MiCMoS
Milano Chemistry Molecular Simulation
Description and User Manual

Tutorials

T7. Monte Carlo: simulation of a liquid flexible molecule (*n*-pentane)

PURPOSE: In this tutorial, it is described how to prepare and equilibrate a liquid box of normal-pentane with the Monte Carlo technique. The aim is to get the user acquainted with the use of slave atoms for the Monte Carlo routine of MiCMoS.

REFERENCE to main manual: Sections 5.2 (**Boxliq**); 5.4 (**Pretop**); 6.2 (construction of molecular frameworks); 6.6.1 (**mcmain**); 6.6.2 (instruction file); 6.6.3 (topology and force field file); 6.6.4 (slave atom 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/T7/pentane.mci
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T7/pentane.oih
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T7/pentane.sla
https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T7/pentane.top
The starting point is the pentane.*oih* structure file, which can be prepared by using **Retcor** as a molecule builder, as detailed in Tutorial T3. File pentane.*mci* contains the MC running commands. You will also need macros to run individual modules **Retcor, Retcha**, **Pretop**, **Boxliq** and **mcmain**. Place .*oih* and pertinent (Windows/Unix) macros into your working directory.

A linear all trans and staggered pentane molecule is built from just the first three carbon atoms (C1-C3), then generating all others by giving bond distances, bond angles and torsion angles (file pentane.*oih*). Tutorial T3 describes in depth how this file can be produced by hand in a few minutes. See the next page for the result.

Pentane: the input pentane.oih file

```
#PNTANE99  n-pentane
   0
    1.0000     1.0000     1.0000     90.00      90.00      90.00
     0.0
   3
    1   0.00000    0.00000    0.00000    1  13    0.
    2   0.00000    1.52500    0.00000    1  13    0.
    3   1.41396    2.09628    0.00000    1  13    0.
   11
    4  -1   0   1   2   3   1  13  0.0000  1.525   180.00   112.000   C4 from C1-C2-C3
    5  -1   0   4   1   2   1  13  0.0000  1.525   180.00   112.000   C5 from C4-C1-C2
    6   7   0   1   2   4   1   3  0.0000  1.080     0.00   108.000   methylene groups
    8   9   0   2   1   3   1   3  0.0000  1.080     0.00   108.000
   10  11   0   4   1   5   1   3  0.0000  1.080     0.00   108.000
   12  -1   0   3   2   1   1   3  0.0000  1.080    60.00   110.500   methyl groups
   13  -1   0   3   2   1   1   3  0.0000  1.080   180.00   110.500
   14  -1   0   3   2   1   1   3  0.0000  1.080   300.00   110.500
   15  -1   0   5   4   1   1   3  0.0000  1.080    60.00   110.500
   16  -1   0   5   4   1   1   3  0.0000  1.080   180.00   110.500
   17  -1   0   5   4   1   1   3  0.0000  1.080   300.00   110.500
    1   0
    1.0    0.0    0.0    0.0    1.0    0.0    0.0    0.0    1.0
   0.000000   0.000000   0.000000
    0
    0
```

The command sequence to generate the .*oeh* file with charges, from the .*oih* file, is as follows (see Tutorial T1 for detailed explanations).

```
./run.retcor pentane
./run.retcha pentane
```

This generates pentane.*oeh*, with explicit atomic coordinates and Extended Hückel charges. The resulting molecular structure is shown in the picture below:
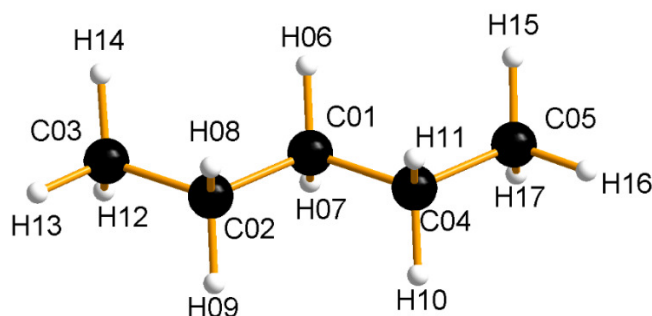
The next step is the preparation of the slave atoms .*sla* file. Remember that **slave connectivity and charges are defined in the topology .*top* file**: we will take care of that in a moment. **The .*sla* file contains the slave-defining parameters (distances, angles and torsions) and tells the MC program which of them is to be varied**. Refer to Table 6.2 in the manual and Section 6.6.4.1 for another practical example (ethanol). First, you have to decide what torsions are free. The two terminal methyl groups (H12-H14 and H15-H17) should be allowed to rotate. This can be accomplished using the "RX$_3$ mode":

```
1.080 110.5   60.0   0   0   3   12 13 14
1.080 110.5   60.0   0   0   3   15 16 17
```

