Exercise 3

Jin Liang

June 19, 2015

In reduced units, the kinetic energy, potential, pressure, temperature, and force are as follows:

Kinetic energy

$$K = \frac{1}{2}\sum_{i=1}^{N} \vec{v}_i^2$$

Potential

$$U(r) = \frac{e^{-r}}{r^2}, \text{ for } r < r_c$$

Tail correction

$$U^{tail} = N\pi e^{-r_c}$$

Pressure

$$P = \rho - \frac{1}{3V}\sum_{j<i}\sum_{i=1}^{N}\frac{\partial U}{\partial r} = \rho + \frac{1}{6N}\sum_{j<i}\sum_{i=1}^{N}(r+2)\frac{e^{-r}}{r^2}$$

Tail correction

$$P^{tail} = \frac{\pi}{6}(r+3)e^{-r_c}$$

Temperature

$$T = \frac{2K}{3N}$$

Force

$$\vec{F} = -\nabla U = \frac{e^{-r}}{r^2}(\frac{2}{r}+1)\frac{\vec{r}}{r}$$

1 Starting configuration

Generate the initial configuration:

a) Generate random positions for N molecules;

b) Generate random velocities, and compute the velocity of the centre of mass, $\vec{v}_{CM} = \frac{1}{N}\sum_{i=1}^{N}\vec{v}_i$. The velocity relative to $\vec{v}_{CM}$ is $\vec{v}_i\prime = \vec{v}_i - \vec{v}_{CM}$, and $\sum_{i=1}^{N}\vec{v}_i\prime = \sum_{i=1}^{N}\vec{v}_i - \sum_{i=1}^{N}\vec{v}_{CM} = 0$.

Then we scale the velocity $\alpha\vec{v}_i\prime$, such that the kinetic energy per particle is one, $\frac{1}{2}\sum_{i=1}^{N}(\alpha\vec{v}_i\prime)^2/N = 1$. In return, the scale is $\alpha = \sqrt{\frac{N}{K}}$.

Then we perform molecular dynamics with the velocity Verlet update

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \tfrac{1}{2}\vec{F}_i(t)(\Delta t)^2$$
$$\vec{v}_i(t+\Delta t) = \vec{v}_i(t) + \tfrac{1}{2}[\vec{F}_i(t) + \vec{F}_i(t+\Delta t)]\Delta t.$$

All the quantities are in reduced units.

2 Time-step dependence

Start with the same initial configuration, for a time duration $t = 30$, we perform four runs with a time step $\Delta t = 0.003, 0.009, 0.027, 0.081$ for each. After each updating step, the total energy, potential energy, the instantaneous pressure and temperature are measured.

2.1 Trajectory divergence

The energy divergence of the last three runs relative to the first run is shown in Figure 1. For a shorter time step, the energy divergence is smaller and fluctuates around zero. For a long time step, like in run 4, the energy divergence is large and increases as time goes on.

The pressure divergence and temperature divergence are shown in Figure 2 and Figure 3, respectively. For pressure divergence, run 2 has the largest fluctuation, while the divergence of run 3 and run 4 remains almost zero. The three runs have similar behaviour for temperature divergence.

2.2 Energy conservation

The total energy of the four runs are shown in Figure 4, which is around 238.5. It means that as the potential energy decreases rapidly at the beginning, the kinetic energy increases with almost the same amount. The total energy is approximately constant over time.

The average and error of the total energy computed with blocking analysis are shown in Table 1.

