

Monte Carlo vs Molecular Dynamics

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MC vs MD for conformational sampling
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Introduction

- Common points:
 1. both of them are widely used methods for atomic-level modeling of fluids.
 2. have the same system setup:
 - representation of molecules as collections of atom-centered interaction sites,
 - utilization of classical force fields for the potential energy terms,
 - implementation of PBC.
 3. the force field controls the total energy (MC) and forces (MD), which determine the evolution of the systems.

- Difference

MC: new configuration generating

selecting a random molecule, translating it, rotating it, and performing any internal structural variations

Acceptance of the new configuration

determined by the Metropolis sampling algorithm

MD: new configuration generating

applying Newton's equations of motion to all atoms simultaneously over a small time step

- There has been surprisingly little comparison of their efficiencies.

e.g. Northrup and McCammon,

MC sampling yield 10 times less atomic diffusion than MD for a given amount of computer time in simulation of bovine pancreatic trypsin inhibitor (BPTI) in the gas phase.

however, Cartesian MC is highly inefficient procedure.

In MC programs like BOSS,

1. we use internal coordinates with specification of the connectivity and bond lengths, bond angles, and dihedral angles in a "Z-matrix"
2. internal variables to be sampled are declared in Z-matrix
3. the structure of the moved molecule is rebuilt from Z-matrix

- In this paper, the conclusions got from the tests are:

1. the MC and MD results for thermodynamic properties and conformer populations are in accord.

2. the conformer populations reach equilibrium in 10^7 MC configurations or 100 ps of MD.

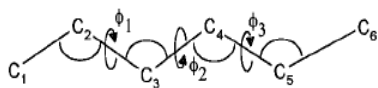
3. the molecular dynamics calculations require 1.6-3.8 times more computer time to achieve the same level of convergence as the MC simulations,

Computation details

- Fluid simulations

NPT ensemble, 25°C and 1 atm with 267 hexane molecules, in a cubic box with periodic boundary conditions.

Intermolecular interactions were computed out to a cutoff of 12Å based on the distance between the C_3 atoms; if the C_3 - C_3 distance was within the cutoff, the entire hexane-hexane interaction was included.



The C-C bond lengths were kept fixed at 1.526Å by not declaring them as variable in the MC simulation or through the SHAKE algorithm in the MD simulation.

- The initial configuration

1. generated by BOSS with its procedure whereby a stored, equilibrated box of liquid argon. This box was then equilibrated with BOSS for $2 \cdot 10^6$ configurations (MC moves), which was long enough for the total energy and density to converge.
2. The hexanes were kept all trans.
3. The equilibrated box of all trans hexane was then used at the start of all comparison simulations.

- MC: BOSS version 3.6
- MD: minmd module of AMBER version 4.0

Monte Carlo Details

- Ranges for the attempted translations, rotations, internal motions, and volume changes to yield an overall acceptance rate: 40% for new configurations
- Default values from BOSS were used except for the change in dihedral angles.
- The length of each MC simulation was 50×10^6 configurations and the energies and coordinates were saved every 25000 configurations for the subsequent analysis.

1. Translation:
in all three Cartesian directions,
[-0.2Å,+0.2Å]
2. Rotation:
choosing one Cartesian axis at random and
rotating about C_3 within [-20°, +20°]
3. Four internal bond angles [-3.8°, +3.8°]
4. Volume change:
performed every 1625 configurations,
 $\Delta V = [-390 \text{Å}^3, +390 \text{Å}^3]$

5. The dihedral angles change:
Three simulations were run with
 $\Delta\phi = [-10^\circ, +10^\circ], [-15^\circ, +15^\circ], [-20^\circ, +20^\circ]$
which is referred to as MC10, MC15, MC20.

So the overall acceptance rates for the three simulations were 37%, 31%, 23%.

The neighbor list was employed with the MC calculations and updated every 4000 configurations. Reduce the computation time by about 20%

BOSS Z-matrix

- The internal coordinate MC requires a Z-matrix that specifies the atomic connectivity and controls the sampling.

