Adsorption of ethanol at a NaCl(100) crystal surface

Free energy profile of ethanol near a solid surface

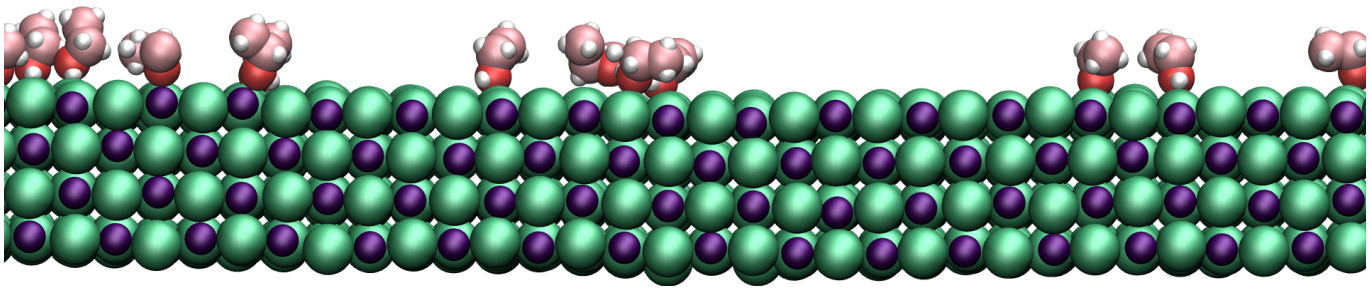


Figure: Ethanol molecules adsorbed at the NaCl(100) surface.

The objective of this exercice is to build a molecular dynamics system made of a flat crystal wall (NaCl) and ethanol molecules, using a molecule topology downloaded from the **ATB repository**. There are three main parts to this exercice:

Molecule topology - First, the molecule topology will be downloaded, and the initial configuration will be generated.

Molecular dynamics - Then, molecular dynamics and umbrella sampling simulations will be performed.

Free energy profile - Third, the WHAM algorithm will be used to re-construct the free energy profile.

Download the files from the ATB

You can skip the creation of the system and go directly to the **molecular dynamics** part by downloading the input data file **here**.

We first need to download the molecule structure and force field information from the Automated Topology Builder (ATB) and repository. Go to the **ATB repository** website (you will need to register). Then go to Existing Molecules, choose a molecule. I am choosing an **ethanol molecule**, but you can choose another one (at your own risk) and follow this tutorial. Then, click on Molecular Dynamics (MD) Files, choose LAMMPS format, and download the GROMOS force field, and the all-atom moltemplate file.

Inside the moltemplate file, there is an example of `system.lt` allowing for the creation of LAMMPS input file. In my case, it looks like that:

```
# system.lt
# simulation of a single molecule in a box of size 50x50x50 Angstroms^3

write_once("Data Boundary") {
-25.0 25.0 xlo xhi
-25.0 25.0 ylo yhi
-25.0 25.0 zlo zhi
}

write_once("In Init") {
# a variable named `cutoff` is required by GROMOS_54A7_ATB.lt
variable cutoff equal 14.0 # Angstroms
boundary p p p
}

# import the forcefield file
import "GROMOS_54A7_ATB.lt"
# import molecule building block file
import "KIR7_allatom_optimized_geometry.lt"

# create a single copy of this molecule at position 0,0,0
mol1 = new KIR7.move(0.0,0.0,0.0)
```

Run it using **Moltemplate**,

```
moltemplate.sh ./system.lt
```

to generate several LAMMPS input files corresponding to a single molecule in vacuum, which you can run using LAMMPS:

```
lmp -in system.in
```

Currently the files contain all bonds, angles, etc., information of the force field, which makes it unpleasant to read. Let us arrange the data and isolate only the useful information. Create four files, name it Positions.dat, Bonds.dat, Angles.dat, and Dihedrals.dat, and copy the respective information in it. Then re-number the atoms types, bonds, angles starting from 1. For the ethanol molecule, the Bonds.dat file looks like that:

```
1 5 1 2
2 2 2 3
3 4 3 4
4 4 3 5
5 3 3 6
6 1 6 7
7 1 6 8
8 1 6 9
```

The first column is the bond index, going from 1 to 8 (8 is the number of bond for the Ethanol molecule), the second column is the identity of the bond. For each bond identity, a bond length and energy are given:

```
bond_coeff      1 349.274 1.0900
bond_coeff      2 399.792 1.4300
bond_coeff      3 299.844 1.5200
bond_coeff      4 349.928 1.1000
bond_coeff      5 442.161 0.9720
```

The third and fourth columns of the Bonds.dat file are the indexes of the atoms linked by the bond.

