PYU33P15: Statistical Thermodynamics
Continuous Assessment CA3 due 27/10/2021

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JS Theoretical Physics

1.

a.

Since the particles do not interact with each other, the internal energy of the system will simply be the total kinetic energy of the particles and the piston, i.e.

$$U = \frac{m}{2} \sum_{i=1}^{N} v_i^2 + \frac{M\,V}{2}.$$

b.

Enthalpy for a 3D system is defined as

$$H = U + P\,V.$$

For a 1D system, this is analogous to pressure being replaced by force and volume replaced by length. In our system, the force acting on the system is F and the length of the line is simply the distance from the wall to the piston, i.e. X. Thus the enthalpy is given by

$$H = \frac{m}{2} \sum_{i=1}^{N} v_i^2 + \frac{M\,V}{2} + F\,X.$$

c.

Before a collision, the position of the ith particle is given by

$$x_i(t) = x_i^0 + v_i(t)\,(t - t_0).$$

Since the particles do not interact with each other, the velocity of a particle is constant until a collision, i.e. $v_i(t) = v_i^0$. We thus have the equations of motion

$$x_i(t) = x_i^0 + v_i^0\,(t - t_0), \qquad v_i(t) = v_i^0.$$

d.

Since the magnitude of the force is F and the piston pushes from the right, we can consider the velocity of the piston as V in the $+x$ direction and the force on the piston as $-F$ in the $+x$ direction. From Newton's equations of motion we have

$$
\begin{aligned}
-F &= M\,\frac{dV(t)}{dt} && \text{(where acceleration is defined as } \tfrac{dV(t)}{dt}\text{)}\\
\implies V(t) &= -\int_{t_0}^{t} \frac{F}{M}\,dt && \text{(rearranging and integrating with respect to } t\text{)}\\
&= -\frac{F}{M}\,(t-t_0) + c_1 && \text{(computing the integral)}\\
V(t_0) = V^0 \implies c_1 &= V^0 && \text{(substituting } t=t_0 \text{ and noticing the first term vanishes)}\\
\implies V(t) = \frac{dX(t)}{dt} &= -\frac{F}{M}\,(t-t_0) + V_0 && \text{(substituting } c_1\text{, velocity is defined as } \tfrac{dX(t)}{dt}\text{)}\\
\implies X(t) &= \int_{t_0}^{t}\left(-\frac{F}{M}\,(t-t_0) + V^0\right)dt && \text{(integrating with respect to } t\text{)}\\
&= \int_{0}^{t-t_0}\left(-\frac{F}{M}\,t' + V^0\right)dt'\\
& && \text{(defining } t' \equiv t-t_0\text{, and thus } dt'=dt\text{, } t_0 \to t' \text{ and } t \to t-t_0\text{)}\\
&= -\frac{F}{2M}\,(t-t_0)^2 + V^0\,(t-t_0) + c_2 && \text{(computing the integral)}\\
X(t_0) = X^0 \implies c_2 &= X^0 && \text{(substituting } t=t_0 \text{ and noticing the first two terms vanish)}\\
\implies X(t) &= -\frac{F}{2M}\,(t-t_0)^2 + V^0\,(t-t_0) + X^0 && \text{(substituting } c_1\text{)}
\end{aligned}
$$

Thus the equations of motion are

$$
X(t) = -\frac{F}{2M}\,(t-t_0)^2 + V^0\,(t-t_0) + X^0 \qquad\qquad V(t) = -\frac{F}{M}\,(t-t_0) + V^0
$$

e.

We will first consider a right moving particle. If we label the time at which a collision happens as t, then the waiting time for a collision is given by $\tau = t - t_0$. If a particle and the piston collide at time t, they will have the same position at time t. We can thus equate the two equations we have for position and solve for τ, i.e.

$$
\begin{aligned}
x(t) &= X(t)\\
x + v\,\tau &= -\frac{F}{2M}\,\tau^2 + V\,\tau + X && \text{(substituting } x(t)\text{, } X(t) \text{ and } \tau = t-t_0\text{)}\\
0 &= \frac{F}{2M}\,\tau^2 - (V-v)\,\tau + (x-X) && \text{(rearranging)}\\
\tau &= \frac{-(-(V-v)) \pm \sqrt{(-(V-v))^2 - 4\left(\frac{F}{2M}\right)(x-X)}}{2\left(\frac{F}{2M}\right)}\\
& && \text{(using } x = \tfrac{-b\pm\sqrt{b^2-4ac}}{2a} \text{ for } a\,x^2 + b\,x + c = 0\text{)}\\
&= \frac{M}{F}\left(V - v \pm \sqrt{(V-v)^2 - 2\frac{F}{M}\,(x-X)}\right) && \text{(simplifying)}
\end{aligned}
$$

