A Study of the Entropy Dynamics of a Gas in Canonical, Microcanonical and Grand Canonical Systems

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One of the great triumphs of 19th and 20th century is the development of Statistical Mechanics and its co-relation with the theory of Thermodynamics. Statistical Mechanics introduces some sophisticated methods like the Ensemble Theory to study the systems. In this project, we intend to study, the Entropy, Energy and other quantities of the systems through the three Ensemble approaches namely Micro-Canonical, Canonical and Grand-Canonical Ensembles with the help of Monte-Carlo simulations using Python.

Keywords: Ensembles, Microcanonical, Canonical, Grand Canonical, System, Reservoir, Entropy, Helmholtz Free Energy.

I. INTRODUCTION:

The science of thermodynamics, which grew essentially out of an experimental study of the macroscopic behaviour of physical systems, had become a secure and stable discipline of physics by the 1850s. The theoretical conclusions following from the first two laws of thermodynamics were found to be in very good agreement with the corresponding experimental results. At the same time, the kinetic theory of gases, which aimed at explaining the macroscopic behaviour of gaseous systems in terms of the motion of their molecules and had so far thrived more on speculation than calculation, began to emerge as a real, mathematical theory. Its initial successes were glaring; however, a real contact with thermodynamics could not be made until about 1872 when Boltzmann developed his H-theorem and thereby established a direct connection between entropy on one hand and molecular dynamics on the other. Almost simultaneously, the conventional (kinetic) theory began giving way to its more sophisticated successor — the ensemble theory. The power of the techniques that finally emerged reduced thermodynamics to the status of an "essential" consequence of the get-together of the statistics and the mechanics of the molecules constituting a given physical system. It was then natural to give the resulting formalism the name Statistical Mechanics.

II. MACROSTATES & MICROSTATES:

Macrostate of a thermodynamic system describes the macroscopic properties of the system while microstate describes the microscopic properties. Generally, the properties of macrostate are averaged over many microstates. All thermodynamic systems are made up of atoms; therefore, it is very important to understand the microstate of the system, which specifies the quantum state of all the atoms in the system. The changes in the microstate can be as small as 10^{35} times than a macrostate, but there are still changes in this scale which may have no effect at the macrostate. A single macrostate contains a very large number of microstates. In other words, we can predict the changes in the macrostate of the thermodynamic system via averaging the changes of microstates. The most commonly measured macroscopic properties include temperature, pressure, volume and density. As described above, some slight changes, which are large changes in the microstate, may not have a considerable change in the macrostate due to this size difference. Therefore, macrostates give a rough measurement of the thermodynamic system, instead of complete details with slight fluctuations. The macrostates are not equally likely, because different macrostates correspond to different numbers of microstates. The most likely macrostate that the system will find itself in is the one that corresponds to the largest number of microstates. Thermal systems behave in a very similar way to the example we have just considered. To specify a microstate for a thermal system, you would need to give the microscopic configurations (perhaps position and velocity, or perhaps energy) of each and every atom in the system. In general, it is impossible to measure which microstate the system is in. The macrostate of a thermal system on the other hand would be specified only by giving the macroscopic properties of the system, such as the pressure, the total energy, or the volume.

III. ENSEMBLES:

We are using probability to describe thermal systems and our approach is to imagine repeating an experiment to measure a property of a system again and again because we cannot control the microscopic properties (as described by the system's microstates). In an attempt to formalize this, Josiah Willard Gibbs in 1878 introduced a concept known as an ensemble. This is an idealization in which one considers making a large number of mental "photocopies" of the system, each one of which represents a possible state the system could be in. As time passes, the system continually switches from one microstate to another, with the result that, over a reasonable span of time, all one observes is a behaviour "averaged" over the variety of microstates through which the system passes. It may, therefore, make sense if we consider, at a single instant of time, a rather large number of systems — all being some sort of "mental copies" of the given system — which are characterized by the same macrostate as the original system but are, naturally enough, in all sorts of possible microstates. Then, under ordinary circumstances, we may expect that the average behaviour of any system in this collection, which we call an ensemble, would be identical to the time-averaged behaviour of the given system. It is on the basis of this expectation that we proceed to develop the so-called ensemble theory.

The microstate of a given classical system, at any time t, may be defined by specifying the instantaneous positions and momenta of all the particles constituting the system. Thus, if N is the number of particles in the system, the definition of a microstate requires the specification of 3N position coordinates q_1, q_2, ..., q_{3N} and 3N momentum coordinates p_1, p_2, ..., p_{3N}. Geometrically, the set of coordinates (q_i, p_i), where i = 1, 2, ..., 3N, may be regarded as a point in a space of 6N dimensions. We refer to this space as the phase space, and the phase point (qi, pi) as a representative point of the given system. As time passes, the set of coordinates (qi, pi), which also defines the microstate of the system, undergoes a continual change. Correspondingly, our representative point in the phase space carves out a trajectory whose direction, at any time t, is determined by the velocity vector $v \equiv (\dot{q_i}, \dot{p_i})$.

$$\Omega(N,q) = \binom{N-1+q}{q} = \frac{(N-1+q)!}{q!(N-1)!}$$

IV. METHODOLOGY:

We have developed Python code for each of the ensemble systems,
(Microcanonical, Canonical and Grand-Canonical)

Algorithms:

1) Microcanonical Ensemble:

a) Set up two systems A and B having nearly equal amount of energy (initially).
b) Within the constraints of microcanonical ensemble theory, particles are not allowed to be exchanged between the two systems. They are constant throughout the time-evolution. Energy is allowed to exchange.
c) Select any two particles at random ri and rj from the composite system A+B.
d) If ri particles have atleast one unit of energy, then decrease the energy of that particle by one unit and increase the energy of the rj particle by one unit. i.e.,

$$E_{ri} = E_{ri} - 1 \text{ and}$$
$$E_{rj} = E_{rj} + 1.$$

e) Calculate the total energy of the system A and B and store it in an array.
f) Calculate the entropy of the system A and B as well as total entropy and store in an array.
g) Calculate the Helmholtz free energy of the system A and B as well as the total Helmholtz Free Energy and store it in an array.
h) Repeat the steps c,d,e,f,g for desired amount of iterations.
i) After desired number of iterations have been completed, plot the quantities such as Energy of system A, system B, composite Energy, entropy of A, entropy of B, composite entropy, Helmholtz Free Energy of A, Helmholtz Free Energy of B and composite Helmholtz Free Energy of A and B vs time (Iterations correspond to the time-evolution).
j) If the plots do not suggest something meaningful, then take out the data and make smaller arrays by averaging the data over desired number of points and plot it.

2) Canonical Ensemble:

a) Set up two systems A and B. Let A be the system and B be the reservoir. System A is very small compared to the reservoir in terms of Energy as well as particles.
b) As within the theory of Canonical Ensemble, particles in both the system A and B remain constant, but energy is allowed to be exchanged between the two.
c) Select any two particles at random ri and rj from the composite system A and B.
d) If the particle ri has atleast one unit of Energy, then decrease the energy of ri particle by one unit and increase the Energy of rj particle by one unit.

$$E_{ri} = E_{ri} - 1$$
$$E_{rj} = E_{rj} + 1$$

e) Calculate the energy, entropy, Helmholtz Free Energy of the system A and store them in respective arrays.
f) Repeat the steps c,d and e for desired number of iterations.
g) After the desired number of iterations have been completed, plot the quantities Energy, Entropy, Helmholtz Free Energy of system vs time (iterations correspond to the time-evolution).
h) If the plots do not suggest something meaningful then take out that data and make smaller arrays by averaging the data over desired number of points and then plot it.

