

MiCMoS

Milano Chemistry Molecular Simulation

Description and User Manual

Tutorials

T9. Molecular Dynamics: liquid benzene

PURPOSE: In this tutorial, it is described how to prepare and equilibrate a very simple liquid (benzene) with the Molecular Dynamics technique.

REFERENCE to main manual: Sections 5.4 (*Pretop*); 6.2 (construction of molecular frameworks); 7.6.1 (*mdmain*); 7.6.2 (instruction file, *.mdi*); 7.6.3 (input box file, *.dat*); 7.6.4 (topology and force field file, *.top*).

FILES: You can find all the files you need to run this tutorial here:

https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T9/b2mco.dat

https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T9/benz.mdi

https://sites.unimi.it/xtal_chem_group/images/MiCMoS_package/T9/benz.oeh

The starting structure file for benzene (*benz.oeh*) is the same described in Tutorial T6. You will also need macros to run *Pretop* and *mdmain*. Place *.oeh* and pertinent (Windows/Unix) macros into your working directory.

The starting topology file (manual, Section 7.6.4) can be produced by running the *Pretop* module (manual, Section 5.4) on the *benz.oeh* structure:

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

The dialog mode will ask for:

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

This time stretching, bending and torsion force fields are needed. Upon request, give 1.2, 1.2 and 1.5 for the scaling factors of stretch, bend and torsion force constants. The *benztry.top* file can now be renamed as *benz.top* and used without editing as it contains all appropriate force field constants (have a look at it on the next page).

There is one stretch for each bond and one bend for each bond angle, with the guessed force constants. The user can obviously modify these values according to any external force field. The *Pretop* module assigns one torsion to each C–C bond with barrier of $2 \times 75 = 150$ kJ/mol, and one improper torsion for each trigonal center with a barrier of $2 \times 150 = 300$ kJ/mol. We can accept these values as they have no real physical origin; they are large values that fill the purpose of keeping the benzene ring as flat as possible, the corresponding potentials being $E(\text{tors}) = K[1 + f \cos(m \cdot \tau)]$ being zero at $\tau = 0$ deg and $2K$ at $\tau = 90$ deg. Obviously, if a more flexible molecule was considered, torsions should have been edited according to parameters summarized in Table A7.5 (manual, Appendix).

benz.top topology file

```
#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 5856.8 C- C
1 6 1.390 5857.0 C- C
1 7 1.080 4320.0 C- H
2 3 1.390 5856.9 C- C
2 8 1.080 4320.0 C- H
3 4 1.390 5856.8 C- C
3 9 1.080 4320.0 C- H
4 5 1.390 5857.0 C- C
4 10 1.080 4320.0 C- H
5 6 1.390 5856.9 C- C
5 11 1.080 4320.0 C- H
6 12 1.080 4320.0 C- H
0 nstr-v
18 nbend-u
1 2 3 120.00 700.5 C- C- C
1 2 8 120.00 606.0 C- C- H
1 6 5 120.00 700.5 C- C- C
1 6 12 120.00 606.0 C- C- H
2 1 6 120.00 700.5 C- C- C
2 1 7 120.00 606.0 C- C- H
2 3 4 120.00 700.5 C- C- C
2 3 9 120.00 606.0 C- C- H
3 2 8 120.00 606.0 C- C- H
3 4 5 120.00 700.5 C- C- C
3 4 10 120.00 606.0 C- C- H
4 3 9 120.00 606.0 C- C- H
4 5 6 120.00 700.5 C- C- C
4 5 11 120.00 606.0 C- C- H
5 4 10 120.00 606.0 C- C- H
5 6 12 120.00 606.0 C- C- H
6 1 7 120.00 606.0 C- C- H
6 5 11 120.00 606.0 C- C- H
0 nbend-v
12 ntors-u
6 1 2 3 75.00 -1.0 1.0 C- C- C- C
2 1 6 5 75.00 -1.0 1.0 C- C- C- C
1 2 6 7 150.00 -1.0 1.0 C- C- C- H
1 2 3 4 75.00 -1.0 1.0 C- C- C- C
2 1 3 8 150.00 -1.0 1.0 C- C- C- H
2 3 4 5 75.00 -1.0 1.0 C- C- C- C
3 2 4 9 150.00 -1.0 1.0 C- C- C- H
3 4 5 6 75.00 -1.0 1.0 C- C- C- C
4 3 5 10 150.00 -1.0 1.0 C- C- C- H
4 5 6 1 75.00 -1.0 1.0 C- C- C- C
5 4 6 11 150.00 -1.0 1.0 C- C- C- H
6 1 5 12 150.00 -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
```

