Numerical Simulations of the Molecular Behavior and Entropy of Supercritical Argon

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Abstract

A numerical model is built, simulating the principles of kinetic gas theory, to predict pressures of molecules in a spherical pressure vessel; the model tracks a single particle and multiplies the force on the spherical walls by a mole of molecules to predict the net pressure. An intermolecular attractive force is added for high-density simulations, to replicate a real fluid; the force is chosen to ensure the fluid matches the Peng-Robinson equation of state as it is compressed to a near supercritical density. The standard deviations of the molecule position and velocity with respect to temperature and density is studied to define the entropy. A parametric study of a Stirling cycle heat engine utilizing near-supercritical densities is modeled, to study how the temperature dependence of the attractive intermolecular Van der Waal forces can affect the net total entropy change to the surrounding environment.

1 Introduction

In the design of any thermodynamic system to convert heat to and from mechanical work, the laws of thermodynamics must always be considered. The first law of thermodynamics
states that the change in internal energy equals the heat and work input into the working fluid \([1–6]\)

\[
\delta u = \delta q - \delta w, \tag{1}
\]

where \(\delta u \ (J/kg)\) is the change in specific internal energy, \(\delta q \ (J/kg)\) is the specific heat transfered, and \(w \ (J/kg)\) is the specific work applied across the boundary \([2–6]\)

\[
\delta w = P \cdot \delta v. \tag{2}
\]

The second law has been described by Rudolph Clausius \([1]\) in 1854 as

\[
\oint \frac{\delta q}{T} \leq 0, \tag{3}
\]

which states that any internally reversible thermodynamic cycle must generate a positive entropy \(\delta s \geq 0\) to the surrounding universe, where the change in entropy \(\delta s \ (J/kg \cdot K)\) is defined as \([2–12]\)

\[
\delta s = \frac{\delta q}{T}, \tag{4}
\]

where \(T \ (K)\) is the absolute temperature, and \(\delta q \ (J/kg)\) represent the heat transferred per unit mass. Because of Clausius’ equation, an ideal gas heat engine has a thermodynamic efficiency limit of the Carnot efficiency

\[
\eta_C = \frac{w_{out}}{q_{in}} = \frac{q_{in} - q_{out}}{q_{in}} = 1 - \frac{T_L}{T_H}, \tag{5}
\]

though exceptions to equation \([5]\) have been observed at the quantum level \([13–15]\) as well as in the presence of supercritical fluids \([16]\).

Entropy is also defined as a level of disorder, characterized by Boltzmann’s entropy
\[ S = k_B \cdot \log(\Omega), \tag{6} \]

where \( S \) (J/K) represents the total entropy, \( k_B \) (1.38065·10\(^{-23}\) J/K) represents Boltzmann’s constant, \( \log \) represents the natural logarithm, and \( \Omega \) represents the number of possible microstates of the system of molecules. If the molecules are at absolute zero (\( T = 0 \) K), when there is no movement of the molecules, then \( \Omega = 1 \), and thus (according to equation 6) \( S = 0 \) J/K.

Equation 6 can be derived from the equation for isothermal (\( \delta T = 0 \)) heating and expansion of an ideal gas. An ideal gas is a fluid at a low enough density where the intermolecular attractive and repulsive Van der Waal forces are negligible, and therefore the equation of state is defined in equation 7

\[ P \cdot V = N \cdot k_B \cdot T, \tag{7} \]

where \( P \) (Pa) represents the pressure, \( V \) (m\(^3\)) represents the total volume of the gas, \( N \) represents the number of molecules of the gas, \( k_B \) is the Boltzmann constant (1.38065·10\(^{-23}\) J/K), and \( T \) (K) represents the absolute temperature. When an ideal gas is undergoing isothermal expansion [3], the heat input \( q_{\delta T = 0} \) (J/kg) is equal to the work output \( W_{\delta T = 0} \) (J/kg) defined by equation 2, and therefore the heat input and work output of an ideal gas undergoing isothermal heating and expansion is defined in equation 8

\[ q_{\delta T = 0} = W_{\delta T = 0} = \int P \cdot dV = N \cdot k_B \cdot T \cdot \int \frac{dV}{V} = N \cdot k_B \cdot T \cdot \log\left(\frac{V_2}{V_1}\right). \tag{8} \]

The change in entropy of an ideal gas is defined by equation 4, and therefore the change in entropy of an ideal gas undergoing isothermal expansion is found by plugging equation 8 into equation 4

\[ \delta s_{\delta T = 0} = \frac{\delta q}{T} = N \cdot k_B \cdot \log\left(\frac{V_2}{V_1}\right) = k_B \cdot \log\left(\frac{V_2}{V_1}\right)^N. \tag{9} \]
By doubling the volume, you are effectively doubling the number of microstates possible (for each molecule), and therefore one can derive equation 6 from 9.

2 Kinetic Theory of an Ideal Gas

The kinetic model of an ideal gas \[ \text{[3,4,17]} \] is a well-established model to predict the kinetic energy of an ideal gas. Internal energy, by definition, is the summation of the kinetic energy from all of the random molecular motion within a fluid, as well as any potential energy from intermolecular forces. In the kinetic model, the gas is assumed to follow the ideal gas equation of state defined in equation 7. For the kinetic model to be applicable, the gas must be ideal, where all of the molecules are moving independent of each other, and there is no interaction between different gas molecules, either by collision or intermolecular forces \[ \text{[4]} \].

If a molecule is moving within the \( x \) direction and hits the boundary of a container or pressure vessel, provided the gas is thermodynamically stable and there is no heat transfer, it will bounce off of the wall in the opposite direction. The change in momentum for each molecular collision is therefore

\[
\Delta p = (m_m \cdot v_x) - (-m_m \cdot v_x) = 2 \cdot m_m \cdot v_x, \tag{10}
\]

where \( \Delta p \) (kg·m/s) is the change in momentum, \( m_m \) (kg) is the mass of an individual molecule, and \( v_x \) is the velocity in the \( x \)-direction. The average time \( \Delta \tau \) (s) for a molecule to cross the length \( L \) (m) of the pressure vessel is

\[
\Delta \tau = \frac{2L}{v_x}. \tag{11}
\]

The force applied to the walls of the pressure vessel with an individual molecular collision \( F_m \) (Newtons) is the change in momentum per unit time

\[
F_m = \frac{\Delta p}{\Delta \tau} = \frac{m_m \cdot v_x^2}{L}, \tag{12}
\]
and the total force on the walls of the pressure vessel $F$ (Newtons) is thus

$$F = N \cdot F_m = \frac{N \cdot m_m \cdot v_{RMS}^2}{L}, \quad (13)$$

where $N$ is the total count of the molecules.

So far this analysis has only been in the $x$-direction, when in reality the molecules are bouncing in three dimensions. Assuming the average speed in all three directions are identical, as is the case in a stable fluid, according to Pythagorean theorem the average Root Mean Square (RMS) total velocity $v_{RMS}$ (m/s) is thus

$$v_{RMS}^2 = v_x^2 + v_y^2 + v_z^2 = 3v_x^2, \quad (14)$$

and thus equation $(13)$ can be rewritten as

$$F = \frac{N \cdot m_m \cdot v_{RMS}^2}{3L}. \quad (15)$$

In the kinetic theory, equation $(15)$ would only apply to molecules that have no rotational or vibrational energies, specifically monatomic molecules such as helium, neon, argon, xenon, krypton, or radon gas [4].

The pressure, by definition, is merely the ratio of the total force over the area of the container, and therefore assuming the container is cubic in shape, the pressure $P$ (Pa) is

$$P = \frac{F}{L^2} = \frac{N \cdot m_m \cdot v_{RMS}^2}{3L^3} = \frac{N \cdot m_m \cdot v_{RMS}^2}{3V}, \quad (16)$$

where $V$ (m$^3$) is the volume of the container.

The total kinetic energy of the gas $KE$ (J) is defined as the sum of the kinetic energies of the gas molecules

$$KE = \frac{1}{2} N \cdot m_m \cdot v_{RMS}^2, \quad (17)$$
and therefore plugging equation 17 into equation 16

\[ P = \frac{2 \cdot KE}{3V}, \]

and therefore the kinetic energy of a monatomic ideal gas can be defined as

\[ KE = \frac{3}{2} P \cdot V. \] (18)

As the kinetic model is dealing with an ideal gas, equation 7 is applicable, and thus

\[ KE = \frac{3}{2} P \cdot V = \frac{3}{2} \cdot m_T \cdot R \cdot T = \frac{3}{2} N \cdot k_B \cdot T, \] (19)

where \( m_T \) (kg) is the total mass of the gas

\[ m_T = N \cdot m_m. \]

The relationship between temperature and kinetic energy is thus defined with equations 17 and 19. This can be rewritten as

\[ KE = \frac{1}{2} N \cdot m_m \cdot v_{RMS}^2 = \frac{3}{2} N \cdot k_B \cdot T, \]

and thus the average total velocity of a particle of an ideal gas is proportional to the square root of the temperature \[4\]

\[ v_{RMS} = \sqrt{\frac{3 k_B \cdot T}{m_m}}. \] (20)

The kinetic heat energy \( \delta q \) of a monatomic ideal gas is simply

\[ U = \frac{3}{2} N \cdot k_B \int_0^T dT = \frac{3}{2} N \cdot k_B \cdot T. \]

The change in entropy of an ideal monatomic gas undergoing isochoric heating at a constant
volume is therefore

\[
\delta s_{V=0} = \frac{3}{2} N \cdot k_B \int_{T_0}^{T} \frac{dT}{T} = \frac{3}{2} N \cdot k_B \cdot \log \left( \frac{T}{T_0} \right) = \frac{3}{2} N \cdot k_B \cdot \log \left( \frac{\frac{m_m v_{RMS}^2}{3k_B}}{\frac{m_m v_{RMS,0}^2}{3k_B}} \right) = \frac{3}{2} N \cdot k_B \cdot \log \left( \frac{v_{RMS}}{v_{RMS,0}} \right)^2 = 3 \cdot N \cdot k_B \cdot \frac{v_{RMS}}{v_{RMS,0}}
\]

This represents the change in entropy for heating an ideal gas at a constant volume; it is different from equation 9, which represents the isothermal heating of an ideal gas with simultaneous expansion in order to maintain a constant temperature. If equation 9 and 21 are combined, the estimated entropy is

\[
S = N \cdot k_B \cdot \{3 \cdot \log(v_{RMS}) + \log \left( \frac{V}{b \cdot MM} \right) \}.
\]

3 Kinetic Gas Simulation

A model was built in the Fortran programming language, to simulate one mole (6.02214086-10^{23}) of argon molecules traveling in a spherical volume. Argon was chosen because it is a simple monatomic molecule, commonly used in industry, and its critical properties are not at excessively low temperatures (ex. Helium). Argon has a molar mass \(MM\) of 39.9 g/mole, a critical pressure \(P_c\) of 4.863 MPa, a critical temperature \(T_c\) of 150.687 K, a critical density of 535 kg/m\(^2\), and a critical specific volume \(V_c\) of 1.8692 cm\(^3\)/g.

