Simulation of 2D Gas Under Constant Pressure

Abstract

This paper explores how classical ideal gas can be computationally modelled, using an event driven molecular dynamics method in 2D with a small number of particles, on the scale of 10^3. The gas is treated under constant pressure using a piston. The results show that the P, V, T and N follow the relationship that the ideal gas law predicts. For reasonable quantitative results the simulation would need to be extended to three dimensions and the number of particles to larger scales.

Introduction

Molecular dynamics modelling is used to analyse how atoms and molecules move while interacting with each other, to determine the dynamical evolution of a system. It has a wide range of uses from simulating biological processes, to uses in materials science for modelling bulk properties of matter from its microscopic properties.

This paper will investigate how gas molecules behave in an enclosed system in two dimensions. The enclosed system is a container with fixed side walls and base, while the top wall is a frictionless piston that can move up or down. (Figure 1) The molecules will be treated as point like particles, carrying all of their energy in translational motion and they do not interact with each other. The gravitational force only acts on the piston, and collisions between the particles, walls and the piston are treated as ideal elastic collisions. Because the gas molecules are treated similarly to the classical ideal gas model the simulation is expected to behave according to what the ideal gas law would suggest. Given a larger initial speed, or equivalently, higher temperature, from the kinetic theory of gases, the particles are expected to occupy more space, hence the piston should remain at a higher position.

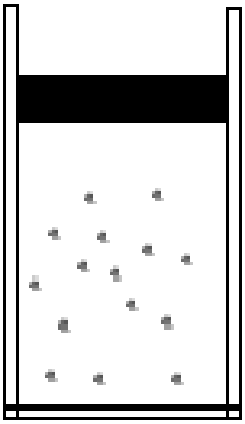

Figure 1. The system.

Theory

The ideal gas law states the connection between the pressure, volume, temperature and number of particles in a gas. [1]

$$PV = nRT = nk_bN_AT \tag{1}$$

Where P is the pressure of the gas, V is the volume, n is the number of moles and T is the temperature. R, k_b and N_A are constants. Since the simulation is in two dimensions and the number of particles is at most a few thousand the model cannot be tested using the exact equation. Instead, set $R = k_b = N_A = 1$, use A, the area of the container, in place of V. And use N, the total number of particles in the system in place of n. Now the general relationship between these state variables is the following:

$$A \propto \frac{N\,T}{P} \tag{2}$$

Since the width of the container is constant and P is linearly proportional to M, the mass of the piston, this can be further simplified to:

$$h \propto \frac{N\,T}{M} \tag{3}$$

Where h is the distance between the piston and the base of the container. This is the general relationship that will be tested in the results section of this paper.

Using the kinetic theory of gases, the temperature and mass of the gas particles can be related to the speed distribution of the particles by the Maxwell-Boltzmann speed distribution in 2D. [2]

$$p(s) = \frac{ms}{k_B T} e^{-\frac{ms^2}{2k_B T}} \tag{4}$$

From this, it can be show that the velocity distribution is (REF)

$$p(v_i) = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\frac{m{v_i}^2}{2k_B T}} \tag{5}$$

Which is a normal distribution with mean $\mu_i = 0$ and standard deviation $\sigma_{v_i} = \sqrt{\frac{k_B T}{m}}$. This equation will be used to initialise the speed of the particles for a given temperature T and mass m.

As mentioned before, the collisions between the particles the walls and the piston are ideal elastic collisions, so the law of conservation of energy and the law of conservation of momentum can be applied. For a general collision problem these laws can be written: [3]

$$\frac{1}{2}m_1 v_{1i}^2 + \frac{1}{2}m_2 v_{2i}^2 = \frac{1}{2}m_1 v_{1i}^2 + \frac{1}{2}m_2 v_{2i}^2 \tag{6}$$

$$m_1 \vec{v}_{1i} + m_2 \vec{v}_{2i} = m_1 \vec{v}_{1f} + m_2 \vec{v}_{2f} \tag{7}$$

When the collision happens with one of the walls, the particle's velocity, tangential to the wall, is conserved since the wall doesn't exert tangential forces. The velocity component normal to the wall is reversed due to energy conservation.

$$v_{1i}^{tan} = v_{1f}^{tan} \tag{8}$$

$$v_{1i}^{norm} = -v_{1f}^{norm} \tag{9}$$

When the particles collide with the piston the tangential component of its velocity is again conserved, for the same reason.

$$v_{1i}^{tan} = v_{1f}^{tan} \tag{10}$$

For the piston there is no sideways motion. So normal component of the particle's velocity can be treated as a one-dimension collision problem between the particle and the piston. So

$$v_f = \frac{m-M}{m+M} v_i + \frac{2M}{m+M} V_i \tag{11}$$

$$V_f = \frac{2m}{m+M} v_i - \frac{m-M}{m+M} V_i \tag{12}$$

[4] Where v_i and v_f are the initial and final normal velocity component of the particle and m is its mass. V_i and V_f are the initial and final velocity of the piston and M is the piston's mass.