Sorting out these file is a tedious task, to follow this tutorial, you can download these files for ethanol by clicking **here**. Alternatively, you can use **the atb2lammps** code to create a clean initial configuration.

If you choose another molecule, you may have additional impropers, or may not have dihedral constraints. In that case you will have to make a few adjustment to the following codes.

Create the initial configuration

Let us replicate the ethanol molecule in between two crystal walls made of NaCl. Create a folder named Ethanol and place the previously generated **files** in it. Create another folder named NaCl, create a file named Positions.dat in it, and copy the following lines corresponding to the initial positions of 8 NaCl atoms:

```
1 1 1 1 0. 0. 0.
2 2 2 -1 0. 2.84 0.
3 3 2 -1 2.84 0. 0.
4 4 1 1 2.84 2.84 0.
5 5 2 -1 0. 0. 2.84
6 6 1 1 0. 2.84 2.84
7 7 1 1 2.84 0. 2.84
8 8 2 -1 2.84 2.84 2.84
```

Then, download this **Python script** , and run it using

```
python3 generatedata.py
```

to generate the data.lammps file containing the initial configuration. This home-made Python script reads the position and molecule information for both NaCl and ethanol, replicate them, and write a LAMMPS data file. Feel free to modify it and add more molecules (or a different molecule).

To properly insert molecules within a structure using a custom script, it is important to detect the positions of the neighbor atoms before inserting a molecule, otherwise atoms will overlap and LAMMPS will crash.

The present Python script rotates the molecules to give them a random orientation, this step is not really necessary as a short molecular dynamics simulation would randomize the molecule orientation anyway.

Alternatively, you can download the LAMMPS file I have generated **here** and use it to continue with the tutorial. Let us also create a parameter file containing all the values of interactions between the atoms:

```
################ mass parameters
mass            1 22.99000
mass            2 35.45000
mass            3 12.011
mass            4 1.008
mass            5 1.008
mass            6 12.011
mass            7 15.9994
################ pair coeffs
pair_coeff      1 1 0.0552 2.31
pair_coeff      2 2 0.1004 4.3
pair_coeff      3 3 0.0663 3.5812
pair_coeff      4 4 0.0281 2.3734
pair_coeff      5 5 0.0000 0.0000
pair_coeff      6 6 0.2450 2.8114
pair_coeff      7 7 0.1195 3.1000
################ bond coeffs
bond_coeff      1 349.274 1.0900
bond_coeff      2 399.792 1.4300
bond_coeff      3 299.844 1.5200
bond_coeff      4 349.928 1.1000
bond_coeff      5 442.161 0.9720
################ angle coeffs
angle_coeff     1 47.694 109.500
angle_coeff     2 55.127 109.500
angle_coeff     3 55.114 111.000
angle_coeff     4 52.477 107.570
angle_coeff     5 47.502 108.530
angle_coeff     6 54.993 110.300
################ dihedral coeffs
dihedral_coeff  1 0.30115 1 3
dihedral_coeff  2 1.415 1 3
dihedral_coeff  3 0.0 1 1
```

Atoms of type 1 and 2 are Na and Cl, and atoms 3 to 7 are the different hydrogen, oxygen, and carbon atoms of the ethanol molecules.

All the force field values for the ethanol's atoms come from the ATB, and from the GROMOS force field. The force field values for NaCl have been taken from **this paper** by Loche et al. The interaction parameters between atoms of types i and j will be calculated using the arithmetic rule of LAMMPS.

Equilibrium

Using LAMMPS, let us bring the system to equilibrium. Open a new text file, name it equilibrium.lammps, and copy the following lines in it:

```
# ethanol at a nacl surface
################ variables
variable        pre equal 1 # desired pressure (Atm)
variable        tem equal 300 # desired temperature (K)
################ main parameters
units           real # style of units (A, fs, Kcal/mol)
atom_style      full # molecular + charge
bond_style      harmonic
angle_style     harmonic
dihedral_style  harmonic
boundary        p p p # periodic boundary conditions
pair_style      lj/cut/coul/long 10 # cut-off 1 nm
kspace_style    pppm 1.0e-4
pair_modify     mix arithmetic tail yes # eij = sqrt(ei*ej), dij = 0.5*(di+dj)
```

The script starts with the definition of two variables: temperature and pressure. Then, units are defined, as well as atom, bond, angle, and dihedral styles. Periodic boundary conditions are used in all directions of space. Atoms interact through a Lennard-Jones potential with a cut off at 1 nm, as well as through long-range Coulomb interactions using the particle-particle particle-mesh solver with an accuracy of 0.0001. Finally, the arithmetic rule is used to control interaction between atoms of different types.

