An Exploration of Ideal and Real Gases Using Event-Based Particle Dynamics

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1 Introduction

The original goal of this project was to implement a simulation of an ideal gas in Python using an algorithm known as Event-Based Particle Dynamics (EBPD), and to then use the simulation to verify that some of the emergent behavior we have studied in the course really does arise from the microscopic behavior of particles, particularly the Maxwell distribution and the ideal gas law. However, realizing that the simulation inherently displays some of the behavior of a real (non-ideal) gas, the scope of my investigation broadened and shifted slightly to include exploring what causes non-ideal behavior and fitting non-ideal gas models to my data. In this paper, I will outline how I implemented the simulation itself, derive the ideal gas law and show how it compares to my data, and discuss which aspects of non-ideality my simulation demonstrates and how it could potentially be modified to be even more realistic.

2 The Simulation

The most basic approach to simulating a physical system is a time-based one. In such a simulation, a timestep is used to advance the state of the system within the simulation loop

and in each iteration every particle checks for collisions with every other particle.

Listing 1: Pseudocode for time-based simulation

```
while t ⩽ t_max:
    t ← t + timestep
    evolve all particles by timestep
    for a in particles:
        for b in particles:
            if a is touching b:
                collide a and b
```

There are two main problems with the time-based approach. First, the timestep must be selected very carefully in order to strike a balance between accuracy and speed. If the timestep is too large some events may be missed entirely, and if it is too small the simulation will take prohibitively long to run. The other problem is that every iteration of the simulation loop involves checking every particle for collisions with every other particle, an $O(n^2)$ operation that does not scale well to large systems.

The alternative to time-based simulation is an algorithm called Event-Based Particle Dynamics [1], which does exactly what its name implies: it treats simulation as a series of events rather than a sequence of times. Essentially, EBPD calculates when all future events will occur, then steps from event to event, evolving the system according to how much time passes between events. This is accomplished by using a priority queue to store future events sorted by when they will occur. The queue is populated initially, then updated lazily (outdated collisions that will no longer actually occur are not removed from the queue, just checked for on each iteration) by adding new events for a particle after it is involved in an event.

Listing 2: Pseudocode for Event-Based Particle Dynamics

```
event_queue ← find_all_events()
while num_events ⩽ max_events:
    event ← event_queue.pop()
    evolve all particles until event.time
    perform event
    add new events for particles involved
```

This approach remedies the shortcomings of the time-based one: Events will never be missed, time is not wasted seeing what happens between collisions, and costly $O(n^2)$ collision checking is mostly avoided. These qualities make EBPD well-suited to simulation problems in which events are sparsely distributed in time yet it is important not to miss any events, and to systems that involve large numbers of particles. A gas fits both of these criteria, so EBPD is an excellent tool for this application[1].

3 Results and Comparison to Theory

3.1 The Maxwell Boltzmann Distribution

Though not the primary focus of this project, it is of interest to examine whether the Maxwell distribution of particle velocities really does arise from the microscopic interactions of gas particles. To do so, I had my simulation produce histograms of particle speeds in each iteration of the event loop, showing how the speed distribution evolves over time. The behavior observed was that the particle speeds, all initialized to the same value v_{ave}, quickly approached the Maxwell distribution, then fluctuated about it, which is expected due to the finite number of particles simulated.

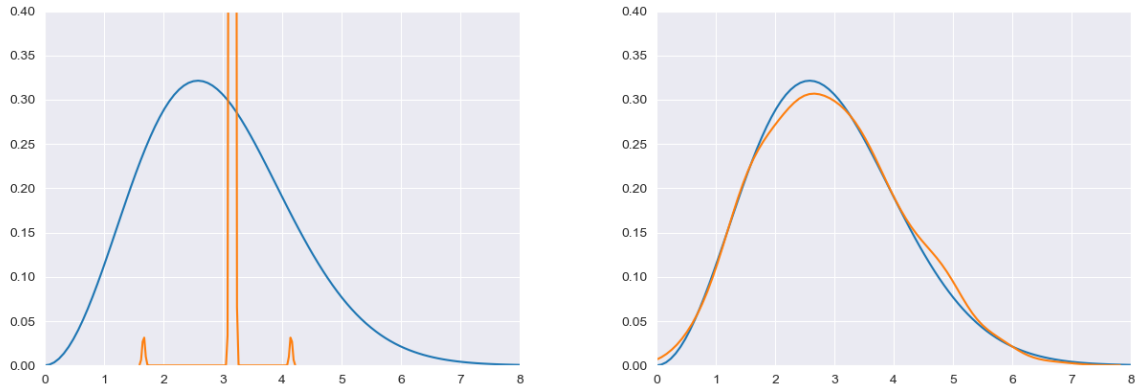


Figure 1: Left: Initial speed distribution (orange) with Maxwell distribution in blue. Right: Speed distribution after 1400 atom-atom collisions.

