A Sample Program of MC Simulation in Canonical Ensemble

(1) The main program

```
program ljmcnvt
include 'header.inc'
call read_data
call preloop
call mcupp
call wrtpar
do istep = 1, nsteps
    itstep = itstep + 1
    call displ
    if (mod(istep, ntraj) .eq. 0) then
        call wrtxyz
    endif
    if (mod(istep, ntrace) .eq. 0) then
        call wrttrace
    endif
endo
call wrtcoord
close(itracef)
stop
end
```

Calculate the total potential energy for the initial configuration. Later in the program, only energy change ($\Delta u$) is calculated.

Perform the particle displacement trail move. This is the core of a NVT MC program.

All other subroutines have been discussed in the MD programs.
1. Examples:

Input file “mcinput.d”

<table>
<thead>
<tr>
<th>ε</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>121.0</td>
<td>3.405</td>
</tr>
<tr>
<td>3.5</td>
<td></td>
</tr>
</tbody>
</table>

Cutoff distance is $3.5\sigma$.

<table>
<thead>
<tr>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.0</td>
</tr>
</tbody>
</table>

Total simulation steps: 10000
Period for coordinates saving: 50
Period for data saving: 1

<table>
<thead>
<tr>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>\begin{array}{c} 1 \text{d-6} \ 1 \text{d-1} \ 1 \text{d-4} \end{array}</td>
</tr>
</tbody>
</table>

Initial displacement

Maximum displacement

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402

2. Performing the particle displacement

- Randomly select a particle.
- Randomly select a position around the selected particle for trial move.
- Calculate the energy change $\Delta u$ due to the trial move.
- Compare $\exp(-\Delta u/kT)$ with a random number $\xi$.
- Accept the move if $\exp(-\Delta u/kT) \geq \xi$;
  Reject the move if $\exp(-\Delta u/kT) < \xi$.

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402
J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402

Comparing results of potential energy from MC and MD for the same system of argon with N=2048, V=3039.7Å³, and T=300K.
Comparing results of pressure from MC and MD for the same system of Argon with \( N=2048 \), \( V=3039.7\text{\AA}^3 \), and \( T=300K \).

The acceptance ratio of the trail displacements is about 50%.
Configurations recorded from the simulations. These configurations do not correspond to the physical trajectories of the system, but they can still reveal the general structural information of the system.

MC and MD give the same radial distribution function. argon at N=2048, V=3039.7Å³, and T=300K.
An NPT Monte Carlo simulation program

1. The main program

```fortran
program ljmcnpt
include 'header.inc'
call read_data
call preloop
  call mcupp
  call wrtpar
do istep = 1, nsteps
    itstep = itstep + 1
    call displ
    call dvolume
    if (mod(istep, ntraj) .eq. 0) then
      call wrtxyz
    endif
    if (mod(istep, ntrace) .eq. 0) then
      call wrttrace
    endif
  enddo
  call wrtcoord
close(itracef)
end
```

One more major subroutine “dvolume” is added to perform the random volume change.

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402

1. Examples:

Input file “mcinput.d”

- Cutoff distance is 3.5σ.
- Cutoff distance is 3.5σ.
- Period for coordinates saving
- Period for coordinates saving
- Total simulation steps
- Total simulation steps
- Minimum displacement
- Minimum displacement
- Maximum displacement
- Maximum displacement
- Minimum volume change
- Minimum volume change
- Maximum volume change
- Maximum volume change

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402
2. Performing the volume change

- Saving the old configuration
- Randomly change the volume
- Scale the particle coordinates due to the volume change
- Calculate the energy and other quantities after the volume change
- Compute the Boltzmann factor and compare it with a random number
- Accept the move if the Boltzmann factor is larger than the random number; Otherwise, reject the move by restoring the old configuration.

