random_seed = 42

[Potential]
potential = eam_al

[Optimizer]
opt_method=lbfgs
converged_force = 1e-4
max_iterations = 1000

[AKMC]
confidence = 0.95

[Process Search]
minimize_first = true

[Prefactor]
default_value=1e12


[Lanczos]
tolerance=0.05

[Saddle Search]
min_mode_method=lanczos
displace_radius = 5.0
displace_magnitude = 0.2
max_energy = 10.0
displace_listed_atom_weight = 1.0
displace_atom_list= -1
```

and then execute eon (the server, not the client). The server will farm out a saddle point searches but the results will not be registered until the next execution of the server. In each execution of EON, the server will register the results of a previous run and begin a new search. To make your life easier, download a simple python script called run_akmc.py from the source `https://notendur.hi.is//~hj/RareEventSummerSchool19.html`. This script will execute the AKMC module N times, where N is a user-supplied system argument, i.e. to execute the script, type: python run_akmc.py 100. This number will be large enough to find the hopping and exchange mechanisms studied previously using NEB, as well as many other mechanisms with somewhat higher activation energy.

In normal AKMC runs the MMF searches will repeatedly visit the same saddle points. When the lowest energy saddle points have been found repeatedly, the confidence level will become high enough and the AKMC algorithm take a Monte Carlo step, advance the time and move on to the next step. Then, this process is repeated at the new state.

However, the objective here is to simply find the two saddle points you calculated earlier with the NEB and a few other higher energy saddle points. In the folder /states/X you can find all transitions out of state X (here, only X=0). Moreover, withon /states/0/ you can find the file 'processtable' which shows all unique transitions already found from this particular initial state. Find a few transitions with unique energy values (several transitions are equivalent by symmetry), write them down and then enter the directory /states/0/procdata. In this folder you have all the reactant (state 0), saddle point and product configurations. To visualize the three configurations simultaneously type: ase-gui reactant_X.con saddle_X.con product_X.con and view the movie.

Q5: *Did you find the saddle points corresponding to the hopping and exchange mechanisms?*

Q6: *Did you find other unique saddle points? How does the energy barrier compare with that of the exchange and hop?*

Typical NEB config.ini file

```
[Main]
job = nudged_elastic_band

[Potential]
potential = eam_al

[Nudged Elastic Band]
images = 8
spring = 5.0
climbing_image_method = True

[Optimizer]
max_iterations = 1000
opt_method = lbfgs
max_move = 0.1
converged_force = 0.01

[Debug]
write_movies = True
```