[1]The code for the simulation can be found at `github.com/carterjswift/gas_sim`

3.2 The Ideal Gas Law

3.2.1 Theory

The ideal gas law is based upon two fundamental assumptions: that gas particles occupy no volume, and that they interact only with the walls of the container and not with other particles. To derive the ideal gas law, we can consider the Helmholtz free energy of the system since we know that $P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$. We begin by writing

$$F = U - TS$$

We can then substitute in the known equations for U and S that assume no interaction between particles (Equipartition theorem for monatomic ideal gas and Sackur-Tetrode Equation) to get:

$$F = \frac{3}{2}Nk_BT - TNk_B\left[ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{\frac{3}{2}}\right) + \frac{5}{2}\right]$$

Taking the partial derivative with respect to V, only one term remains:

$$\frac{\partial F}{\partial V} = -\frac{Nk_BT}{V}$$

Substituting in P for the partial derivative and rearranging, we obtain the ideal gas law:

$$PV = Nk_BT$$

Therefore, we should expect to see that any system conforming to the two basic assumptions of this derivation should obey the ideal gas law.

3.2.2 Simulation

Now that the derivation of the ideal gas law from the two basic assumptions has been shown, it is possible to examine the results of the simulation and compare them to the theory. First, the ideal gas law predicts that there should be a linear relationship between pressure and temperature at constant volume and number of particles. To examine this, I ran the simulation over a range of temperatures, plotting pressure against Nk_bT and fitting it with a line. As seen in Figure 2, the data agree very well with the prediction of the ideal gas law, with an r^2 value of 0.9999996.

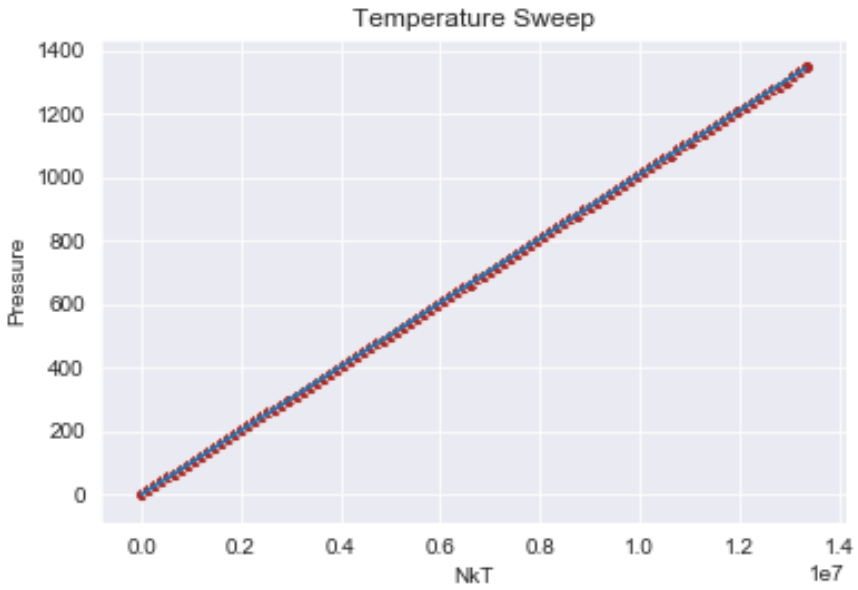
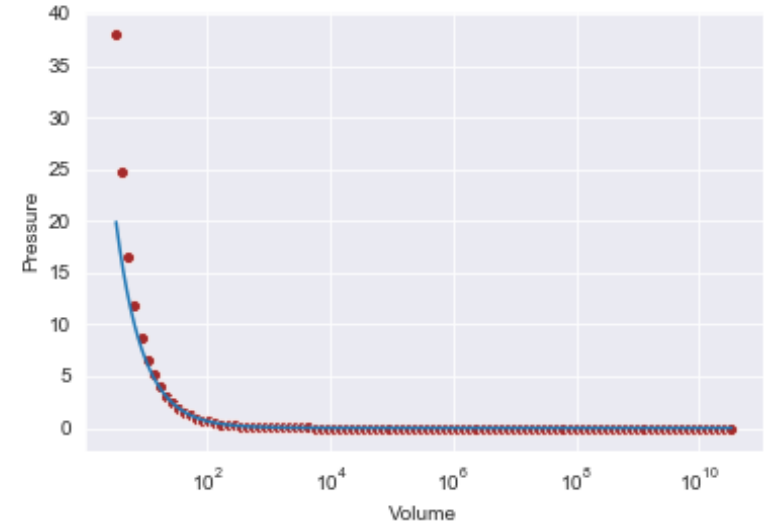
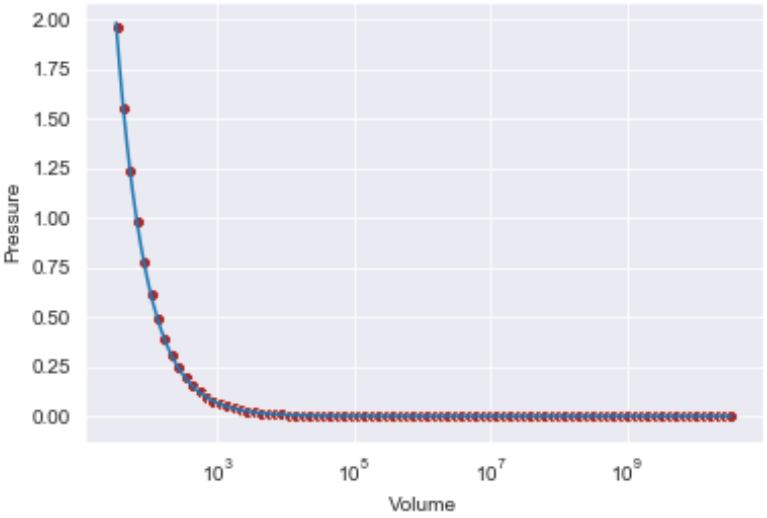