Now open an empty *benz.mdi* file and type in the run control commands as follows (see manual, Section 7.6.2 for full information on various parameters):

run control commands in benz.mdi

```
liquid benzene clp potential minimal barostat
# n.steps irvel ipri ibox idstr timestep Emolim iengt ibias +Ebias Nbias tinon tinof
10000 0 0 1 0 0.002 -5.0 0 0
# cutoffu cutoffv cutoffw factin ipots ianh inano
15.0 0.0 0.0 0.0 0 0 0
# N(T) Tset Tstart Trelax 0/1/2 weak/stiff/CSVR
350 298 298 0.6 0
# N(P) Pset comprs 0/lianis ipr ww iexstr + strall 22, 33, 12 13 23, GPa
400 1.0 0.35 0 0 0.0 0
# N(com) nwbox nwre npri
50 200 200 200
```

This run asks for 10,000 steps (10 ps = 10,000 x 0.002 ps) with periodic box (ibox=1), cutoff of 15 Å, CLP potentials (ipots=0). Irvel=0 means guessed velocities at the beginning, no writing of velocities on the *.mdc* trajectory file (very useful to save a lot of disk space). The timestep is 2 fs, the best value from experience; a larger value makes sampling faster but also causes large structure changes at the risk of crashes. Temperature is set at 298 K and checked every 350 steps with a weak coupling algorithm and relaxation parameter 0.6. Pressure is set at 1 atm and monitored every 400 steps with minimal barostat (ipr=0), isotropic control (ianis=0) and relaxation parameter 0.35. Center of mass is reset every 50 steps, very frequently, to update appropriately the center of mass distance list used in intermolecular cutoff evaluations. Trajectories are written on file every 200 steps. The standard leapfrog algorithm is employed (iengt=0), with no kinetic bias (ibias=0) and no anharmonicity correction (ianh=0).

CAUTION: small values of nwbox with large systems may cause extremely large output files.

Key parameters of any simulation are the two relaxation "times", "Trelax" and "comprs". The latter is especially critical, because a larger value makes convergence faster but also involves larger density changes that may lead to unpredictable crashes of the simulation. It should be adjusted for each system by cautious trials. The two control frequencies N(T) and N(P) should not be too small to prevent an excessive tampering with system relaxation. Something in the range 500-1000 steps (but sometimes even less) should be appropriate. They are small for the present short simulation for sampling purposes. A regular liquid simulation should run for some 10 million steps, or 10 ns.

We have now to define the starting box. A possibility is to call **Boxliq** (manual, Section 5.2) and then to run preliminary Monte Carlo with a very low value of T (see Tutorials T6 and T7) to dispose of hard contacts and avoid unstable molecular configurations in the phase space. An even smarter strategy consists in starting from the output of a former Monte Carlo equilibration, if available. In this exercise, we will use the *b2mco.dat* file corresponding to the last frame of the former Monte Carlo work (Tutorial T6). The *b1mco.dat* file obtained from the preliminary MC equilibration is also suitable, though. They both contain a total of 250 benzene molecules, more or less with the correct density at room temperature. These files can be used for MD without modification, sparing the MD simulation a time-consuming and sometimes uncertain preliminary resetting of hard contacts. Now everything is ready for starting the MD simulation:

```
./run.mdmain benz b2mco.dat b3
```

and the outputs are found in *b3md.pri*, *b3mdc.dat*, *b3.mde* and *b3mdo.dat*. Note that the starting energy in *b3md.pri* is identical to the final energy in *b2mc.pri* of Tutorial T6; this is a useful check that things are working properly. If you look at the *b3md.pri* output, you will see that box dimensions are identical to those in the final frame of the Monte Carlo trajectory (see Tutorial T6), but energies are slightly different as we now employed a 15 Å cutoff rather than a 16 Å one.