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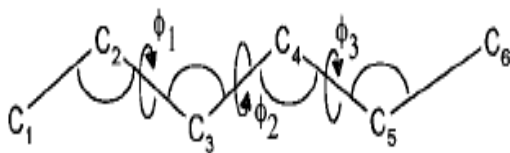
Hexane
1 C3      71      71      0      0.000000      0      0.000000      0      0.000000
2 DUM     -1     -1      1      0.500000      0      0.000000      0      0.000000
3 DUM     -1     -1      2      0.500000      1      90.000000      0      0.000000
4 C4      71      71      1      1.526000      2      124.000000      3      180.000000
5 C5      71      71      4      1.526000      1      112.400000      2      0.000000
6 C6      68      68      5      1.526000      4      112.400000      1      180.000000
7 C2      71      71      1      1.526000      4      112.400000      5      180.000000
8 C1      68      68      7      1.526000      1      112.400000      4      180.000000

Variable Bonds follow      (14)
Additional Bonds follow    (214)
Variable Bond Angles follow (14)

0005      Additional Bond Angles follow (314)
0006      Variable Dihedrals follow (314,F12.6)
0007
0008

000600650065 20.0
000700650065 20.0
000800650065 20.0

Additional Dihedrals follow (614)
Domain Definitions follow (414)
Final blank line
    
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The atoms are constructed in order, which can affect the sampling efficiency e.g. in this hexane case, it is best to build out from the center, rather than proceeding from one end to the other.

Molecular Dynamics

A leap-frog algorithm is used by the minmd module of AMBER to integrate the equation of motion, and the NPT ensemble is approximated by velocity rescaling and coupling to a constant pressure bath.

500 ps in total and energies and coordinates were saved for subsequent analysis every 0.1ps.

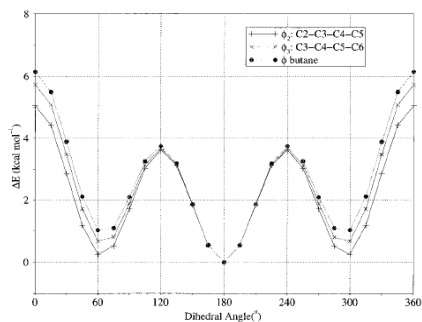
- Computational environment
 - * Silicon Graphics Indigo workstation with a MIPS R4000 processor.
 - * FORTRAN 77 compilation was performed with the highest optimization levels for both programs.
- In 95.4s of CPU time
 - MD: 10ps, 5000 MD time steps
 - MC: 1.63×10^6 configurations, 6105 MC passes (equals the number of configurations/the number of molecules)

Potential Functions

- The intermolecular interactions consist of L-J 12-6 terms between all atoms with the OPLS united-atom values for σ ϵ
- The form of the torsional potential is:

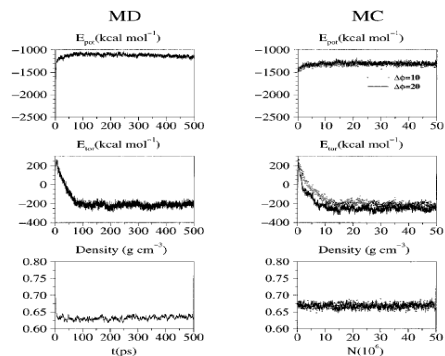
$$E_{\text{torsion}} = \sum_i \{V_1(1 + \cos \phi_i)/2 + V_2(1 - \cos 2\phi_i)/2 + V_3(1 + \cos 3\phi_i)/2\}$$
- Intramolecular L-J interactions are also included between atoms separated by three or more bonds .

Results



Potential energy profiles for variation of the two dihedral angles of hexane with the other two fixed at 180° and for variation about the central CC bond of butane.

- Thermodynamic properties



Convergence plots from the MD and MC10 and MC20 simulations for the potential Energy, torsional energy and density.

