MiCMoS
Milano Chemistry Molecular Simulation
Description and User Manual

Tutorials

T6. Monte Carlo: simulation of a liquid rigid molecule (benzene)

PURPOSE: In this tutorial, it is described how to prepare and equilibrate a liquid box of benzene with the Monte Carlo technique.

REFERENCE to main manual: Sections 5.2 (***Boxliq***); 5.4 (***Pretop***); 6.6.1 (***mcmain***); 6.6.2 (instruction file); 6.6.3 (topology and force field file).

FILES: You can find all the files you need to run this tutorial here:
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T6/benz.mci
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T6/benz.oeh
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T6/benz.top
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T6/benz_preliminary.mci
The starting point is the benz.*oeh* structure file, which was prepared based on obvious geometrical criteria (regular hexagon, all C-C 1.40 Å, all C-H 1.08 Å). See Tutorial T3 to know how to do that automatically with ***Retcor***. CLP charges were assigned by ***Retcha*** (see Tutorial 1). File benz.*mci* contains the MC running commands. You will also need macros to run individual modules ***Pretop***, ***Boxliq*** and ***mcmain***. Place .*oeh* and pertinent (Windows/Unix) macros into your working directory.

Open the benz.*oeh* file.

Structure file .oeh for benzene

```
#BENZNE99  benzene
0          0.0
1.0000   1.0000   1.0000   90.000   90.000   90.000
0.0000
12
 1   0.00000   1.39000   0.00000  1 12 -0.2878
 2   1.20378   0.69500   0.00000  1 12 -0.2878
 3   1.20378  -0.69500   0.00000  1 12 -0.2878
 4   0.00000  -1.39000   0.00000  1 12 -0.2878
 5  -1.20377  -0.69500  -0.00000  1 12 -0.2878
 6  -1.20377   0.69500  -0.00000  1 12 -0.2878
 7  -0.00000   2.47000   0.00000  1  2  0.2878
 8   2.13909   1.23500   0.00000  1  2  0.2878
 9   2.13909  -1.23500  -0.00000  1  2  0.2878
10   0.00000  -2.47000   0.00000  1  2  0.2878
11  -2.13908  -1.23500  -0.00000  1  2  0.2878
12  -2.13908   1.23500  -0.00000  1  2  0.2878
 0
 1    1
1.0   0.0   0.0   0.0   1.0   0.0   0.0   0.0   1.0
0.00000   0.00000   0.00000
 0
 0
```

Note that the reference system indicator in the penultimate line (see manual, Section 1.4.3) is 0, meaning that input coordinates are going to be transferred as such to the topology file. The 0 on the last line means that no extra potential parameters are required. Moreover, coordinates are expressed in Cartesian form, with a formal unit cubic cell of 1x1x1 Å and no symmetry operations apart the identity.

The starting topology file (manual, Section 6.6.3) can be produced by running the ***Pretop*** module (manual, Section 5.4):

```
./run.pretop benz
```

The dialog mode will ask for:

```
give factors for ks,kb,kt force consts.
```

On prompt for force constant scaling factors answer 1. 1. 1., as these will anyway be useless. This is a very simple rigid molecule and there are no slave atoms. The program prints general information on a benzpre.*pri* output file; you may want to check solute connectivity to ensure that all is ok:

*Output of **Pretop**:*

```
pretop module 2017-2018 for
    #BENZNE99  benzene
 operation on asymmetric unit n.  1

  original coordinates and reference coordinates
    0.0000    1.3900    0.0000      0.0000    1.3900    0.0000
    1.2038    0.6950    0.0000      1.2038    0.6950    0.0000
    1.2038   -0.6950    0.0000      1.2038   -0.6950    0.0000
    0.0000   -1.3900    0.0000     -0.0000   -1.3900    0.0000
   -1.2038   -0.6950   -0.0000     -1.2038   -0.6950   -0.0000
   -1.2038    0.6950   -0.0000     -1.2038    0.6950   -0.0000
   -0.0000    2.4700    0.0000      0.0000    2.4700    0.0000
    2.1391    1.2350    0.0000      2.1391    1.2350    0.0000
    2.1391   -1.2350   -0.0000      2.1391   -1.2350   -0.0000
    0.0000   -2.4700    0.0000     -0.0000   -2.4700    0.0000
   -2.1391   -1.2350   -0.0000     -2.1391   -1.2350   -0.0000
   -2.1391    1.2350   -0.0000     -2.1391    1.2350   -0.0000
 molecular volumes   83.27    0.00

   solute connectivity
 atom   1 type  12     2   6   7
   1.390   1.390   1.080
 atom   2 type  12     1   3   8
   1.390   1.390   1.080
 atom   3 type  12     2   4   9
   1.390   1.390   1.080
 atom   4 type  12     3   5  10
   1.390   1.390   1.080
 atom   5 type  12     4   6  11
   1.390   1.390   1.080
 atom   6 type  12     1   5  12
   1.390   1.390   1.080
 atom   7 type   2     1
   1.080
 atom   8 type   2     2
   1.080
 atom   9 type   2     3
   1.080
 atom  10 type   2     4
   1.080
 atom  11 type   2     5
   1.080
 atom  12 type   2     6
   1.080
 normal end of operation
```

Pretop also produces a benztry.*top* topology file; the flag "try" should warn you that it is just a tentative file, which must be edited to suit your needs.

Tentative topology file for benzene, .top. Red: lines to be cancelled; green: lines to be edited

```
#BENZNE99  benzene topology
12
 1   0.00000   1.39000   0.00000  12   -0.2878
 2   1.20378   0.69500   0.00000  12   -0.2878
 3   1.20378  -0.69500   0.00000  12   -0.2878
 4  -0.00000  -1.39000   0.00000  12   -0.2878
 5  -1.20377  -0.69500  -0.00000  12   -0.2878
 6  -1.20377   0.69500  -0.00000  12   -0.2878
 7   0.00000   2.47000   0.00000   2    0.2878
 8   2.13909   1.23500   0.00000   2    0.2878
 9   2.13909  -1.23500  -0.00000   2    0.2878
10  -0.00000  -2.47000   0.00000   2    0.2878
11  -2.13908  -1.23500  -0.00000   2    0.2878
12  -2.13908   1.23500  -0.00000   2    0.2878
 0  nslav-u
 0  ncore-v
 0  nslav-v
83.3    0.0 volu-u,volu-v
12  nstr-u
 1    2   1.390  4880.7   C- C
 1    6   1.390  4880.9   C- C
 1    7   1.080  3600.0   C- H
 2    3   1.390  4880.8   C- C
 2    8   1.080  3600.0   C- H
 3    4   1.390  4880.7   C- C
 3    9   1.080  3600.0   C- H
 4    5   1.390  4880.9   C- C
 4   10   1.080  3600.0   C- H
 5    6   1.390  4880.8   C- C
 5   11   1.080  3600.0   C- H
 6   12   1.080  3600.0   C- H
 0  nstr-v
18  nbend-u
 1    2    3  120.00   583.8   C- C- C
 1    2    8  120.00   505.0   C- C- H
 1    6    5  120.00   583.8   C- C- C
 1    6   12  120.00   505.0   C- C- H
 2    1    6  120.00   583.8   C- C- C
 2    1    7  120.00   505.0   C- C- H
 2    3    4  120.00   583.8   C- C- C
 2    3    9  120.00   505.0   C- C- H
 3    2    8  120.00   505.0   C- C- H
 3    4    5  120.00   583.8   C- C- C
 3    4   10  120.00   505.0   C- C- H
 4    3    9  120.00   505.0   C- C- H
 4    5    6  120.00   583.8   C- C- C
 4    5   11  120.00   505.0   C- C- H
 5    4   10  120.00   505.0   C- C- H
 5    6   12  120.00   505.0   C- C- H
 6    1    7  120.00   505.0   C- C- H
 6    5   11  120.00   505.0   C- C- H
 0  nbend-v
12  ntors-u
6   1   2   3  50.00   -1.0    1.0   C- C- C- C
2   1   6   5  50.00   -1.0    1.0   C- C- C- C
1   2   6   7 100.00   -1.0    1.0   C- C- C- H
1   2   3   4  50.00   -1.0    1.0   C- C- C- C
2   1   3   8 100.00   -1.0    1.0   C- C- C- H
2   3   4   5  50.00   -1.0    1.0   C- C- C- C
3   2   4   9 100.00   -1.0    1.0   C- C- C- H
3   4   5   6  50.00   -1.0    1.0   C- C- C- C
4   3   5  10 100.00   -1.0    1.0   C- C- C- H
4   5   6   1  50.00   -1.0    1.0   C- C- C- C
5   4   6  11 100.00   -1.0    1.0   C- C- C- H
6   1   5  12 100.00   -1.0    1.0   C- C- C- H
 0  ntors-v
 0  nlist-u
 0  nlist-v
0.410   235.0   650.0   77000.0
 0  nextr
```

