1 Introduction

The fundamental principles behind the physical properties of gases stems from the collision between the individual gas particles. There are various models to simulate the collision between particles. The inverse power law model [2] is an accurate model of particle collisions but is considered a slow model due to the high computational time required at its conception. In 1981, Bird [1] introduced the Variable Hard Sphere (VHS) model as an approximation of the inverse power law model. In the VHS model, particles interact only when they are in contact. In general, the VHS model is considered as a good approximation of the inverse power law model at room temperature. However, the difference between these two models has never been quantitatively demonstrated. This report discusses the implementation of these two models and their results when simulating the collision of gas particles at various temperatures and number densities. The result can provide a guide to estimate the reliability of results in the simulation of real gases. In our simulation, we use C++ programming language to implement both models. Averagely, the simulation of 2000 particle collisions is below 0.70 seconds.

2 Methodology

2.1 Inverse Power Law Model

To obtain the final velocities for the two molecules we will first start off by examining the linear momentum and energies of both molecules, then move onto constants defined by the Inverse Power Law model. The pre-collision velocities of the two molecules will be denoted by $\vec{\mathbf{c_1}}$ and $\vec{\mathbf{c_2}}$ while the post-collision velocities of each respective molecule will similarly be $\vec{\mathbf{c_1}}^*$ and $\vec{\mathbf{c_2}}^*$. We shall also assume that linear momentum and energy will be conserved throughout the collision, and since we are using two similar molecules in each collision, i.e. $m_1 = m_2$. We have

$$m\vec{\mathbf{c_1}} + m\vec{\mathbf{c_2}} = m\vec{\mathbf{c_1}}^* + m\vec{\mathbf{c_2}}^* \implies \vec{\mathbf{c_1}} + \vec{\mathbf{c_2}} = \vec{\mathbf{c_1}}^* + \vec{\mathbf{c_2}}^* \tag{1}$$

and

$$m||\mathbf{c_1}||^2 + m||\mathbf{c_2}||^2 = m||\mathbf{c_1}^*||^2 + m||\mathbf{c_2}^*||^2 \implies ||\mathbf{c_1}||^2 + ||\mathbf{c_2}||^2 = ||\mathbf{c_1}^*||^2 + ||\mathbf{c_2}^*||^2 \tag{2}$$

The relative velocity $\vec{\mathbf{c_r}}$ and $\vec{\mathbf{c_r}}^*$ may be defined as

$$\vec{\mathbf{c_r}} = \vec{\mathbf{c_1}} - \vec{\mathbf{c_2}} \tag{3}$$

$$\vec{\mathbf{c_r}}^* = \vec{\mathbf{c_1}}^* - \vec{\mathbf{c_2}}^* \tag{4}$$

The equations (1) and (2) may be combined with (3) and (4) to give

$$\vec{\mathbf{c_1}} = \frac{1}{2}(\vec{\mathbf{c_1}} + \vec{\mathbf{c_2}} + \vec{\mathbf{c_r}}) \tag{5}$$

$$\vec{\mathbf{c_2}} = \frac{1}{2}(\vec{\mathbf{c_1}} + \vec{\mathbf{c_2}} - \vec{\mathbf{c_r}}) \tag{6}$$

This shows that the velocities are anti-parallel in the frame of reference and assuming the molecules are point centres of force, the force between them remains in the plane containing the two molecules meaning we can view the 3D collision on a 2D frame of reference, and the final velocities in this plane is similarly

$$\vec{\mathbf{c_1}}^* = \frac{1}{2}(\vec{\mathbf{c_1}} + \vec{\mathbf{c_2}} + \vec{\mathbf{c_r}}^*) \quad (7) \qquad \vec{\mathbf{c_2}}^* = \frac{1}{2}(\vec{\mathbf{c_1}} + \vec{\mathbf{c_2}} - \vec{\mathbf{c_r}}^*) \quad (8)$$