The model will take the dimensionless reduced temperature \(T_R\) and reduced specific volume \(V_R\) as inputs. The temperature is easily calculated as \(T = T_R \cdot T_c\), and the volume (for one mole) is calculated as \(V = V_R \cdot V_c \cdot MM\). From the known volume of the sphere, the radius and surface area are easily calculated as

\[
R_{sphere} = \left( \frac{3}{\pi \cdot 4} V_{sphere} \right)^{\frac{1}{3}},
\]

\[
A_{sphere} = 4 \cdot \pi \cdot R_{sphere}^2.
\]

The model has the option of simulating the particle at a constant speed for a given
temperature, if so the speed is constantly the $v_{RMS}$ speed for the given temperature defined in equation 20. The model also gives the option of simulating a profile of faster and slower speeds; the speed profile will maintain the same $RMS$ average speed defined in equation 20, and the average speed $v_{avg}$ (m/s) will be determined as

$$v_{avg} = v_{RMS} \sqrt{\frac{8}{3 \pi}} \tag{24}$$

If the model calls for $N_Y$ velocity increments to be simulated, a subroutine in the Fortran code will generate a $N_Y \cdot 1$ vector-array, ranging from 0.2 to 1.8, averaging 1.0, with a standard deviation of 0.71. This vector-array will be multiplied by the average molecule velocity at the boundary $v_{avg}$; the $RMS$ of the velocity vector-array will be equal to $v_{RMS}$ determined with 20.

The time-step $\delta \tau$ (s) is determined by the estimated time for an argon molecule traveling at the average speed $v_{avg}$ (m/s) across the diameter of the sphere $2 \cdot R_{sphere}$ (m). This time is divided by the integer value $N_{\delta \tau}$ that is specified by the model, to give a time-step.

$$\delta \tau = \left( \frac{2 \cdot R_{sphere}}{v_{avg}} \right) \cdot \frac{1}{N_{\delta \tau}} \tag{25}$$

It is necessary to record the molecule’s position and velocity with each increment, but with different angles and speeds, it is impossible to know exactly how many time steps will be needed for each test parameter. In this Fortran code, an array length of $10 \cdot N_{\delta \tau}$ was found to be more than enough to avoid any risk of running out of array space. In this study, a resolution of $N_{\delta \tau} = 300$ was used; increasing the resolution beyond this number was not observed to have any significant impact on the results.

At each velocity increment, the model simulates a molecule leaving the surface of the sphere at different angles. As a sphere is effectively identical at all surface locations, the point of initial contact will be defined as ($-R,0,0$). The initial velocity will be defined in
three dimensions as

\[
\begin{align*}
V_x &= V_i \sin(\theta) \cdot \cos(\phi) \\
V_y &= V_i \sin(\theta) \cdot \sin(\phi) \\
V_z &= V_i \cos(\theta),
\end{align*}
\] (26)

where \(\phi\) ranges from 0 to \(\pi/2\), and \(\theta\) ranges from 0 to \(\pi\), both in 361 increments, resulting in \(361^2 = 130,321\) different simulations for each temperature and volume increment. The velocity magnitude \(V_i\) (m/s) for the individual increment is determined from the temperature (equation 20); the initial velocity magnitude is kept constant at \(v_{RMS}\) for each temperature, and \(N_Y = 1\).

The kinetic gas theory assumes the molecule travels across the long length of the volume and directly impacts the wall; in reality molecules will travel at all possible angles. If a molecule were to travel directly through the center of the sphere, the time \(\tau\) (s) to travel will simply be \(\tau = 2 \cdot R_{sphere}/v_{avg}\), and the force due to the change in momentum for a single molecule will be derived from equation 15, where \(F = m_m \cdot v_{RMS}^2 / (3 \cdot 2 \cdot R_{sphere})\). Assuming the spherical volume, if a molecule were to travel at an angle from the center of the sphere, the travel time \(\tau\) (s) will be reduced, but the force will also be reduced as the molecule is hitting the surface at an angle, and will only transmit part of its energy to changing momentum and direction.

The simulation starts off with a molecule at position \((-R,0,0)\). With each time-step, it increments the three dimensions based on the 3-dimensional velocity described in equation 26. The model uses a \texttt{while} loop until the radius \(r_{ii}\) (m) of the position

\[
r_{ii} = \sqrt{x^2 + y^2 + z^2};
\] (27)

exceeds the radius of the sphere, \(r_{ii} > R_{sphere}\). At this point, the molecule has impacted the cylinder wall. If the molecule travels right through the center and impacts the other end at position \((R,0,0)\), then the velocity will be \(V_i \cdot (1,0,0)\), and the force impacted will be
at a maximum; the travel time \( \tau \) (s) will also be the maximum \( \tau = 2R_{\text{sphere}}/V_i \). If the molecule were to travel at a 90° perpendicular direction, where the velocity were \( V_i\cdot(0, 1, 0) \) or \( V_i\cdot(0, 0, 1) \), the position will remain at (-R,0,0) and the travel time \( \tau \) will effectively be 0. For all the molecules traveling at angles in between the two extremes, the force applied is simply the dot product of the velocity with the position of the impact

\[
V X_{\text{rat}} = X_x V_x + X_y V_y + X_z V_z,
\]

(28)

and the dimensionless \( V X_{\text{rat}} \) is applied to the equation for the force applied by a single molecule \( F_m \) (N) defined in equation (29)

\[
F_m = \frac{V X_{\text{rat}} m_i \sqrt{V_x^2 + V_y^2 + V_z^2}}{3 \cdot 2 \cdot R_{\text{sphere}}}.
\]

(29)

Throughout this simulation, for all initial angles and velocities, the position and velocity in three dimensions is tabulated and recorded. Each position and velocity is stored in a large data file, and at the conclusion of the simulation, the average, RMS, and standard deviation of both the positions and the velocities are determined. The purpose of determining the standard deviation is to find the relationship between the standard deviation of the position and velocity, as it relates to entropy, determined with equations 4, 9, and 21.

4 Kinetic-Potential Simulation

The ideal gas equation breaks down in the presence of intermolecular attractive and repulsive Van der Waal forces, and therefore empirical equations of states are used, such as the
Redlich-Kwong \[18\] and the Peng-Robinson equation of state \[19,20\]

\[ P = \frac{R \cdot T}{v - B} - \frac{A \cdot \alpha}{v^2 + 2 \cdot B \cdot v - B^2}, \]  
(30)

\[ A = 0.45724 \cdot \frac{R^2 \cdot T^2}{P_c}, \]

\[ B = 0.07780 \cdot \frac{R \cdot T_c}{P_c}, \]

\[ \alpha = (1 + \kappa \cdot (1 - \sqrt{T_R}))^2, \]

\[ \kappa = 0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2, \]

where \( \omega \) is Pitzer’s acentric factor, defined as

\[ \omega = \log_{10} (\frac{P_c}{P'_s}) - 1, \]  
(31)

where \( P'_s \) (Pa) is the saturated pressure at a reduced temperature of \( T_R = 0.7 \), and \( P_c \) (Pa) is the critical pressure. For all of the monatomic fluids including argon, \( \omega = 0 \). The coefficient \( A \) represents the intermolecular attractive force, and the coefficient \( B \) represents the actual volume of the molecules at absolute zero. As the specific volume \( v \) (m\(^3\)/kg) increases (and the density decreases), equation (30) matches the ideal gas law defined in equation (7).

As the density of a fluid increases to the point of being a saturated liquid, saturated gas, or supercritical fluid, intermolecular attractive (and repulsive) forces \[21–26\] can impact the pressure and temperature of the fluid. As the molecules get closer together in the presence of attractive intermolecular forces, the internal potential energy will decrease. The thermodynamic data yields an empirical equation that closely predicts the change in specific internal energy \( \Delta u \) (J/kg) during isothermal compression and expansion

\[ \Delta u = \frac{a'}{\sqrt{T}} \cdot (\frac{1}{v_1} - \frac{1}{v_2}), \]  
\[ a' = \frac{R^2 \cdot T^{2.5}}{9 \cdot (2^{\frac{3}{2}} - 1) \cdot P_c}, \]  
(32)

where \( v_1 \) and \( v_2 \) (m\(^3\)/kg) represent the specific volume, \( T \) represents the temperature, \( R \)
(J/kg·K) represents the gas constant,

\[ R = \frac{R_U}{MM} = \frac{A \cdot k_B}{MM}, \quad (33) \]

where \( A \) is Avogadro’s Number \( 6.02214 \times 10^{23} \) (J/K), \( k_B \) is Boltzman’s Constant \( 1.38 \times 10^{-23} \) (J/K), \( MM \) (kg/mole) is the molar mass, \( T_C \) (K) represents the critical temperature, and \( P_C \) (Pa) represents the critical pressure. The intermolecular attractive parameter \( a' \) defined in equation \( 32 \) is thus \( 1,063.8 \) Pa·K\(^{0.5}\)·m\(^{6}\)·kg\(^{-2}\) for argon.

The value of \( a' \) happens to be the same coefficient used in the Redlich-Kwong \([18]\) equation of state; equation \( 32 \) does not actually use any equation of state, as it is an empirical equation based on published data by NIST in the literature. The change in internal energy equation \( 32 \) during evaporation has been observed on many different molecules, including the highly polar fluid water; the monatomic fluids of argon, krypton, and xenon; the diatomic fluid nitrogen; ammonia; the hydrocarbons of methane, ethane, propane, and both normal and iso-butane; and the refrigerants Freon R-12, R-22, and R-134a. All of the data provided utilized the available online tables from NIST \([27]\), which are based on previously published experimental and empirical thermodynamics data \([28–53]\). First, equation \( 32 \) matched remarkably for the change in internal energy during isothermal expansion during vaporization, all over a wide temperature range \( \Delta T \) (K). The calculated coefficient \( a' \) (Pa·K\(^{0.5}\)·m\(^{6}\)·kg\(^{-2}\)) and the coefficient of determination \( R^2 \) between the NIST values and equation \( 32 \) are all tabulated in Table 1.