Copy benztry.*top* into benz.*top*:

```
cp benztry.top benz.top
```

Now work on benz.*top*. You have no need to probe bond stretching and bending in Monte Carlo; moreover, benzene is very rigid and no free torsions are present. All useless stretch,

bend and torsion functions must be deleted. Remember also to change the corresponding indicators nstr-u, nbend-u and ntors-u to 0. In the end, you should have the following file:

Topology file to be used in MC simulation for benzene

```
   #BENZNE99  benzene topology
   12
    1   0.00000   1.39000   0.00000  12   -0.2878
    2   1.20378   0.69500   0.00000  12   -0.2878
    3   1.20378  -0.69500   0.00000  12   -0.2878
    4  -0.00000  -1.39000   0.00000  12   -0.2878
    5  -1.20377  -0.69500  -0.00000  12   -0.2878
    6  -1.20377   0.69500  -0.00000  12   -0.2878
    7   0.00000   2.47000   0.00000   2    0.2878
    8   2.13909   1.23500   0.00000   2    0.2878
    9   2.13909  -1.23500  -0.00000   2    0.2878
   10  -0.00000  -2.47000   0.00000   2    0.2878
   11  -2.13908  -1.23500  -0.00000   2    0.2878
   12  -2.13908   1.23500  -0.00000   2    0.2878
    0  nslav-u
    0  ncore-v
    0  nslav-v
   83.3    0.0 volu-u,volu-v
    0  nstr-u
    0  nstr-v
    0  nbend-u
    0  nbend-v
    0  ntors-u
    0  ntors-v
    0  nlist-u
    0  nlist-v
   0.410   235.0   650.0   77000.0
    0  nextr
```

The starting liquid box is constructed by the invoking ***Boxliq*** (manual, Section 5.2):

```
./run.boxliq benz
```

The program will answer:

```
mol.diameter and liquid cell length     6.535     7.546

   give nrep,expans.factor,randT,tauspread,ichir
```

On prompt, answer: *nrep* 4, exp factor 1.1, other three numbers: 0.5, 10.0, 0. ***Boxliq*** will print on screen:

```
box on x, y, z   38.0796   38.0389   38.0534  averaged to   38.0573
 normal end of operation, n.mols., dens  250   0.588
 Thank you for using MiCMoS
```

The result is a box with 250 molecules written as rigid-body position parameters, of approximate density 0.59. Information on position and orientation of all the molecules in the box is written in file benzliq.*bxi* (manual, Section 5.1.1) produced by ***Boxliq***. The approximate box dimension is averaged to 38.057 Å.