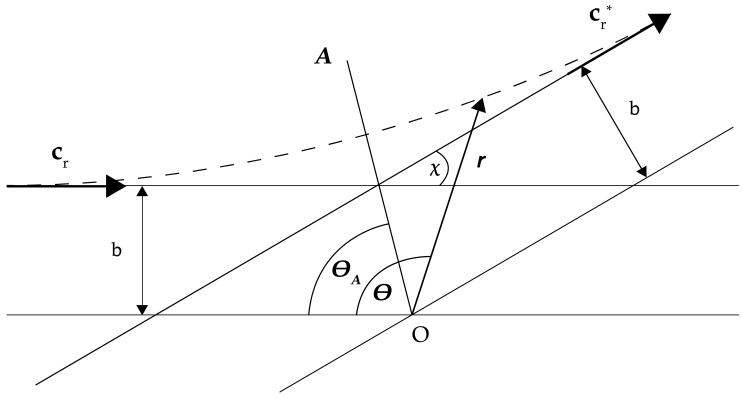


Figure 1: Collision Dynamics

Our next task in finding the components of $\vec{\mathbf{c_r}}^*$ requires finding the change in direction, χ, of the relative velocity vector $\vec{\mathbf{c_r}}$. Using polar coordinates r and θ to represent the incoming molecule with respect to the frame of reference, the equation for the angular momentum would be

$$r^2(\frac{d\theta}{dt}) = const = b\vec{\mathbf{c_r}} \quad (9)$$

The magnitude of the force field affecting the molecules is the sum of the kinetic and potential energies but if the molecules are very far away, i.e. $r \to \infty$, the magnitude of force may be equated as just the asymptotic kinetic energy where $m_r = \frac{1}{2}m$

$$\frac{1}{2}m_r(\frac{dr}{dt}^2 + r^2\frac{d\theta}{dt}^2) + \phi = const = \frac{1}{2}m_r(\vec{\mathbf{c_r}}^2) \quad (10)$$

ϕ is the inter-molecular potential which is related to the spherically symmetrical force F between molecules

$$\phi = \int_r^\infty F \, \mathrm{d}r \quad (11)$$

Removing time t from equations (10) and (11) and combining them will five the following

$$\frac{dr}{dt}^2 + r^2\frac{d\theta}{dt}^2 + \frac{\phi}{\frac{1}{2}m_r} = \frac{r^4}{b^2}(\frac{d\theta}{dt})^2$$
$$\implies (\frac{dr}{d\theta}\frac{d\theta}{dt})^2 + \frac{\phi}{\frac{1}{2}m_r} = (\frac{d\theta}{dt})^2(\frac{r^4}{b^2} - r^2)$$
$$\implies (\frac{dr}{d\theta})^2 = \frac{r^4}{b^2} - r^2 - \frac{\phi r^4}{\frac{1}{2}m_r\vec{\mathbf{c_r}}^2 b^2}$$

Introducing the dimensionless coordinate

$$W = \frac{b}{r} \quad (12)$$

We can get

$$(\frac{dW}{d\theta})^2 = 1 - W^2 - \frac{\phi}{\frac{1}{2}m_r\vec{\mathbf{c_r}}^2} \quad (13)$$

$$\theta = \int_0^W (1 - W^2 - \frac{\phi}{\frac{1}{2} m_r \vec{\mathbf{c}_\mathbf{r}}^2})^{-\frac{1}{2}} \, \mathrm{d}W \tag{14}$$

The inverse power law model defines

$$\phi = \frac{\kappa}{(\eta - 1) r^{\eta - 1}} \tag{15}$$

where κ is a constant evaluated from [2]. The viscosity coefficient of the gas μ can also be found in [2]

$$\mu = \frac{(\frac{15}{8}\pi m k)^{\frac{1}{2}} (\frac{2mRT}{\kappa})^{\frac{2}{\eta - 1}}}{8 A_2(\eta) \Gamma(4 - \frac{2}{\eta - 1})} \tag{16}$$

Since $\theta = \theta_A$, we can get the following from the previous 3 equations

$$\theta_A = \int_0^{W_1} (1 - W^2 - \frac{\kappa}{\frac{1}{2} m_r \vec{\mathbf{c}_\mathbf{r}}^2 (\eta - 1) r^{\eta - 1}})^{-\frac{1}{2}} \, \mathrm{d}W \tag{17}$$

where W_1 is the positive root of the equation

$$1 - W^2 - \frac{\kappa}{\frac{1}{2} m_r \vec{\mathbf{c}_\mathbf{r}}^2 (\eta - 1) r^{\eta - 1}} = 0 \tag{18}$$