If dealing with a purely ideal gas, molecules have no interaction with each other, and the pressure and velocities can be solved with the purely analytical approach of the kinetic gas theory. To model real fluids, with intermolecular Van der Waal fluids, assumptions for the intermolecular forces are necessary. In Lennard Jones’ equation, the attractive VDW force \( F_{VDW} \) (N) for two molecules is proportional to the distance between particles to the sixth exponent \([5, 54]\)

\[ F_{VDW} = \frac{a'}{r^6}, \quad (34) \]
| Fluid          | M (g/Mole) | $T_C$ (K) | $P_C$ (MPa) | $a'$  | $\Delta T$ (K) | $R^2$  |
|---------------|------------|-----------|-------------|-------|----------------|-------|
| Water (H$_2$O)| 18.02      | 647.14    | 22.064      | 43.971| 274-647        | 0.98572|
| Argon (Ar)    | 39.948     | 150.687   | 4.863       | 1.062 | 84-150         | 0.98911|
| Krypton (Kr)  | 83.798     | 209.48    | 5.525       | 484   | 116-209        | 0.98858|
| Xenon (Xe)    | 131.3      | 289       | 5.84        | 417   | 162-289        | 0.98972|
| Nitrogen (N$_2$) | 28.0134   | 126.2     | 3.4         | 1.982 | 64-126         | 0.98565|
| Ammonia (NH$_3$) | 17.0305 | 405.4     | 11.3119     | 29.824| 196-405        | 0.98603|
| Methane (CH$_4$) | 16.043   | 190.53    | 4.598       | 12.520| 91-190         | 0.97818|
| Ethane (C$_2$H$_6$) | 30.07   | 305.34    | 4.8714      | 10.937| 91-305         | 0.94881|
| Propane (C$_3$H$_8$) | 44.098 | 369.85    | 4.2477      | 9.418 | 86-369         | 0.93372|
| Butane (C$_4$H$_{10}$) | 58.125  | 425.16    | 3.796       | 8.594 | 135-424        | 0.9631 |
| Iso-Butane (C$_4$H$_{10}$) | 58.125  | 407.85    | 3.64        | 8.078 | 114-407        | 0.95368|
| Freon R-12    | 120.91     | 385.12    | 4.1361      | 1.423 | 175-384        | 0.98465|
| Freon R-22    | 86.47      | 369.295   | 4.99        | 2.077 | 172-369        | 0.98741|
| Freon R-134a  | 102.03     | 374.21    | 4.0593      | 1.896 | 170-374        | 0.9884 |

Table 1: The calculated coefficient $a'$ (Pa$\cdot$K$^{0.5}\cdot$m$^6\cdot$kg$^{-2}$) and the coefficient of determination $R^2$ between the NIST values and equation 32 over a specified temperature range $\Delta T$ (K).

where $a'$ is a constant and $r$ (m) is the distance between two molecules. While the Lennard Jones potential equation [54] also includes a twelfth power for the repulsive forces, these are not based in reality, and the repulsive forces due to the Pauli Exclusion Principle are considered by subtracting the minimum possible volume $B$ (m$^3$/kg) in the VDW equation of state.

For the sake of simplicity, assume that the volume is a perfect sphere of a real, monatomic fluid molecules following the VDW equation of state. The surface area $A_{sphere}$ (m$^2$) and volume of this sphere $V_{sphere}$ (m$^3$) is simply

$$V_{sphere} = \frac{4}{3}\pi R_{sphere}^3,$$

$$A_{sphere} = 4\pi R_{sphere}^2,$$

where $R_{sphere}$ (m) represents the sphere radius. Next, assume a molecule is on the far edge of this sphere; to determine the net attractive forces one must determine the summation of the average distances of the other molecules within the volume.

$$\hat{P}(x) = \frac{A(x)}{A_{avg}}$$
The cross-section area of the sphere at a given $X$-axis point $A(x)$ can be found from the radius of the cross section

$$A(x) = \pi \cdot R_{\text{sphere}}^2 \cdot \cos^2 \left( \sin^{-1} \left( \frac{x}{R_{\text{sphere}}} \right) \right),$$

(37)

while the average cross section area is simply the total volume of the sphere over the diameter of the sphere

$$A_{\text{avg}} = \frac{4}{3} \frac{\pi \cdot R_{\text{sphere}}^3}{2 \cdot R_{\text{sphere}}},$$

(38)

$$= \frac{2}{3} \frac{\pi \cdot R_{\text{sphere}}^2}{},$$

and now the probability $\tilde{P}(x)$ can be found by plugging the results of equation 37 and 38 into equation 36

$$\tilde{P}(x) = \frac{3}{2} \cos^2 \left( \sin^{-1} \left( \frac{x}{R_{\text{sphere}}} \right) \right).$$

(39)

The next step is to integrate across the diameter of the sphere along the $X$-axis in order to find the overall average distance to the sixth power $\bar{\delta x}^6$ (m)

$$\delta x^6 = \int_{-R}^{R} (R - x)^6 \cdot \tilde{P}(x) dx,$$

(40)

$$= \int_{-R_{\text{sphere}}}^{R_{\text{sphere}}} (R_{\text{sphere}} - x)^6 \frac{3}{2} \cos^2 \left( \sin^{-1} \left( \frac{x}{R_{\text{sphere}}} \right) \right) dx,$$

$$= \frac{16}{3} R_{\text{sphere}}^6.$$

It is desired not just for the average distance to a particle at the edge of the sphere, but all throughout the radius. A particle moving on the $X$-axis will experience attraction from particles both in front of and behind it, and therefore the proper average $\tilde{\delta x}^6$, for the purpose of determining net total attraction towards the center of the sphere

$$\tilde{\delta x}^6(r) = \int_{-R_{\text{sphere}}}^{r} (r - x)^6 \frac{3}{2} \cos^2 \left( \sin^{-1} \left( \frac{x}{R_{\text{sphere}}} \right) \right) dx - \int_{r}^{R_{\text{sphere}}} (R_{\text{sphere}} - x)^6 \frac{3}{2} \cos^2 \left( \sin^{-1} \left( \frac{x}{R_{\text{sphere}}} \right) \right) dx,$$

(41)
which can be simplified by the approximate equation

\[ \delta x^6(r) \approx \frac{16}{3} r^3, \]  

(42)

where \( r \) (m) represents the radial position on the X-axis, where \( 0 < r < R_{\text{sphere}} \). The correlation coefficient between the two equations \( \text{eq. 41} \) and \( \text{eq. 42} \), where \( \delta r = 0.001 \), is \( R = 0.99936 \).

| \( r \)  | \( \delta x^5(r) \) eq. 41 | \( \delta x^9(r) \) eq. 42 |
|-------|--------------------------|--------------------------|
| 0.05005 | 0.033158                | 0.00066867               |
| 0.1001  | 0.06865                 | 0.0053494                |
| 0.15015 | 0.10887                 | 0.018054                 |
| 0.2002  | 0.15633                 | 0.042795                 |
| 0.25025 | 0.21373                 | 0.083584                 |
| 0.3003  | 0.28399                 | 0.14443                  |
| 0.35035 | 0.37035                 | 0.22935                  |
| 0.4004  | 0.4764                  | 0.34236                  |
| 0.45045 | 0.60615                 | 0.48746                  |
| 0.4995  | 0.76063                 | 0.66467                  |
| 0.54955 | 0.95109                 | 0.88515                  |
| 0.5996  | 1.1803                  | 1.1497                   |
| 0.64965 | 1.4545                  | 1.4623                   |
| 0.6997  | 1.7809                  | 1.827                    |
| 0.74975 | 2.1671                  | 2.2477                   |
| 0.7998  | 2.6218                  | 2.7286                   |
| 0.84985 | 3.1547                  | 3.2736                   |
| 0.8999  | 3.7763                  | 3.8867                   |
| 0.94995 | 4.4982                  | 4.5719                   |
| 1       | 5.3333                  | 5.3333                   |

Table 2: Comparison of \( \delta x^6(r) \) functions between equation 41 and 42. The correlation coefficient between the two equations (\( \delta r = 0.001 \)) is \( R = 0.99936 \).

While typical conservative forces such as gravity, electrostatic forces, and VDW attractive forces increase as the distance between two attractive objects decreases, it is clear from equation 41 that the forces will decrease when a given molecule moves closer to the center of the volume, proportional to the radial position cubed. This makes physical sense, as near the center of the sphere, the attractive forces of neighboring molecules on one side of the molecule counteract the attractive forces from the other side.

When modeling the effects of intermolecular attractive forces, it is not enough to simply
take the pressure reduced from the intermolecular attractive Van der Waal force, multiply it by the spherical surface area, divide it by the number of molecules, and reduce it by the relative radius cubed. The reason for this is that the overall change in pressure of the real fluid includes the pressure reduced from the attractive force, as well as the change in time for the molecule to travel across the spherical volume. An increasing force will inherently accelerate the molecule towards the center, and decelerate it towards the other side, reducing the travel time, and thus increasing the pressure. It is necessary to select a force that balances these two impacts on the final pressure, in order to achieve the correct pressure for the equation of state.

A parametric study of the supercritical argon molecules propagating in the sphere was conducted to determine the exact function for the intermolecular force on each molecule. The maximum such a force will be is that which will cause the drop in pressure observed in most empirical equations of states, such as the Peng-Robinson defined in equation 30

\[
\delta P = - \frac{A \cdot \alpha}{v^2 + 2B^*v - B^2}. \tag{43}
\]

The derivative of the change in internal energy defined in equation 32 gives a very close approximation for \(\delta P\)

\[
\delta P \approx - \frac{R^2T_c^{2.5}}{9(2^* - 1)P_c} \frac{1}{\sqrt{T}} \frac{1}{v^2}.
\]

The force needs to be some ratio of this, as increasing the force will increase the average speed of a molecule (for a given \(v_{RMS}\) (m/s) at the surfaces), reducing the time in between impacted the sphere’s surface, and increasing the pressure.