The floating entries specify, for each methyl, 1 C-H distance (1.080 Å), 1 H-C-C angle (110.5º) and 1 H-C-C-C torsion (60º); the 3 H-C distances and H-C-C angles are equal, whereas the other 2 torsions are set by default at 60+120º and 60+240º. The integer code 0 0 3 specifies that H-C and H-C-C bond lengths and angles are fixed (0 0), whereas torsions are assigned to step type number 3. This means that this parameter will be varied by (*rand*- 0.5)·*step*, where *rand* is a random number, and step is the third element of the maximum stepsize array specified in the *.mci* file (see below and manual, instruction 8 in Section 6.6.2). The last 3 integer specify the atom id required in "RX$_3$ mode", according to Table 6.2.

Then, you have three methylene groups (H6-H7, H8-H9 and H10-H11), which may be specified in "methylene mode" rows:

```
 1.080 108.0    0.0  0   0   0    6   7   0
 1.080 108.0    0.0  0   0   0    8   9   0
 1.080 108.0    0.0  0   0   0   10  11   0
```

This instruction defines 3 CH$_2$ groups, each bearing two identical H-C distances (1.080 Å), and H-C-H angles (108.0º). According to manual (Table 6.2), no torsions are to be defined. During Monte Carlo, we want to change neither the H-C distance nor the H-C-H angle, as we are concerned just with torsions. Therefore, the step type numbers are all 0 (0 0 0). Finally, for each methylene you must specify atom id's of the two defining hydrogens (see manual, Table 6.2).

The last two rotatable bonds are C1-C2 and C1-C4. These shall be specified in "Z-matrix mode"; to do so, atoms C4 and C5 must be generated according to:

```
 1.525 112.0 180.0  0   0   3    4   0   0
 1.525 112.0 180.0  0   0   3    5   0   0
```

As the reference hydrocarbon chain is antiperiplanar, all torsions equal 180º and will be changed using the same step type number 3 as described above. As usual, neither C-C bond distances (1.525 Å) nor C-C-C bond angles will change and their corresponding step type numbers are 0. According to Table 6.2 in the manual, the last three integer must specify only the pivot atom id (C4 or C5).

Putting together these instructions, you end with 7 slave atom lines. Open a new pentane.*sla* file (manual, Section 6.4.4) and type in the instructions. Remember to write atom id numbers in the correct ascending order.

```
                              vi pentane.sla
```

pentane.sla file

```
   7
 1.525 112.0 180.0  0   0   3    4   0   0   one C4 atom variable torsion from 180°
 1.525 112.0 180.0  0   0   3    5   0   0   same as for C5
 1.080 108.0    0.0  0   0   0    6   7   0   methylene groups, fixed
 1.080 108.0    0.0  0   0   0    8   9   0
 1.080 108.0    0.0  0   0   0   10  11   0
 1.080 110.5   60.0  0   0   3   12  13  14   methyl groups variable torsion from 60,180,300°
 1.080 110.5   60.0  0   0   3   15  16  17
```

Now invoke **Pretop** and answer the dialog mode as detailed in Tutorial T6:

```
./run.pretop pentane
give factors for ks,kb,kt force consts.
1 1 1
normal end of  operation
  Thank you for using MiCMoS
```

This produces a tentative pentanetry.*top* file that looks like the printout in the following page. As detailed in Tutorial T6, stretching and bending functions highlighted in red are useless and must be deleted. As **Pretop** has found a not empty .*sla* file, it has printed also the lines highlighted in green, which serve as a template to define the slave atoms. For this reason, explicit coordinates of atoms 4-17 are redundant and must be deleted. The torsional parameters (highlighted in green) are tentative too, and must be changed by hand based on potentials listed in the manual Appendix, Section A7.3 and Table A7.5.
First, save a copy of the try.*top* file:

```
cp pentanetry.top pentane.top
```

Open pentane.*top* and get rid of unwanted lines (the red ones in the printout, next page). Mind to update the instructions nstr-u and nbend-u, setting them to 0.