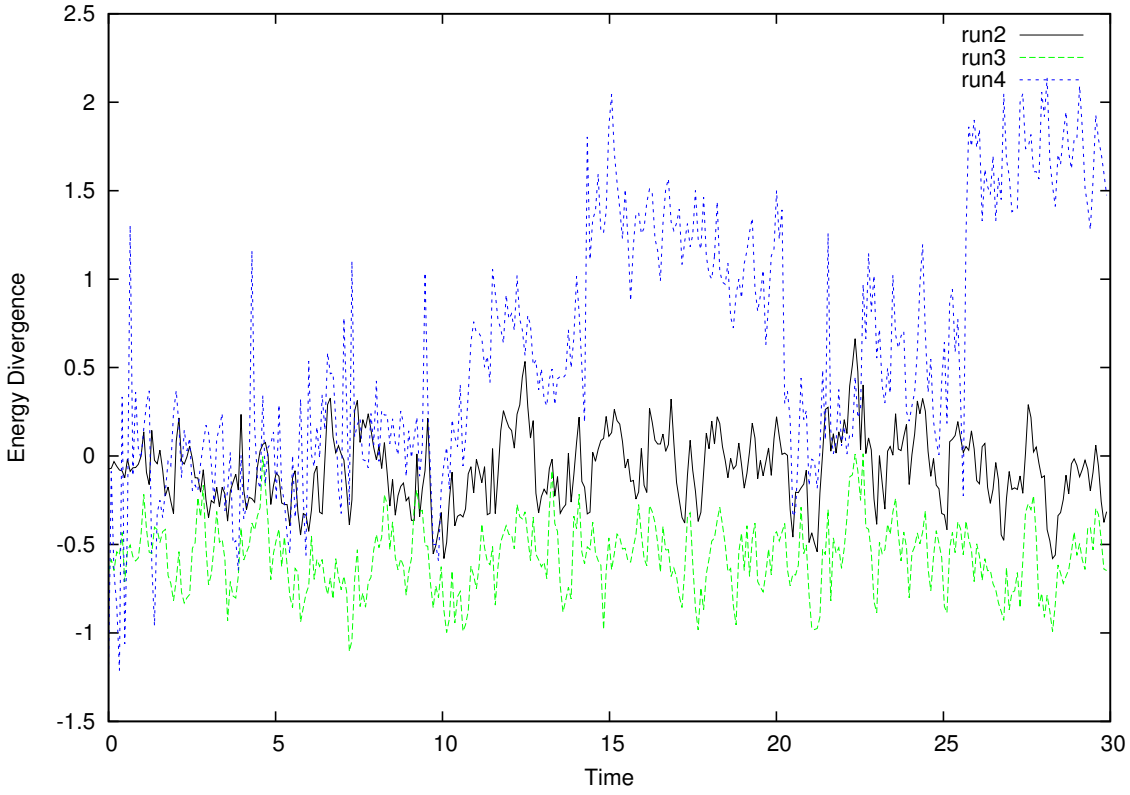

Figure 1: Energy Divergence

Table 1: Average and Error of Energy

Run	Energy	Error
1	238.459795	0.015885
2	238.385998	0.013857
3	237.883926	0.012388
4	239.030273	0.176397

