# Thermodynamics Snookered

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***Abstract*—The temperature and pressure of the system are calculated by the python codes and the effect of different parameters, such as radii of the balls, are investigated to derive the underlying thermodynamics laws.**

## I. Introduction

In this project python codes are first written to describe elastic 2-D collisions of one hard sphere in side a circular container, then it expands to multiple balls interacting with the container and each other. The accuracy of the simulation will be tested by comparing the agreement between different plots and their corresponding theory.

## II. Theory

### A. Collision

The equation describing the dynamics of the balls with the container is[1]:

$$(\vec{r}_1 + \vec{v}_1\delta t - \vec{r}_2 - \vec{v}_2\delta t)^2 = (R_1 \pm R_2)^2 \quad (1)$$

Where it accounts for any two balls, including the container. $R, \vec{v}, \vec{r}$ are the radius, velocity, and position of the center of a corresponding ball. If the collision is between a ball and the container, a minus sign will be used between the radii of the two balls. Rearranging the equation, we can get an expression for $\delta t$, the time to collision[1]:

$$\delta t = \frac{-2\vec{r}\cdot\vec{v} \pm \sqrt{(2\vec{r}\cdot\vec{v})^2 - 4|\vec{v}|^2(|\vec{r}|^2 - R^2)}}{2|\vec{v}|^2} \quad (2)$$

Where $R, v, r$ are $R_1 \pm R_2$, $\vec{v}_1 - \vec{v}_2$, and $\vec{r}_1 - \vec{r}_2$ respectively. When two balls collide, their velocities will change. Using conservation of momentum, the velocity of the balls after collision in 2-D can be expressed as[2]:

$$\vec{v'}_1 = \vec{v}_1 - \frac{2m_2}{m_1 + m_2}\frac{\langle \vec{v}_1 - \vec{v}_2, \vec{r}_1 - \vec{r}_2 \rangle}{\|\vec{r}_1 - \vec{r}_2\|^2}(\vec{r}_1 - \vec{r}_2) \quad (3)$$

$$\vec{v'}_2 = \vec{v}_2 - \frac{2m_1}{m_1 + m_2}\frac{\langle \vec{v}_2 - \vec{v}_1, \vec{r}_2 - \vec{r}_1 \rangle}{\|\vec{r}_2 - \vec{r}_1\|^2}(\vec{r}_2 - \vec{r}_1) \quad (4)$$

Where $\vec{r}_1, m_1, \vec{v}_1$ and $\vec{r}_2, m_2, \vec{v}_2$ are the position, mass, and velocity of the first and second ball respectively.

### B. Pressure

In 2-D, the pressure on the container due to the balls is defined by:

$$P = \frac{F}{A} = \frac{dp}{dt}A^{-1} \quad (5)$$

Where $P$ is pressure, $F$ is force, $p$ is momentum, $t$ is time and $A$ is the circumference of the container. The pressure on the container due to the balls can be found by calculating the average change of momentum of the balls that collide with the container divided by the container circumference.

### C. Maxwell Speed Distribution

After starting the simulation, the system will reach equilibrium after a certain number of collisions. The distribution of the speed of the particles when a system reaches equilibrium is determined by the 2-D Maxwell speed distribution[3]:

$$P(s < |\vec{v}| < s + ds) = \frac{ms}{k_B T}exp(-\frac{ms^2}{2k_B T})ds \quad (6)$$

Where $s$ is speed, $m$ is the mass of one ball and $k_B$ is the Boltzmann constant.

### D. Ideal Gas and van der Waal's Law

The ideal gas equation is:

$$PV = Nk_BT \quad (7)$$

Where N is the number of particles. However, the ideal gas law only holds when the particles have negligible volume(in this simulation area). So van der Waals law is introduced instead to obtain more accurate representations of state[1]:

$$(P + a(\frac{N^2}{V^2}))(V - Nb) = Nk_BT \quad (8)$$

Where $a$ represents the average attraction between particles. However, it will not be considered in this simulation. So $a$ will be 0 and the equation above will be reduced to:

$$P = \frac{Nk_B}{V - Nb}T \quad (9)$$

Where $b$ is a constant related to the volume of the particle. However $b$ is not equal to the volume of a particle since more volume need to be subtracted to find the volume remaining for motion. It turns out that in the extremely dilute state $b$ is four times the volume of a particle and can fall down to half with decreasing external volume[4]. Note that since the simulation is in 2-D, the theoretically value for b will not be four times ball area. Lastly, the relationship between the average kinetic energy and the temperature is:

$$KE = \frac{n_d}{2}k_BT \quad (10)$$

Where $n_d$ is the degree of freedom, which is 2 since the simulation is 2-D.