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402

```fortran
subroutine dvolume
  include 'header.inc'
  real*8 boxold(3)

  nv = nv + 1
  boxold(1) = cube(1)
  boxold(2) = cube(2)
  boxold(3) = cube(3)
  uppold = upp
  wppold = wpp
  psold = pstar
  vold = vstar
  rosold = rostar
  stepv = nv * vstar
  vstar = vstar + stepv * (ran2(idum) - 0.5d0)
  rostar = rostar * vold / vstar
  cube(1) = (vstar / sxy / sxz)**(1.0d0 / 3.0d0)
  cube(2) = sxy * cube(1)
  cube(3) = sxz * cube(1)
  do i = 1, np
    do j = 1, 3
      r0(i,j) = r0(i,j) * cube(j) / boxold(j)
    enddo
  enddo
  call mcupp
  hdif = upp - uppold + p0s * (vstar - vold)
    .  - dble(np) * tstar * dlog(vstar / vold)
```

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402
if (hdif.gt.0.d0) then
    eph=dexp(-hdif/tstar)
    if (eph.lt.ran2(idum)) then
        do i = 1, np
            do j = 1, 3
                r0(i,j) = r0(i,j) * boxold(j)/cube(j)
            enddo
        enddo
        do j = 1, 3
            cube(j) = boxold(j)
        enddo
        upp = uppold
        wpp = wppold
        vstar = vold
        pstar = psold
        else
            nvs = nvs + 1
        endif
    else
        nvs = nvs + 1
    endif
end

Get the Boltzmann factor.

Compare the Boltzmann factor with a random number.

Restore the original state if the move is rejected. No need to do anything if it is accepted as the change has been made already.

Calculate the successful rate.

Adjust the volume change step so that the successful rate is about 0.5.

Comparing of potential energies from MC and MD for the system of argon at N=2048, P=0.0, T=50K.

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402
Pressure calculated from virial oscillates around the target pressure (0 in this example).

Density fluctuates as a result of volume fluctuation. After the initial equilibration, density fluctuates around its average value.

A sample GCMC program

1. The main program

Three types of MC moves are selected randomly.

- Particle displacement (have been discussed).
- Particle creation (new)
- Particle destruction (new)
2. Different from the other programs, potential is just cut at the half of the simulation box. Long-range correction is added.

Long range correction (LRC) is obtained by assuming the radial distribution function \( g(r) = 1 \), when \( r \) is larger than the cutoff distance.

For LJ potential, the LRCs of potential energy and the pressure are:

\[
U_{LRC} = \frac{8}{9} \pi N \rho \sigma^3 \left( \frac{\sigma}{r_c} \right)^9 - \frac{3}{2} \left( \frac{\sigma}{r_c} \right)^3 \\
P_{LRC} = \frac{32}{9} \pi \rho^2 \sigma^6 \left( \frac{\sigma}{r_c} \right)^9 - \frac{3}{2} \left( \frac{\sigma}{r_c} \right)^3
\]

3. Performing particle creation

subroutine creation
include 'header.inc'

\[\begin{align*}
nii &= nii + 1 \\
nnew &= np + 1 \\
rho &= dble(nnew)/vstar \\
call lrcup(rcut,nnew,rho,ulr,plr) \\
cx &= \text{cube}(1) \times (\text{ran2(idum)} - 0.5) \\
cy &= \text{cube}(2) \times (\text{ran2(idum)} - 0.5) \\
cz &= \text{cube}(3) \times (\text{ran2(idum)} - 0.5) \\
cx &= \text{cx-cube}(1) \times \text{anint}(\text{cx/cube}(1)) \\
cy &= \text{cy-cube}(2) \times \text{anint}(\text{cy/cube}(2)) \\
cz &= \text{cz-cube}(3) \times \text{anint}(\text{cz/cube}(3)) \\
is &= np + 1 \\
call daltau \\
udif &= \text{dupi} + \text{ulr} - \text{ulrc} \\
dcb &= \text{udif}/tstar - \text{dlog(zact/rho)} \\
\text{if (dcb .gt. 0.d0)} \\
& \quad \text{egu} = \text{dexp}(-\text{dcb}) \\
\text{if (egu.lt.ran2(idum))goto 250} \\
\text{endif}
\end{align*}\]
nis = nis + 1
np = nnew
iatom=now(np)
if(iatom.eq.0) then
  now(np)=np
  iatom=np
endif
r0(iatom, 1) = cx
r0(iatom, 2) = cy
r0(iatom, 3) = cz
rostar = rho
ulrc = ulr
plrc = plr
upp = upp + udif
wpp = wpp + dwpi
pstar = rostar*tstar + wpp/vstar + plrc
250 continue
return end