Method

The simulation uses an event driven approach. Each molecule has a randomly initialised starting position,(x_i, y_i) and velocity components (v_{xi}, v_{yi}), initialised using equation 5. A typical speed distribution for the particles is on Figure 2.

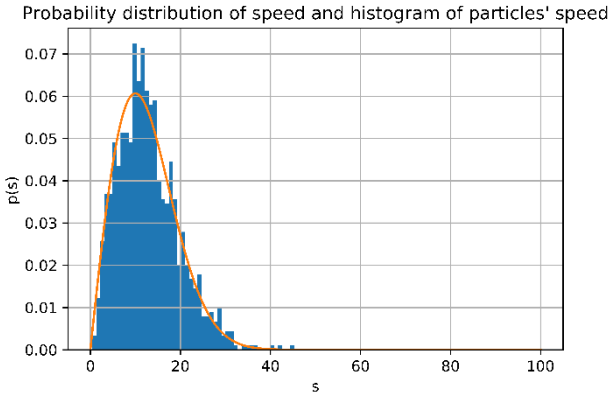

Figure 2. Maxwell-Boltzmann peed distribution.

From these values, Δt_i, the time for a particle to reach a boundary, is calculated for every particle. Since the molecules don not experience gravitational acceleration, and do not collide with each other, they move in a straight line. This means that the time until they reach one of the side walls, or the base, can be calculated using

$$\Delta t = \frac{\Delta x}{v_x} \qquad \Delta t = \frac{\Delta y}{v_y} \tag{13}$$

When the molecule is travelling towards the piston the piston's motion must be accounted for which follows the equation

$$h = h_0 + V\Delta t + v_y \frac{g}{2} \Delta t^2 \tag{14}$$

h is the distance of the piston from the base. Equating this to the molecule's equation of motion

$$v_y t + y_0 = h_0 + Vt + \frac{g}{2} t^2 \tag{15}$$

From which

$$\Delta t = \frac{-(V - v_y) \pm \sqrt{(V - v_y)^2 - 2g(h_0 - y_0)}}{g} \tag{16}$$

Next, Δt_i, the solution to equation 16, is calculated for every molecule, and the simulation is stepped forward with the minimum value of Δt_i. At each new timestep the position and velocity of every particle and the piston are recalculated after Δt. For the particle that Δt_i belongs to, either equation 8 and 9 or equation 10 and 11 are applied to recalculate its velocity components, depending on if the particle hit the piston or a wall. If the particle collided with the piston the piston's velocity is also recalculated using equation 12.

The simulation can be represented by a simple flow chart diagram. (Figure 3.) First the necessary parameters are initialised, the temperature, number of particles, mass of a particle, mass of the piston and the number of steps to run the simulation for, this will be represented by N_{steps}. A typical value for this is from 5000 to 50 000.

Next, the code enters the main loop, which executes one step of the simulation every iteration. In the main loop, first the calc_hit_time() function is called which calculates Δt for every particle with every enclosing surface using equation 13 and 16. The function returns the minimum Δt, True of False, specifying whether the hit is with the piston or not, and the particle's number in the storage arrays, storing the positions and velocities of the particles. Next the positions of the particles, the piston and the piston's velocity are recalculated Δt later. Then depending on whether the particle hit a wall or the piston the new velocity is recalculated. After that, data, that is necessary for future plotting, is saved and the next iteration begins.

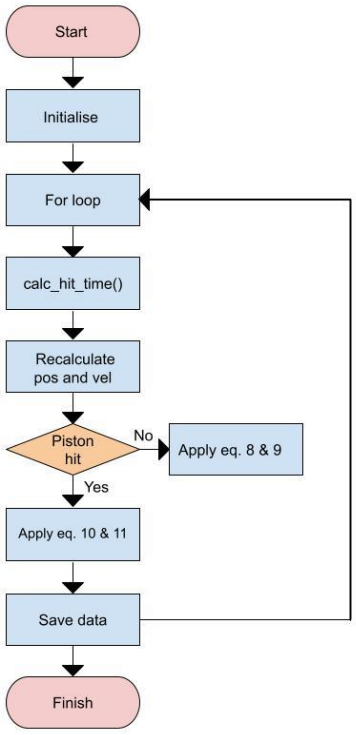

Figure 3. Flow chart diagram of the simulation.