## III. Computing Methods

In the Ball class, the value for time to collision is calculated. However, there can be more than one solution and one of the solutions may be negative. Therefore it is important to filter out unwanted solutions with if statements. Moreover, due to floating point error, 0 cannot be used directly in the conditions and instead *1e-8* is used. When calculating the time until the next collision, all non repeating pairs of balls will be used to find their non-negative time until next collision by using a double loop. The value for the shortest time will be updated when the calculated time to collision is smaller than the current time until collision. However if the balls are already touching, they will not be counted. so after counting all the time until collision, all the balls will be moved by the shortest time until collision

To make sure that the code will not be changed accidentally, the position, mass, radius, and velocity parameters are saved as hidden attributes of the object. The collision algorithm is optimized such that the balls remain hard spheres even when multiple balls collide on the container at the same time, as a list is used to store the index of balls that will collide at the same time.

In the simulation, the velocity of the balls are randomized using normal distribution and the kinetic energy hence temperature is varied by changing the $\sigma$ of the distribution.

Beyond that, a method is written to investigate the relationship between the parameter $b$ in Eqn. 9 and the area of a ball by fitting the constant for different ball radii and plotting a best fit line. In this plot, the particles are called for each radius, and the value for b is determined by using the curve fit method from scipy.optimize. After all the points are plotted, the poly1d method from numpy is used to determine the gradient of the line.

## IV. Results and Analysis

In Fig.1, the histogram for ball distance between the center shows that the frequency increased linearly as the distance increases, and there is a spike at the end due to the container wall stopping the balls from travelling further. It shows that the balls distribute randomly after reaching equilibrium as the histogram demonstrates radial increase. In Fig.2, the histogram for ball distance ranges from 1 to 19. Since the radii of the balls are 0.5 the closest the centers can be is 1, similarly the furthest they can be apart from is 19 since the radius of the container is 10. The maximum frequency is when the distance from two balls is around 8, which means that the distribution is not symmetrical. Since there is no inter-ball attraction, the probability of finding finding a ball anywhere in the container should be uniform, apart from along the wall of the container where the probability is slightly higher than expected, which can be approximated as point processes. Furthermore, according to the shape of the distribution, it can be determined that the distribution of the distance between centers of particles follow a nearest neighbor distribution[5]. As the ball radius decreases to infinitesimal, the left side of the histogram also reduce to zero.

Fig. 3 and 4 show the conservation of kinetic energy and momentum of the system. Both lines are quite stationary with minimal change in gradient. This is an indication that the simulation works as expected.

In Fig.5, the gradient of the pressure against temperature divided by $k_B$ is very close to the gradient of the ideal gas line, which is $N/V$ where $N, V$ are the number of particles and area of the container respectively. This result is expected as the system is closer to an ideal gas system as the radius of the balls decrease. Fig.6(a) shows the same plot but with 4 different simulations, for each simulation the ball radius is set to a different value. It can be clearly observed that as the ball radius increases the gradient for the corresponding line increases, making it further away from the ideal gas line. The rate of increase of gradient however, is not directly proportional to that of the radius. Fig.6(b) shows how the change in radius affects the gradient difference from the ideal gas line gradient. The plot shows an exponential increase as radius increases from 0.2 to 1.0.

In Fig.7, the histogram resembles the shape of the theoretical speed distribution obtained from Eqn.6. In general, as the number of collisions increase, the histogram will tend to fit the Maxwell speed distribution better.

Eqn.9 shows the relationship between pressure and temperature for balls with a finite radius, the constant $b$ is related to the area of the ball and needs to be solved graphically. Fig.8 shows the plot of $b$ against different ball areas and the gradient of the fitted line is approximately 2. This result is in accord with the theory of van der Waals law.