Performing the particle destruction

subroutine destruction
include 'header.inc'

ndd=ndd+1
nnew=np - 1
rho = dble(nnew)/vstar
call lrcup(rcut,nnew,rho, ulr, plr)
if (nnew.eq.0) then
  write(isterr,* ) 'only one atom exists'
  stop
endif
is = int(ran2(idum)*dble(np)) + 1
if (is .gt. np) is = np
it = now(is)
cx = r0(it, 1)
 cy = r0(it, 2)
 cz = r0(it, 3)
c call daltau
c get the Boltzmann factor and compare it
  with a random number
  udif = -dupi + ulr - ulrc
ddb = udif/tstar - dlog(rostar/zact)
  if(ddb.gt.0.0) then
    educ=dexp(-ddb)
    if(educ.lt.ran2(idum)) goto 250
  endif
  accept the change
  nds = nds + 1
  if (is .lt. np) then
    do i = is, np-1
      now(i) = now(i+1)
    enddo
  endif
  now(np) = it
  np = nnew
  rostar = rho
  ulrc = ulr
  plrc = plr
  upp = upp + udif
  wpp = wpp - dwpi
  pstar = rostar*tstar + wpp/vstar + plrc
*      + plrc
250 continue
return end

Array now() is used to handle the particle index number.

Update the data if the creation is accepted.
5. Examples:

Input file “mcinput.d”

\[ \mu_c \text{ in ev} \]

- \[ \varepsilon \]
- \[ T \]
- \[ 121.0 \] \[ 3.405 \] \[ 39.948 \]
- \[ 139.15 \]
- \[ -0.0372 \]
- \[ 500000 \] \[ 2500 \] \[ 500 \] \[ 1.d-6 \] \[ 1.d-1 \] \[ 1.d-4 \]

\( \sigma \)

Period for coordinates saving

Total simulation steps

Minimum displacement

Maximum displacement

Initial displacement

Note: \( \mu_c \) is called configurational chemical potential.

\[ A = \exp(\beta \mu_c); \text{ Here } A \text{ is activity, so the relation of } \mu_c \text{ and } \mu \text{ is:} \]

\[ \mu_c = \mu - 3k_B T \ln \Lambda. \]

---

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402

Particle number fluctuates in GCMC simulation. This results in density fluctuates as well.

---

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402
GCMC simulation of confined fluids

1. The system

Fluid is confined between two flat narrow smooth walls.
2. Potential models

\[ U = U_{ff} + U_{fw} \]

\( U_{ff} \): fluid-fluid interactions -- LJ potential.

\( U_{fw} \): fluid-wall interactions – Steele potential for carbon surfaces.

\[ U_{fw} = A \left[ \frac{2}{5} \left( \frac{\sigma_{fw}}{z} \right)^{10} - \left( \frac{\sigma_{fw}}{z} \right)^{4} - \left( \frac{\sigma_{fw}}{3\Delta(0.61\Delta + z)} \right)^{4} \right] \]

(Parameters can be found in: Steele, W. A., 1973, Surface Sci., 36, 317)

Potential energy of a fluid particle inside a slit pore. The energy and the distance are shown in the reduced units of the fluid LJ parameters.

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402
Particle number in the system is the function of chemical potential.

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402

Density profiles of the fluid show different layer structures formed at the two chemical potential values.

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402
Fluid-fluid interaction energies recorded in the simulations at the two values of chemical potential.
Fluid-wall interaction energies recorded in the simulations at the two values of chemical potential.

J. A. Harrison & G. T. Gao, Chemistry Department, US Naval Academy, Annapolis, MD 21402