A parametric study was performed to find the exact ratio of this pressure, and a function for the force (N) on a given molecule, accelerating it as it travels towards the center and decelerating it as it travels back towards the surface, was determined in order that the molecule satisfy the Peng-Robinson equation of state defined in equation 30. The Van der
Waal attractive force $F_{VDW}$ (N) is thus

$$F_{VDW} = \chi \cdot \frac{R^2 T_{c}^{2.5}}{9(2^{4} - 1)P_{c}} \cdot \frac{1}{\sqrt{T}} \cdot \frac{1}{\sqrt{v^2}} \cdot \frac{A_{sphere}}{N},$$

(44)

where $N$ is the number of molecules in the sphere (one mole for this simulation), and $\chi$ is a dimensionless coefficient

$$\chi = 2.3246 - \frac{0.8441}{\sqrt(V_R)} - 0.8670 \cdot T_R, \quad T_R \leq 1$$

$$= 2.3246 - \frac{0.8441}{\sqrt(V_R)} - 0.8670 \cdot \sqrt{T_R}, \quad T_R \geq 1$$

(45)

determined from a parametric study. This force $F_{VDW}$ (N) is the force at the surface of the sphere towards the center; this force decreases in each of the three dimensions as the molecule gets closer to the center

$$F_x = -F_{VDW} \cdot \left(\frac{x}{R}\right)^3.$$  

$$F_y = -F_{VDW} \cdot \left(\frac{y}{R}\right)^3.$$  

$$F_z = -F_{VDW} \cdot \left(\frac{z}{R}\right)^3.$$  

5 Kinetic Simulation to Determine Entropy

Two parametric simulations of this model were conducted, with negligibly low intermolecular attractive forces applied, for one mole of near-ideal gas argon. The first parametric simulation (run 1) started off at a reduced specific temperature $T_R$ of 2.0, and increased to 3.0, while maintaining a constant reduced specific volume $V_R$ of 100. The second parametric simulation (run 2) started off with a reduced specific volume $V_R$ of 100, expanded up to a reduced specific volume $V_R$ of 1,000, all at a constant reduced temperature $T_R$ of 2.0 (approximately 300 K). The actual volume of the sphere $V_{sphere}$ (m$^3$) for one mole of argon was determined from the reduced volume $V_R$, the specific density $\rho_c = 535$ kg/m$^3$, and the
molar mass $MM = 39.9$ g/mole simply by

$$V_{sphere} = \frac{V_R \cdot MM}{\rho_c},$$

and thus the radius $R_{sphere}$ (m) and surface area $A_{sphere}$ (m$^2$) of the sphere can be determined from $V_{sphere}$ (m$^3$) with equation (46).

The reduced specific volumes $V_R$ and reduced specific temperatures $T_R$, as well as the pressures determined with the model $P_{kin}$ (kPa), the pressures determined with the Peng-Robinson equation of state $P_{PR}$ (kPa) defined in equation (30) as well as the internal energy $U$ (kJ), are tabulated in Table 3 for run 1 and Table 6 for run 2. In both simulation, the numerical prediction for the pressure matched the Peng-Robinson pressures within less than 1%. The internal energy for run 1 went up with increasing temperatures based on the specific heat $C_V$ (J/kg·K), whereas the internal energy for run 2 was nearly constant; the minimal increase is due to the increase in internal potential energy, due to the reduced loss in pressure from the attractive Van der Waal intermolecular forces (equation (43)).

The average molecular positions $\text{Avg} \ X$, $\text{Avg} \ Y$, and $\text{Avg} \ Z$ (m); and RMS molecular velocities $\text{RMS} \ V_X$, $\text{RMS} \ V_Y$, and $\text{RMS} \ V_Z$ (m/s) are tabulated in Tables 4 and 7 for run 1 and run 2, respectively. The standard deviations of the molecular position $X_{STD}$, $Y_{STD}$, and $Z_{STD}$ (m); and standard deviations of the molecular velocities $V_{X,STD}$, $V_{Y,STD}$, and $V_{Z,STD}$ (m/s) are tabulated in Tables 5 and 8 for run 1 and run 2, respectively. As expected, in run 1, with increasing temperatures at a constant volume, the standard deviations of the velocity increases, whereas the standard deviations of the position remains relatively unchanged. Also expected, in run 2, with increasing volume and a constant temperature, the standard deviations of the position increases, whereas the standard deviations of the velocity remains relatively unchanged.

Entropy is a measure of the disorder of a system, and the number of possible positions and velocities of a molecular system, and so it would make logical sense that as the entropy of a system of molecules increases, the standard deviations of the molecular positions and/or velocities would increase. The entropy $S$ (J/kg·K) as estimated in equation (22) was compared
to the standard deviations of the molecular positions and velocities, and empirical equation (47) was generated from the numerically obtained standard deviations of run 1 and run 2. The comparisons in entropy are tabulated in Table 9 and the correlation coefficient $R$ between equation 22 and 47 for both run 1 and run 2 was $R=0.9923$.

\[
S = \Phi_1 + \Phi_2 \cdot V_{STD} + \Phi_3 \cdot X_{STD}, \tag{47}
\]

\[
X_{STD} = \sqrt{X_{X,STD}^2 + X_{Y,STD}^2 + X_{Z,STD}^2}
\]

\[
V_{STD} = \sqrt{V_{X,STD}^2 + V_{Y,STD}^2 + V_{Z,STD}^2}
\]

\[
\Phi_1 = 172.2593,
\]

\[
\Phi_2 = 1.2793 \cdot 10^{-4},
\]

\[
\Phi_3 = 2168.8433.
\]
Table 3: The reduced temperature $T_R$, reduced specific volume $V_R$, pressure (obtained with the model) $P_{\text{kin}}$ (kPa), pressure obtained with the Peng-Robinson equation of state defined in equation 30 $P_{PR}$ (kPa), the % errors between the numerical and empirical pressure, and the internal energy $U$ (kJ) determined with the RMS velocity (Table 4) for run 1.
\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Trial & Avg X (m) & Avg Y (m) & Avg Z (m) & RMS $V_X$ (m/s) & RMS $V_Y$ (m/s) & RMS $V_Z$ (m/s) \\
\hline
1 & -0.066977 & 0.027098 & -2.778e-09 & 289.2383 & 204.4911 & 250.8883 \\
2 & -0.06695 & 0.027107 & -2.7757e-09 & 293.2069 & 207.0102 & 254.0916 \\
3 & -0.066952 & 0.027107 & -2.0865e-09 & 296.7418 & 209.5186 & 257.1673 \\
4 & -0.066953 & 0.027106 & -2.7759e-09 & 300.2352 & 211.9975 & 260.207 \\
5 & -0.066954 & 0.027106 & -2.776e-09 & 303.6895 & 214.4473 & 263.2111 \\
6 & -0.066956 & 0.027105 & -2.7761e-09 & 307.105 & 216.8698 & 266.1814 \\
7 & -0.066957 & 0.027105 & 9.4804e-09 & 310.4831 & 219.2653 & 269.1193 \\
8 & -0.066958 & 0.027104 & 5.1647e-09 & 313.8248 & 221.635 & 272.0258 \\
9 & -0.066959 & 0.027104 & -2.776e-09 & 317.1318 & 223.9793 & 274.9017 \\
10 & -0.06696 & 0.027103 & -2.7764e-09 & 320.405 & 226.2995 & 277.7475 \\
11 & -0.066961 & 0.027103 & 7.976e-09 & 323.6448 & 228.5964 & 280.5649 \\
12 & -0.066962 & 0.027103 & -1.9462e-09 & 326.8527 & 230.8708 & 283.3541 \\
13 & -0.066963 & 0.027103 & -2.7766e-09 & 330.0303 & 233.1222 & 286.116 \\
14 & -0.066963 & 0.027102 & -2.7767e-09 & 333.1775 & 235.352 & 288.852 \\
15 & -0.066964 & 0.027102 & -2.7767e-09 & 336.2957 & 237.5618 & 291.5612 \\
16 & -0.066964 & 0.027102 & -2.7768e-09 & 339.3856 & 239.75 & 294.2463 \\
17 & -0.066965 & 0.027102 & -2.7768e-09 & 342.4478 & 241.92 & 296.9058 \\
18 & -0.066966 & 0.027102 & -2.7769e-09 & 345.4824 & 244.0701 & 299.543 \\
19 & -0.066966 & 0.027101 & -2.7769e-09 & 348.4907 & 246.2012 & 302.1575 \\
20 & -0.066967 & 0.027101 & -2.777e-09 & 351.4736 & 248.314 & 304.7493 \\
21 & -0.066967 & 0.027101 & -1.8002e-09 & 354.4316 & 250.4091 & 307.319 \\
\hline
\end{tabular}
\caption{The mean position and RMS velocity for run 1.}
\end{table}