*pentanetry.top, as produced by **Pretop**. Red: lines to be erased. Green: lines to be edited.*

```
PNTANE99  n-pentane   topology
  17
   1   0.00000    0.00000    0.00000  13  -0.5622
   2   0.00000    1.52500    0.00000  13  -0.5522
   3   1.41396    2.09628    0.00000  13  -0.8988
   4  -1.41396   -0.57127   -0.00000  13  -0.5522
   5  -1.41396   -2.09627   -0.00000  13  -0.8988
   6   0.52628   -0.35498    0.87374   3   0.2818
   7   0.52628   -0.35498   -0.87374   3   0.2818
   8  -0.52628    1.87998    0.87374   3   0.2824
   9  -0.52628    1.87998   -0.87374   3   0.2824
  10  -1.94023   -0.21629   -0.87374   3   0.2824
  11  -1.94024   -0.21629    0.87374   3   0.2824
  12   1.95412    1.76899   -0.87608   3   0.2952
  13   1.38569    3.17591    0.00000   3   0.2950
  14   1.95412    1.76899    0.87608   3   0.2952
  15  -0.90815   -2.47450    0.87608   3   0.2952
  16  -2.42556   -2.47450   -0.00000   3   0.2950
  17  -0.90815   -2.47450   -0.87607   3   0.2952
   7  nslav-u
   4   0   0      0   0   0    0   0.0000
   5   0   0      0   0   0    0   0.0000
   6   7   0      0   0   0    0   0.0000
   8   9   0      0   0   0    0   0.0000
  10  11   0      0   0   0    0   0.0000
  12  13  14      0   0   0    0   0.0000
  15  16  17      0   0   0    0   0.0000
   0  ncore-v
   0  nslav-v
  90.4    0.0 volu-u,volu-v
  16  nstr-u
   1    2   1.525  2038.1   C- C
   1    4   1.525  2038.0   C- C
   1    6   1.080  3600.0   C- H
   1    7   1.080  3600.0   C- H
   2    3   1.525  2037.9   C- C
   2    8   1.080  3600.0   C- H
   2    9   1.080  3600.0   C- H
   3   12   1.080  3600.0   C- H
   3   13   1.080  3600.0   C- H
   3   14   1.080  3600.0   C- H
   4    5   1.525  2038.1   C- C
   4   10   1.080  3600.0   C- H
   4   11   1.080  3600.0   C- H
   5   15   1.080  3600.0   C- H
   5   16   1.080  3600.0   C- H
   5   17   1.080  3600.0   C- H
   0  nstr-v
  30  nbend-u
   1    2    3  112.00   527.6   C- C- C
   1    2    8  109.00   642.5   C- C- H
   1    2    9  109.00   642.5   C- C- H
   1    4    5  112.00   527.6   C- C- C
   1    4   10  109.00   642.5   C- C- H
   1    4   11  109.00   642.5   C- C- H
   2    1    4  112.00   527.6   C- C- C
   2    1    6  109.00   642.5   C- C- H
   2    1    7  109.00   642.5   C- C- H
   2    3   12  110.00   630.0   C- C- H
   2    3   13  111.00   617.5   C- C- H
   2    3   14  110.00   630.0   C- C- H
   3    2    8  109.00   642.5   C- C- H
   3    2    9  109.00   642.5   C- C- H
   4    1    6  109.00   642.5   C- C- H
   4    1    7  109.00   642.5   C- C- H
   4    5   15  111.00   617.5   C- C- H
   4    5   16  111.00   617.5   C- C- H
   4    5   17  111.00   617.5   C- C- H
   5    4   10  109.00   642.5   C- C- H
   5    4   11  109.00   642.5   C- C- H
   6    1    7  108.00   470.0   H- C- H
   8    2    9  108.00   470.0   H- C- H
  10    4   11  108.00   470.0   H- C- H
  12    3   13  108.00   470.0   H- C- H
  12    3   14  108.00   470.0   H- C- H
  13    3   14  108.00   470.0   H- C- H
  15    5   16  108.00   470.0   H- C- H
  15    5   17  108.00   470.0   H- C- H
  16    5   17  108.00   470.0   H- C- H
   0  nbend-v
   4  ntors-u
   4   1    2    3  50.00   -1.0    3.0   C- C- C- C
   2   1    4    5  50.00   -1.0    3.0   C- C- C- C
   1   2    3   12  50.00   -1.0    3.0   C- C- C- H
   1   4    5   15  50.00   -1.0    3.0   C- C- C- H
   0  ntors-v
   0  nlist-u
   0  nlist-v
  0.410   235.0   650.0   77000.0
   0  nextr
```

```
PNTANE99  n-pentane  topology
  17
   1   0.00000   0.00000   0.00000  13   -0.5622
   2   0.00000   1.52500   0.00000  13   -0.5522
   3   1.41396   2.09628   0.00000  13   -0.8988
   7  nslav-u
   4   0   0     0   0   0    0   0.0000                    [templates for slave atom construction]
   5   0   0     0   0   0    0   0.0000
   6   7   0     0   0   0    0   0.0000
   8   9   0     0   0   0    0   0.0000
  10  11   0     0   0   0    0   0.0000
  12  13  14     0   0   0    0   0.0000
  15  16  17     0   0   0    0   0.0000
   0  ncore-v
   0  nslav-v
  90.4     0.0 volu-u,volu-v
   0  nstr-u
   0  nstr-v
   0  nbend-u
   0  nbend-v
   4  ntors-u
   4   1   2   3  50.00   -1.0   3.0   C- C- C- C        [tentative torsion parameters]
   2   1   4   5  50.00   -1.0   3.0   C- C- C- C
   1   2   3  12  50.00   -1.0   3.0   C- C- C- H
   1   4   5  15  50.00   -1.0   3.0   C- C- C- H
   0  ntors-v
   0  nlist-u
   0  nlist-v
  0.410   235.0   650.0   77000.0
   0  nextr
```