3) Grand Canonical Ensemble:

a) Set up a Big system, divide that system into some desired number of smaller areas. Select any one area and consider that as system A and name it area1. The remaining number of areas form the large reservoir B. The system A is very small compared to the reservoir in terms of Energy as well as particles.

b) As within the theory of Grand Canonical Ensemble, both, particles as well as Energy are allowed to be exchanged between the system area1 and the reservoir (all other areas).

c) Select any two areas randomly Ai and Aj from the composite system (area1 + all other areas).

d) If the Area Ai has more than one particle and has at least one unit of energy, then decrease the energy of the Area Ai by the average energy per particle in the area Ai and increase the Energy of the Area Aj by the amount of which energy has been taken out from the Area Ai. Also, decrease the number of particles in Area Ai by one unit and increase the number of particles in the Area Aj by one unit.

EAi = EAi – (average energy per particle in Ai)
EAj = EAj + (average energy per particle in Ai)
NAi = NAi – 1
NAj = NAj + 1

e) Calculate the energy, entropy and the number of particles of system A (area1) and store them in respective arrays.

f) Repeat the steps c,d and e for desired number of iterations.

g) After the desired number of iterations have been completed, plot the quantities Energy, Entropy, number of particles of system A (area1) vs time. (Iterations correspond to time-evolution).

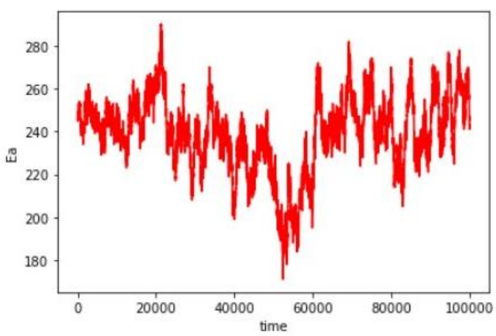
h) If the plots do not suggest something meaningful, then take out the data and make smaller arrays by averaging the data over desired number of points and plot it.

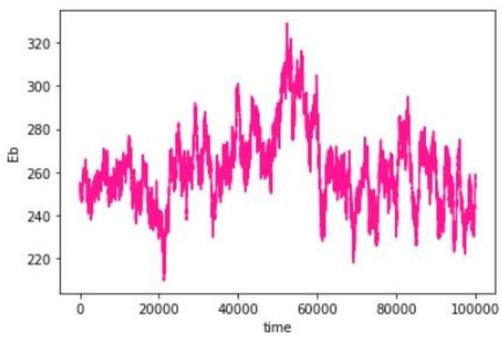
V. RESULTS:

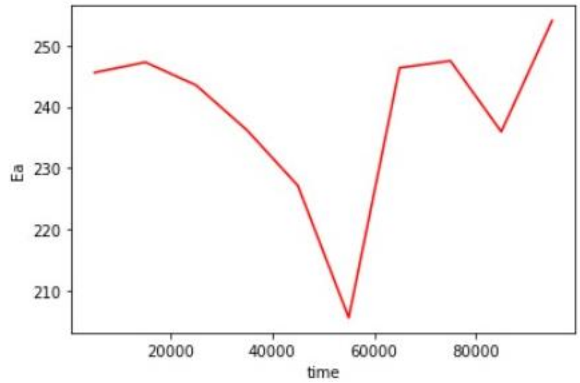
1. Microcanonical

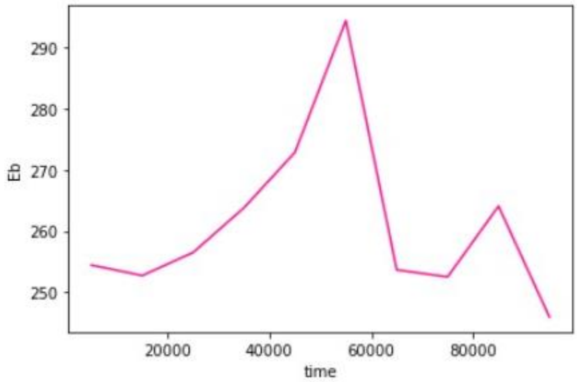
a. Case I:

```
Case 1: Micro-Canonical Ensemble
Na =  100
Nb =  100
qa =  250
qb =  250
The initial qa/Na =  2.5
The initial qb/Nb =  2.5
No.of Iterations =  100000
```






Ea
time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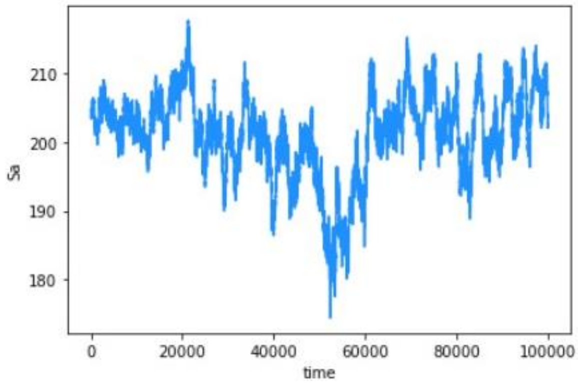
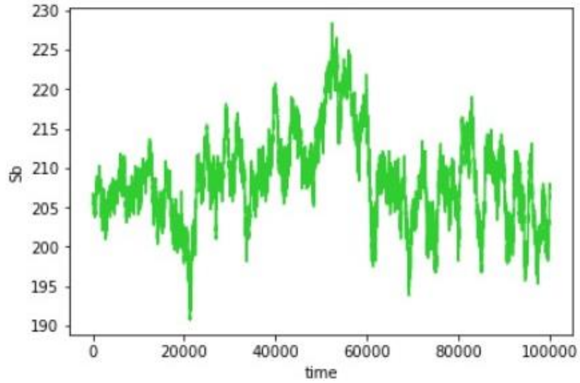
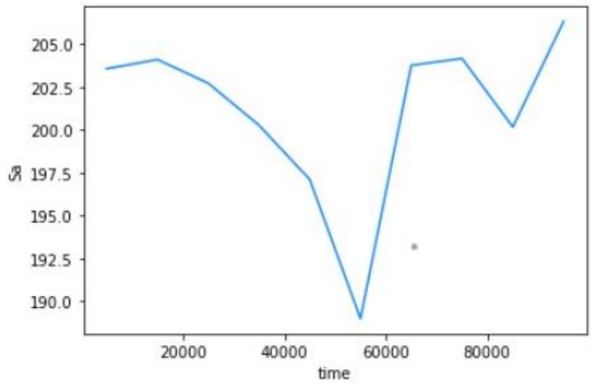
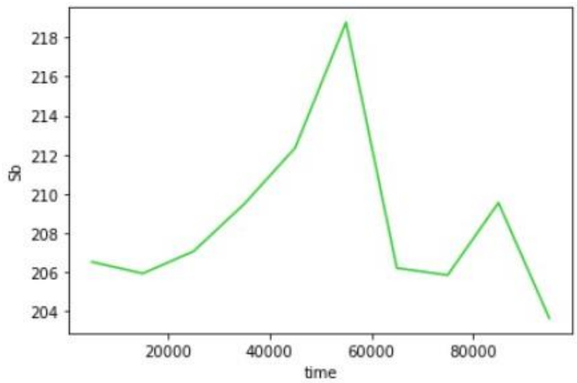
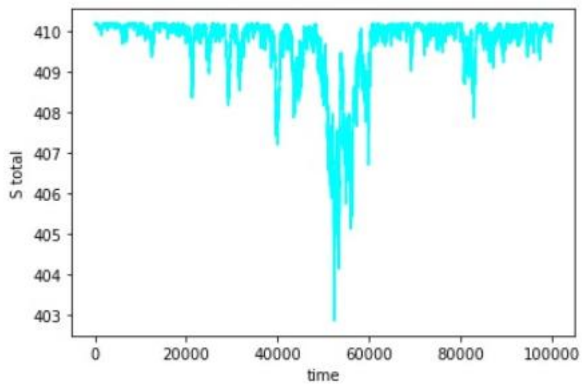
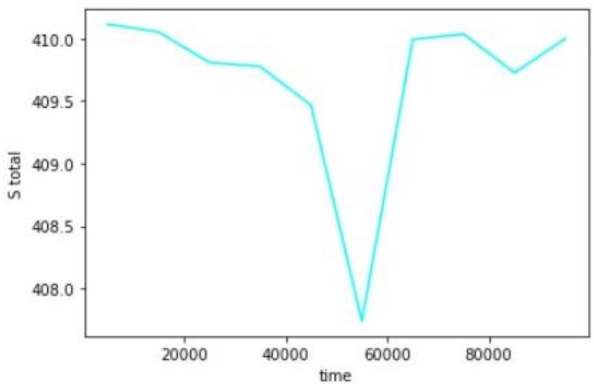