Here we can use GNU Scientific Library's (GSL) integration and root finding functions for equations (17) and (18) respectively. The deflection angle of the relative velocity $\vec{\mathbf{c}_\mathbf{r}}$ is thus

$$\chi = \pi - 2\theta_A \tag{19}$$

After finding χ, we can get to finding $\vec{\mathbf{c}_\mathbf{r}}^*$. We shall introduce a new set of Cartesian coordinates, $\vec{x}'$, $\vec{y}'$, and $\vec{z}'$ alongside our reference plane where $\vec{x}'$ is in the direction of $\vec{\mathbf{c}_\mathbf{r}}$. The components of $\vec{\mathbf{c}_\mathbf{r}}^*$ along the new set of axes are

$$\vec{\mathbf{c}_\mathbf{r}} \cos\chi \;\; , \;\; \vec{\mathbf{c}_\mathbf{r}} \sin\chi \cos\varepsilon \;\; , \;\; \vec{\mathbf{c}_\mathbf{r}} \sin\chi \sin\varepsilon$$

where ε is the angle between the collision plane $\vec{\mathbf{CP}}$ and the new $\vec{y}'$ plane

$$\vec{\mathbf{CP}} = (\vec{\mathbf{P}_1} - \vec{\mathbf{P}_2}) \times (\vec{\mathbf{c}_\mathbf{r}}) \tag{20}$$

where $\vec{\mathbf{P}_1}$ and $\vec{\mathbf{P}_2}$ are the 3D coordinates of the first and second molecule respectively and since we can choose the $\vec{y}'$ plane arbitrarily, we can choose it such that it will be normal to the x-axis. The directional cosines of $\vec{y}'$ are then

$$0, w_r (v_r^2 + w_r^2)^{-\frac{1}{2}}, -v_r (v_r^2 + w_r^2)^{-\frac{1}{2}} \tag{21}$$

The difference between these two planes will then simply be

$$\varepsilon = \arccos(\frac{\vec{\mathbf{y}}' \cdot \vec{\mathbf{CP}}}{||\mathbf{y}'|| \times ||\mathbf{CP}||}) \tag{22}$$

Switch the axes back to the original x, y, and z axes to get the direction cosines of $\vec{\mathbf{c}_\mathbf{r}}^*$.

$$\begin{aligned}
u_r^* &= \cos\chi u_r + \sin\chi \sin\varepsilon (v_r^2 + w_r^2)^{\frac{1}{2}} \\
v_r^* &= \cos\chi v_r + \sin\chi (\vec{\mathbf{c}_\mathbf{r}} w_r \cos\varepsilon - u_r v_r \sin\varepsilon)(v_r^2 + w_r^2)^{\frac{1}{2}} \\
w_r^* &= \cos\chi w_r + \sin\chi (\vec{\mathbf{c}_\mathbf{r}} v_r \cos\varepsilon + u_r w_r \sin\varepsilon)(v_r^2 + w_r^2)^{\frac{1}{2}}
\end{aligned}$$

Here u, v, and w are the x, y, and z components of $\vec{\mathbf{c}_\mathbf{r}}$ respectively. Finally, substitute the $\vec{\mathbf{c}_\mathbf{r}}^*$ vector back into equations (7) and (8) to obtain $\vec{\mathbf{c}_\mathbf{r}}$.

2.2 Variable Hard Sphere Model

The VHS model is similar to the Hard Sphere model where upon contact, the force between the molecules is directed along an imaginary line that connects their centers.