CAUTION: Changing the value of the expansion factor (now 1.1) generates boxes of different density: too low, will take a long time to equilibrate; too high, the box will contain too many hard contacts. Try with experience.

You now have to prepare the MC run control file, benz.*mci*: open it as a new file and write the following instructions. Refer to manual, Section 6.6.2 for the meaning of the various parameters.

Monte Carlo running command file, .mci, for preliminary disposal of hard contacts

```
  benzene standard liquid run
#  iprint ivarib iwrh  ipots  factin
      0     0     0      0      0.0
#  cutoff  boxx    boxy    boxz   alf   bet   gam   var.indices      irbox
   15.0   0.000   0.000   0.000    0.0   0.0   0.0   2  2  2  0  0  0   1
# temp  n.moves,ncom reset,nbox reset  nwri  nwre   npri/steps
   200.0  100000     1000       0       5000  5000      1000
  0.50  30.0  10.0  0.0  0.0  0.  0.  0.  0.  0.
#   P    npres ianis
   1.0    900    3
```

The CLP potentials are used (ipots=0), the temperature is kept low (200 K) for a more efficient optimization of the box that at the start contains a number of hard contacts. Irbox=1 means that starting box dimensions are read from the input benzliq.*bxi* file and not from the .*mci* file. Box edges are varied with a maximum step length of 0.02 Å each (2 2 2 below "var. indices"), and 100,000 steps are asked writing coordinate and energy trajectory every 5,000 steps. Pressure and box edges are updated every 900 steps with isotropic control (ianis=3). The reference pressure is 1 bar.

The command

```
./run.mcmain benz benzliq.bxi b1
```

runs the MC program; benz corresponds to .*mci* and .*top* files; benzliq.*bx*i the starting box in condensed format and b1 will flag all outputs.

The first task is to dispose of hard contacts with highly repulsive energies (they do not fit the output format and are written as a ******* field). The output of this run is an almost equilibrated box with cohesive energy (the rough equivalent of vaporization energy) 29 kJ/mol and density 0.83 g/mL.

```
final result at last MC step
       0.0  -6558.2   -528.7      0.0  -7086.9
  33.9752 33.9752 33.9752   90.00   90.00   90.00

    #BENZNE final Ecoh,Et per mol.,vbox,dens   -28.3   -28.3  39218.08   0.827
 normal end of operation
```

File b1mc.*pri* has the printed output, Files b1mcc.*dat*, b1mc.*ene* and b1mco.*dat* have the trajectories (manual, Section 5.1.3), list of energies (manual, Section 8.5.1) and final frame (manual, Section 5.1.1) data. In particular, file b1mc.*bxo* has the final frame in symbolic form (like .*bxi*) that can be used to restart the job. Actually, longer runs and a higher cutoff would be needed to better reproduce experimental data.

Let's now set up a full Monte Carlo calculation. Open the *.mci* file and edit some key parameters. First, increase cutoff to 16.0 Å; then, raise T to 298 K (25 ºC) to simulate liquid benzene at room temperature; finally, increase the number of moves to 500,000 and set nwri = nwre = 10,000 and npri=5,000 to have output files not too large. Eventually, you should have:

Monte Carlo running command file, .mci

```
  benzene standard liquid run
#  iprint ivarib iwrh  ipots  factin
      0     0     0      0      0.0
#  cutoff  boxx    boxy    boxz   alf   bet   gam   var.indices      irbox
   16.0   0.000   0.000   0.000    0.0   0.0   0.0   2  2  2  0  0  0   1
# temp  n.moves,ncom reset,nbox reset  nwri  nwre   npri/steps
   298.0  500000     1000       0      10000 10000      5000
  0.50  30.0  10.0  0.0  0.0  0.  0.  0.  0.  0.
#   P    npres ianis
   1.0    900    3
```

Now execute again ***mcmain***:

```
./run.mcmain benz b1mc.bxo b2
```

Note that this command calls benz.*top*, which is of course left unchanged, the same benz.*mci* input that you edited a moment ago, and uses the final frame of the previous MC run (b1mc.*bxo*) as a starting box for this calculation. It is wise to change the label for output files (b2) to avoid overwriting of files generated by the previous run.