Then, add the following lines to the script:

```
################ import positions and parameters
read_data       data.lammps
include         PARM.lammps
################ groups # descriptions
group           nacl type 1 2 # nacl wall
group           eth type 3 4 5 6 7 # ethanol molecules
################ dynamics
timestep        1 # (fs)
fix             mymme nacl momentum 1 linear 1 1 1
velocity        all create ${tem} 4928459 rot yes mom yes dist gaussian
fix             mynpt all npt temp ${tem} ${tem} 100 x ${pre} ${pre} 1000 y ${pre} ${pre} 1000
################ output
thermo          1000
dump            dp1 all atom 1000 dump.lammpstrj # print every 1 ps
################ run
run             100000 # 100 ps
write_data      data.npt
```

The read_data and include commands are used to import the previously generated data and parameter files, respectively. Then, two groups are defined from the atoms types, and a timestep of 1 fs is set. The linear momentum of the NaCl block is canceled in all three directions to avoid drifting. Initial velocities are given to the atoms , with a starting temperature equal to the chosen value of 300 K. An anisotropic NPT thermostat is used, with the volume being adjusted only along the x and y directions, and not along the z direction to avoid the collapse of the two walls.

Trajectories are printed in a dump file every 1 ps, and information to the terminal every 1 ps. The simulation runs for 100 ps and finally the final state is printed in the data.npt file. You can visualize the trajectory by opening the dump file using VMD or Ovito.

Umbrella sampling

From the previously equilibrated configuration, let us perform the umbrella sampling simulation step. To do so, we are going to pick one of the ethanol molecule, and force it to move along an axis normal to the NaCl surface, by adding a harmonic potential to it. The actual position of the molecule around the center of the harmonic potential will be recorded,

and used later to reconstruct the free energy profile.

Create another input file within the same folder, call it umbrella.lammps, and copy the following lines in it:

```
# ethanol at a nacl surface
################ variables
variable        pre equal 1 # desired pressure (Atm)
variable        tem equal 300 # desired temperature (K)
variable        k1 equal 0.5 # spring constant
variable        k2 equal 5 # spring constant
################ main parameters
units           real # style of units (A, fs, Kcal/mol)
atom_style      full # molecular + charge
bond_style      harmonic
angle_style     harmonic
dihedral_style  harmonic
boundary        p p p # periodic boundary conditions
pair_style      lj/cut/coul/long 10 # cut-off 1 nm
kspace_style    pppm 1.0e-4
pair_modify     mix arithmetic tail yes # eij = sqrt(ei*ej), dij = 0.5*(di+dj)
################ import positions and parameters
read_data       data.npt
include         PARM.lammps
################ groups # descriptions
group           nacl type 1 2 # nacl wall
group           eth type 3 4 5 6 7 # ethanol molecules
group           oxy type 7 # ethanol molecules
group           mol2 molecule 2
group           topull intersect mol2 oxy
################ dynamics
timestep        1 # (fs)
fix             mynpt all npt temp ${tem} ${tem} 100 x ${pre} ${pre} 1000 y ${pre} ${pre} 1000
variable        zini equal xcm(nacl,z)
fix             mytth1 nacl spring tether ${k2} NULL NULL ${zini} 0
################ output
thermo          1000
dump            dp1 all atom 50000 dump.lammpstrj
################ run
variable        zave equal xcm(topull,z)
variable        cpt loop 24
label           loop
variable        zdes equal -20+0.5*(${cpt}-1)
fix             mytth2 topull spring tether ${k1} 0 0 ${zdes} 0
run             50000
fix             myat1 all ave/time 10 10 100 v_zave v_zdes file position.${cpt}.dat
run             500000
unfix           myat1
next            cpt
jump            SELF loop
```

The first difference between this script and the previous one is the definition of two spring constants k_1 and k_2 that will be used respectively to maintain the ethanol molecule, and the nacl wall near given positions. A second difference is that new groups have been defined, with the group 'topull' being made of one single oxygen atom that is part of the chosen ethanol molecule. This group is itself build from the intersection between the group 'oxy' made of all the oxygen atoms of type 7, and the group 'mol2' made of all the atoms of the molecule of index 2 (the wall is index 1, and the ethanol molecules are indexes 2, 3, 4 etc.). Finally, a loop made of 24 iterations is defined, the variable 'zdes' is the desired position we want to impose to the atom of group 'topull', it goes from -20 Å (very close to the bottom wall) to -8 Å (far from the wall). The fix 'mytth2' is used to add the harmonic potential to the atom 'topull'. Note that the fix 'mytth1' is used to prevent the NaCl wall for drifting from its original position 'zini'.