One problem with this time sliced method is that the value of Δt decreases sharply with higher temperatures. This is because for higher temperatures particles have higher initial speeds, so they reach the boundaries in shorter times. This limitation had its largest effect on creating plots for high temperatures as those required a larger number of timesteps to reach the same elapsed time in the simulation. These simulations would run for more than an hour for 60s simulation time.

Results

The behaviour of the model can be tested by changing the initial parameters and investigating how the system reacts to it. The main parameters are the temperature T, the number of particles N, the mass of the piston M, and the mass of a particle m. As mentioned in the theory section, the model is expected to behave similarly to what the ideal gas law would suggest.

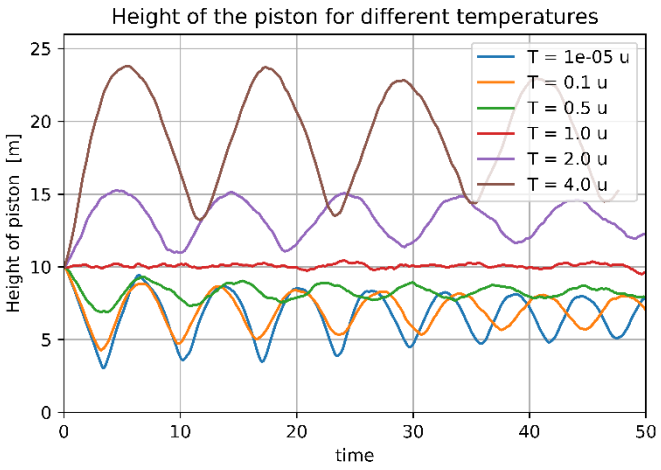

Figure 4. (m=0.1, M=10, N =1000)

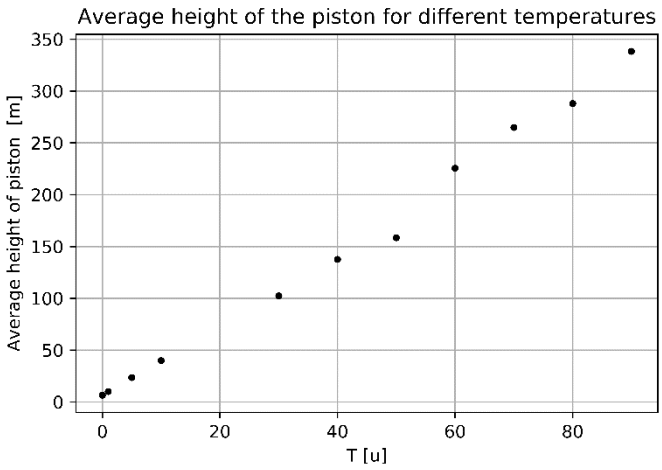

Figure 5. (m=0.1, M=10, N=1000)

First investigating how the system reacts to different temperatures, the average height of the piston scales linearly with T (Figure 5), which is also what equation 3. suggests, note that this is not always as clear as this plot, particularly for high temperatures N_{steps} needs to be much higher to get reasonable results. The higher average height for higher temperature is due to the relationship between the particles speeds and temperature (equation 4), higher temperature leads to higher average particle speeds which leads to more frequent collisions and a larger force exerted on the piston, as the change of momentum is larger. On figure 4 the height of the piston is shown against time. Even for close to zero temperatures the piston seems to remain relatively heigh, which doesn't agree with the ideal gas law. This is due to the way the particles are initialised. Even for $T = 0$ the particles are distributed from the bottom of the container up to the piston, so when the piston starts accelerating downwards it collides with the particles on its way down and loses energy while the particles gain kinetic energy. Figure 4 also shows that the further away the piston's starting position is from its equilibrium the higher it will be oscillating and the longer it takes to reach equilibrium.