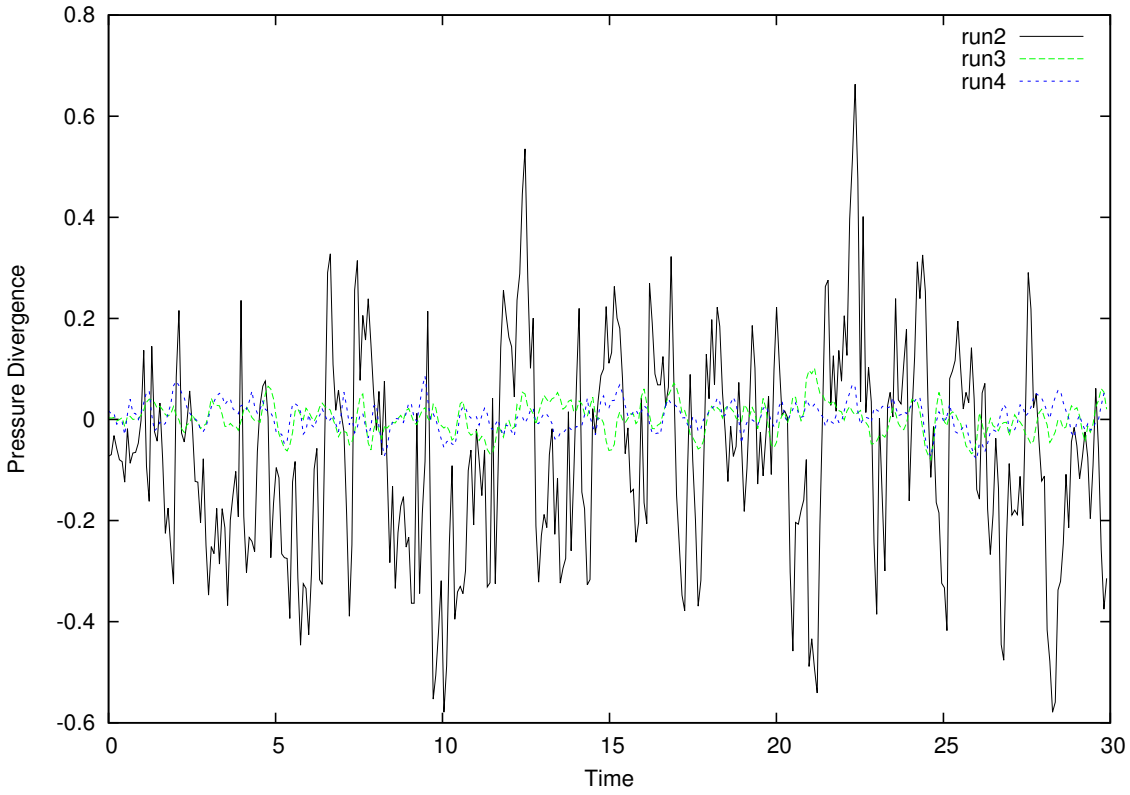

Figure 2: Pressure Divergence

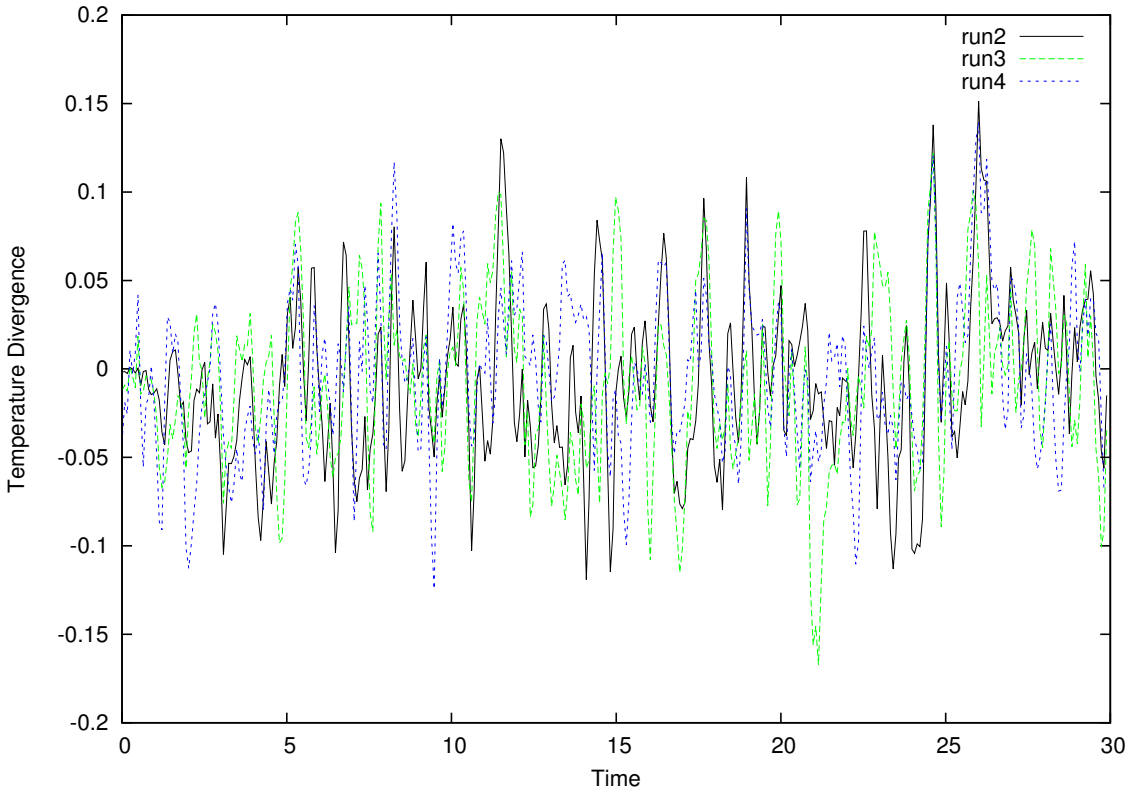

Figure 3: Temperature Divergence

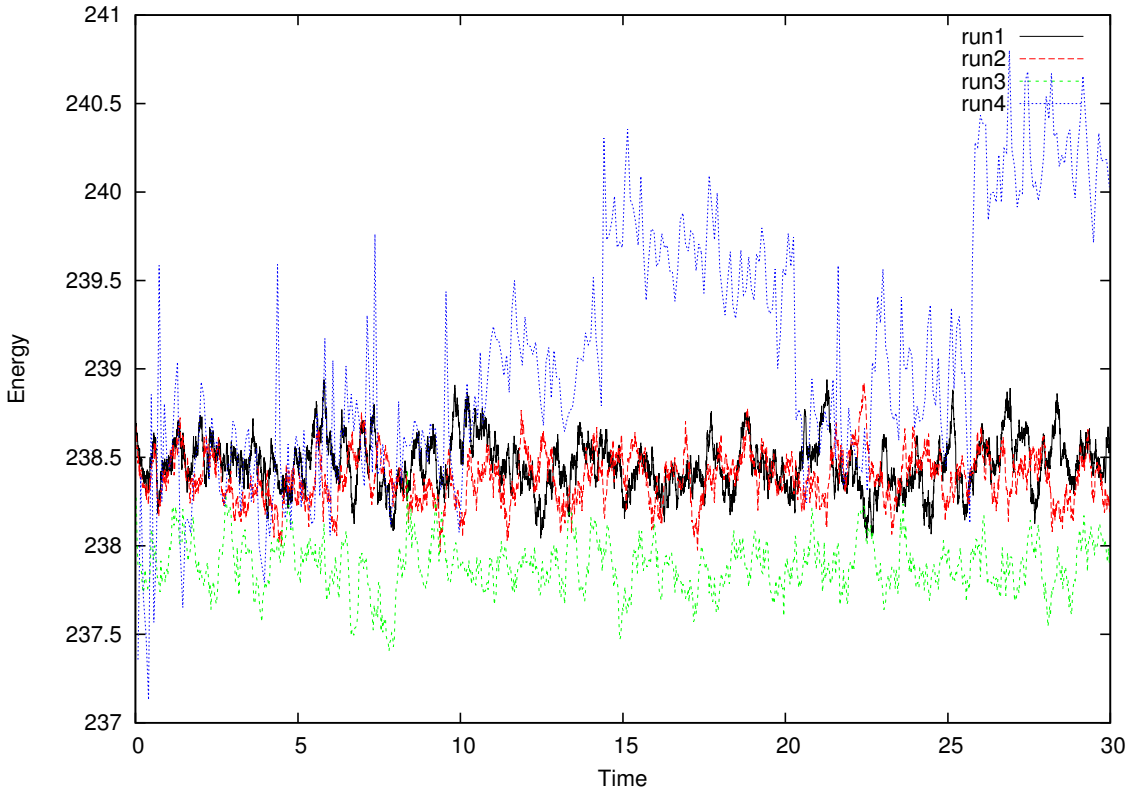

Figure 4: Energy Conservation

2.3 Thermalization

The thermalization of pressure and temperature are shown in Figure 5 and Figure 6, respectively. The pressure and temperature of all the four runs reach equilibrium at an equelibrium time $t^*_{eq} \approx 0.5$