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| Trial | $X_{X,STD}$ (m) | $X_{Y,STD}$ (m) | $X_{Z,STD}$ (m) | $V_{X,STD}$ (m/s) | $V_{Y,STD}$ (m/s) | $V_{X,STD}$ (m/s) |
|-------|----------------|----------------|----------------|-------------------|-----------------|-------------------|
| 1     | 0.0026905      | 0.00067387     | 0.0017681      | 12111.056         | 12864.746       | 62944.914         |
| 2     | 0.0026915      | 0.00067418     | 0.0017701      | 12427.305         | 13188.486       | 64562.535         |
| 3     | 0.0026915      | 0.00067416     | 0.00177        | 12729.76          | 13510.059       | 66135.008         |
| 4     | 0.0026914      | 0.00067414     | 0.0017699      | 13032.178         | 13831.644       | 67797.68          |
| 5     | 0.0026914      | 0.00067412     | 0.0017698      | 13334.629         | 14153.262       | 69280.078         |
| 6     | 0.0026914      | 0.00067411     | 0.0017697      | 13636.997         | 14474.855       | 70852.547         |
| 7     | 0.0026912      | 0.00067409     | 0.0017696      | 13939.477         | 14796.468       | 72425.211         |
| 8     | 0.0026912      | 0.00067408     | 0.0017695      | 14242.004         | 15117.968       | 73998.047         |
| 9     | 0.0026911      | 0.00067406     | 0.0017695      | 14544.544         | 15439.505       | 75570.953         |
| 10    | 0.0026911      | 0.00067405     | 0.0017694      | 14847.077         | 15761.027       | 77143.688         |
| 11    | 0.0026911      | 0.00067404     | 0.0017693      | 15149.649         | 16082.619       | 78716.648         |
| 12    | 0.002691      | 0.00067404     | 0.0017693      | 15452.23           | 16404.287       | 80289.547         |
| 13    | 0.002691      | 0.00067402     | 0.0017692      | 15754.771         | 16725.828       | 81862.352         |
| 14    | 0.002691      | 0.00067401     | 0.0017692      | 16057.435         | 17047.375       | 83435.445         |
| 15    | 0.002691      | 0.00067401     | 0.0017691      | 16359.894         | 17368.988       | 85007.906         |
| 16    | 0.002691      | 0.000674       | 0.0017691      | 16662.418         | 17690.438       | 86580.891         |
| 17    | 0.0026909     | 0.000674       | 0.001769       | 16964.77          | 18012.127       | 88153.094         |
| 18    | 0.0026909     | 0.00067399     | 0.001769       | 17267.299         | 18333.793       | 89726.031         |
| 19    | 0.0026909     | 0.00067398     | 0.0017689      | 17569.984         | 18655.346       | 91299.148         |
| 20    | 0.0026909     | 0.00067398     | 0.0017689      | 17872.594         | 18976.932       | 92872.109         |
| 21    | 0.0026909     | 0.00067397     | 0.0017689      | 18175.207         | 19298.521       | 94444.992         |

Table 5: The position and velocity standard deviations for run 1.
| Trial | $V_R$ | $T_R$ | $P_{\text{kin}}$ (kPa) | $P_{PR}$ (kPa) | $P_{\text{error}}$ (%) | $U$ (kJ) |
|-------|-------|-------|-------------------|---------------|----------------|--------|
| 1     | 100   | 2     | 345.4537          | 335.0073      | 0.31           | 93.8471 |
| 2     | 120   | 2     | 287.8502          | 279.3072      | 0.31           | 93.9061 |
| 3     | 140   | 2     | 246.6736          | 239.4888      | 0.3            | 93.9482 |
| 4     | 160   | 2     | 215.8105          | 209.607       | 0.3            | 93.9798 |
| 5     | 180   | 2     | 191.8241          | 186.355       | 0.29           | 94.0044 |
| 6     | 200   | 2     | 172.6565          | 167.7467      | 0.29           | 94.0241 |
| 7     | 220   | 2     | 156.9532          | 152.5172      | 0.29           | 94.0402 |
| 8     | 240   | 2     | 143.8597          | 139.8229      | 0.29           | 94.0537 |
| 9     | 260   | 2     | 132.7964          | 129.0794      | 0.29           | 94.065  |
| 10    | 280   | 2     | 123.3077          | 119.8691      | 0.29           | 94.0748 |
| 11    | 300   | 2     | 115.0808          | 111.8856      | 0.29           | 94.0832 |
| 12    | 320   | 2     | 107.8863          | 104.8991      | 0.28           | 94.0906 |
| 13    | 340   | 2     | 101.5342          | 98.7339       | 0.28           | 94.0971 |
| 14    | 360   | 2     | 95.8966           | 93.2532       | 0.28           | 94.1029 |
| 15    | 380   | 2     | 90.8398           | 88.3489       | 0.28           | 94.1081 |
| 16    | 400   | 2     | 86.3029           | 83.9347       | 0.28           | 94.1128 |
| 17    | 420   | 2     | 82.1948           | 79.9406       | 0.28           | 94.117  |
| 18    | 440   | 2     | 78.4569           | 76.3093       | 0.28           | 94.1209 |
| 19    | 460   | 2     | 75.041            | 72.9937       | 0.28           | 94.1244 |
| 20    | 480   | 2     | 71.912            | 69.9541       | 0.28           | 94.1276 |
| 21    | 500   | 2     | 69.0377           | 67.1576       | 0.28           | 94.1305 |

Table 6: The reduced temperature $T_R$, reduced specific volume $V_R$, pressure (obtained with the model) $P_{\text{kin}}$ (kPa), pressure obtained with the Peng-Robinson equation of state defined in equation $P_{PR}$ (kPa), the % errors between the numerical and empirical pressure, and the internal energy $U$ (kJ) determined with the RMS velocity (Table 7) for run 2.
| Trial | Avg X (m) | Avg Y (m) | Avg Z (m) | RMS $V_X$ (m/s) | RMS $V_Y$ (m/s) | RMS $V_Z$ (m/s) |
|-------|-----------|-----------|-----------|----------------|----------------|----------------|
| 1     | -0.066977 | 0.027098  | -2.778e-09| 289.2383       | 204.4491       | 250.8883       |
| 2     | -0.071174 | 0.028796  | -2.9521e-09| 289.2383      | 204.4491       | 250.8883       |
| 3     | -0.074927 | 0.030314  | -3.1077e-09| 289.2383      | 204.4491       | 250.8883       |
| 4     | -0.078337 | 0.031694  | -3.2492e-09| 289.2383      | 204.4491       | 250.8883       |
| 5     | -0.081474 | 0.032963  | -3.3793e-09| 289.2383      | 204.4491       | 250.8883       |
| 6     | -0.084386 | 0.034141  | -3.5001e-09| 289.2383      | 204.4491       | 250.8883       |
| 7     | -0.08711  | 0.035243  | -3.6131e-09| 289.2383      | 204.4491       | 250.8883       |
| 8     | -0.089674 | 0.03628   | -3.7194e-09| 289.2383      | 204.4491       | 250.8883       |
| 9     | -0.092098 | 0.037261  | -3.82e-09   | 289.2383      | 204.4491       | 250.8883       |
| 10    | -0.094402 | 0.038193  | -3.9155e-09| 289.2383      | 204.4491       | 250.8883       |
| 11    | -0.096598 | 0.039082  | -4.0066e-09| 289.2383      | 204.4491       | 250.8883       |
| 12    | -0.098699 | 0.039932  | -4.0937e-09| 289.2383      | 204.4491       | 250.8883       |
| 13    | -0.10071  | 0.040747  | -4.1773e-09| 289.2383      | 204.4491       | 250.8883       |
| 14    | -0.10265  | 0.041531  | -4.2577e-09| 289.2383      | 204.4491       | 250.8883       |
| 15    | -0.10452  | 0.042286  | -4.3351e-09| 289.2383      | 204.4491       | 250.8883       |
| 16    | -0.10632  | 0.043015  | -4.4098e-09| 289.2383      | 204.4491       | 250.8883       |
| 17    | -0.10806  | 0.04372   | -4.4821e-09| 289.2383      | 204.4491       | 250.8883       |
| 18    | -0.10975  | 0.044404  | -4.5522e-09| 289.2383      | 204.4491       | 250.8883       |
| 19    | -0.11139  | 0.045066  | -4.6201e-09| 289.2383      | 204.4491       | 250.8883       |
| 20    | -0.11298  | 0.04571   | -4.6862e-09| 289.2383      | 204.4491       | 250.8883       |
| 21    | -0.11453  | 0.046337  | -4.7504e-09| 289.2383      | 204.4491       | 250.8883       |

Table 7: The mean position and RMS velocity for run 2.
| Trial | $X_{X,STD}$ (m) | $X_{Y,STD}$ (m) | $X_{Z,STD}$ (m) | $V_{X,STD}$ (m/s) | $V_{Y,STD}$ (m/s) | $V_{Z,STD}$ (m/s) |
|-------|-----------------|-----------------|-----------------|-------------------|-------------------|-------------------|
| 1     | 0.0026905       | 0.00067387      | 0.0017681       | 12111.056         | 12864.746         | 62944.914         |
| 2     | 0.0030382       | 0.0076096       | 0.0019966       | 12111.056         | 12864.746         | 62944.914         |
| 3     | 0.0033671       | 0.0084333       | 0.0022127       | 12111.056         | 12864.746         | 62944.914         |
| 4     | 0.0036806       | 0.0092184       | 0.0024187       | 12111.056         | 12864.746         | 62944.914         |
| 5     | 0.0039812       | 0.0099715       | 0.0026162       | 12111.056         | 12864.746         | 62944.914         |
| 6     | 0.0042709       | 0.010697        | 0.0028066       | 12111.056         | 12864.746         | 62944.914         |
| 7     | 0.0045511       | 0.011399        | 0.0029907       | 12111.056         | 12864.746         | 62944.914         |
| 8     | 0.0048229       | 0.01208         | 0.0031693       | 12111.056         | 12864.746         | 62944.914         |
| 9     | 0.0050873       | 0.012742        | 0.0033431       | 12111.056         | 12864.746         | 62944.914         |
| 10    | 0.0053449       | 0.013387        | 0.0035124       | 12111.056         | 12864.746         | 62944.914         |
| 11    | 0.0055965       | 0.014017        | 0.0036777       | 12111.056         | 12864.746         | 62944.914         |
| 12    | 0.0058425       | 0.014633        | 0.0038394       | 12111.056         | 12864.746         | 62944.914         |
| 13    | 0.0060835       | 0.015237        | 0.0039977       | 12111.056         | 12864.746         | 62944.914         |
| 14    | 0.0063198       | 0.015829        | 0.004153        | 12111.056         | 12864.746         | 62944.914         |
| 15    | 0.0065518       | 0.01641         | 0.0043054       | 12111.056         | 12864.746         | 62944.914         |
| 16    | 0.0067797       | 0.01698         | 0.0044552       | 12111.056         | 12864.746         | 62944.914         |
| 17    | 0.0070038       | 0.017542        | 0.0046025       | 12111.056         | 12864.746         | 62944.914         |
| 18    | 0.0072244       | 0.018094        | 0.0047475       | 12111.056         | 12864.746         | 62944.914         |
| 19    | 0.0074417       | 0.018639        | 0.0048903       | 12111.056         | 12864.746         | 62944.914         |
| 20    | 0.0076559       | 0.019175        | 0.005031        | 12111.056         | 12864.746         | 62944.914         |
| 21    | 0.0078671       | 0.019704        | 0.0051698       | 12111.056         | 12864.746         | 62944.914         |

Table 8: The position and velocity standard deviations for run 2.
Table 9: The entropy, both theoretical (equation 22) and with the empirical equation 47. The correlation coefficient between equation 22 and 47 for both run 1 and run 2 is R=0.9923.
6 The Supercritical Stirling Cycle Heat Engine

A Stirling engine cycle is defined by isothermal compression at the cold sink (stage 1-2), isochoric heating from the cold to the hot temperature (stage 2-3), isothermal expansion at the hot source (stage 3-4), and isochoric cooling back from the hot temperature to the cold temperature (stage 4-1). An ideal Stirling cycle heat engine, with perfect regeneration from the isochoric cooling (stage 4-1) to the isochoric heating (stage 2-3) will have the Carnot thermodynamic efficiency defined in equation 5.