Since the equation for τ is quadratic, it is natural that there can be two possible values of τ where the particles collide. If we have that $v \geqslant V$, then to have positive τ we must have a positive square root. If we have $v < V$ then we must compare the square root term with the non-square root term. Label $\alpha \equiv V - v$. Since $x < X$ at any point in time, we can label $\beta \equiv -2\frac{F}{M}\,(x-X) > 0$ since $X > x$. Inside the brackets we then have $\alpha \pm \sqrt{\alpha^2 + \beta}$. Since $\beta > 0$, we know that $\sqrt{\alpha^2+\beta} > \alpha$, and so to avoid having a negative result for τ we must take the positive square root, i.e.

$$
\tau = \frac{M}{F}\left(V - v + \sqrt{(V-v)^2 - 2\frac{F}{M}\,(x-X)}\right)
$$

If we now have a left moving particle, we can construct an analogous problem where. Since the particle bounces elastically off of the wall, it will have the same speed when it bounces back. We can thus instead consider a similar problem where the piston is moved to the other side of the wall and acts in the $+x$ direction, and the wall is removed, as the particle and piston will travel the same distance in this alternative problem. The change of problems is equivalent to the transformation $F \to -F$, $V \to -V$, and $X \to -X$. We can derive the equation in a similar manner, i.e.

$$\begin{aligned}
x(t) &= X(t) && \text{(as before)} \\
x + v\,\tau &= \frac{F}{2M}\,\tau^2 - V\,\tau - X && \text{(as before but with } F \to -F,\ V \to -V, \text{ and } X \to -X) \\
0 &= \frac{F}{2M}\,\tau^2 - (V+v)\,\tau - (x+X) && \text{(rearranging)} \\
\tau &= \frac{-(-(V+v)) \pm \sqrt{(-(V+v))^2 - 4\left(\frac{F}{2M}\right)(-(x+X))}}{2\left(\frac{F}{2M}\right)} \\
& && \text{(using } x = \tfrac{-b\pm\sqrt{b^2-4ac}}{2a} \text{ for } a\,x^2 + b\,x + c = 0) \\
&= \frac{M}{F}\left(V + v \pm \sqrt{(V+v)^2 + 2\frac{F}{M}\,(x+X)}\right) && \text{(simplifying)}
\end{aligned}$$

Similarly to before, if we take the negative square root we result in a negative waiting time, which is unphysical. Thus we have for a left moving particle

$$\tau = \frac{M}{F}\left(V + v + \sqrt{(V+v)^2 + 2\frac{F}{M}\,(x+X)}\right) \qquad \text{(simplifying)}$$

f.

Since collisions are elastic, we can use the principles of conservation of momentum and energy to find expressions for w and W. First consider a right moving particle.

$$\begin{aligned}
m\,v + M\,V &= m\,w + M\,W && \text{(conservation of momentum)} \\
M\,(W - V) &= m\,(v - w) && \text{(rearranging)} \\
W &= V + \frac{m\,(v-w)}{M} && \text{(rearranging)}
\end{aligned}$$

$$
\begin{aligned}
\frac{m\,v^2}{2} + \frac{M\,V^2}{2} &= \frac{m\,w^2}{2} + \frac{M\,W^2}{2} && \text{(conservation of energy)}\\
m\,v^2 + M\,V^2 &= m\,w^2 + M\left(V^2 + \frac{2m\,V\,(v-w)}{M} + \frac{m^2\left(v^2 - 2v\,w + w^2\right)}{M^2}\right)\\
& && \text{(multiplying across by 2, substituting } W \text{ obtained above and computing } W^2\text{)}\\
M\,v^2 &= M\,w^2 + 2M\,v\,V - 2M\,w\,V + m\,v^2 - 2m\,v\,w + m\,w^2\\
& && \text{(expanding, cancelling } M\,V^2 \text{ from both sides and multiplying across by } \tfrac{M}{m}\text{)}\\
0 &= (M+m)\,w^2 - 2\,(M\,V + m\,v)\,w + \left(m\,v^2 + 2M\,v\,V - M\,v^2\right) && \text{(rearranging to get a quadratic in } w\text{)}\\
w &= \frac{2(M\,V + m\,v) \pm \sqrt{4\,(M^2\,V^2 + 2m\,M\,v\,V + m^2\,v^2) - 4(M+m)\,(m\,v^2 + 2M\,v\,V - M\,v^2)}}{2(M+m)}\\
& && \text{(using } x = \tfrac{-b\pm\sqrt{b^2-4ac}}{2a} \text{ for } a\,x^2 + b\,x + c = 0\text{)}\\
&= \frac{M\,V + m\,v \pm \sqrt{M^2\,V^2 + 2m\,M\,v\,V + m^2\,v^2 - m\,M\,v^2 - m^2\,v^2 - 2M^2\,v\,V - 2m\,M\,v\,V + M^2\,v^2 + m\,M\,v^2}}{m+M}\\
& && \text{(expanding and simplifying)}\\
&= \frac{M\,V + m\,v \pm \sqrt{M^2\,(V^2 - 2v\,V + v^2)}}{m+M} && \text{(cancelling and factoring)}\\
&= \frac{M\,V + m\,v \pm M\sqrt{(V-v)^2}}{m+M} && \text{(simplifying)}\\
&= \frac{M\,V + m\,v \pm (M\,V - M\,v)}{m+M} && \text{(simplifying)}
\end{aligned}
$$