Figure 2: Plot of pressure vs. temperature at constant volume

Secondly, the ideal gas law predicts an inverse proportionality between pressure and volume for constant temperature and number of particles. I followed a similar procedure to test this, only sweeping over a range of volumes rather than a range of temperatures. Figure 3a shows the plot of pressure vs. volume that resulted from this analysis, plotted against the ideal relation determined by the ideal gas law. It can be clearly seen that the gas did not behave ideally at low volumes, which I will discuss in the next section, but focusing in on the higher volumes in Figure 3b the prediction is accurate to a very good approximation.



(a)



(b)

Figure 3: a: Logarithmic plot of pressure vs. volume. b: The same plot, but omitting small volumes

3.3 Non-Ideality

As seen in Figure 3a, the simulation clearly does not follow ideal behavior at low volumes. In order to understand why, we have to recall the two basic assumptions of the ideal gas model, that particles occupy zero volume and interact only with the walls of the container.

This therefore implies two types of non-ideality, one due to particles having nonzero volume, and another due to particles interacting with each other via some mechanism. For a non-ideal gas, the first type of non-ideality should dominate at high pressures where a significant fraction of the total volume is occupied by the particles themselves, while the second type should dominate at low pressures, where attractive interactions between particles reduce the volume they occupy compared to what is predicted by the ideal gas law. This simulation exhibits only the first kind of non-ideality, as the event-driven algorithm inherently requires the particles to have some volume and also prevents particles from interacting over long-distances between events. One of the first attempts to develop an equation of state for non-ideal gases was the van der Waals equation of state, for which van der Waals won the Nobel Prize in Physics in 1910 [2]. The van der Waals equation compensates for the two non-ideal characteristics of a gas with two terms and corresponding parameters, as seen below:

$$P = \frac{Nk_bT}{V-b} - \frac{a}{V^2}$$

Comparing the van der Waals equation to the ideal gas law, one can see that the first term on the righthand side is simply the ideal gas law with a correction factor b subtracted from the volume, while the second term is entirely new. The parameter b is related to the total volume occupied by the particles themselves, therefore accounting for the space occupied by particles, and the righthand term accounts for the attraction between particles, with the parameter a being a measure of the average attractive force between particles [2].

Since my simulation does not have any attractive forces between particles, $a = 0$, so the equation $P = \frac{Nk_bT}{V-b}$ should be a good fit for the data. In order to verify this, I found the value of b that minimized the sum of squared errors between the model and the simulation results, plotting the resulting model against the data and finding its correlation coefficient. The result of this analysis is shown in Figure 4, where we can see a fairly good fit, with $r^2 = 0.9985$ and the parameter $b = \frac{V_{particles}}{0.53}$.