This simulation will take 10-15', depending on your CPU speed. Open the b2mc.*pri* file. First, the program prints a resume of atomic coordinates and charges, plus some operational parameters, such as the CLP fudge scaling factors and the cutoff for centre of mass distance.

```
  Run control .mci file header line    benzene standard li
topology file header line
    #BENZNE99  benzen

core atoms, solute
    1    0.0000    1.3900    0.0000   12 -0.2878
    2    1.2038    0.6950    0.0000   12 -0.2878
    3    1.2038   -0.6950    0.0000   12 -0.2878
    4   -0.0000   -1.3900    0.0000   12 -0.2878
    5   -1.2038   -0.6950   -0.0000   12 -0.2878
    6   -1.2038    0.6950   -0.0000   12 -0.2878
    7    0.0000    2.4700    0.0000    2  0.2878
    8    2.1391    1.2350    0.0000    2  0.2878
    9    2.1391   -1.2350   -0.0000    2  0.2878
   10   -0.0000   -2.4700    0.0000    2  0.2878
   11   -2.1391   -1.2350   -0.0000    2  0.2878
   12   -2.1391    1.2350   -0.0000    2  0.2878

solute atoms,total,core,slaves   12   12    0
solvent atoms,total,core,slaves    0    0    0
using CLP potentials,parameters     0.41  235.00  650.00  77000.00
cutoff for center-of-mass distances  16.0
```

In the second output block, atomic parameters are summarized, including effective atomic charges, polarizabilities, diffuseness factors and acceptor-donor ("acdo") indices:

```
atomic parameters,solute
 n.,type,species,charge,wt,polar.,diffu, acdo
    1   C    12  -0.1180   12.011    1.350    1.000    0.000
    2   C    12  -0.1180   12.011    1.350    1.000    0.000
    3   C    12  -0.1180   12.011    1.350    1.000    0.000
    4   C    12  -0.1180   12.011    1.350    1.000    0.000
    5   C    12  -0.1180   12.011    1.350    1.000    0.000
    6   C    12  -0.1180   12.011    1.350    1.000    0.000
    7   H     2   0.1180    1.008    0.390    0.620    0.100
    8   H     2   0.1180    1.008    0.390    0.620    0.100
    9   H     2   0.1180    1.008    0.390    0.620    0.100
   10   H     2   0.1180    1.008    0.390    0.620    0.100
   11   H     2   0.1180    1.008    0.390    0.620    0.100
   12   H     2   0.1180    1.008    0.390    0.620    0.100
 net charge on solute and solvent   -0.0000    0.0000
 molecular weight, solute and solvent
     78.1134    0.0000
 sum of + and - charges, solute and solvent
      0.7080   -0.7080      0.0000    0.0000
```

Note that atomic charges are rescaled by 0.41, as specified in the input *.mci* file. Then, information on the simulation box is given:

```
box dimensions and max steps
   33.9752  0.0200 33.9752  0.0200 33.9752  0.0200  90.00   0.00  90.00   0.00  90.00   0.00
 N.solutes-atoms, N.solvents-atoms
     250    12     0     0
 total parameters in solutes and solvents  1500     0
 actual variables, total,solute,solvent  1500  1500     0
 ivarib   0 number of particles for P control    250.
 initial nonzero intramolecular energies
 solute, solvent, tot intramolecular energy       0.0       0.0       0.0
```