Sa
time

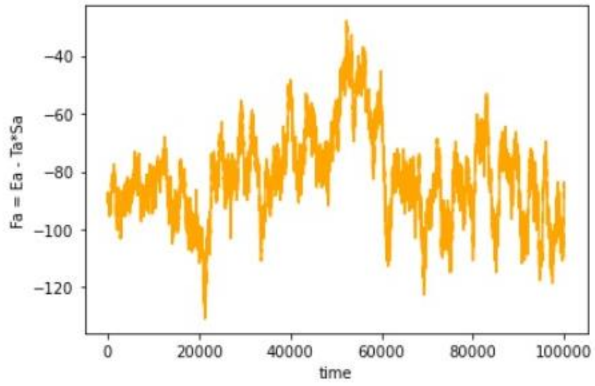

Sb
time

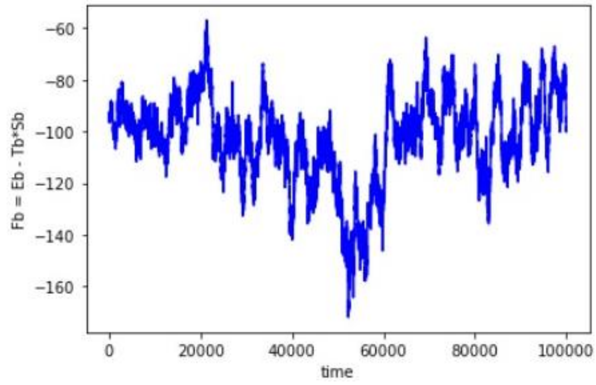

Sa
time

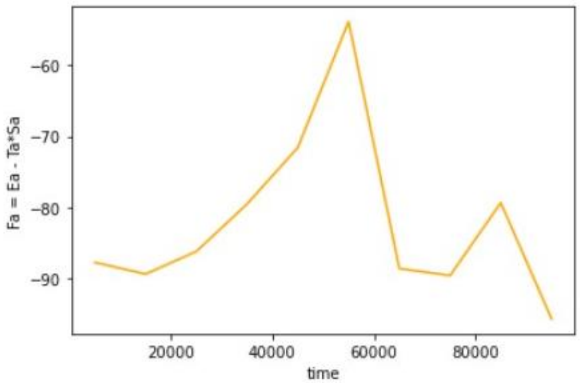

Sb
time

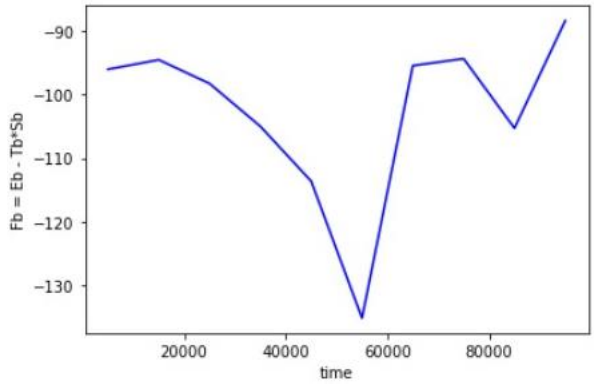

S total
time

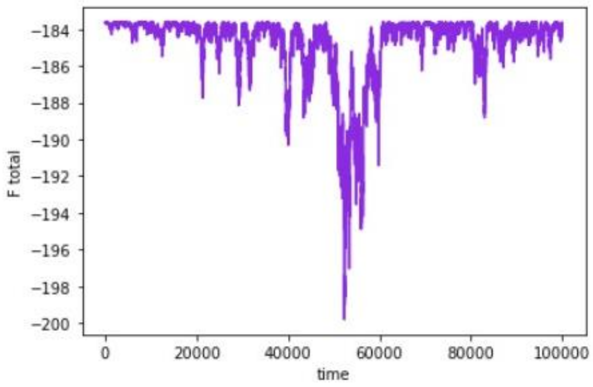

S total
time

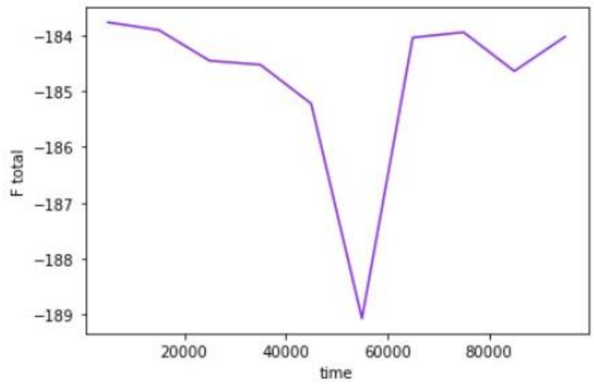






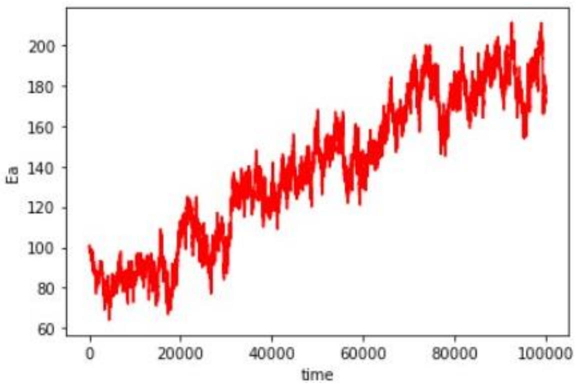


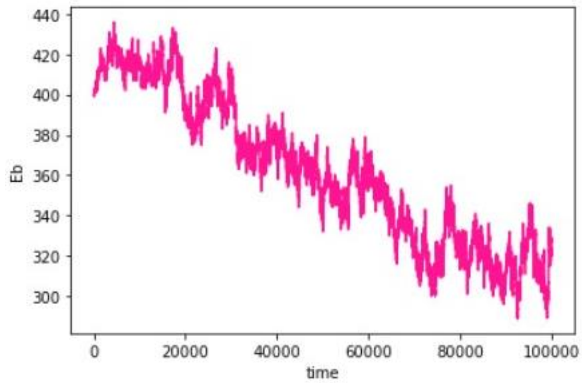


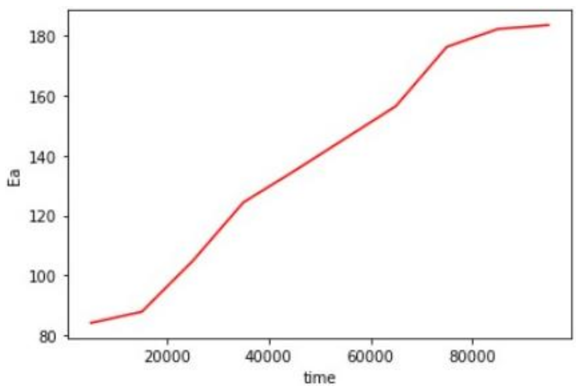


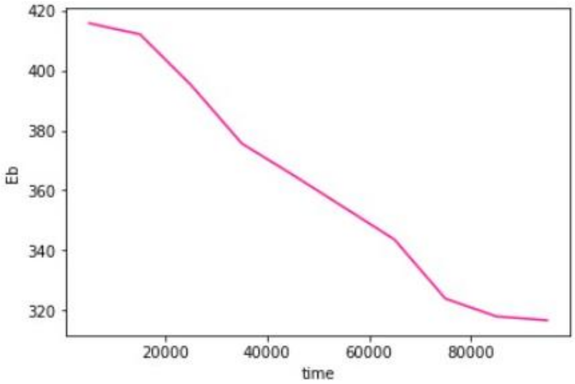
b. Case II:

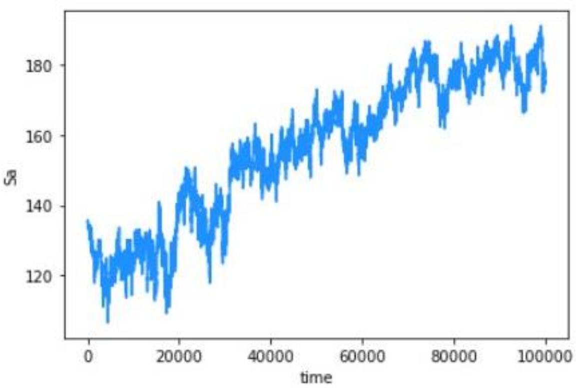
```
Case 2: Micro-Canonical Ensemble
Na =  100
Nb =  100
qa =  100
qb =  400
The initial qa/Na =  1.0
The initial qb/Nb =  4.0
No.of Iterations =  100000
```