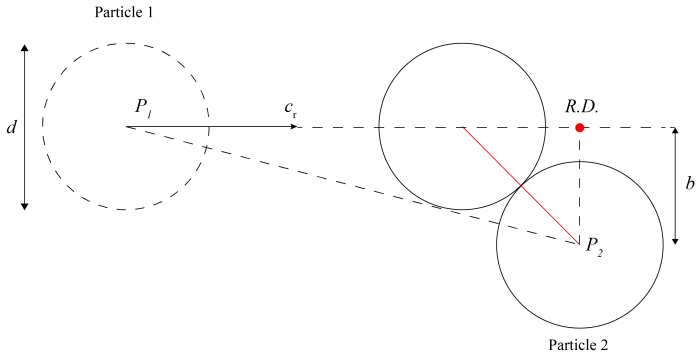


Figure 2: Hard Sphere Collision, where d is the diameter of the particle and b is the miss impact parameter

Changing the reference frame to that of particle 2, we first find the coordinate denoted by the red dot above to find the position of particle 1 upon contact.

$$\mathbf{P}_{\text{red dot}} = \mathbf{P}_1 + \left(\frac{\vec{\mathbf{c}}_\mathbf{r} \cdot (\mathbf{P}_2 - \mathbf{P}_1)}{\vec{\mathbf{c}}_\mathbf{r} \cdot \vec{\mathbf{c}}_\mathbf{r}}\right)\vec{\mathbf{c}}_\mathbf{r} \tag{23}$$

$$\mathbf{P}_{\text{at contact}} = \mathbf{P}_{\text{red dot}} - \left(\sqrt{d^2 - b^2}\right)\hat{\vec{\mathbf{c}}}_\mathbf{r} \tag{24}$$

We can then calculate the normal velocities that would be imparted on the particles.

$$\text{Red line vector} = \mathbf{R}_v = \mathbf{P}_{\text{at contact}} - \mathbf{P}_2 \tag{25}$$

$$\text{Normal Velocity} = \mathbf{N}_v = (\vec{\mathbf{c}}_\mathbf{r} \cdot \hat{\mathbf{R}}_v)\hat{\mathbf{R}}_v \tag{26}$$

The final velocities for the particles are then,

$$\vec{\mathbf{c}}_\mathbf{1}{}^* = \vec{\mathbf{c}}_\mathbf{1} - \mathbf{N}_v \text{ and } \vec{\mathbf{c}}_\mathbf{2}{}^* = \vec{\mathbf{c}}_\mathbf{2} + \mathbf{N}_v \tag{27}$$

The VHS model differs from the HS model where its diameter d is a function of $\vec{\mathbf{c}}_\mathbf{r}$ [2] as follows,

$$d = d_{\text{ref}}(c_{\text{r,ref}}/|\mathbf{c}_r|)^{\upsilon} \tag{28}$$

2.3 Data Generation

2.3.1 Random initial velocities

The random velocities of the particles are generated from a normal distribution whose mean is 0 and standard deviation $\sqrt{\frac{kT}{m}}$. This is run three times to generate a 3D velocity vector.

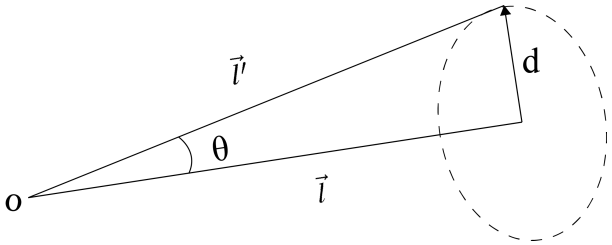


Figure 3: Relative Coordinates of colliding particle

2.3.2 Relative coordinates of particle at contact

In order to ensure constant collisions in our simulation we will first place one molecule at the origin O, and the impact point of the incoming molecule at an arbitrarily chosen distance l, generated from a gamma distribution whose shape is 1.0 and rate is $\frac{1}{\pi nd^2}$, where d is the diameter of the molecule, and n is the number density which is obtained from

$$n = \frac{p}{kT} \tag{29}$$

where p is the pressure at STP, and k is the Boltzmann constant. Next we will need to get the vector l

$$\vec{\mathbf{l}} = \frac{l}{c_1}\vec{\mathbf{c_1}} \tag{30}$$

Having the molecules collide at an arbitrarily chosen point a circle with radius d at the end of $\vec{\mathbf{l}}$ where d can be chosen using a normal distribution with mean 0 and standard deviation d^2. Here the angle θ is simply