As a fluid gets more and more dense, the molecules get closer to each other, and the impact of intermolecular forces increases. When a Stirling Engine uses a dense real fluid as its working fluid, the internal energy will in fact change during isothermal compression and expansion, and can be simply and accurately approximated with empirical equation 32. To improve on the accuracy, the potential energy of the real argon will be determined by integrating the reduced pressure from the intermolecular Van der Waal forces defined in equation 43, as well as the kinetic energy of a mole of argon traveling at the numerically simulated RMS average velocity $\bar{v}_{RMS} \text{ (m/s)}$, and therefore the internal energy of a mole of argon is defined in equation 48

$$U(V,T) = \frac{1}{2}MM(\bar{v}_{RMS})^2 - MM\int_{V}^{\infty} \frac{A\alpha}{V^2 + 2B V - B^2} dv. \quad (48)$$

This argon model will simulate the entropy of a theoretical high-density Stirling cycle engine 16, using one mole of argon gas as the working fluid. The reduced specific volume at top and bottom dead center are $V_R = 1.5$ and $V_R = 15.0$, whereas the reduced specific temperatures are $T_R = 1.3 \approx -78^\circ\text{C}$ and $T_R = 2.0 \approx 25^\circ\text{C}$ at the low and hot temperature range. The thermodynamic properties of the argon working fluid at each stage of this cycle are tabulated in Table 10; the specific work $\delta w \text{ (J/kg)}$ and specific heat $\delta q \text{ (J/kg)}$ inputs, as well as the changes in specific internal energy $\delta u \text{ (J/kg)}$ and specific entropy $\delta s \text{ (J/kg-K)}$ as determined with equation 4 are tabulated in Table 11.

The reduced specific volumes $V_R$ and reduced specific temperatures $T_R$, as well as the pressures determined with the model $P_{kin} \text{ (MPa)}$, the pressures determined with the Peng-
Robinson equation of state $P_{PR}$ (MPa) defined in equation 30, as well as the internal energy (equation 48), are tabulated in Tables 12, 15, 18, and 21 for stages 1-2, 2-3, 3-4, and 4-1, respectively. In both simulation, the numerical prediction for the pressure matched the Peng-Robinson pressures within less than 3% error.

The average molecular position $Avg X$, $Avg Y$, and $Avg Z$ (m); and average RMS molecular velocity $RMS V_X$, $RMS V_Y$, and $RMS V_Z$ (m/s), are tabulated in Tables 13, 16, 19, and 22 for stages 1-2, 2-3, 3-4, and 4-1, respectively. The standard deviations of the molecular position $X_{X,STD}$, $X_{Y,STD}$, and $X_{Z,STD}$ (m); and standard deviations of the molecular velocities $V_{X,STD}$, $V_{Y,STD}$, and $V_{Z,STD}$ (m/s) are tabulated in Tables 14, 17, 20, and 23 for stages 1-2, 2-3, 3-4, and 4-1, respectively. The change in entropy, including the difference in entropy $\delta s_0$ (J/K) due to standard deviation of the molecule location and velocity as determined with empirical equation 47, as well as the change in entropy $\delta s_1$ (J/K) to the universe from the heat input and output as determined by equation 4, is tabulated in Table 24. The cumulative change in entropy $\int \delta s_0$ (J/K) and $\int \delta s_0$ (J/K) throughout this cycle is tabulated in Table 25.

| Stage | $P$ (MPa) | $v$ (cm$^3$/g) | $T$ (°C) | $P_R$ | $v_R$ | $T_R$ |
|-------|-----------|---------------|---------|-------|-------|-------|
| 1     | 1.3744    | 28.0374       | -78     | 0.28263 | 15    | 1.3   |
| 2     | 9.6737    | 2.80374       | 25      | 1.9893 | 1.5   | 1.3   |
| 3     | 20.6058   | 2.80374       | 25      | 4.2373 | 1.5   | 2.0   |
| 4     | 2.1744    | 28.0374       | 25      | 0.44713 | 15    | 2.0   |

Table 10: Pressure $P$ (MPa) as determined from the Peng-Robinson equation of state (equation 30), specific volume $v$ (cm$^3$/g), temperature $T$ (°C), reduced pressure $P_R$, reduced specific volume $v_R$, and reduced temperature $T_R$, for the Stirling cycle heat engine utilizing supercritical argon gas as the working fluid.
Stage Change | $\delta u$ (J/kg) | $\delta w$ (J/kg) | $\delta q$ (J/kg) | $\delta s$ (J/kg·K)
--- | --- | --- | --- | ---
Stage 1-2 | -609 | 2670 | -3279 | 15.8933
Stage 2-3 | 1378 | 318 | 1060 | -2.5789
Stage 3-4 | 603 | -5300 | 5903 | -19.8044
Stage 4-1 | -1372 | -115 | -1257 | 4.8796

Table 11: The change in specific internal energy $\delta u$ (J/kg), specific work $\delta w$ (J/kg), specific heat transfer $\delta q$ (J/kg), and specific entropy $\delta s$ (J/kg·K) obtained by equation 4 between each of the four stages of the high-pressure Stirling cycle heat engine.

| Trial | $V_R$ | $T_R$ | $P_{\text{kin}}$ (MPa) | $P_{\text{PR}}$ (MPa) | $P_{\text{error}}$ (%) | $U$ (kJ) | $S$ (J/K)
--- | --- | --- | --- | --- | --- | --- | ---
1 | 15 | 1.3 | 1.5047 | 1.3803 | 0.9 | 2.3263 | 186.1793
2 | 14.325 | 1.3 | 1.5759 | 1.4418 | 0.93 | 2.3209 | 186.1226
3 | 13.65 | 1.3 | 1.6545 | 1.509 | 0.96 | 2.3149 | 186.065
4 | 12.975 | 1.3 | 1.7409 | 1.5828 | 1 | 2.3084 | 186.0064
5 | 12.3 | 1.3 | 1.8373 | 1.6643 | 1.04 | 2.3012 | 185.9468
6 | 11.625 | 1.3 | 1.9447 | 1.7545 | 1.08 | 2.2931 | 185.8862
7 | 10.95 | 1.3 | 2.0658 | 1.8551 | 1.14 | 2.2841 | 185.8242
8 | 10.275 | 1.3 | 2.2028 | 1.968 | 1.19 | 2.2739 | 185.761
9 | 9.6 | 1.3 | 2.3591 | 2.0955 | 1.26 | 2.2623 | 185.6964
10 | 8.925 | 1.3 | 2.5395 | 2.2406 | 1.33 | 2.249 | 185.6303
11 | 8.25 | 1.3 | 2.7495 | 2.4074 | 1.42 | 2.2336 | 185.5625
12 | 7.575 | 1.3 | 2.9976 | 2.601 | 1.52 | 2.2156 | 185.4928
13 | 6.9 | 1.3 | 3.2948 | 2.8285 | 1.65 | 2.1941 | 185.421
14 | 6.225 | 1.3 | 3.8526 | 3.0997 | 0.8 | 2.2783 | 185.5059
15 | 5.55 | 1.3 | 3.1184 | 3.4286 | 0.9 | 2.2573 | 185.4435
16 | 4.875 | 1.3 | 3.4368 | 3.8359 | 1.04 | 2.2303 | 185.3809
17 | 4.2 | 1.3 | 3.8257 | 4.3537 | 1.21 | 2.1945 | 185.3191
18 | 3.525 | 1.3 | 4.3101 | 5.035 | 1.44 | 2.1447 | 185.2591
19 | 2.85 | 1.3 | 4.9259 | 5.9747 | 1.76 | 2.0708 | 185.2027
20 | 2.175 | 1.3 | 5.7384 | 7.3689 | 2.21 | 1.95 | 185.1532
21 | 1.5 | 1.3 | 6.9257 | 9.7546 | 2.9 | 1.7175 | 185.1134

Table 12: The reduced temperature $T_R$, reduced specific volume $V_R$, pressure (obtained with the model) $P_{\text{kin}}$ (MPa), pressure obtained with the Peng-Robinson equation of state defined in equation 30 $P_{\text{PR}}$ (MPa), the % errors between the numerical and empirical pressure, the internal energy $U$ (kJ) obtained with equation 48 utilizing the RMS velocities tabulated in Table 13 and the entropy $S$ (J/K) as defined with empirical equation 47 for stage 1-2.
Table 13: The mean position and RMS velocity, for stage 1-2.