$$
\begin{aligned}
w &= \frac{M\,V + m\,v + M\,V - M\,v}{m+M} & w &= \frac{M\,V + m\,v - M\,V + M\,v}{m+M} && \text{(taking each of + and −)}\\
&= \frac{2M\,V + (m-M)\,v}{m+M} & &= v && \text{(simplifying)}
\end{aligned}
$$

The first case corresponds to the particle colliding with the piston and bouncing back, whereas the second case corresponds to the particle passing right through the piston without colliding. Although both of these cases conserve momentum and energy, only the first is realistic, and so we take this as w. Substituting this into our expression for W obtained earlier gives

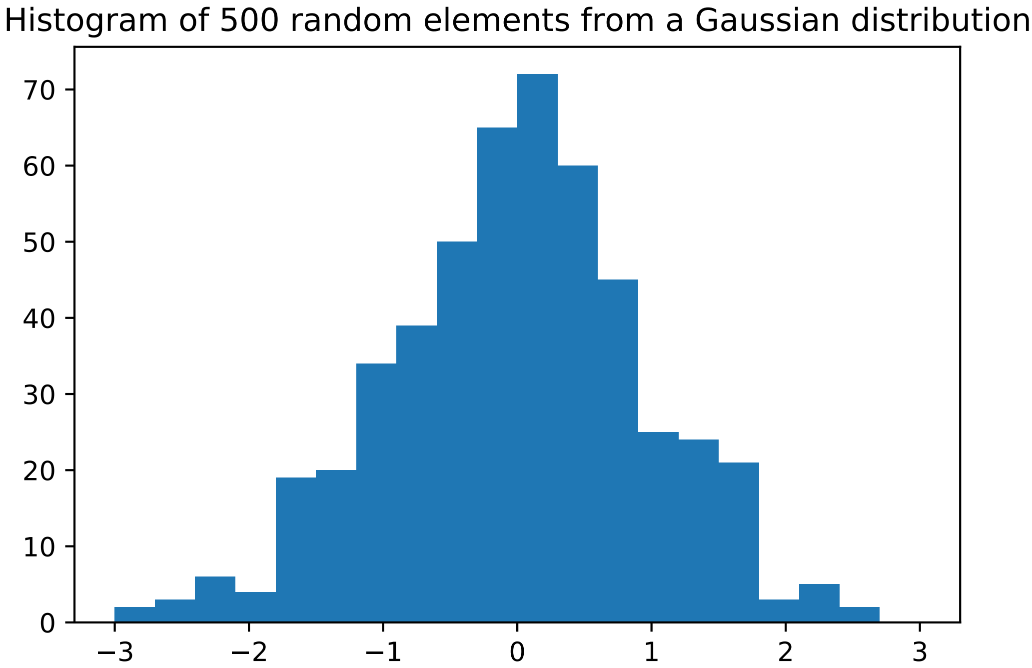
$$
\begin{aligned}
W &= V + \frac{m\,(v-w)}{M} && \text{(expression for } W \text{ obtained before)}\\
&= V + \frac{m}{M}\left(v - \frac{2M\,V + (m-M)\,v}{m+M}\right) && \text{(substituting } w\text{)}\\
&= V + \frac{m}{M}\left(\frac{m\,v + M\,v - 2M\,V - m\,v + M\,v}{m+M}\right) && \text{(simplifying into one fraction)}\\
&= V + \frac{2m\,v - 2m\,V}{m+M} && \text{(cancelling } mv \text{ and bringing the factor into the fraction)}\\
&= \frac{m\,V + M\,V + 2m\,v - 2m\,V}{m+M} && \text{(simplifying into one fraction)}\\
&= \frac{2m\,v + (M-m)\,V}{m+M} && \text{(simplifying)}
\end{aligned}
$$

As before, if we instead consider a left moving particle, we can simply switch the signs of V and W to mimic the problem of the piston on the other side of the wall. We thus get