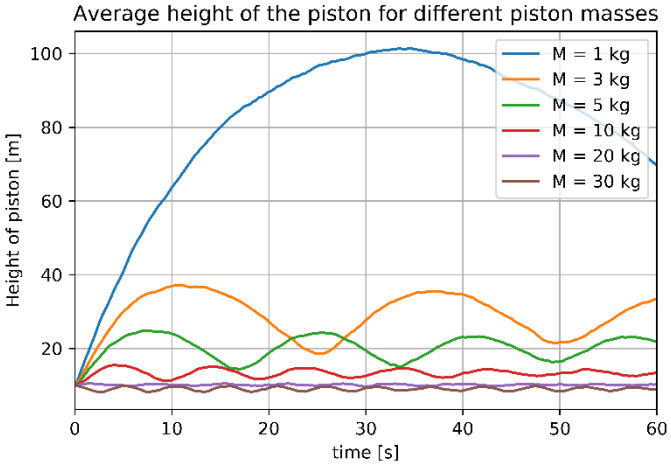

Figure 6. (m=0.1, T=2, N=1000)

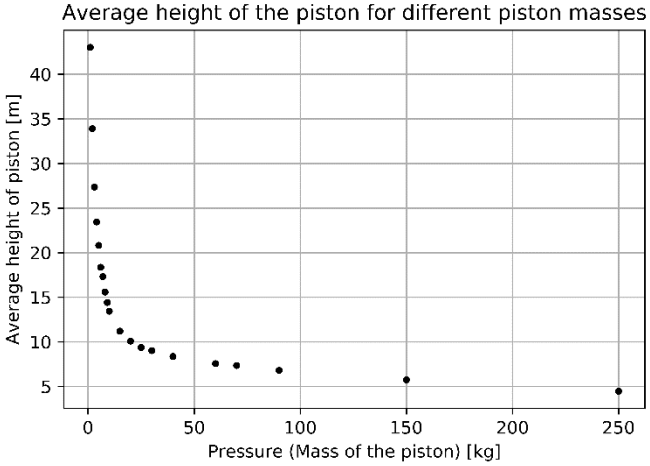

Figure 7. (m=0.1, T=2, N=1000)

Varying the mass of the piston, which corresponds to varying the pressures, shows that a lower mass generally means a higher piston position (Figure 6.) and the hyperbolic relationship between the M and h can be seen on Figure 6. Even for low N_{steps} this hyperbolic relation is generally visible. This inverse relationship could be explained by comparing two cases, two pistons with different masses, while every other parameter is the same. The piston with higher mass would generally "feel" similar forces as a piston with lower mass, but Newton's second law states that an object's acceleration is inversely proportional to its mass, so the lower mass piston will have a higher acceleration and this higher acceleration explains the larger oscillations for smaller masses on Figure 6. The larger acceleration also means that to reach an equilibrium, the frequency of the collisions must drop lower compared to the high mass piston, which is achieved by a less dense gas, or equivalently, higher average height of the piston, as shown on Figure 7.

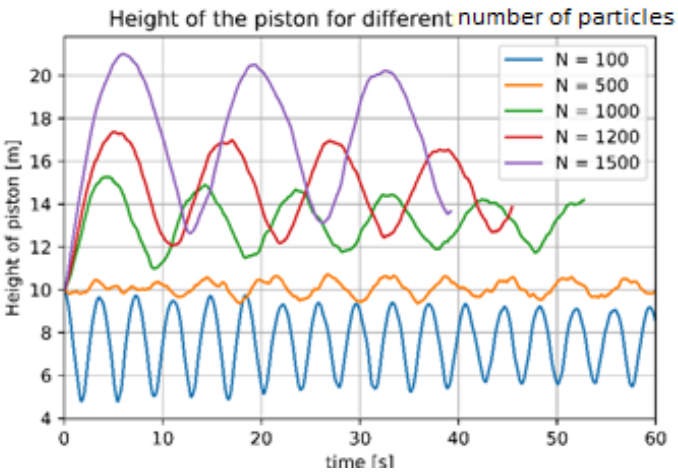

Figure 7. (m=0.1, T=2, M=10)

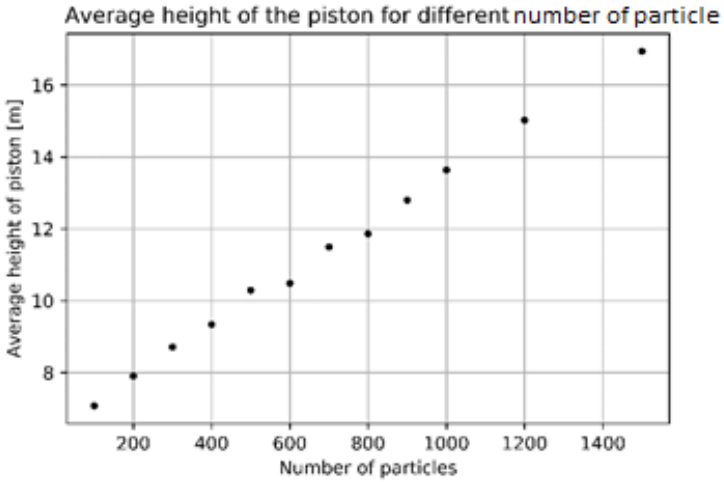

Figure 8. (m=0.1, T=2, M=10)

For a changing number of particles, the general linear relationship between h and N is seen on Figure 8, which also follows equation 3. This can be explained similarly to the previous cases. For two systems with the exact same initial parameters, but different number of particles, the system with less particles will initially have less frequent collisions with the piston until the density of the particles increases. This increase in density of particles will only happen, if the volume, or in our case, area decreases, which means that the height of the piston decreases compared to the higher number of particles system.