$$\theta = \arctan(\frac{d}{l}) \tag{31}$$

To find the vector $\vec{\mathbf{l}}'$ we will opt to use geometry instead of a rotation matrix. We will first project $\vec{\mathbf{l}}$ on to the x-y plane, then find the vector $\vec{\mathbf{l}}'$ in terms of ψ and θ. The components of vectors $\vec{\mathbf{l_p}}$, $\vec{\mathbf{l}}$, and $\vec{\mathbf{l}}'$ respectively would be

$$\vec{\mathbf{l_p}} = (r\cos\phi, r\sin\phi, 0)$$
$$\vec{\mathbf{l}} = (l\cos\psi\cos\phi, l\cos\psi\sin\phi, l\sin\psi)$$
$$\vec{\mathbf{l}}' = (l\cos(\psi+\theta)\cos\phi, l\cos(\psi+\theta)\sin\phi, l\sin(\psi+\theta))||$$

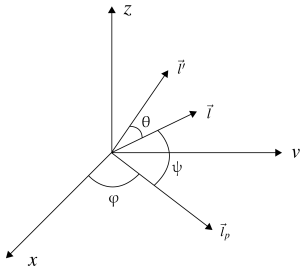


Figure 4: Projections

where

$$\psi = \arcsin(\frac{l_z}{l}) \tag{32}$$

The components of $\vec{\mathbf{l}}'$ would then be

$$\frac{l_x}{\cos\psi}\cos(\psi+\theta)\ ,\ \frac{l_y}{\cos\psi}\cos(\psi+\theta)\ ,\ \frac{l_z}{\sin\psi}\sin(\psi+\theta) \tag{33}$$

The last variable we will have to determine is the angle θ_r in which the molecules collide, which can be chosen using a uniform distribution with mean 0 and standard deviation 2π. Finally, we can determine the exact position where the incoming molecule will reach after time t

$$\text{Coordinate} = ||\vec{\mathbf{l}}' - \vec{\mathbf{l}}||\left(\frac{\cos\theta_r}{||\vec{\mathbf{l}}' - \vec{\mathbf{l}}||}(\vec{\mathbf{l}}' - \vec{\mathbf{l}}) + \frac{\sin\theta_r}{||\vec{\mathbf{c}}_\mathbf{r} \times (\vec{\mathbf{l}}' - \vec{\mathbf{l}})||}(\vec{\mathbf{c}}_\mathbf{r} \times (\vec{\mathbf{l}}' - \vec{\mathbf{l}}))\right) + \vec{\mathbf{l}} \tag{34}$$

Now we can shift the collision and the molecule's positions relatively, but since it will not affect the angle at which the collision occurs, and in turn the final velocity, we shall not change the relative positions of the molecules, i.e. one of the molecules will still start at the origin O.

2.3.3 Reference Velocity

The reference velocity, $c_{\text{r,ref}}$ in the VHS model is given by [3],

$$c_{\text{r,ref}} = \sqrt{\frac{(15/8)(\pi mk)^{1/2}(4k/m)^{\upsilon}T^{1/2+\upsilon}}{\sigma_{\text{T,ref}}\Gamma(4-\upsilon)\mu}}^{1/\upsilon} \tag{35}$$