| Trial | Avg X (m) | Avg Y (m) | Avg Z (m) | RMS $V_X$ (m/s) | RMS $V_Y$ (m/s) | RMS $V_Z$ (m/s) |
|-------|-----------|-----------|-----------|----------------|----------------|----------------|
| 1     | -0.035587 | 0.014398  | -1.476e-09| 233.1914       | 164.8321       | 202.2726       |
| 2     | -0.035045 | 0.014179  | -1.4536e-09| 233.1914       | 164.8321       | 202.2726       |
| 3     | -0.034486 | 0.013952  | -1.4304e-09| 233.1914       | 164.8321       | 202.2726       |
| 4     | -0.033908 | 0.013718  | -1.4064e-09| 233.1914       | 164.8321       | 202.2726       |
| 5     | -0.032688 | 0.013225  | -1.3558e-09| 233.1914       | 164.8321       | 202.2726       |
| 6     | -0.032043 | 0.012964  | -1.329e-09 | 233.1914       | 164.8321       | 202.2726       |
| 7     | -0.031371 | 0.012692  | -1.3012e-09| 233.1914       | 164.8321       | 202.2726       |
| 8     | -0.030668 | 0.012408  | -1.272e-09 | 233.1914       | 164.8321       | 202.2726       |
| 9     | -0.029932 | 0.01211   | -1.2415e-09| 233.1914       | 164.8321       | 202.2726       |
| 10    | -0.029157 | 0.011796  | -1.2094e-09| 233.1914       | 164.8321       | 202.2726       |
| 11    | -0.028339 | 0.011466  | -1.1754e-09| 233.1914       | 164.8321       | 202.2726       |
| 12    | -0.027471 | 0.011114  | -1.1394e-09| 233.1914       | 164.8321       | 202.2726       |
| 13    | -0.026218 | 0.010851  | -9.3108e-09| 242.5788       | 165.3416       | 204.4496       |
| 14    | -0.025204 | 0.010454  | -9.0304e-09| 243.4964       | 165.3842       | 204.6685       |
| 15    | -0.024103 | 0.010023  | -9.838e-10 | 244.6179       | 165.4364       | 204.9353       |
| 16    | -0.022895 | 0.0095513 | -9.3251e-10| 246.0186       | 165.4973       | 205.2718       |
| 17    | -0.021547 | 0.0090258 | -9.0961e-10| 247.8141       | 165.5699       | 205.7093       |
| 18    | -0.020014 | 0.0084283 | -8.3083e-09| 250.1926       | 165.6579       | 206.2937       |
| 19    | -0.018218 | 0.0077264 | -7.3337e-10| 253.4464       | 165.7632       | 207.1082       |
| 20    | -0.016012 | 0.0068541 | -5.7272e-10| 257.9062       | 165.8705       | 208.2573       |
| 21    | -0.016012 | 0.0068541 | -5.7272e-10| 257.9062       | 165.8705       | 208.2573       |
| Trial | $X_{X, STD}$ (m) | $X_{Y, STD}$ (m) | $X_{Z, STD}$ (m) | $V_{X, STD}$ (m/s) | $V_{Y, STD}$ (m/s) | $V_{Z, STD}$ (m/s) |
|-------|-----------------|-----------------|-----------------|-------------------|-------------------|-------------------|
| 1     | 0.00075956      | 0.00019024      | 0.00049914      | 7872.1855         | 8362.085          | 40914.195         |
| 2     | 0.0007366       | 0.00018449      | 0.00048405      | 7872.1855         | 8362.085          | 40914.195         |
| 3     | 0.00071328      | 0.00017865      | 0.00046872      | 7872.1855         | 8362.085          | 40914.195         |
| 4     | 0.00068956      | 0.00017271      | 0.00045314      | 7872.1855         | 8362.085          | 40914.195         |
| 5     | 0.00064093      | 0.00016667      | 0.00043729      | 7872.1855         | 8362.085          | 40914.195         |
| 6     | 0.00061581      | 0.00015424      | 0.00042114      | 7872.1855         | 8362.085          | 40914.195         |
| 7     | 0.00059023      | 0.00014128      | 0.00040467      | 7872.1855         | 8362.085          | 40914.195         |
| 8     | 0.00056409      | 0.00013458      | 0.00038787      | 7872.1855         | 8362.085          | 40914.195         |
| 9     | 0.00053733      | 0.00012771      | 0.0003531       | 7872.1855         | 8362.085          | 40914.195         |
| 10    | 0.00050988      | 0.00012064      | 0.00031651      | 7872.1855         | 8362.085          | 40914.195         |
| 11    | 0.00048168      | 0.00011336      | 0.00029744      | 7872.1855         | 8362.085          | 40914.195         |
| 12    | 0.00045262      | 0.00010734      | 0.00028797      | 8137.1377         | 8409.0684         | 41799.648         |
| 13    | 0.00042695      | 0.00010374      | 0.00028797      | 8409.0684         | 41799.648         | 41799.648         |
| 14    | 0.00039586      | 9.9569e-05      | 0.00026773      | 8163.0317         | 8413.8047         | 41889.188         |
| 15    | 0.00036346      | 9.1474e-05      | 0.00024665      | 8194.3926         | 8419.2754         | 41998.473         |
| 16    | 0.0003295       | 8.2989e-05      | 0.00022457      | 8233.542          | 8426.04           | 42136.496         |
| 17    | 0.00029362      | 7.403e-05       | 0.00020125      | 8283.9036         | 8434.9443         | 42316.305         |
| 18    | 0.00025533      | 6.4468e-05      | 0.00017636      | 8350.0996         | 8446.5508         | 42557.098         |
| 19    | 0.00021373      | 5.4084e-05      | 0.00014926      | 8440.4346         | 8462.3477         | 42893.82          |
| 20    | 0.00016731      | 4.2474e-05      | 0.0001187       | 8563.1191         | 8483.8496         | 43371.117         |

Table 14: The position and velocity standard deviations, for stage 1-2.
| Trial | $V_R$ | $T_R$ | $P_{kin}$ (MPa) | $P_{PR}$ (MPa) | $P_{error}$ (%) | $U$ (kJ) | $S$ (J/K) |
|-------|-------|-------|-----------------|----------------|-----------------|-------|---------|
| 21    | 1.5   | 1.3   | 6.9257          | 9.7546         | 2.9             | 1.7175 | 185.1134 |
| 22    | 1.5   | 1.335 | 7.6201          | 10.3281        | 2.62            | 1.7855 | 185.2743 |
| 23    | 1.5   | 1.37  | 8.3064          | 10.8998        | 2.38            | 1.8537 | 185.4357 |
| 24    | 1.5   | 1.405 | 8.9868          | 11.4697        | 2.16            | 1.922  | 185.5979 |
| 25    | 1.5   | 1.44  | 9.6619          | 12.038         | 1.97            | 1.9905 | 185.7609 |
| 26    | 1.5   | 1.475 | 10.3307         | 12.6046        | 1.8             | 2.059  | 185.9242 |
| 27    | 1.5   | 1.51  | 10.9932         | 13.1697        | 1.65            | 2.1277 | 186.0882 |
| 28    | 1.5   | 1.545 | 11.6497         | 13.7332        | 1.52            | 2.1965 | 186.2526 |
| 29    | 1.5   | 1.58  | 12.3019         | 14.2953        | 1.39            | 2.2653 | 186.4177 |
| 30    | 1.5   | 1.615 | 12.9485         | 14.856         | 1.28            | 2.3343 | 186.5829 |
| 31    | 1.5   | 1.65  | 13.589          | 15.4153        | 1.18            | 2.4033 | 186.7486 |
| 32    | 1.5   | 1.685 | 14.2238         | 15.9733        | 1.1             | 2.4724 | 186.9148 |
| 33    | 1.5   | 1.72  | 14.8548         | 16.53          | 1.01            | 2.5415 | 187.0811 |
| 34    | 1.5   | 1.755 | 15.479          | 17.0855        | 0.94            | 2.6107 | 187.2477 |
| 35    | 1.5   | 1.79  | 16.1041         | 17.6397        | 0.87            | 2.6799 | 187.415  |
| 36    | 1.5   | 1.825 | 16.7196         | 18.1928        | 0.81            | 2.7492 | 187.5825 |
| 37    | 1.5   | 1.86  | 17.3336         | 18.7448        | 0.75            | 2.8185 | 187.7503 |
| 38    | 1.5   | 1.895 | 17.9406         | 19.2956        | 0.7             | 2.8878 | 187.9181 |
| 39    | 1.5   | 1.93  | 18.5432         | 19.8454        | 0.66            | 2.9571 | 188.0862 |
| 40    | 1.5   | 1.965 | 19.1431         | 20.3941        | 0.61            | 3.0265 | 188.2546 |
| 41    | 1.5   | 2     | 19.7386         | 20.9418        | 0.57            | 3.0959 | 188.4232 |

Table 15: The reduced temperature $T_R$, reduced specific volume $V_R$, pressure (obtained with the model) $P_{kin}$ (MPa), pressure obtained with the Peng-Robinson equation of state defined in equation 30 $P_{PR}$ (MPa), the % errors between the numerical and empirical pressure, the internal energy $U$ (kJ) obtained with equation 48 utilizing the RMS velocities tabulated in Table 16 and the entropy $S$ (J/K) as defined with empirical equation 47 for stage 2-3.
| Trial | Avg X (m) | Avg Y (m) | Avg Z (m) | RMS $V_X$ (m/s) | RMS $V_Y$ (m/s) | RMS $V_Z$ (m/s) |
|-------|-----------|-----------|-----------|----------------|----------------|----------------|
| 21    | -0.016012 | 0.0068541 | -5.727e-10| 257.9062       | 165.8705       | 208.2573       |
| 22    | -0.016038 | 0.0068454 | -6.4225e-10| 259.9315       | 168.0591       | 210.6734       |
| 23    | -0.016062 | 0.0068374 | 1.6952e-09 | 261.9767       | 170.2163       | 213.0688       |
| 24    | -0.016086 | 0.0068295 | -6.4905e-10| 264.0343       | 172.3413       | 215.4502       |
| 25    | -0.016108 | 0.0068221 | -6.4905e-10| 266.1017       | 174.4399       | 217.8147       |
| 26    | -0.016128 | 0.0068152 | -6.5104e-10| 268.1809       | 176.5127       | 220.1578       |
| 27    | -0.016148 | 0.0068087 | 5.2874e-10  | 270.2665       | 178.5588       | 222.4862       |
| 28    | -0.016167 | 0.0068024 | 2.4662e-09  | 272.3582       | 180.5813       | 224.7963       |
| 29    | -0.016184 | 0.0067966 | 2.3627e-10  | 274.4534       | 182.58         | 227.0909       |
| 30    | -0.016201 | 0.006791  | -6.5776e-10 | 276.5556       | 184.5551       | 229.3649       |
| 31    | -0.016217 | 0.0067855 | -6.5916e-10 | 278.6596       | 186.5104       | 231.6213       |
| 32    | -0.016231 | 0.0067806 | 2.559e-09   | 280.7635       | 188.4435       | 233.8631       |
| 33    | -0.016245 | 0.0067758 | -6.6179e-10 | 282.8697       | 190.3584       | 236.0845       |
| 34    | -0.016259 | 0.0067712 | -6.6298e-10 | 284.9751       | 192.2531       | 238.2907       |
| 35    | -0.016272 | 0.006767  | 9.6614e-10  | 287.076        | 194.1292       | 240.4836       |
| 36    | -0.016284 | 0.0067627 | -6.6518e-10 | 289.178        | 195.986        | 242.6583       |
| 37    | -0.016295 | 0.0067588 | 1.0292e-09  | 291.2759       | 197.8251       | 244.8188       |
| 38    | -0.016306 | 0.0067551 | -6.6714e-10 | 293.3735       | 199.6489       | 246.9593       |
| 39    | -0.016317 | 0.0067517 | -6.6804e-10 | 295.4665       | 201.4549       | 249.0864       |
| 40    | -0.016326 | 0.0067484 | 3.5112e-10  | 297.5555       | 203.2462       | 251.1972       |
| 41    | -0.016336 | 0.0067449 | -4.8459e-10 | 299.6399       | 205.0207       | 253.2946       |