Snapshots of the system after N_{steps} for a general run. The oscillation of the piston is clearly visible.

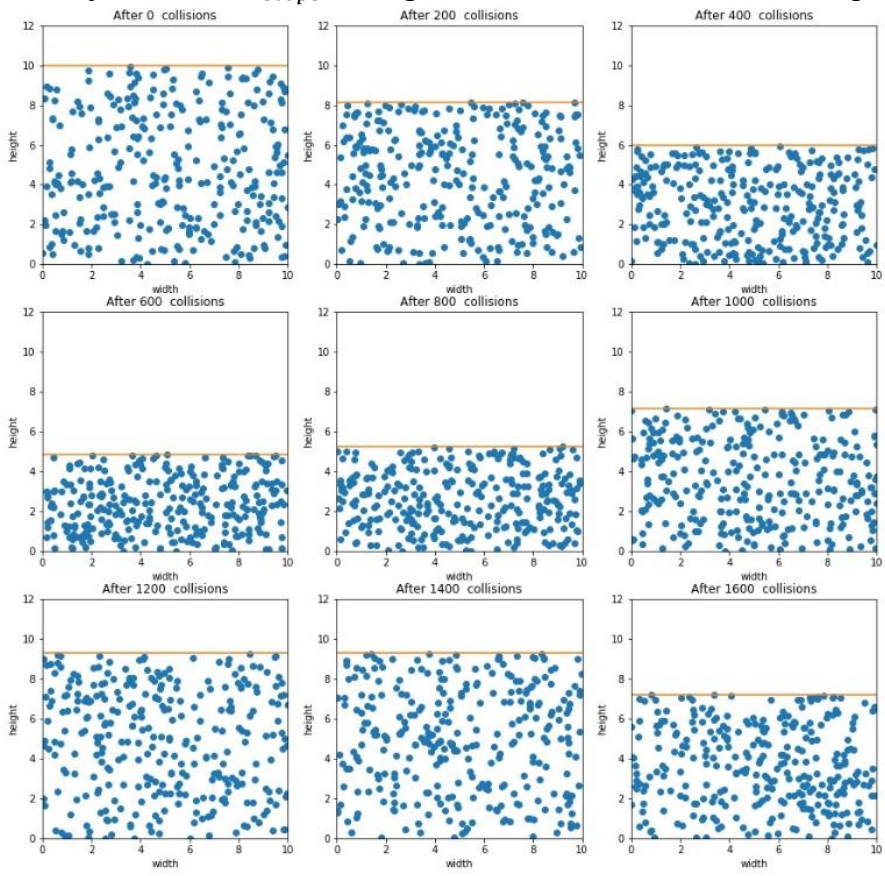

Figure 9. (T=2, m=0.1, M=20, N=300)

Conclusion

The 2D gas simulation showed qualitative agreement with the ideal gas law. The relationship of h, M, N and T is what equation 3 predicts. This exact model could be improved by increasing the number of particles, this can easily be adopted provided more computational power is available. A further expansion to three dimensions should also be investigated, so that the model can be tested against actual calculations using the ideal gas law. A time sliced method is likely needed for any further extension, like particle-particle collisions or including interatomic potentials.

References

[1] Ford, I., n.d. *Statistical thermodynamics*. 1st ed. London: John Wiley & Sons, Ltd., p.8.

[2] Salinger, G., Aiken, J. and Sears, F., 1975. *Solutions manual for Sears, Salinger Thermodynamics, kinetic theory, and statistical thermodynamics, third edition*. Reading, Mass.: Addison-Wesley Pub. Co., pp.352-362.

[3] Halliday, D., Resnick, R., Walker, J. and Liao, S., 2013. *Fundamentals of physics*. Hoboken, N.J.: Wiley, p.195.

[4] Salinger, G., Aiken, J. and Sears, F., 1975. *Solutions manual for Sears, Salinger Thermodynamics, kinetic theory, and statistical thermodynamics, third edition*. Reading, Mass.: Addison-Wesley Pub. Co., pp.352-362.