Slave atom connectivities are now to be defined. Always refer to main manual, Table 6.2. Note that they can be easily guessed from the corresponding *.oih* file above. The atomic charges can be found in the pentane.*oeh* file produced by **Retcha**.

pentane.sla slave atom file

```
   7  nslav-u
   4  -1   0     1   2   3   13   -0.5522
   5  -1   0     4   1   2   13   -0.8988
   6   7   0     1   2   4    3    0.2818
   8   9   0     2   1   3    3    0.2824
  10  11   0     4   1   5    3    0.2824
  12  13  14     3   2   1    3    0.29513
  15  16  17     5   4   1    3    0.29513
```

CAUTION: For each line, the first 6 entries are very similar to that specified for implicit atoms in the starting pentane.*oih* file. The 7th entry is the atomic specie code number (manual, Table 1.1), which is also equal to that specified in the pentane.*oih* file.

After completing the section on slave atom construction and rearranging, you need to define potentials for the 4 torsions that are expected to vary, as established in pentane.*sla* file (step type numbers ≠ 0). **Pretop** knows that and prepares 4 lines (highlighted in green) that need to be edited. Recall that the basic functional for the torsional potential is $E(tors) = k_{tors}[1 + f\cos m\varphi]$ (manual, Section 6.4.1). From Table A7.5, you see that the recommended values for k_{tors}, f and m of a C-C-C-C chain are 6, 1 and 3 in pentane (nº 16). As for H-C-C-C torsions, the most similar case is nº 5 (propylbenzene), which gives k_{tors} = 7.5, f = 1 and m = 3.

```
    4   ntors-u
    4    1    2    3   6.00      1.0      3.0      CCCC
    2    1    4    5   6.00      1.0      3.0      CCCC
    1    2    3   12   7.50      1.0      3.0      HCCC
    1    4    5   15   7.50      1.0      3.0      HCCC
```

A few (12) intramolecular contacts between methyl groups and opposite methylene groups are protected from possible jump of the pentane chain into a gauche, or worse cis, conformation. See manual, Section 6.6.3 for more information.

```
   12   nlist-u
  8 15    8 16    8 17   9 15   9 16   9 17
 10 12 10 13 10 14 11 12 11 13 11 14
```