## V. Conclusion

In this project, the simulation is successfully written and tested through different plots. In general, the simulation is in agreement with theory. Beyond the script requirements, the significance of the distribution of ball distance was explored and determined and the correlation between the $b$ constant in van der Waals law and ball area was successfully determined.

## References


[1] MacKinnon, A. and Kingham, R. (2020) Project B: Thermodynamics Snookered.

[2] Love, A. E. H. (1897) "Principles of Dynamics" p. 262. Cambridge. Cambridge University Press

[3] Halliday, D., Resnick, R. and Walker, J. (2011) "THE KINETIC THEORY OF GASES," in Fundamentals of physics. Hoboken, NJ: Wiley.

[4] van der Waals, J.D. (1910) "The equation of state for gases and liquids," Nobel Lectures, 12 December.

[5] Daley, D.J. and Vere-Jones, D. (2005) " Basic Properties of the Poisson Process," in An introduction to the theory of Point Processes. New York: Springer.

## VI. PLOTS FROM SIMULATION

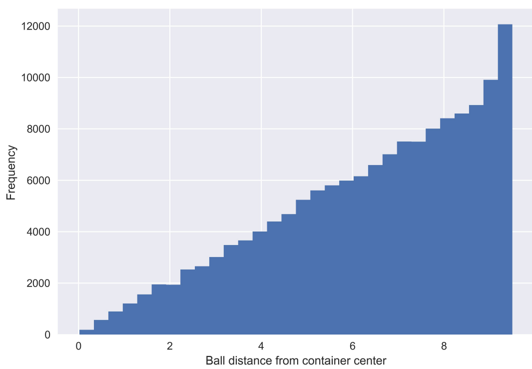



Fig. 1: The histogram for distance from container center for 30 balls with mass=1, radius=0.5, and average KE=5.21. The histogram is plotted from 5000 collisions

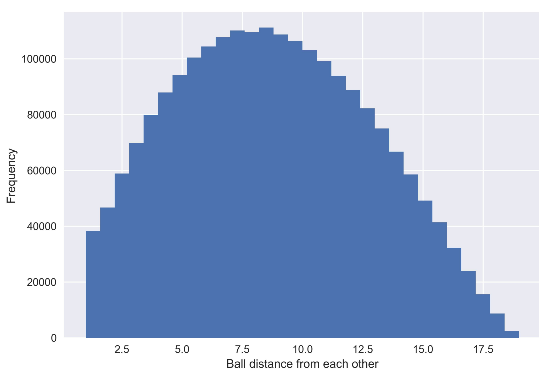



Fig. 2: The histogram for distance from the center of each ball excluding the container for 30 balls with mass=1, radius=0.5, and average KE=5.21. The histogram is plotted from 5000 collisions

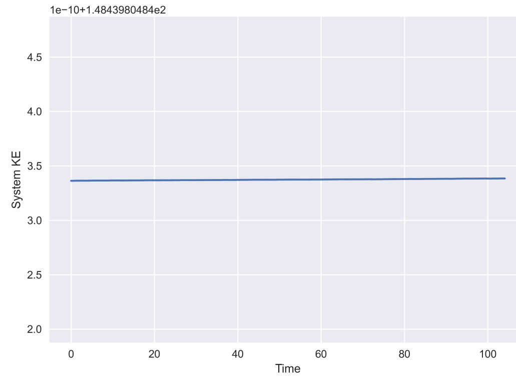



Fig. 3: The plot for system kinetic energy against time for 30 balls with mass=1, radius=0.1, and average KE=4.95, plotted from 2000 collisions

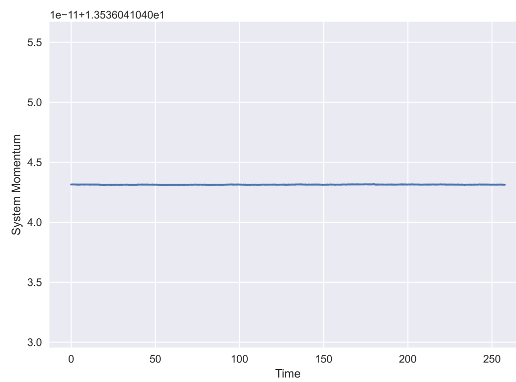



Fig. 4: The plot for system momentum against time for 30 balls with mass=1, radius=0.1, and average KE=4.82, plotted from 5000 collisions