Run the script using LAMMPS. 24 files named position.1.dat, position.2.dat, etc. must appear inside the folder. If you visualize the dump file with VMD, you see one molecule being progressively moved out from the wall. The other molecules remain unperturbed and free to diffuse and adsorb.

Building the free energy profile

In order to treat the data, we are going to use the WHAM algorithm. You can download and compile the version of **Alan Grossfield**. In order to apply the WHAM algorithm to our simulation, we first need to create a metadata file. This file simply contains the paths of the data file, the value of x_{des}, and the values of k. To generate the file more easily, you can run this script using Octave (assuming that the wham algorithm is located in the same folder as the LAMMPS simulations).

```
file=fopen('metadata.dat','wt');
for a=1:24
X=['./position.',num2str(a),'.dat ',num2str(-20+0.5*(a-1)),' 0.5'];
fprintf(file,X);
fprintf(file,'\n');
end
```

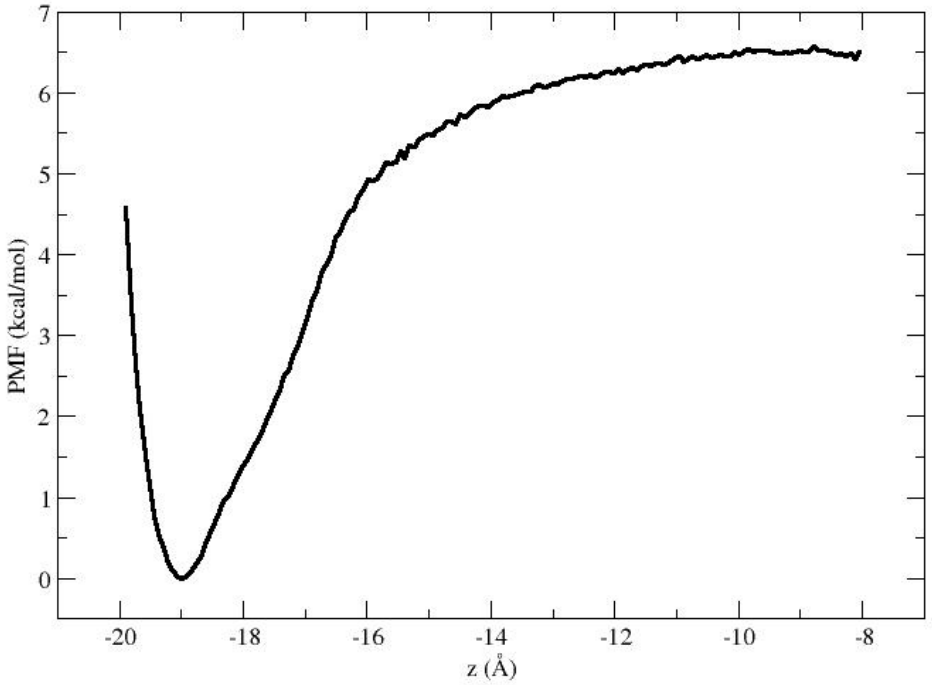
The generated file named metadata.dat looks like that (alternatively you can download it **here**):

```
./position.1.dat -99 0.0205
./position.1.dat -20 0.5
./position.2.dat -19.5 0.5
./position.3.dat -19 0.5
./position.4.dat -18.5 0.5
(...)
./position.23.dat -9 0.5
./position.24.dat -8.5 0.5
```

Then, simply run the following command

```
 ./wham -20 -8 160 1e-8 300 0 metadata.dat PMF.dat
```

where -20 and -8 are the boundaries, 160 the number of bins, 1e-8 the tolerance, and 300 the temperature. A file named PMF.dat has been created, and contains the free energy profile in Kcal/mol:



The profile indicates that it is more energetically favorable for an ethanol molecule to adsorb at the surface rather than remaining far from it, which is consistent with what we observe with the unperturbed molecules (they stick to the surface). The energy well is about 6.5 kcal/mol, which is about $11 \times k_\mathrm{B}T$.