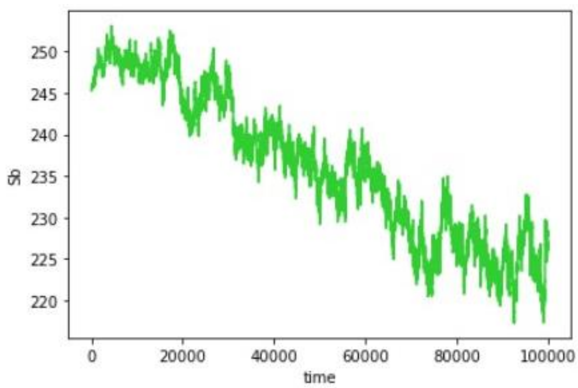

Ea
time
60
80
100
120
140
160
180
200
0
20000
40000
60000
80000
100000

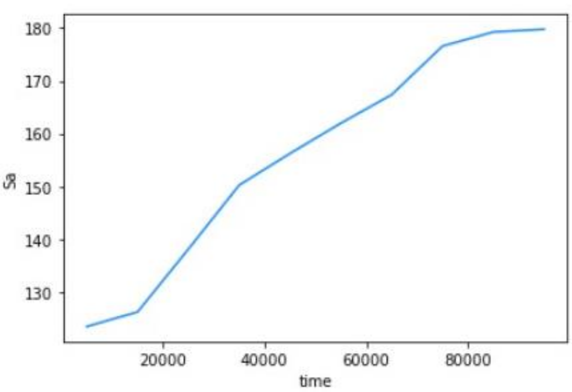

Eb
time
300
320
340
360
380
400
420
440
0
20000
40000
60000
80000
100000

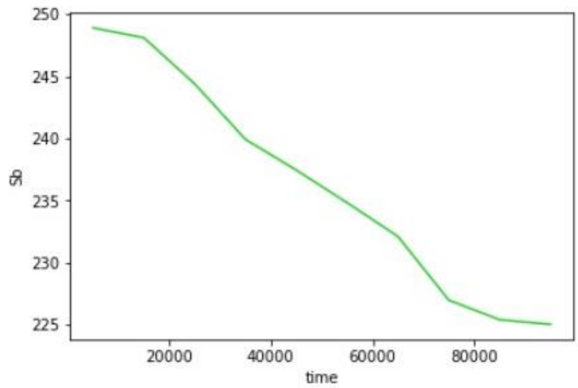

Ea
time
80
100
120
140
160
180
20000
40000
60000
80000

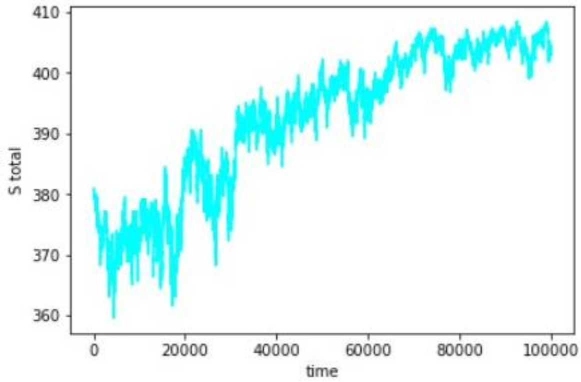

Eb
time
320
340
360
380
400
420
20000
40000
60000
80000

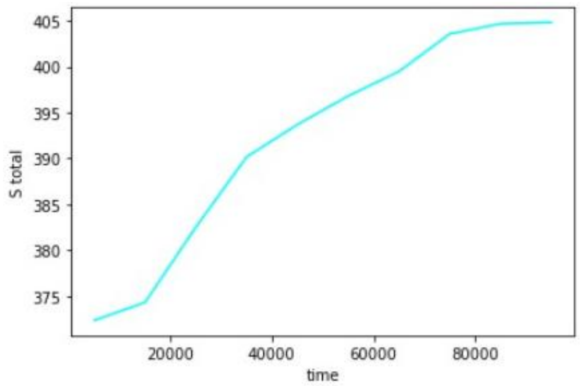

Sa
time
120
140
160
180
0
20000
40000
60000
80000
100000

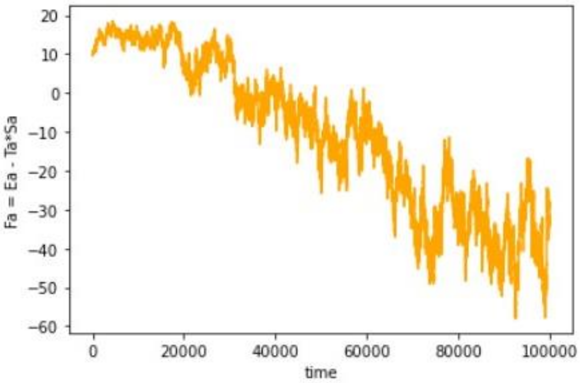

Sb
time
220
225
230
235
240
245
250
0
20000
40000
60000
80000
100000

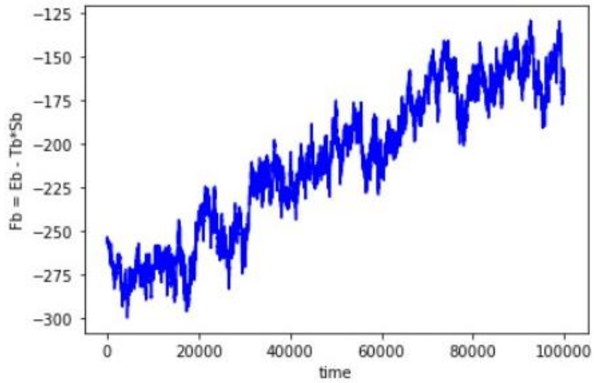

Sa
time
130
140
150
160
170
180
20000
40000
60000
80000

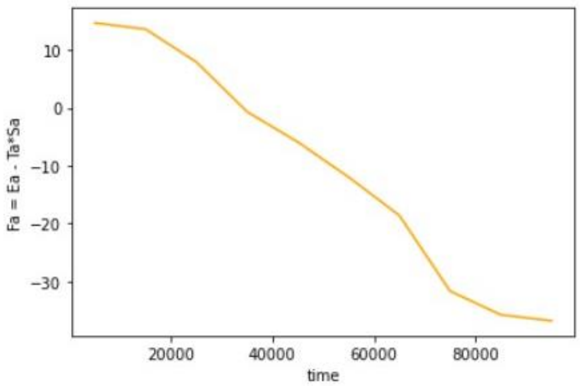

Sb
time
225
230
235
240
245
250
20000
40000
60000
80000

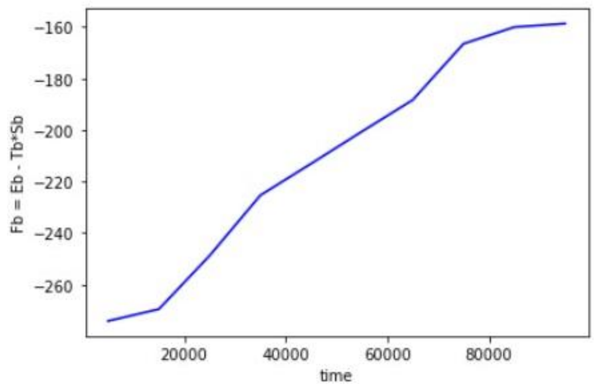

S total
time
410
400
390
380
370
360
0
20000
40000
60000
80000
100000

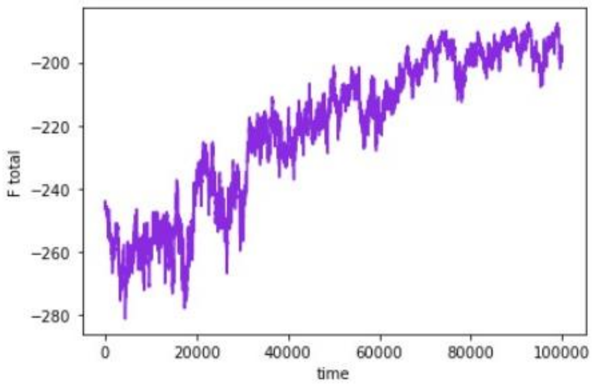