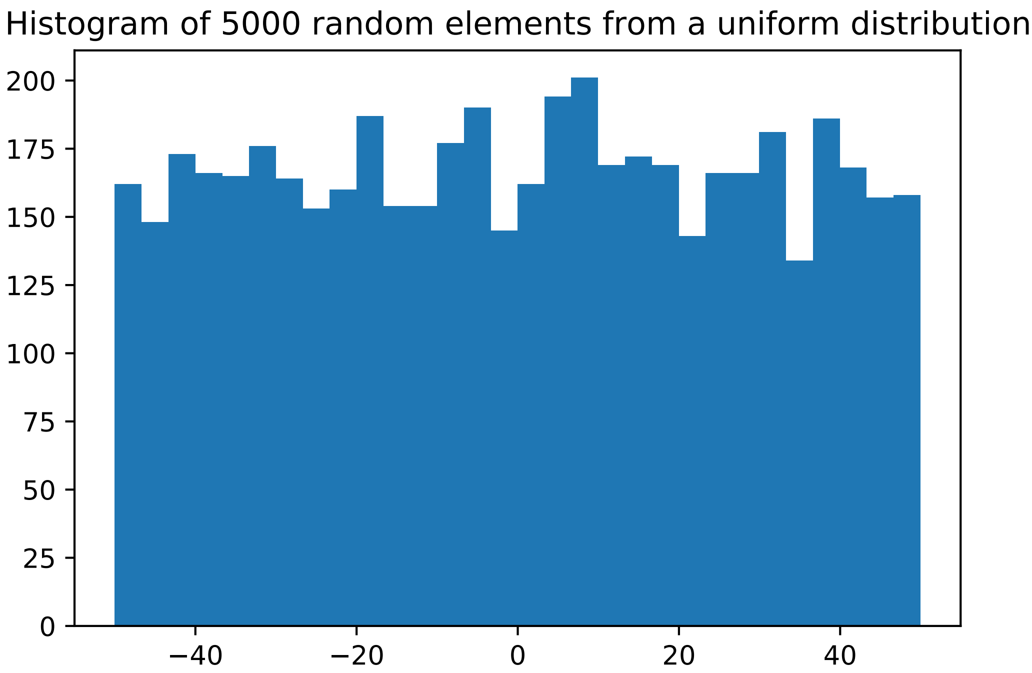
$$
\begin{aligned}
w &= \frac{-2M\,V + (m-M)\,v}{m+M} & -W &= \frac{2m\,v - (M-m)\,V}{m+M} && \text{(switching signs of } V \text{ and } W\text{)}\\
& & \implies W &= \frac{-2m\,v + (M-m)\,V}{m+M} && \text{(simplifying)}
\end{aligned}
$$

2.

c.


Histogram of 500 random elements from a Gaussian distribution
0
10
20
30
40
50
60
70
−3
−2
−1
0
1
2
3

e.


Histogram of 5000 random elements from a uniform distribution
0
25
50
75
100
125
150
175
200
−40
−20
0
20
40

3.

a.

From the 3D ideal gas law

$$P\,V = N\,k_B\,T$$

we can change pressure to force and volume to position to obtain the 1D ideal gas law

$$F\,X = N\,k_B\,T.$$

Since the length of the system is simply the piston position, we can rearrange for X and substitute the given values to find the starting position

$$X_0 = 2\,\frac{N\,k_B\,T_0}{F}.$$

From assuming

$$\frac{m\,v^2}{2} = \frac{k_B\,T}{2}$$

for each particle, we can rearrange to find the average square of velocity

$$\langle v^2 \rangle = \frac{k_B\,T}{m}.$$

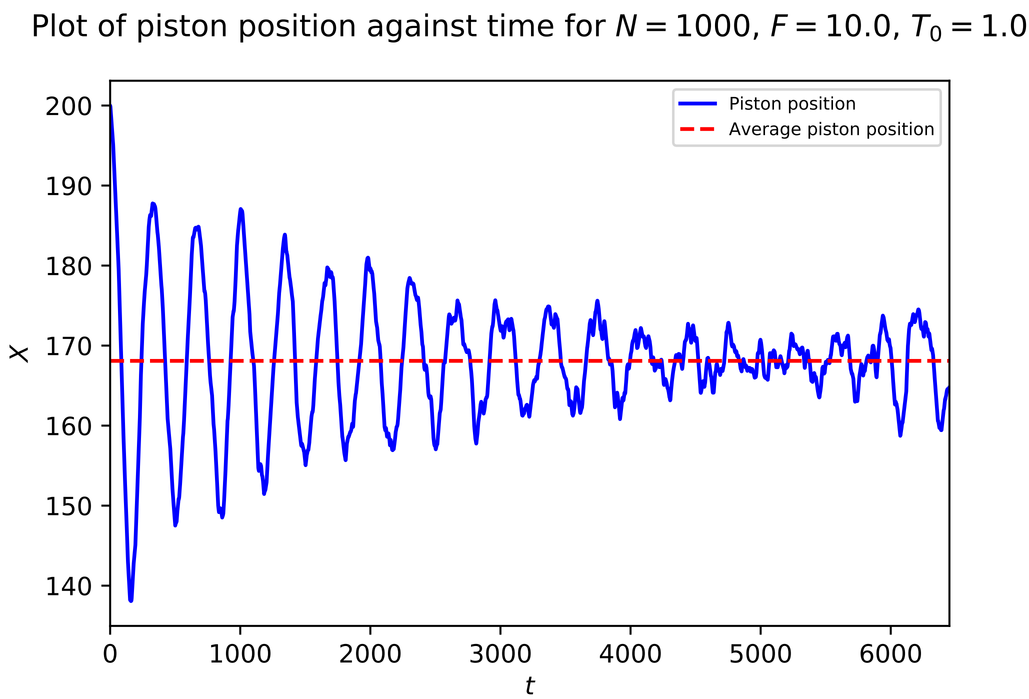
For this simulation, we want to initially have the particles travelling in both directions, the mean of the velocity distribution should be at 0. For a Gaussian distribution $G(x)$, the expected value of x^2 is simply the square of the standard deviation, i.e.