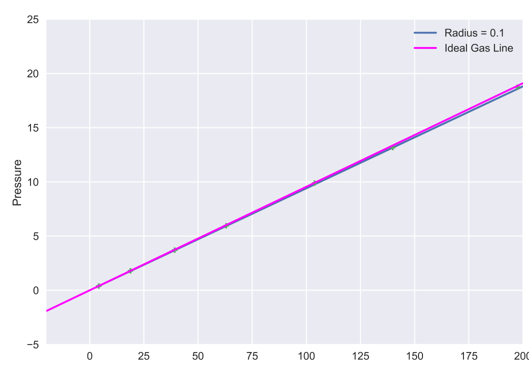
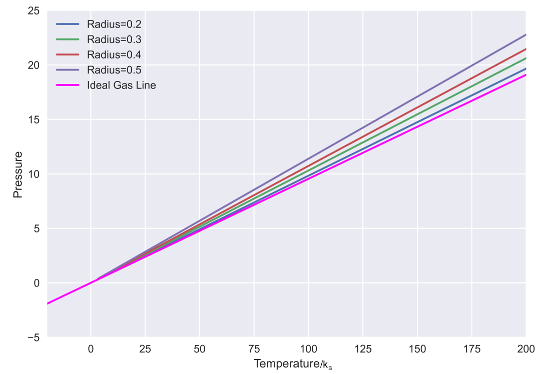
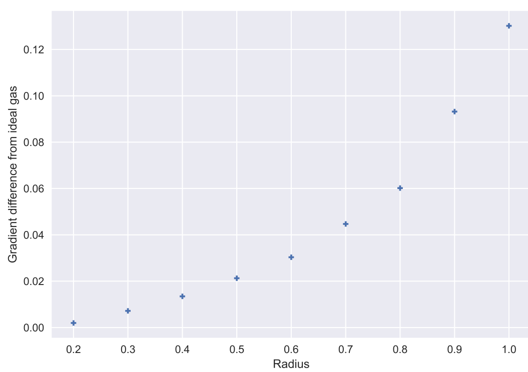



Fig. 5: The plot for pressure against temperature divided by the Boltzmann constant for 30 balls with mass=1 and radius=0.1




(a) The plot for pressure against temperature divided by the Boltzmann constant for balls with different radii in each simulation




(b) Plot of gradient difference from ideal gas against ball radius

Fig. 6: Plots of how radius affect the equation of state

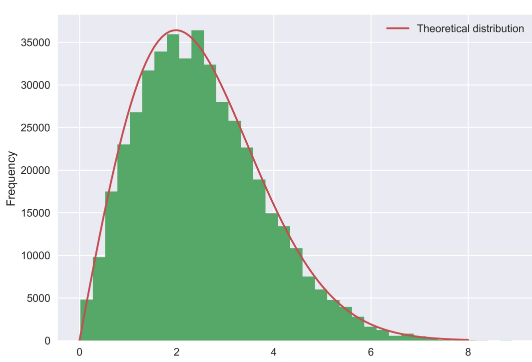



Fig. 7: The histogram and theoretical distribution of ball speed for 30 balls with mass=1 and radius=0.1, plotted from 15000 collisions

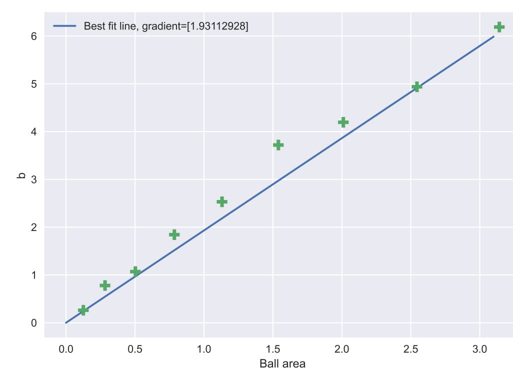



Fig. 8: The plot of fitted value of b against ball area