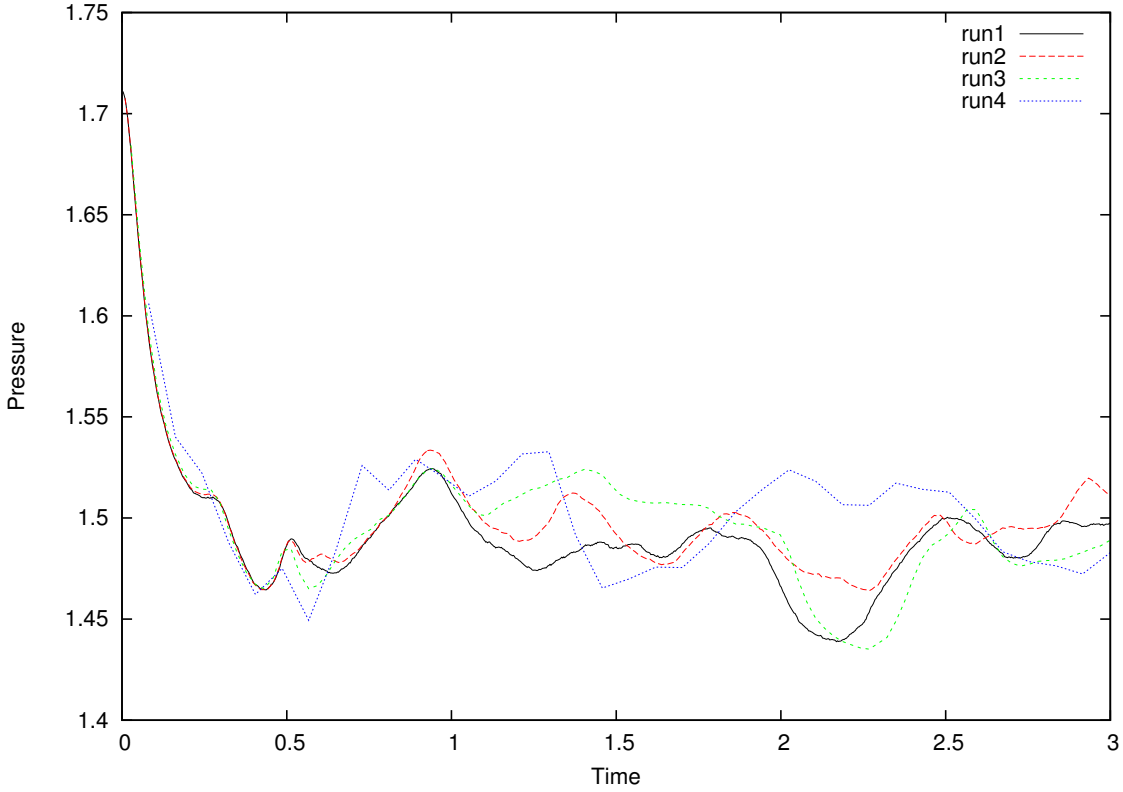

Figure 5: Pressure Thermalization

2.4 Errors and correlations

The average and error after equilibrium of pressure, temperature, and potential energy for the four runs are collected in Table 2. Blocking analysis is used for the computation.

