Computer simulation of physical systems I

Task III: NVT molecular dynamics with Nosé-Hoover thermostat

In this exercise you will practice with MD simulations in the NVT ensemble for the same system of LJ-atoms of the previous exercise (Task II). We will use the same code of Task II, which also implements the equations for the Nosé-Hoover (NH) thermostat. As usual, you can find illustrative examples in each subdirectory, together with comments and scripts which will help you in the understanding and accomplishment of the following steps.

1. *Startup* the simulation: equilibrate the sample and then study the velocity distribution.

- perform an equilibration run in the NVT ensemble (by runnning `run_NVT()`) starting from the sample which was equilibrated at $T = 94$ K in the previous exercise; monitor the evolution of the (instantaneous) temperature during the run
- plot the velocity distribution and compare it with the theoretical distribution appropriate for the NVT ensemble; check the conservation of the constant of motion, H_{NH} (NH hamiltonian, reported on output in the rightmost column)

2. Study how the distribution of the velocities and the response of the system to a change of temperature depend on the choice of Q (*thermal inertia parameter* of the thermostat)

- evolve the system using different values of Q and compare the velocity distributions
- for the same values of Q, change the ensemble temperature and monitor the evolution of the instantaneous temperature during the transitory
- (Optional) study how the accuracy in the conservation of H_{NH} depends on Q

3. Study the distribution of the velocities and the fluctuations of the (instantaneous) temperature at *different ensemble temperatures*:

- prepare a set of samples equilibrated at different values of T in a range of interest
- compute the velocity distribution and the temperature fluctuations and compare them with the theoretical values expected for the NVT ensemble
- (Optional) compare the temperature fluctuations of the NVT ensemble with those of the NVE ensemble (at the same values of T); study a system of different size and check if the temperature fluctuations scale with the appropriate law for the NVT ensemble (additionally, you can do the same for the NVE ensemble)

4. Compute the *diffusion coefficient* and compare it with that obtained in the NVE simulations. (Optional) Investigate how the diffusion coefficient changes as a function of the ensemble temperature (for instance, using the set of temperatures studied previously) and check if it obeys the Arrhenius law by fitting to $D(T) = D(0)\exp(-E/RT)$, where E and $D(0)$ are the fit parameters.

Instructions

Step 1: Startup

1. EQUILIBRATE THE SAMPLE IN THE NVT

We start from the same sample at $T \approx 94K$ that was equilibrated in the NVE ensemble (copy that file into the current directory before going on).

In order to perform a dynamics in the NVT ensamble using the Nose'-Hoover thermostat, you need to use the function `run_NVT()` and specify a value of the thermal inertia parameter Q (see file `Step1.py`):

```
N, L, pos, vel = read_pos_vel('sampleT94.4.dat')

# Run MD simulation in NVT ensemble
output = run_NVT(pos, vel, L, nsteps, N, dt, T, Q)

# Plot E_NH vs step
plt.plot(output['nsteps'],output['EnNH'])
plt.plot(output['nsteps'],output['EnKin']+output['EnPot'])
plt.show()
```

See the evolution of T during equilibration, you should see a transitory at the beginning and then the fluctuations should reach a stable amplitude. Since the starting values for the Nose'-Hoover variables may not be very good it can take several time steps to reach an equilibrium condition, even if the starting temperature is close to the target temperature.

2. STUDY THE FLUCTUATIONS

In the next simulation, you will sample the temperature and velocity fluctuations by uncommenting the second part of `Step1.py`:

```
Q = 10.              # thermal intertia parameter
T = 0.7807           # requested temperature
nsteps = 900         # number of steps
dt = 0.0046          # integration step

N, L, pos, vel, xi, lns = read_pos_vel('sampleNVT94.4.dat')

# Run MD simulation in NVT ensemble
output = run_NVT(pos, vel, L, nsteps, N, dt, T, Q, xi, lns)

# Plot temperature distribution
plt.hist(output['EnKin']/3*2, bins=np.linspace(0,10,499),fc='none',
        histtype='step', density = True)
plt.show()

# Plot p(v) distribution
v = np.linspace(-10,10,499)
plt.plot(v, np.mean(output['pv'], axis=0))
```

```
plt.plot(v,norm.pdf(v,0,np.sqrt(T)))
plt.show()

# Plot p(v**2) distribution
v = np.linspace(0,10,499)
plt.plot(v, np.mean(output['pv2'], axis=0))
plt.plot(v, maxwell.pdf(v, 0, np.sqrt(T)))
plt.show()
```

Here, `xi` and `lns` are NH-variables that are read from `sampleNVT94.4.dat` and required in order to start with the fully equilibrated state.

Examine the conservation of E_{NH} (the energy corresponding to the Nose'-Hoover Hamiltonian, which is stored in the output, e.g. `EnNH`). Compare its fluctuations with those of the "real" total energy.

Plot the distribution function of the velocity vector and of the speed which are written in the output dictionary by `run_NVT()` and compare with the corresponding Maxwell-Boltzmann distribution (at the correct temperature). You can now verify if the particle velocities obtained by integrating the Nose'-Hoover equations actually correspond to the dynamics of the NVT ensemble.

Step 2: Check Q

1. TEST N-H FOR SEVERAL VALUES OF Q

By changing the value of Q in the code, examine the conservation of E_{NH} for several values of Q: what do you notice? The integration step adopted so far does it lead to the same degree of accuracy for all values of Q? Can you explain why? (see also next point)

Plot the distribution function of the velocity vector for all those Q values. Does it reproduce the correct Maxwell-Boltzmann distribution in all cases?

2. STUDY A CHANGE OF TEMPERATURE

Here, the aim is to see how the temperature behaves (as a function of Q) when we impose a sudden change from T_{old} to T_{new}. For this purpose we use the second part of the script `Step2.py`, which performs an equilibration run at T_{old} followed by a run at a different temperature T_{new}. This is done for several values of the Nose'-Hoover thermodinamic inertia parameter Q.

Look at the evolution of T straight after the temperature change. Compare the amplitude of the temperature fluctuations at the starting and final temperatures. Compare the frequency of the temperature oscillations and the transition from T_{new} to T_{new} for different values of Q (make also a link with the previous point). Make some comments.

Step 3: Distributions

1. TEST N-H AT SEVERAL TEMPERATURES

You are now asked to verify that the N.-H. velocity distribution reproduces the Maxwell-Boltzmann distribution also at other temperatures. Following the same lines of the previous exercises, you should be able to setup your system at different temperatures (choose a small set of values in a range of interest) and sample the velocity distribution.

2. TEMPERATURE FLUCTUATIONS NVE vs NVT

Compare the temperature fluctuations at different temperatures and verify that obey to the relation expected for the NVT ensemble.

Consider also systems of different sizes and investigate how the temperature fluctuations scale with that number of particles in the canonic and microcanonic ensembles.

Step 4: Diffusion coefficient

1. COMPUTE DIFFUSION COEFFICIENT IN NVT

Use the techniques that you have learned so far to compute the diffusion coefficient in the NVT ensemble at different temperatures and compare it with that already obtained in the NVE simulations. Verify that $D(T)$ follows the Arrhenius-like relation with temperature:

$D(T) = D(0) exp(-E/RT)$