$$\langle x^2 \rangle = \sigma^2.$$

Thus the standard deviation of the velocity distribution is

$$\sigma = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{k_B\,T}{m}}.$$

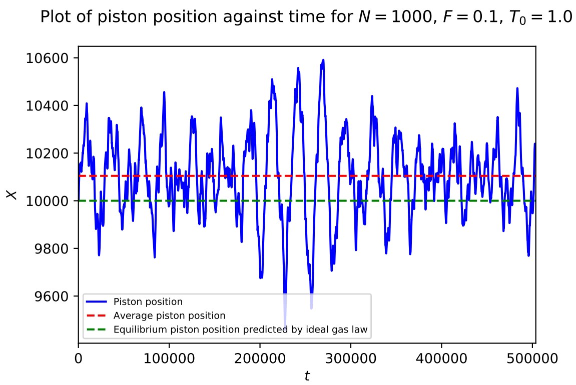
The following graphs of piston position against time were plotted:

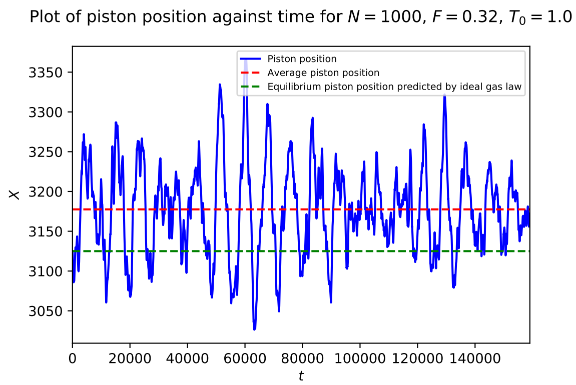


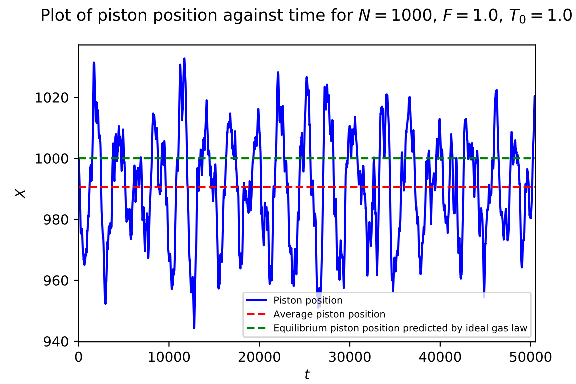
Here we can see that the piston tends to an equilibrium position of approximately 168. This is not the equilibrium position predicted by the ideal gas law for $T_0 = 1$ as, since we do not start at an equilibrium position, the piston contracting will increase the temperature of the system and thus change the equilibrium position.

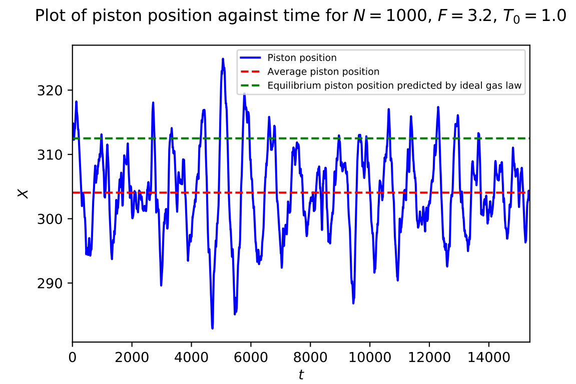
b.