3 Dependence on the starting configuration

Then we generate a new starting configuration, and perform a new molecular dynamics run with a time step 0.009. From the thermalization behaviour of pressure and temperature,

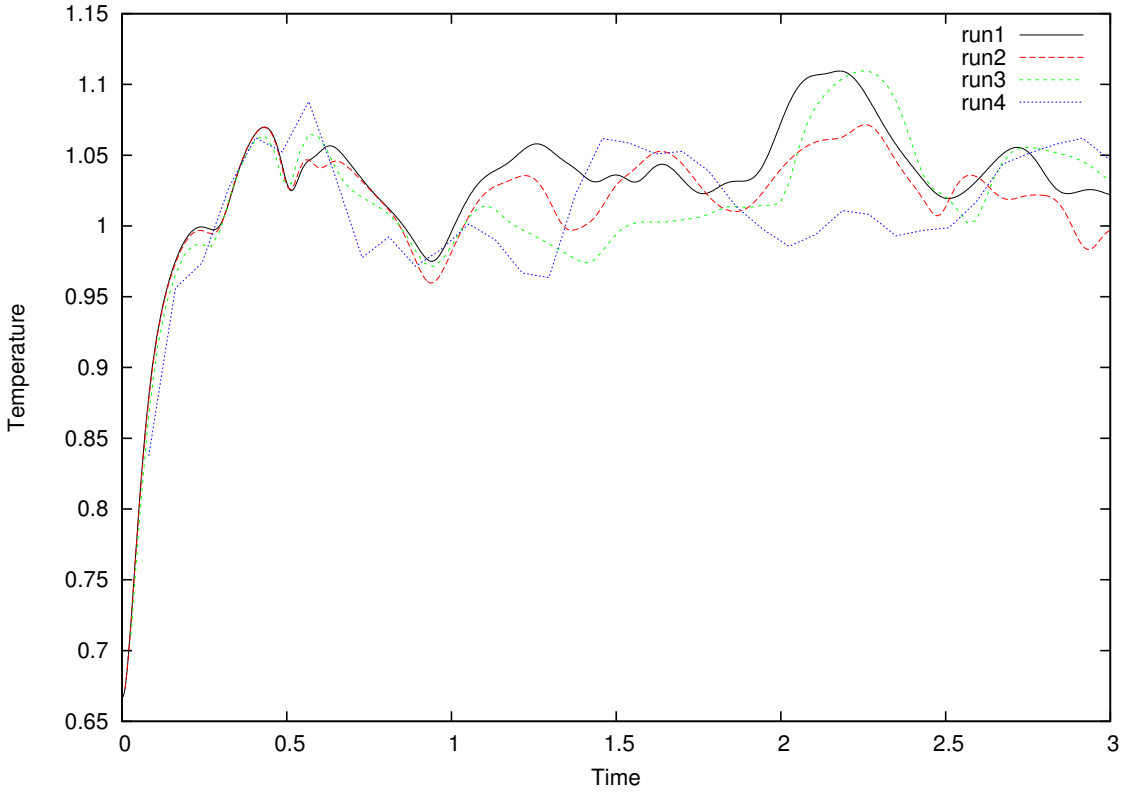

Figure 6: Temperature Thermalization

Table 2: Average and Error of Pressure, Temperature, and Potential

Run	Pressure	σ_P	Temperature	σ_T	Potential	σ_p
1	1.486791	0.001946	1.035526	0.002869	121.964097	0.325954
2	1.491382	0.002296	1.028010	0.003621	122.738961	0.403414
3	1.488568	0.002597	1.028302	0.003831	122.202709	0.434929
4	1.492280	0.002211	1.032828	0.003342	122.877294	0.363085

The equilibrium time is estimated as $t^*_{eq} \approx 0.3$.

The average and error of pressure, temperature, and potential energy are shown in Table 3. The variation in the starting configuration results in a change of the potential and kinetic energy, and accordingly, the pressure and temperature.

Table 3: Average and Error of the new configuration

	Average	Error
Energy	300.725673	0.031950
Pressure	1.528001	0.004997
Temperature	1.523283	0.006643
Potential	129.352790	0.767607