S total
time
405
400
395
390
385
380
375
20000
40000
60000
80000

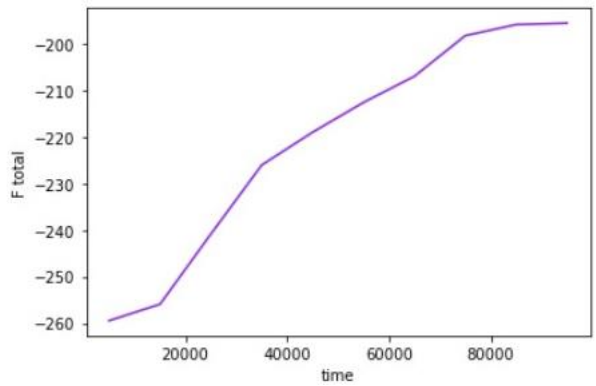

Fa = Ea - Ta*Sa
time
20
10
0
−10
−20
−30
−40
−50
−60
0
20000
40000
60000
80000
100000


Fb = Eb - Tb*Sb
time
−125
−150
−175
−200
−225
−250
−275
−300
0
20000
40000
60000
80000
100000


Fa = Ea - Ta*Sa
time
10
0
−10
−20
−30
20000
40000
60000
80000


Fb = Eb - Tb*Sb
time
−160
−180
−200
−220
−240
−260
20000
40000
60000
80000

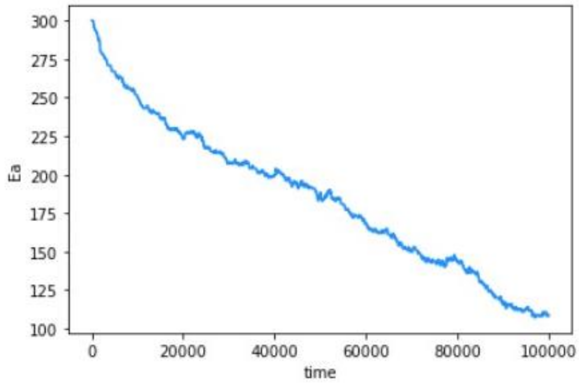

F total
time
−200
−220
−240
−260
−280
0
20000
40000
60000
80000
100000

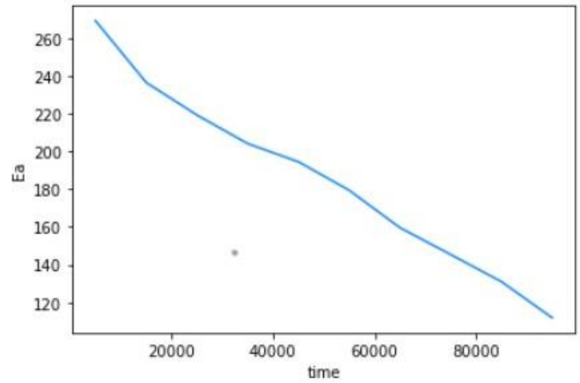

F total
time
−200
−210
−220
−230
−240
−250
−260
20000
40000
60000
80000

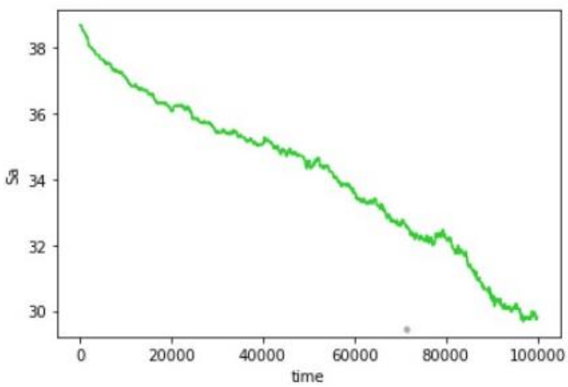
2. **Canonical:**

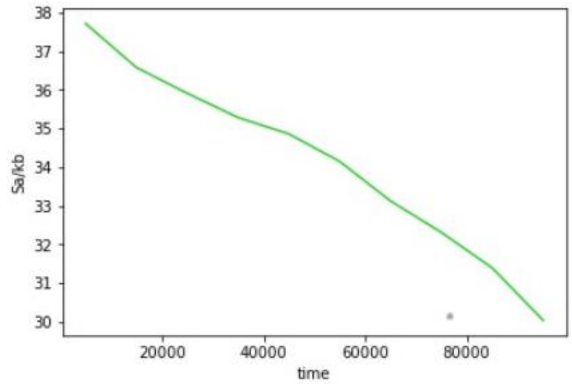
   a. **Case I:**

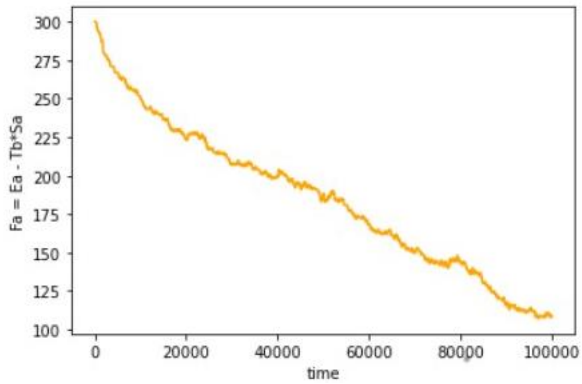
```
Case 1: Canonical Ensemble
Na =  10
Nb =  990
qa =  300
qb =  9700
The initial qa/Na =  30.0
The initial qb/Nb =  9.797979797979798
No. of Iterations =  100000
```