Note that max steps on the box edges are 0.02 Å, again as specified in the input file. In the next output block, the initial energies are provided. No solvent molecules are present; thus, the corresponding entries (those marked with "v", such as "v" and "uv") are 0.

```
Intermolecular energies
   LP energies, u,v,uv  -6595.49      0.00      0.00
 Coul energies, u,v,uv   -528.76      0.00      0.00
 Total LP,Coul,total E  -6595.49   -528.76  -7124.24
   box dipole energy        0.00
 multiples of box dim
       1.0     1.0     1.0

 Eintra,Elp,Eq,Edip,Et,box,initial values
       0.0  -6595.5   -528.8     0.0  -7124.2 33.9752 33.9752 33.9752   90.00   90.00   90.00
 Ecoh,Et per mol.,vbox,dens,initial values
     -28.5   -28.5  39218.06   0.827
```

Relevant boundary conditions, including barostat and thermostat, are then specified:

```
Temperature,n.moves,nboxc,ncomc,nwribox,nwrie
     298.00    500000         0      1000     10000     10000
 MC steps
   0.50 30.00 10.00  0.00  0.00  0.00  0.00  0.00  0.00  0.00
 set P, interval for P control    1.0       900
 isotropic box ch. or pressure control
 Isobaric-Isothermal ensemble (IIE) P control
```

Then, values of box parameters and total energies are printed according with to the printout frequency specified in the *.mci* running command file. For example:

```
MC moves initial
       1800   34.153   34.153   34.153   90.000   90.000   90.000       1. box data
       5000      0.0  -6433.2   -513.2      0.0  -6946.5          ens data
   -6433.2      0.0      0.0   -513.2      0.0      0.0
       7200   34.193   34.193   34.193   90.000   90.000   90.000       1. box data
      10000      0.0  -6432.4   -484.4      0.0  -6916.8          ens data
   -6432.4      0.0      0.0   -484.4      0.0      0.0
      11700   34.250   34.250   34.250   90.000   90.000   90.000       1. box data
      12600   34.176   34.176   34.176   90.000   90.000   90.000       1. box data
      13500   34.198   34.198   34.198   90.000   90.000   90.000       1. box data
      14400   34.164   34.164   34.164   90.000   90.000   90.000       1. box data
      15000      0.0  -6365.2   -490.6      0.0  -6855.8          ens data
   -6365.2      0.0      0.0   -490.6      0.0      0.0
[...]
```

Thus, we see that the simulation box was successfully updated at steps 1800, 7200 and so on (see lines marked as (`1. box data`). As required, energies in kJ/mol are always printed every 5,000 steps (lines marked as `ens data`); numbers have the usual meaning: dispersive-repulsive terms, Coulomb terms, dipole correction (always 0 in this case) and total energy.

Finally, the program ends by printing last step parameters (final box edges, energies), and also summarized how many MC moves have been attempted, plus how many have been accepted or rejected. Box statistics is printed aside. In the last lines, energies are normalized to "per mole" values.

```
last step
     500000
 general,tot,acc,rej,  box,tot,acc,rej
      499445    303396    196049       555       144       411
    #BENZNE acceptance ratio, total,box      60.75     25.95

 final result at last MC step
       0.0  -7434.9   -701.5      0.0  -8136.4
  32.8075 32.8075 32.8075   90.00   90.00   90.00

 Intermolecular energies
   LP energies, u,v,uv  -7434.87      0.00      0.00
 Coul energies, u,v,uv   -701.51      0.00      0.00
 Total LP,Coul,total E  -7434.87   -701.51  -8136.38
   box dipole energy        0.00

    #BENZNE final Ecoh,Et per mol.,vbox,dens   -32.5   -32.5  35311.66   0.918
 normal end of operation
```

The calculation has ended with an approximate vaporization energy of 32.5 kJ/mol and liquid density of 0.92 g/mL, which are both rather good if compared with the corresponding experimental estimates at room temperature (33.9 kJ/mol and 0.88 g/mL).

See Tutorial T11 to learn how to use analysis programs to analyze in depth *.mcc*, *.mco* and *.ene* files.