File b3md.pri: starting energies

Intermolecular energies					
LP energies, u,v,uv,ubar,vbar	-7395.52	0.00	0.00	0.00	0.00
Coul energies, u,v,uv,ubar,vbar	-701.01	0.00	0.00	0.00	0.00
total intram,LP,Coul,total	0.0	-7395.5	-701.0	-8096.5	
cohesive E per mol. solute,solvent,solvation	-32.4	0.0	0.0		

To the sake of comparison, ending MC energies were -7434.87 (LP), -701.51 (Coulomb) and -8136.38 (total). This short tutorial run serves the purpose of a quick description of the main features of MD in MiCMoS, but it could be implemented by proceeding the simulation for some ns. Note that *ubar* and *vbar* (total interaction energies with the barrier) are always zero as the simulation is not confined. If you have a look at the *.pri* file, you should note the following:

- 1) In a Linux/Unix environment, use the command

```
grep 'nmove,Pset, Pcurrent' b3md.pri
```

to highlight how pressure has changed during the simulation. Pressure oscillates between positive and negative values, as it should around the 1 atm preset value; this is in fact a symbolic number because internal pressure in liquids can instantly be hundreds of atmospheres.

- 2) The *grep* command can help in keeping record of temperature as well:

```
grep 'old and new temperatures' b3md.pri
```

The weak-coupling barostat takes about 1000 steps to bring the system to the desired temperature, as it should.

- 3) The intramolecular and intermolecular energies are provided in the output, throughout lines ending with the `'ens data'` label. You can extract them, again, with the command *grep*:

```
grep 'ens data' b3md.pri
```

This will produce a table like

200	1676.9	1423.8	1540.0	0.0	0.0	0.0	0.0	0.0	-7587.4	-691.5	-3638.2	-33.1	0.918	ens data
400	2700.4	1886.7	1727.7	0.0	0.0	0.0	0.0	0.0	-7527.3	-638.2	-1850.7	-32.7	0.919	ens data
600	3041.3	2142.5	1781.2	0.0	0.0	0.0	0.0	0.0	-7541.6	-717.2	-1293.8	-33.0	0.919	ens data
600	3041.3	2142.5	1781.2	0.0	0.0	0.0	0.0	0.0	-7541.6	-717.2	-1293.8	-33.0	0.919	ens data

Where, from left to right, you have step number; stretching, bending and torsion energies of the solute; a dummy zero; stretching, bending and torsion energies of the solvent; a dummy zero; Lennard–Jones intermolecular energies; Coulomb intermolecular energies; total energies; cohesive energies per molecule per asymmetric unit; total density, in g/mL. All energies are expressed in kJ/mol. The intramolecular stretch and bend energies are zero at the beginning and level out at about 4000 and 2800 kJ/mol. Having 250 x 12 stretch degrees of freedom (d.o.f) and 250 x 16 bend

d.o.f., the average energy per d.o.f. is 1.3 kJ/mol and 0.7 kJ/mol, respectively, both comparable with ($\frac{1}{2} RT$) at ~ 300 K.

- 4) Total energies would have a meaning only if a comparison with gas-phase intramolecular energies were available. As a reasonable guide, the cohesive energy, that is the sum of Lennard–Jones and Coulomb energies, is about -30 kJ/mol, which is of the correct order of magnitude of the vaporization enthalpy of benzene (33.9 kJ/mol). The current final results predict indeed a vaporization enthalpy of 32.5 kJ/mol. The steady-state liquid density of about 0.93 g/mL also compares favorably with the experimental density (0.88 g/mL), with an absolute error of 5 %. These two quantities can be used to gauge the performance of the potential energy schemes.

The last lines in the output are as follows:

```
Intermolecular energies
  LP energies, u,v,uv,ubar,vbar -7440.25      0.00      0.00      0.00      0.00
  Coul energies, u,v,uv,ubar,vbar -683.26      0.00      0.00      0.00      0.00
  final box edges, multiplicities 32.713 32.713 32.713 1 1 1
  final unit cell 32.713 32.713 32.713 90.0 90.0 90.0 0.926

  %edges, abs angles, %density variations
  -0.3 -0.3 -0.3 -0.0 -0.0 -0.0 0.87
  final cohesive Ens, solute,solvent,solvation -32.5 0.0 0.0
  cohesive energy variations -0.1 0.0 0.0
  normal end of operation at
  4 July 2023 17:08:12.311
  Thank you for using MiCMoS Molecular Dynamics
```