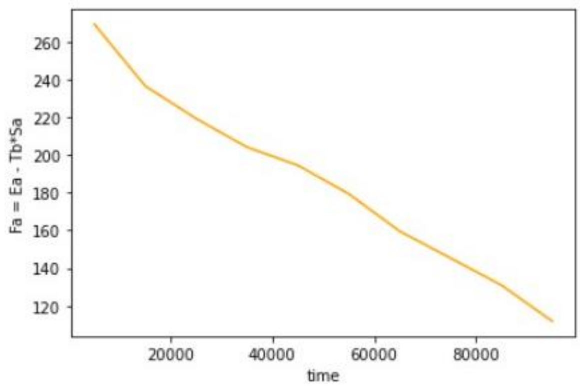






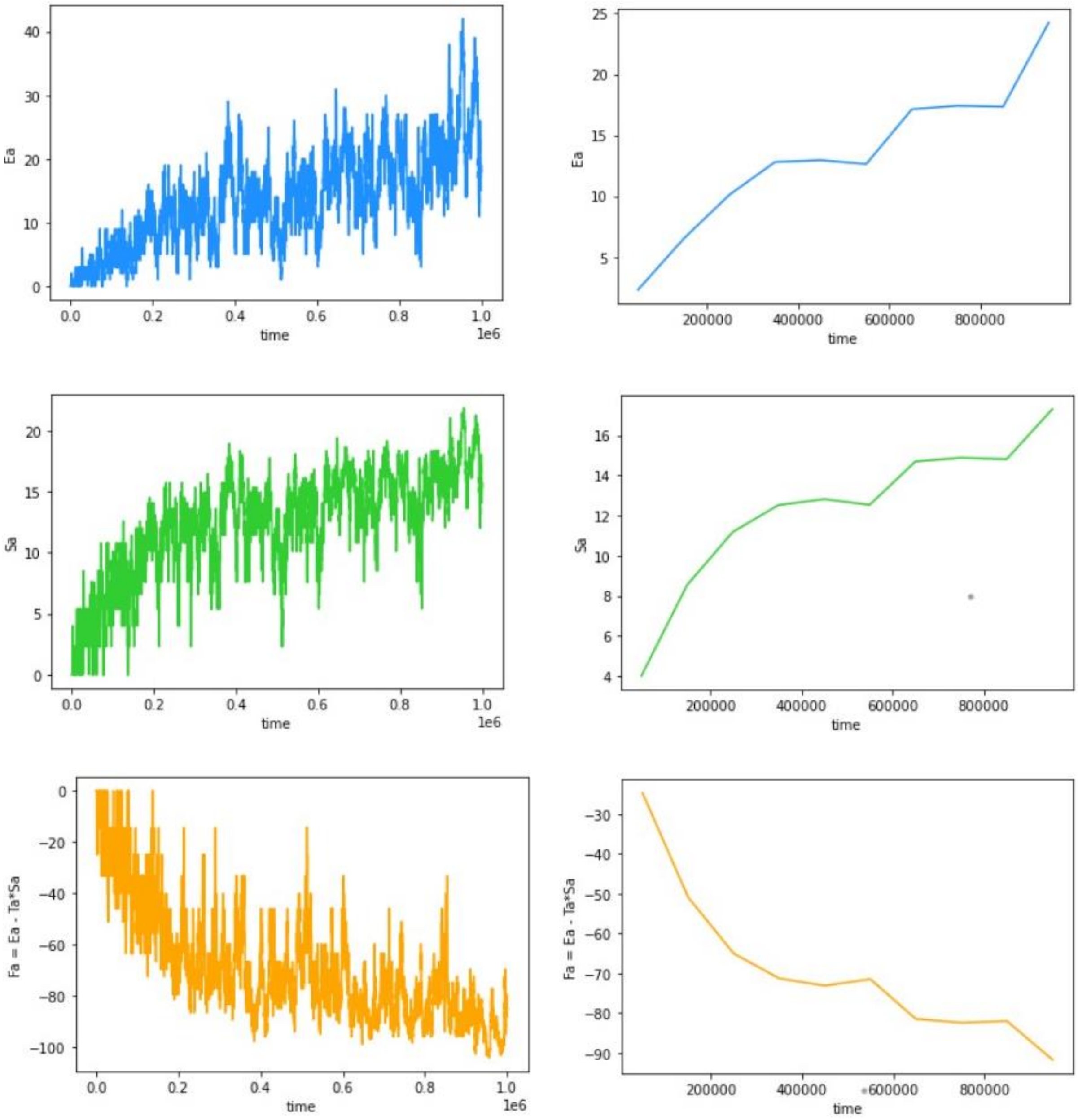






b. Case II:

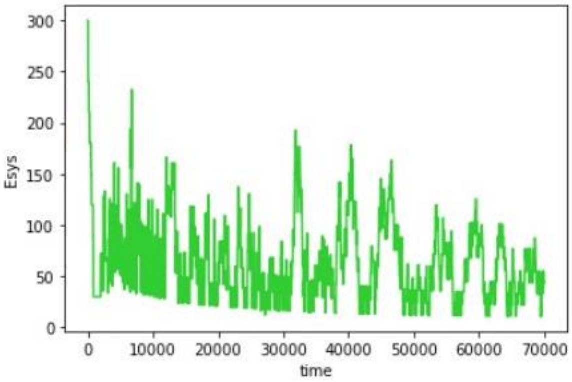
```
Case 2: Canonical Ensemble
Na =  10
Nb =  990
qa =  0
qb =  10000
The initial qa/Na =  0.0
The initial qb/Nb =  10.1010101010101
No. of Iterations =  100000
```

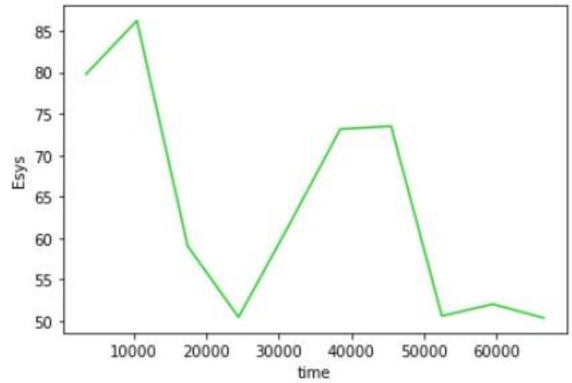


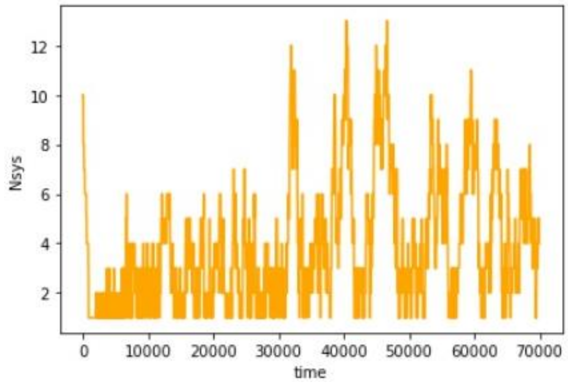
3. Grand Canonical Ensemble:

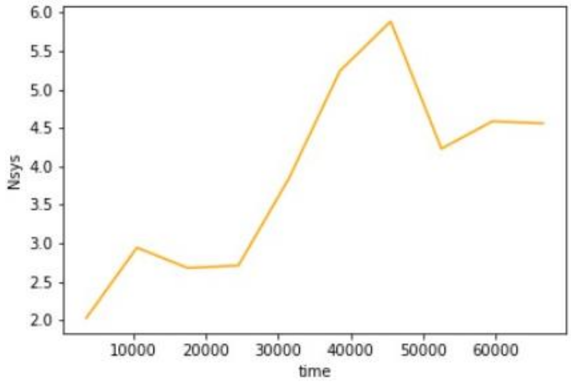
a. Case I:

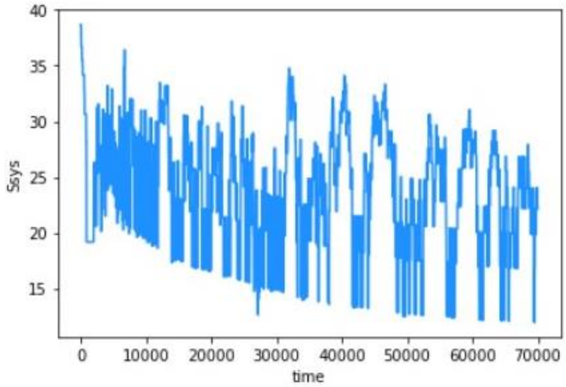
```
Case 1: Grand-Canonical Ensemble
Nsystem =  10
Nreservoir =  990
Esystem =  300
Ereservoir =  9700
The initial Esys/Nsys =  30.0
The initial Eres/Nres =  9.797979797979798
No.of Iterations =  70000
```

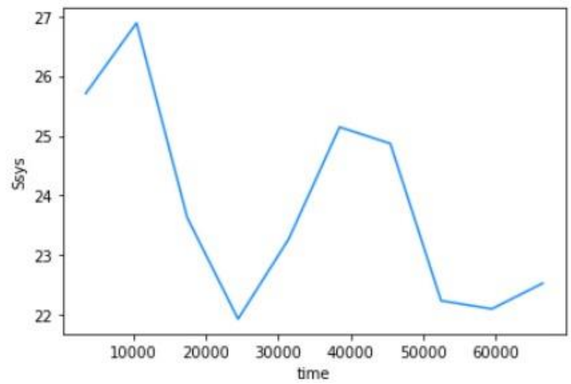

Esys
300
250
200
150
100
50
0
0
10000
20000
30000
40000
50000
60000
70000
time

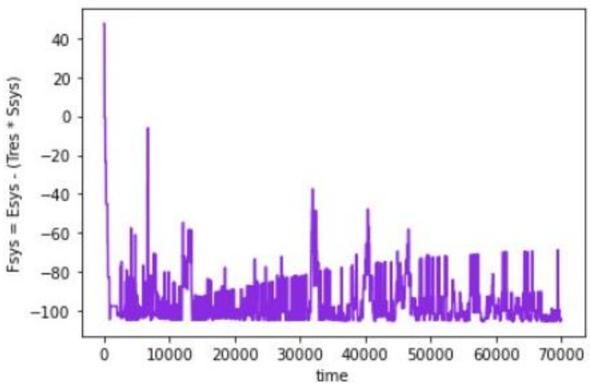

Esys
85
80
75
70
65
60
55
50
10000
20000
30000
40000
50000
60000
time

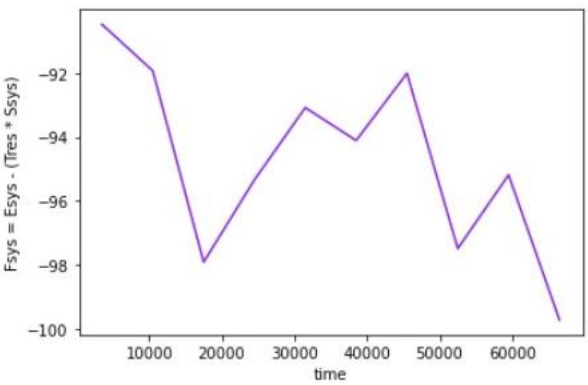

Nsys
12
10
8
6
4
2
0
10000
20000
30000
40000
50000
60000
70000
time


Nsys
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
10000
20000
30000
40000
50000
60000
time


Ssys
40
35
30
25
20
15
0
10000
20000
30000
40000
50000
60000
70000
time

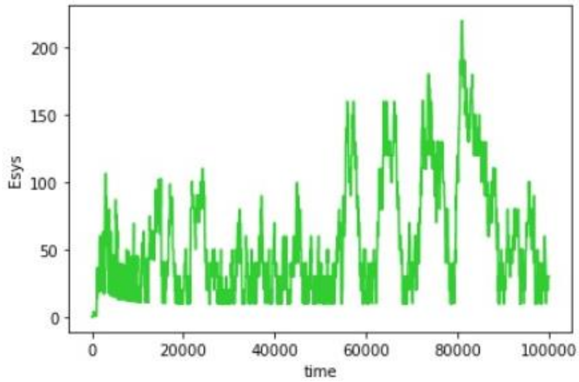

Ssys
27
26
25
24
23
22
10000
20000
30000
40000
50000
60000
time

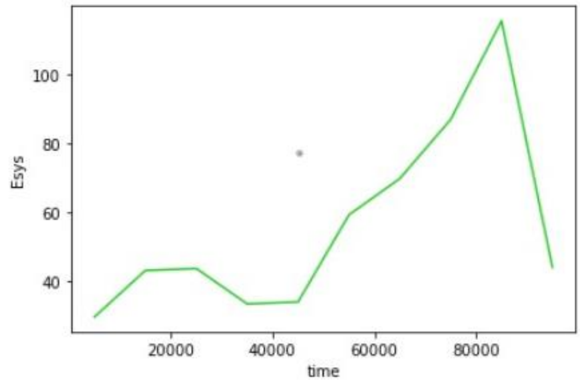

Fsys = Esys - (Tres * Ssys)
40
20
0
−20
−40
−60
−80
−100
0
10000
20000
30000
40000
50000
60000
70000
time

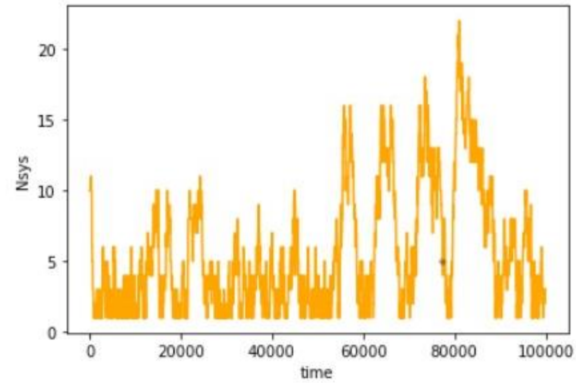

Fsys = Esys - (Tres * Ssys)
−92
−94
−96
−98
−100
10000
20000
30000
40000
50000
60000
time