The final .*top* file looks like this:

pentane.top file. Green: instructions edited.

```
#PNTANE99   n-pentane topology
   3
   1    0.00000    0.00000    0.00000   13    -0.5622
   2    0.00000    1.52500    0.00000   13    -0.5522
   3    1.41396    2.09628    0.00000   13    -0.8988
   7   nslav-u
   4   -1    0       1   2   3    13    -0.5522
   5   -1    0       4   1   2    13    -0.8988
   6    7    0       1   2   4     3     0.2818
   8    9    0       2   1   3     3     0.2824
  10   11    0       4   1   5     3     0.2824
  12   13   14       3   2   1     3     0.29513
  15   16   17       5   4   1     3     0.29513
   0   ncore-v
   0   nslav-v
  90.4      0.0 volu-u,volu-v
   0   nstr-u
   0   nstr-v
   0   nbend-u
   0   nbend-v
   4   ntors-u
   4    1    2    3   6.00      1.0      3.0      CCCC
   2    1    4    5   6.00      1.0      3.0      CCCC
   1    2    3   12   7.50      1.0      3.0      HCCC
   1    4    5   15   7.50      1.0      3.0      HCCC
   0   ntors-v
  12   nlist-u
  8 15    8 16    8 17   9 15   9 16   9 17
 10 12 10 13 10 14 11 12 11 13 11 14
   0   nlist-v
  0.410    235.0    650.0    77000.0
   0   nextr
```

The input box file can now be prepared by the command (manual, Section 5.2)

```
                    ./run.boxliq pentane

     mol.diameter and liquid cell length      7.361      8.499

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

on prompt, answer 4 1.05 0.5 5. 0, producing a box (pentaneliq.*bxi*) with 250 molecules, side 40.88, density 0.44. Attempts with expansion factor of 1.0 and a higher density would fail to produce the necessary optimization in MC because molecules would be too much entangled (this conclusion was reached by trial and error).

You are now ready to prepare the MC run control file, pentane.*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.

```
   pentane standard liquid run
#   iprint ivarib iwrh   ipots   factin
      0      0      0      0       0.7
#   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
   20.0  200000      1000        0       0     0      2000
   0.70  50.0  10.0  0.0  0.0  0.  0.  0.  0.  0.
#   P     npres ianis
   1.0    700    3
```

Note that the maximum stepsize vector in the 8ᵗʰ line (manual, Section 6.6.2) is

```
   0.70  50.0  10.0  0.0  0.0  0.  0.  0.  0.  0.
```

The first two vector elements (0.7 and 50.0) determine stepsize for molecular translations and rotations and are controlled by corresponding 1 and 2 "step type numbers" in the *.bxi* file. The third element, 10.0, determines the stepsize for torsional parameters ("step type number" 3 in file pentane.*sla*). As usual, "var.indices" of 2 2 2 in the command file pentane.*mci* set to 0.02 Å the maximum cell change per step.

The differences with the benzene case treated in Tutorial T6 are: 1) the *factin* parameter is 0.7, meaning that the 12 intramolecular nonbonded contacts (see *nlist-u* above) are calculated by the same intermolecular potentials but damped by a factor of 0.7; 2) the temperature is set very low (20 K) so that the MC run is in fact an energy minimizer; 3) the steps for rigid translation and rotation of molecules are larger (0.7 and 50.0) to allow more freedom; 4) the box update frequency is higher; 5) the simulation is longer (200,000 moves) in prevision of the higher difficulty of landing into a stable arrangement with a flexible molecule.

The MC run is then started by the command

```
            ./run.mcmain pentane pentaneliq.bxi p1
```

Output files are p1mc.*pri*, p1mco.*dat,* p1.*bxo*. Notice that during the minimization the box dimension increase up to 44 Å, while the system expands to disentangle too close molecular pairs. After a reasonable configuration is attained, energy minimization bring back the box dimension to a lower value. Total energies are different from cohesive energies: E(tot) = E(cohes)+E(intram). The comparison with thermodynamic quantities like vaporization energies is problematic because E(intram) might be different in the liquid and in the vapor phases. Anyway, the simulation is far too short to produce really significant results. Typical production runs for thorough equilibration being in the range of millions of steps. The intramolecular nonbonded energy is negligible, revealing that the molecules stay in a nearly all-trans conformation. If desired a longer simulation can be restarted using the p1mc.*bxo* output box and giving more realistic temperature and pressure rescaling parameters, in conjunction with smaller maximum stepsizes.