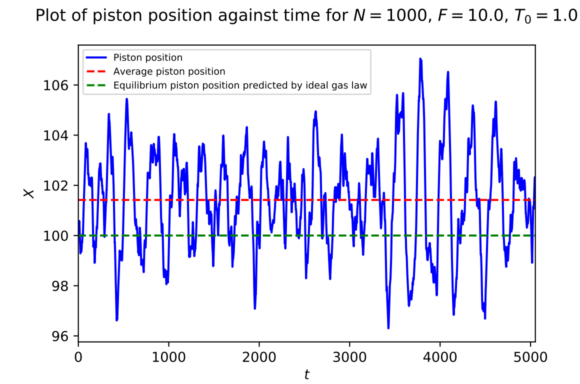
For $F = 0.1, 0.32, 1, 3.2, 10, 32, 100$, the following graphs of piston position against time were plotted:

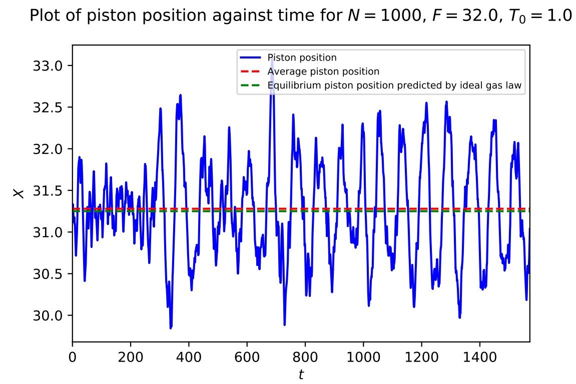


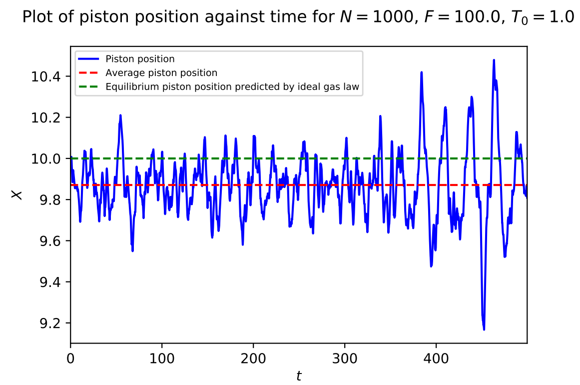




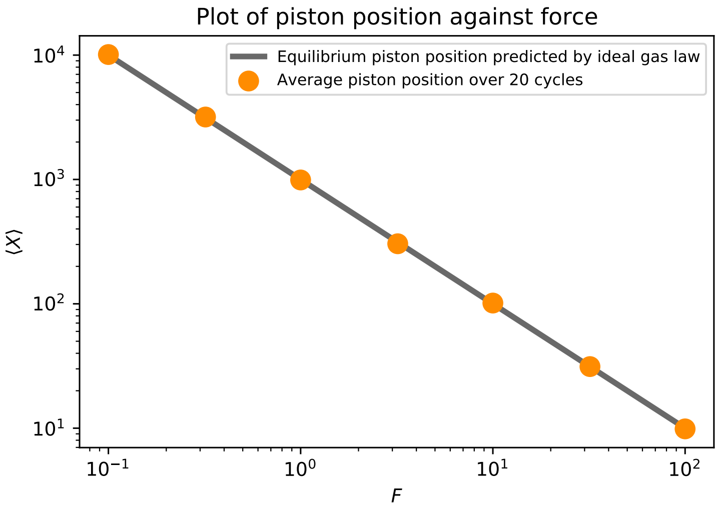








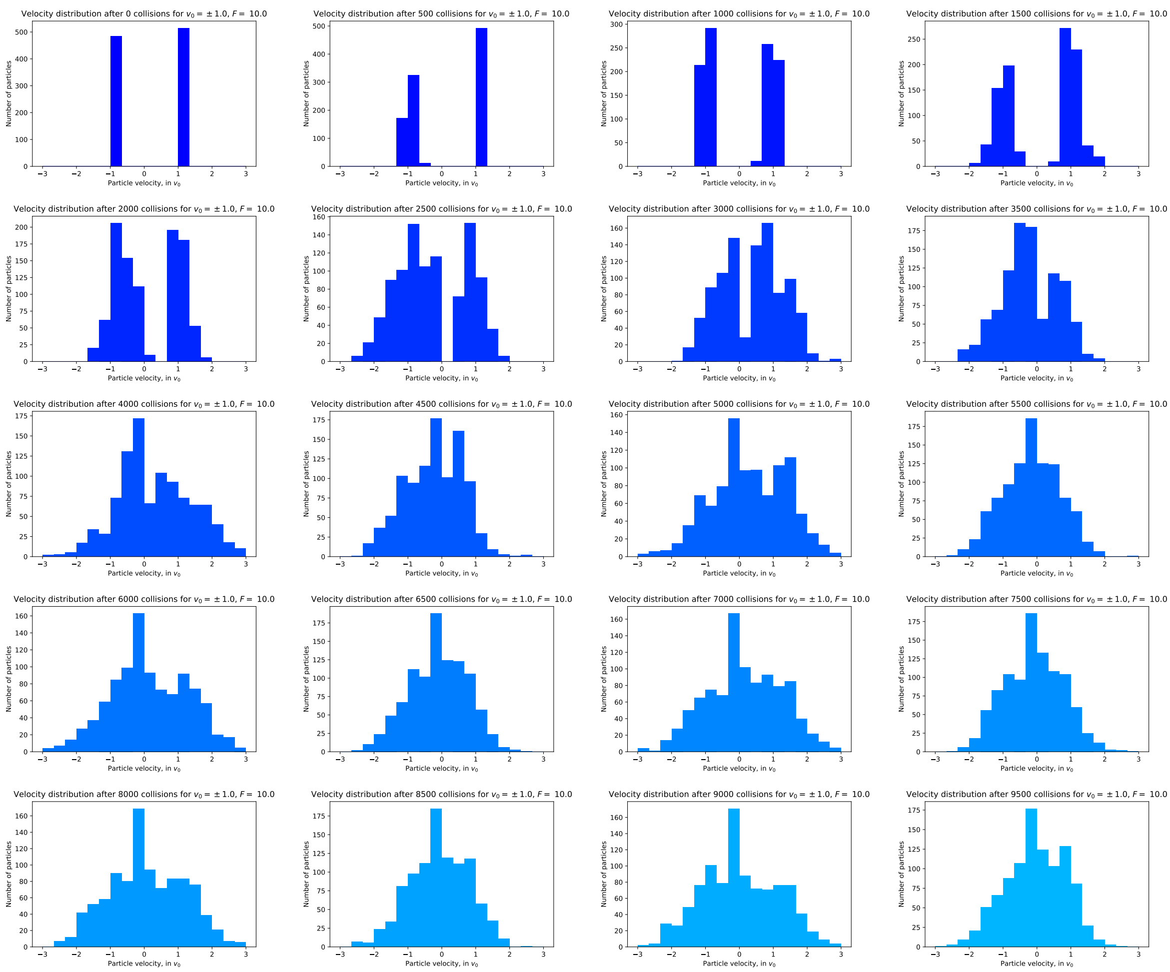