TABLE 1: Summary of Results from Simulations of Liquid Hexane^a

simulation	MC10	MC15	MC20	MC20n	MD	exp ^b
$\Delta\phi$	10	15	20	20		
cutoff correction	yes	yes	yes	no	no	
acceptance %	36.9	31.2	22.6	23.1		
E_t^c	-1313(1)	-1303(3)	-1307(2)	-1157(3)	-1134(4)	
E_{tors}^c	462(2)	472(3)	474(1)	489(2)	445(2)	
E_{tot}^c	-211(3)	-244(3)	-247(3)	-256(3)	-214(3)	
ΔH_{vap}^d	7.869(0.004)	7.831(0.010)	7.846(0.007)	7.264(0.010)	7.190(0.016)	7.541
$C_p(\text{water})$	14.50(0.8)	13.00(0.7)	13.60(0.8)	12.90(0.8)		
$C_p(l)$	46.80(0.8)	45.30(0.7)	45.90(0.8)	45.20(0.8)		46.7
α	124(7)	119(8)	133(9)	123(8)		139
ϵ	152(7)	142(8)	147(7)	172(10)		173
density	0.66920(0.0003)	0.66800(0.0005)	0.66900(0.0006)	0.65490(0.0007)	0.63380(0.0008)	0.655
$\phi_1 g^+$	18.40(5)	13.70(3)	14.90(3)	16.60(2)	16.00(3)	
$\phi_1 t$	68.80(3)	70.50(6)	69.10(6)	66.00(5)	71.00(5)	
$\phi_1 g^-$	12.80(4)	15.80(4)	16.00(4)	17.40(4)	13.00(3)	
$\phi_2 g^+$	23.50(4)	22.40(3)	22.00(5)	20.70(6)	23.40(4)	
$\phi_2 t$	60.20(4)	54.30(8)	53.50(4)	55.60(7)	56.20(4)	
$\phi_2 g^-$	16.30(3)	23.30(7)	24.50(5)	23.70(2)	20.40(4)	
$\phi_3 g^+$	15.50(3)	15.10(3)	14.70(3)	15.30(4)	14.80(3)	
$\phi_3 t$	70.90(3)	68.30(5)	69.90(5)	69.20(4)	72.70(3)	
$\phi_3 g^-$	15.40(2)	16.60(4)	15.40(3)	15.50(3)	12.50(3)	

^a Reported averages and standard deviations are calculated over the last 2004 for MC or over the last 200 ps for MD. Acceptances and populations are reported in percentages, energies and enthalpies in kcal mol⁻¹, heat capacities in cal mol⁻¹ K⁻¹, α in 10⁻³ K⁻¹, ϵ in 10⁻⁶ amu⁻¹, and densities in g cm⁻³. ^b Experimental data from ref 14. ^c E_t corresponds to total energy for MC and potential energy for MD.

Obtained by averaging over the final 200 ps of the MD simulation and from the final 20*10⁴ configurations for the MC calculations.

- Conformer Populations
gauche+ (0-120°), trans (120°-240°),
gauche- (240°-360°)

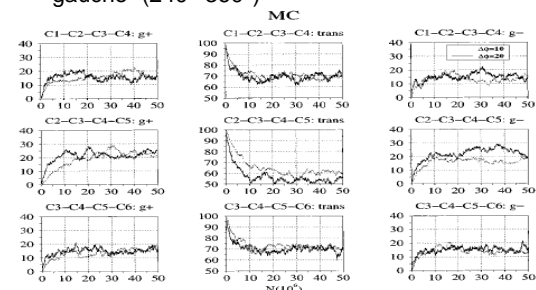
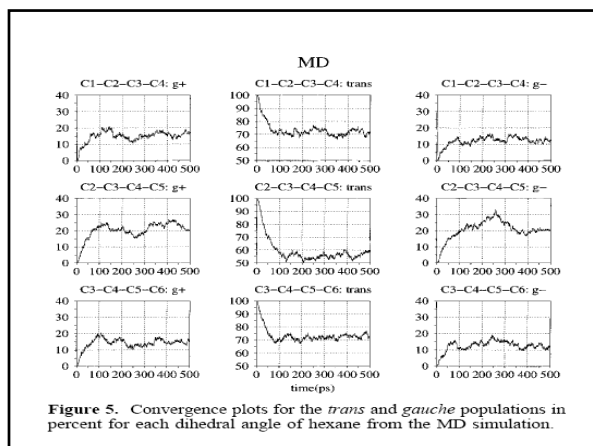


Figure 4. Convergence plots for the *trans* and *gauche* populations in percent for each dihedral angle of hexane from the MC10 and MC20 simulations.



Conclusion

- The overall consistency of the thermodynamic and conformational results for liquid hexane from two different programs, BOSS and AMBER, with very different sampling algorithms, MC and MD, is reassuring.
- From the behavior of the torsional energy profiles and conformer populations over the full runs,
 - MC needs 10×10^6 configurations for conformational convergence, (584s)
 - MD needs 100ps to get the same convergence, (954s) $954/584=1.63$