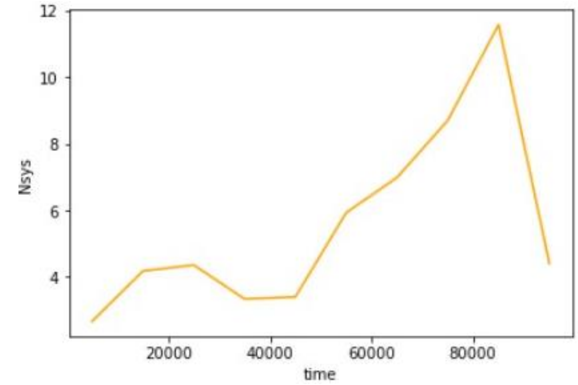
b. Case II:

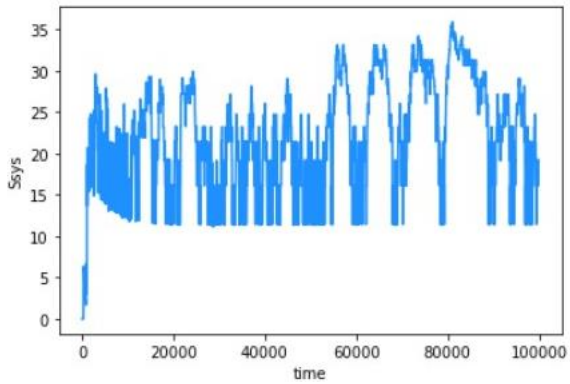
```
Case 2: Grand-Canonical Ensemble
Nsystem =  10
Nreservoir =  990
Esystem =  0
Ereservoir =  10000
The initial Esys/Nsys =  0.0
The initial Eres/Nres =  10.1010101010101
No.of Iterations =  100000
```

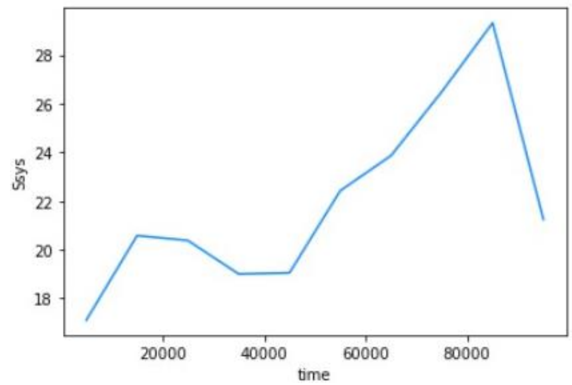


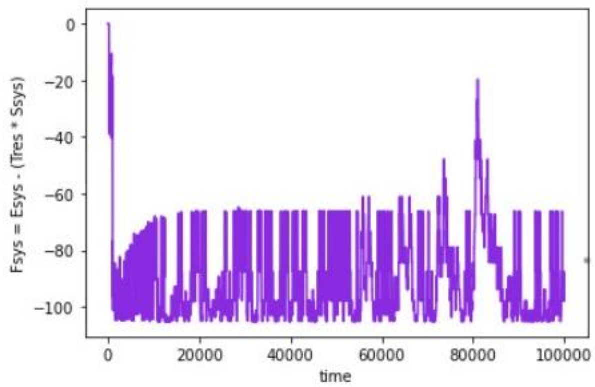


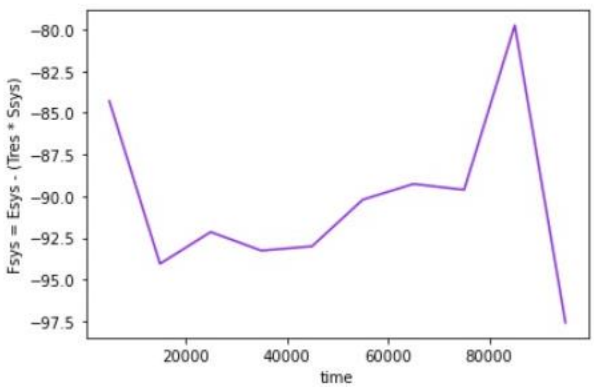












VI. DISCUSSIONS:

1. Microcanonical Ensemble:

a. Case I:

Energy, Entropy, Helmholtz Free Energy of both systems as well as total entropy and total Helmholtz free energy do not change and their final value is nearly equal to their initial value. This outcome is expected since Na = Nb and qa = qb, the average energy per particle is equal, hence, equilibrium is expected.

b. Case II:

Na = Nb, qa = 100, qb = 400, i.e., qa<qb. Therefore, qb/Nb > qa/Na, which is not an equilibrium situation, hence, after 10^5 iterations, Ea increases, Eb decreases, Fa decreases, Fb increases, Sa increases and Sb decreases. Both the systems are trying to reach equilibrium.

Also, for equilibrium, the total Entropy must increase and Helmholtz free energy should decrease and this is reflected in the results obtained.

2. Canonical Ensemble:

a. Case I:

System A : system of our choice.

System B : reservoir.

Na<<Nb and qa/Na > qb/Nb. It is observed that after 10^5 iterations, system A is more energetic and must lose energy to reach equilibrium. Also, the Helmholtz Free Energy should decrease at equilibrium as is seen in the output. But an interesting thing to be noted is that the entropy is also showing a decreasing trend, which is counter intuitive.

b. Case 2:

Na = 10, Nb = 990, i.e., Na<<Nb. Also, qa = 0 while qb is the total energy.
i.e., qa/Na < qb/Nb.

When system is allowed to exchange energy, it gains energy as expected. Helmholtz Free Energy also decreases as expected to decrease at equilibrium.
Also, the Entropy increases at equilibrium as expected.

3. Grand Canonical Ensemble:

a. Case I:

$N_{system} << N_{reservoir}$, $E_{system}/N_{system} > E_{reservoir}/N_{reservoir}$.

The system is more energetic; hence it is expected for the system to lose energy to attain equilibrium. This is evident from the plots. The entropy also decreases, which is counter intuitive. Initially the number of particles also decreases, but over a longer duration (greater number of iterations), the number of particles somewhat attains an equilibrium value. Helmholtz free energy shows a decreasing trend which is expected.

b. Case II:

$N_{system} << N_{reservoir}$, $E_{system} = 0 << E_{reservoir}$.

As time increases, the system gains energy and tries to attain equilibrium as should be the case for a less energetic system in a more energetic environment.

Also, average number of particles also increases in the system with time and eventually saturates or reaches equilibrium. Initially the entropy is zero, it increases as the system gains energy and particles and reaches equilibrium value. Helmholtz free energy shows a decreasing trend.

VII. CONCLUSIONS:

1. As we can see, in a Microcanonical Ensemble, total entropy of the composite system always increases, while the Helmholtz free energy increases or decreases depending upon the case.
   Hence, we can conclude that the BEST parameter to describe Microcanonical Ensemble is Entropy which is always greater than or equal to zero. (Zero when only one microstate is possible).
   Here we have considered total composite entropy as both systems are not much different, so no preferred system.
2. In case of the Canonical as well as the Grand Canonical Ensembles, it is the Helmholtz Free Energy which is always decreasing in the equilibrium state while the entropy might increase or decrease depending upon the energies of the system. Therefore, there is a preferred system, which is different from the reservoir.
   Hence, we can conclude that the BEST parameter to describe the Canonical and the Grand Canonical Ensemble system is Helmholtz Free Energy which is less than or equal to zero.

Monte-Carlo Simulations:

1. With a very simple mathematical form and use of Random generators, the process is quite fast and often depicts or even mimics the results like an actual experiment.
2. The limitation with these methods is that sometimes some random numbers are preferred more consecutively in a row and that sometimes deviates from the actual physical situation.

Acknowledgement:

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*We are also thankful to **Dr. Katherine Rawlins** Ma'am for her constant support and guidance.*

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Python Code File.