3 Results and Discussion

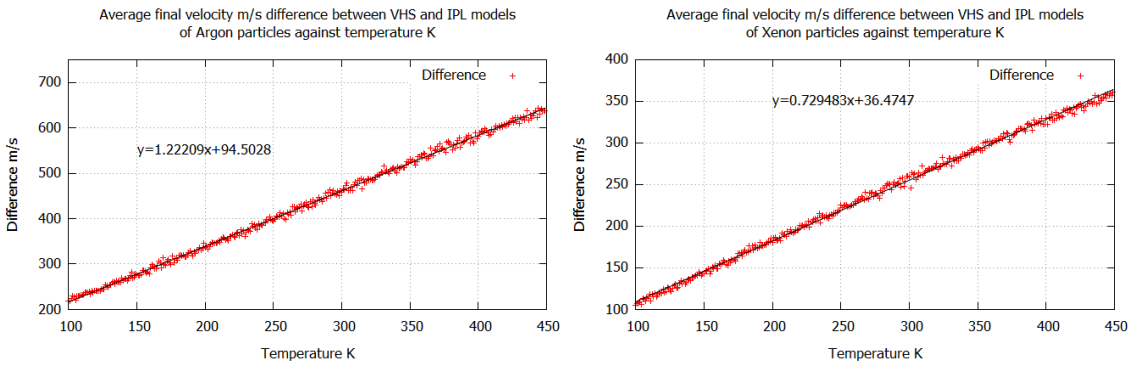
Our goal now is to find the difference between the Inverse Power Law and the Variable Hard Sphere models, specifically the difference between their final velocities of both molecules. We can find the difference for each collision using

$$\text{Difference} = \sqrt{|\vec{\mathbf{c}}'_{1,\text{ VHS}} - \vec{\mathbf{c}}'_{1,\text{ IPL}}|^2 + |\vec{\mathbf{c}}'_{2,\text{ VHS}} - \vec{\mathbf{c}}'_{2,\text{ IPL}}|^2} \tag{36}$$

We will then run the simulation 10000 times and sum up the difference

$$\text{Difference} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}|\vec{\mathbf{c}}'^{(i)}_{1,\text{ VHS}} - \vec{\mathbf{c}}'^{(i)}_{1,\text{ IPL}}|^2 + |\vec{\mathbf{c}}'^{(i)}_{2,\text{ VHS}} - \vec{\mathbf{c}}'^{(i)}_{2,\text{ IPL}}|^2} \tag{37}$$

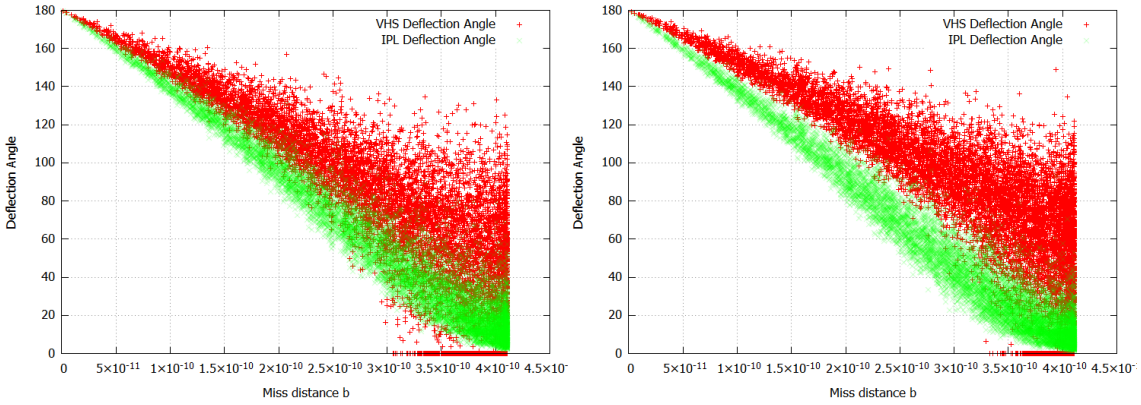
Lastly, we will do this for a range of temperatures for Argon and Xenon.



(a) Argon **(b)** Xenon

Figure 5: Graph of differences

From figures 5a and 5b we can clearly see that as temperature increases, the difference between the models also increases linearly for both Argon and Xenon particles. We



(a) 200K **(b)** 300K

Figure 6: Graph of deflection angles of Argon particles

can thus deduce that at high temperatures, the VHS model becomes less accurate as an approximation for the IPL model.

Figures 6a and 6b show the decrease in overlap of the deflection angles between temperatures 200K and 300K which further shows the deviation of the VHS model as an approximation of the IPL model as we approach higher temperatures. The opacity of IPL deflection angles has been decreased to show the degree of overlap.

4 Future Work

We can make further improve on the IPL and VHS models to include the simulation of diatomic molecules, accounting for their rotation and structure and further study the results of both models by using a wider range of temperatures.