The following graph of average position and expected equilibrium position against force was plotted:

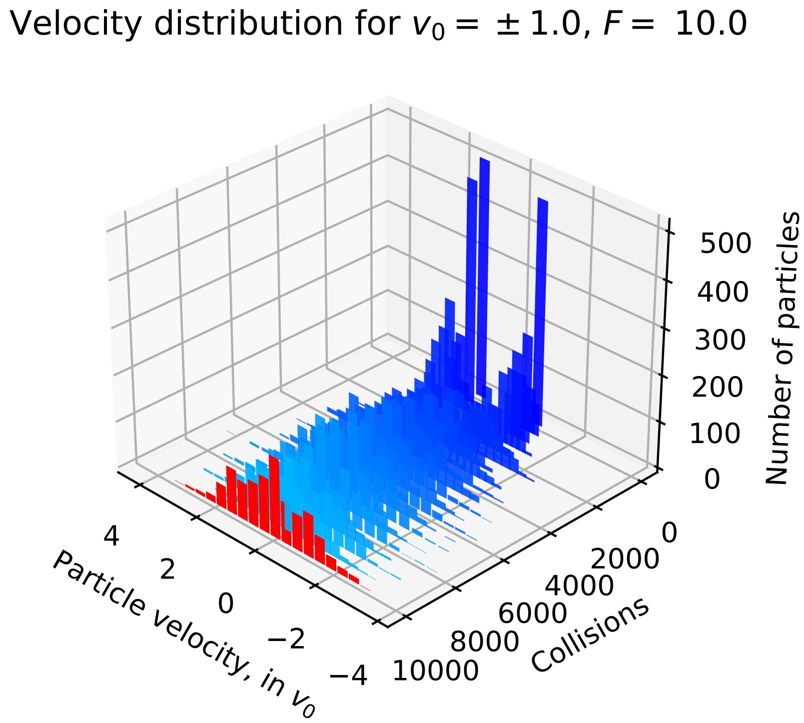


From these graphs we can see that the programmed simulation matches the case for the ideal graph to a high degree of accuracy.

c.

The following graphs of the velocity distribution after certain collisions were plotted:



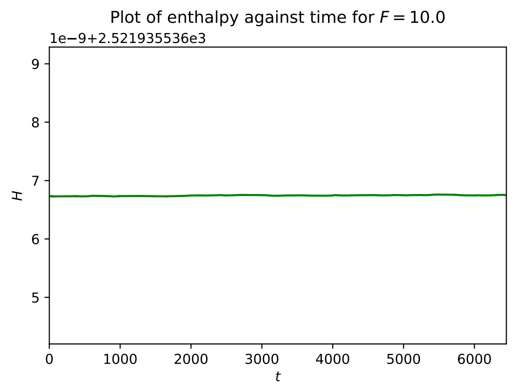


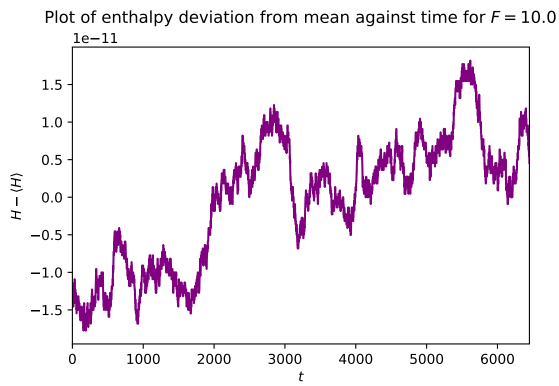
From these graphs we can see that, starting with a particle speed of v_0, the velocity distribution tends to a Maxwell distribution.

d.

i.

The following graph of enthalpy and enthalpy deviation from mean against time were plotted (for the same simulation as in 3. a.):

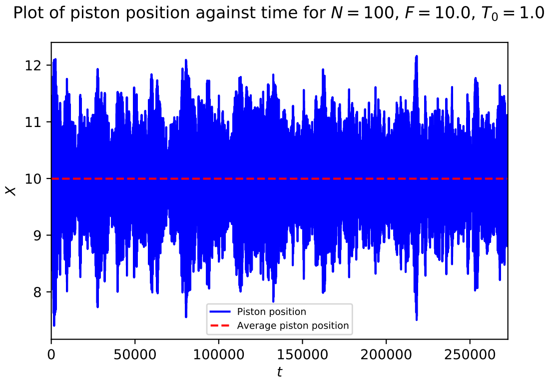


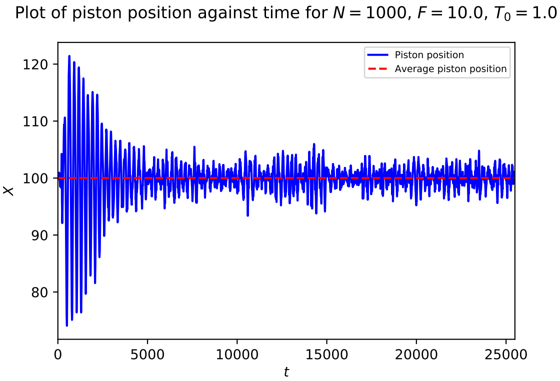


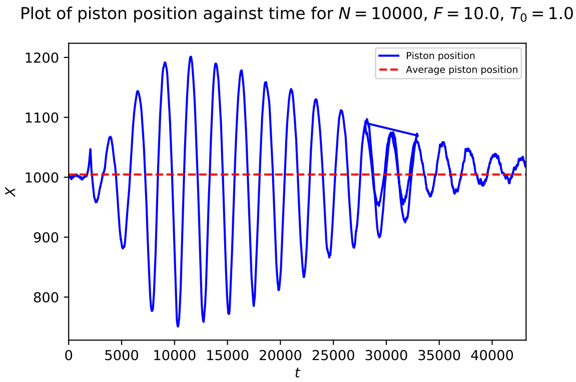
From these graphs we can see that the enthalpy of the system is approximately constant to a high degree of accuracy (deviation of 10^{-11} from a constant 2.5×10^3).

iii.

The following graphs of piston position against time for various number of particles were plotted:







For 100 particles, even after 500000 collisions or roughly 5000 cycles the system does not seem to asymptote to an equilibrium position. This is likely due to the fact that the system does not contain many particles and thus is not a good model of an ideal gas.

For 1000 particles, the piston fluctuates quite a lot for the first 10 cycles or 5000 units of time, after which it only fluctuates a small amount. This is a better model of an ideal gas, but it is clearly not an excellent one due to the remaining fluctuation.

For 10000 particles, I was only able to compute the piston position for 200000 collisions or 20 cycles. We can clearly see that this system is the best model of an ideal gas of the three, which is to be expected due to the number of particles in the system. If I had the computing power, it could easily be shown that the system asymptotes to the predicted equilibrium position after sufficient time. (The straight line between peaks is due to a small error in my code, and I did not have enough time to run the code again)

iv.

One could add interaction between particles by considering Van der Waals forces. If we give each particle a radius r, then the force on each particle is given by[1]

$$f(x_i) = -\frac{A\,r}{12}\sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{1}{(x_i - x_j)^2},$$

where A is the Haymaker coefficient. This force can be approximated by only considering adjacent particles interacting with each other, rather than all particles in the system. Since this force is non-constant, we cannot simply find the equations of motion as we did for the piston. One way we could get around this is by taking very small time steps over which we assume the force is constant and find the positions and velocities of each particle after each of these timesteps and checking after each time step if a collision has occurred, as the expression for the waiting time would be quite complicated.

[1] H. C. Hamaker, Physica, 4(10), 1058–1072 (1937)