Interestingly, the parameter b is not simply equal to $V_{particles}$, but rather that value

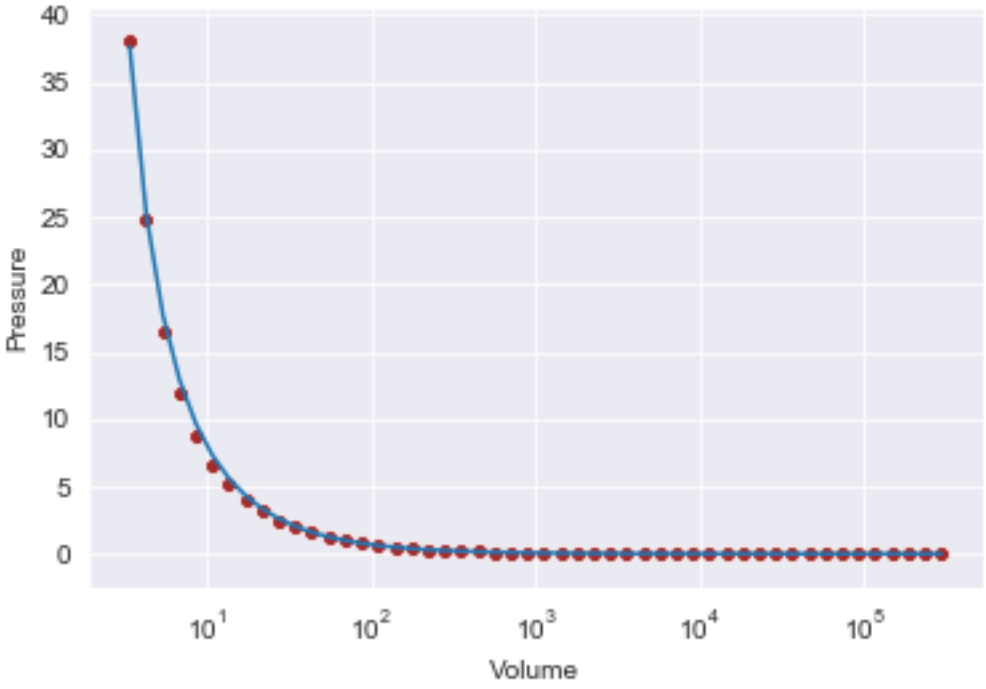


Figure 4: Logarithmic plot of pressure vs. volume fit against the van der Waals model

divided by 0.53. I suspect that the reason for this is that spheres cannot be packed perfectly such that there are no voids between them, so the space each particle takes up in the limit of all particles being pressed against each other is somewhat greater than its own volume. In this case, the ratio of particle volume to b is 0.53, which it turns out is very close to the random loose packing fraction of spheres, which is how tightly spheres can be packed without deliberately organizing them or agitating them in a gravity field to achieve better packing ratios [3]. This is unsurprising because the conditions of the simulation seem to be in agreement with the conditions of a random loose pack.

4 Potential Future Work

It would be interesting to expand this simulation to also account for attractions between particles, though I do not believe this could be done in a way that preserves the event-

based nature of the simulation, so a time-based algorithm would have to be used instead, which would bring with it the disadvantages highlighted in Section 1. However, this would allow for verification of the second term of the van der Waals equation and comparison with more-recently developed non-ideal equations of state. Additionally, it would be intriguing to explore how the results change if a gravitational field is applied, as it could potentially lead to a tighter packing of particles and therefore a lower value for the parameter b.

References

[1] Aleksandar Donev. *Asynchronous Event-Driven Particle Algorithms*. URL: https://cims.nyu.edu/~donev/DSMC/AED_Review.pdf.

[2] Georgios Kontogeorgis, Romain Privat, and Jean-Noël Jaubert. "Taking Another Look at the van der Waals Equation - Almost 150 Years Later". In: *J. Chem. Eng. Data* (2019). DOI: https://doi.org/10.1021/acs.jced.9b00264.

[3] George Y. Onoda and Eric G. Liniger. "Random loose packings of uniform spheres and the dilatancy onset". In: *Phys. Rev. Lett.* 64 (22 May 1990), pp. 2727–2730. DOI: 10.1103/PhysRevLett.64.2727.