A Appendix

A.1 Variables

Gas constant $R = \frac{k}{m}$, where k is the Boltzmann constant.

A.2 Particle Parameters

Element	Molecular Mass \kg	Viscosity Coefficient	Viscosity Index	Diameter \m
Neon	33.5×10^{-27}	2.975×10^{-5}	0.66	2.77×10^{-10}
Argon	66.3×10^{-27}	2.117×10^{-5}	0.81	4.17×10^{-10}
Krypton	139.1×10^{-27}	2.328×10^{-5}	0.80	4.76×10^{-10}
Xenon	218×10^{-27}	2.107×10^{-5}	0.85	5.74×10^{-10}

A.3 Figures

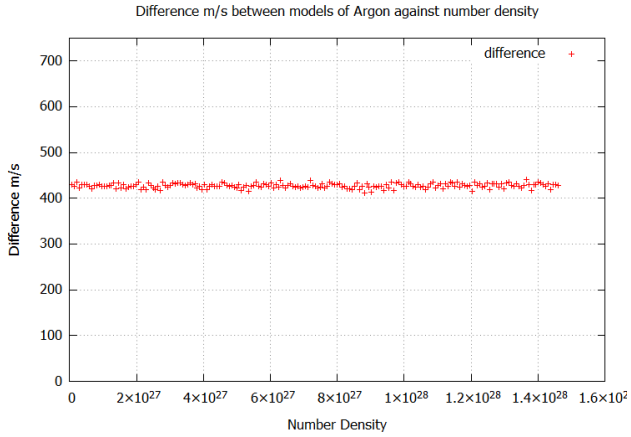


Figure 7: Difference between models against number density

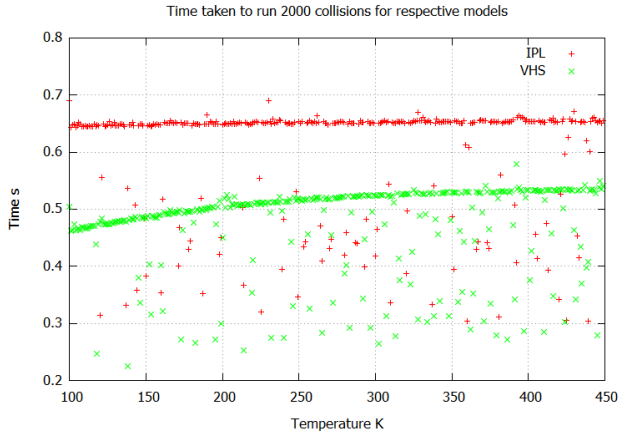


Figure 8: Time taken to run 2000 collisions for both VHS and IPL models. On modern hardware, the VHS model is still twice as fast as the IPL model.

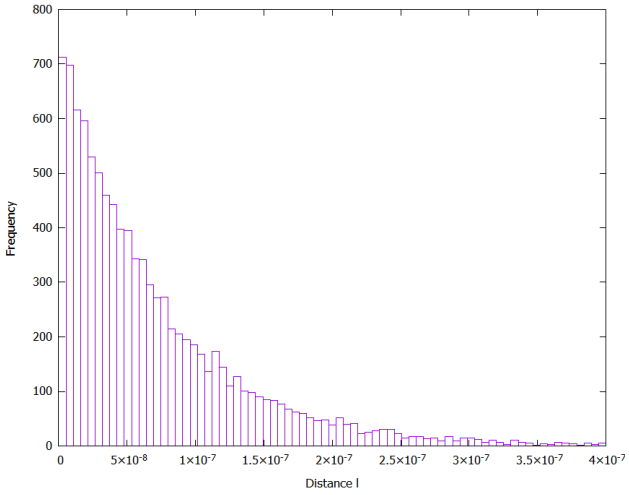


Figure 9: Frequency graph of distance l

References

[1] Vincenti and Kruger (1965). *Introduction to physical gas dynamics.*

[2] Bird, G.A. (1981). *Monte Carlo simulation in an engineering context.*

[3] Bird, G.A. (1994). *Molecular gas dynamics*.