Table 16: The mean position and RMS velocity, for stage 2-3.
| Trial | $X_{X,STD}$ (m) | $X_{Y,STD}$ (m) | $X_{Z,STD}$ (m) | $V_{X,STD}$ (m/s) | $V_{Y,STD}$ (m/s) | $V_{X,STD}$ (m/s) |
|-------|----------------|----------------|----------------|------------------|----------------|------------------|
| 21    | 0.00016731     | 4.2474e-05     | 0.0001187      | 8563.1191        | 8483.8496      | 43371.117        |
| 22    | 0.00016717     | 4.2395e-05     | 0.00011801     | 8754.4951        | 8705.7207      | 44383.273        |
| 23    | 0.00016703     | 4.2319e-05     | 0.00011736     | 8945.7754        | 8927.0146      | 45398.32         |
| 24    | 0.0001669      | 4.2246e-05     | 0.00011676     | 9138.0107        | 9148.5137      | 46418.77         |
| 25    | 0.00016676     | 4.2176e-05     | 0.00011621     | 9330.9297        | 9370.1973      | 47443.227        |
| 26    | 0.00016664     | 4.2115e-05     | 0.0001157      | 9524.1729        | 9592.1318      | 48469.469        |
| 27    | 0.00016652     | 4.2057e-05     | 0.00011523     | 9717.8438        | 9814.0869      | 49500.113        |
| 28    | 0.00016639     | 4.2001e-05     | 0.00011479     | 9911.874         | 10036.352      | 50533.391        |
| 29    | 0.00016627     | 4.195e-05      | 0.00011438     | 10106.753        | 10258.5        | 51570.262        |
| 30    | 0.00016616     | 4.1901e-05     | 0.000114      | 10301.739        | 10480.549      | 52608.262        |
| 31    | 0.00016605     | 4.1852e-05     | 0.00011364     | 10497.555        | 10702.74       | 53648.422        |
| 32    | 0.00016595     | 4.1811e-05     | 0.00011331     | 10693.362        | 10925.292      | 54691.938        |
| 33    | 0.00016585     | 4.1769e-05     | 0.000113      | 10889.772        | 11147.769      | 55735.875        |
| 34    | 0.00016574     | 4.1727e-05     | 0.0001127      | 11086.111        | 11369.986      | 56782.465        |
| 35    | 0.00016566     | 4.1693e-05     | 0.00011243     | 11284.201        | 11592.922      | 57832.363        |
| 36    | 0.00016557     | 4.1655e-05     | 0.00011217     | 11481.937        | 11815.598      | 58883.035        |
| 37    | 0.00016548     | 4.1622e-05     | 0.00011193     | 11680.159        | 12038.313      | 59936.227        |
| 38    | 0.0001654     | 4.1591e-05     | 0.00011169     | 11878.296        | 12261.111      | 60988.887        |
| 39    | 0.00016531     | 4.1562e-05     | 0.00011147     | 12076.861        | 12483.627      | 62044.059        |
| 40    | 0.00016524     | 4.1534e-05     | 0.00011127     | 12275.724        | 12706.661      | 63100.047        |
| 41    | 0.00016517     | 4.1502e-05     | 0.00011107     | 12475.365        | 12929.374      | 64158.133        |

Table 17: The position and velocity standard deviations, for stage 2-3.
Table 18: The reduced temperature $T_R$, reduced specific volume $V_R$, pressure (obtained with the model) $P_{\text{kin}}$ (MPa), pressure obtained with the Peng-Robinson equation of state defined in equation 30 $P_{PR}$ (MPa), the % errors between the numerical and empirical pressure, the internal energy $U$ (kJ) obtained with equation 48 utilizing the RMS velocities tabulated in Table 19, and the entropy $S$ (J/K) as defined with empirical equation 47 for stage 3-4.

| Trial | $V_R$ | $T_R$ | $P_{\text{kin}}$ (MPa) | $P_{PR}$ (MPa) | $P_{\text{error}}$ (%) | $U$ (kJ) | $S$ (J/K) |
|-------|-------|-------|------------------------|----------------|------------------------|---------|-----------|
| 41    | 1.5   | 2     | 19.7386                | 20.9418        | 0.57                   | 3.0959  | 188.4232  |
| 42    | 2.175 | 2     | 13.6818                | 14.3757        | 0.48                   | 3.3078  | 188.5157  |
| 43    | 2.85  | 2     | 10.611                 | 11.04          | 0.39                   | 3.4181  | 188.5957  |
| 44    | 3.525 | 2     | 8.7097                 | 8.989          | 0.31                   | 3.4855  | 188.672   |
| 45    | 4.2   | 2     | 7.402                  | 7.5913         | 0.25                   | 3.531   | 188.7459  |
| 46    | 4.875 | 2     | 6.429                  | 6.5744         | 0.2                    | 3.5637  | 188.8181  |
| 47    | 5.55  | 2     | 5.7077                 | 5.8001         | 0.16                   | 3.5883  | 188.8886  |
| 48    | 6.225 | 2     | 5.1254                 | 5.1902         | 0.12                   | 3.6075  | 188.9576  |
| 49    | 6.9   | 2     | 4.6519                 | 4.6972         | 0.1                    | 3.6229  | 189.0251  |
| 50    | 7.575 | 2     | 4.2593                 | 4.2901         | 0.07                   | 3.6355  | 189.0911  |
| 51    | 8.25  | 2     | 3.9285                 | 3.9482         | 0.05                   | 3.646   | 189.1558  |
| 52    | 8.925 | 2     | 3.6454                 | 3.657          | 0.03                   | 3.6548  | 189.2192  |
| 53    | 9.6   | 2     | 3.4009                 | 3.4059         | 0.01                   | 3.6624  | 189.2814  |
| 54    | 10.275| 2     | 3.187                  | 3.187          | 0                   | 3.669   | 189.3425  |
| 55    | 10.95 | 2     | 2.9986                 | 2.9949         | 0.01                   | 3.6747  | 189.4026  |
| 56    | 11.625| 2     | 2.8315                 | 2.8246         | 0.02                   | 3.6798  | 189.4617  |
| 57    | 12.3  | 2     | 2.682                  | 2.6726         | 0.04                   | 3.6843  | 189.5199  |
| 58    | 12.975| 2     | 2.5478                 | 2.5362         | 0.05                   | 3.6883  | 189.5773  |
| 59    | 13.65 | 2     | 2.4261                 | 2.413          | 0.05                   | 3.6919  | 189.6338  |
| 60    | 14.325| 2     | 2.3158                 | 2.3013         | 0.06                   | 3.6952  | 189.6896  |
| 61    | 15    | 2     | 2.2151                 | 2.1995         | 0.07                   | 3.6982  | 189.7445  |
| Trial | Avg X (m) | Avg Y (m) | Avg Z (m) | RMS Vx (m/s) | RMS Vy (m/s) | RMS Vz (m/s) |
|-------|-----------|-----------|-----------|--------------|--------------|--------------|
| 41    | -0.016336 | 0.0067449 | -4.8459e-10 | 299.6399     | 205.0207     | 253.2946     |
| 42    | -0.018512 | 0.0076267 | -7.6001e-10 | 298.4725     | 204.9624     | 253.0187     |
| 43    | -0.020283 | 0.0083371 | 1.2691e-09  | 297.2648     | 204.9016     | 252.7355     |
| 44    | -0.021795 | 0.0089414 | -8.97e-10   | 296.2813     | 204.8495     | 252.5075     |
| 45    | -0.023125 | 0.0094727 | -9.5257e-10 | 295.4987     | 204.8082     | 252.3243     |
| 46    | -0.02432  | 0.0099494 | -1.0025e-09 | 294.8679     | 204.7732     | 252.179      |
| 47    | -0.025408 | 0.010384  | -1.0479e-09 | 294.3521     | 204.7452     | 252.059      |
| 48    | -0.026411 | 0.010785  | 1.6399e-09  | 293.922      | 204.7215     | 251.9608     |
| 49    | -0.027344 | 0.011158  | -1.1287e-09 | 293.5596     | 204.7004     | 251.8781     |
| 50    | -0.028217 | 0.011507  | -1.1652e-09 | 293.2509     | 204.6827     | 251.8061     |
| 51    | -0.02904  | 0.011837  | -2.853e-10  | 292.9823     | 204.6683     | 251.7451     |
| 52    | -0.029819 | 0.012149  | -1.8103e-10 | 292.7488     | 204.6553     | 251.6911     |
| 53    | -0.030559 | 0.012445  | -1.2629e-09 | 292.5424     | 204.6442     | 251.6441     |
| 54    | -0.031265 | 0.012728  | -1.2924e-09 | 292.3616     | 204.6334     | 251.6005     |
| 55    | -0.03194  | 0.012999  | -1.3205e-09 | 292.2        | 204.6233     | 251.5622     |
| 56    | -0.032589 | 0.013259  | -1.3476e-09 | 292.0529     | 204.6156     | 251.5285     |
| 57    | -0.033212 | 0.013509  | 7.5363e-09  | 291.9213     | 204.6066     | 251.4982     |
| 58    | -0.033813 | 0.013751  | -1.3986e-09 | 291.8004     | 204.6001     | 251.4708     |
| 59    | -0.034394 | 0.013984  | -1.4227e-09 | 291.6908     | 204.5937     | 251.4456     |
| 60    | -0.034956 | 0.014209  | -1.0421e-09 | 291.5905     | 204.5857     | 251.4229     |
| 61    | -0.0355   | 0.014428  | -1.4688e-09 | 291.4971     | 204.5832     | 251.4015     |

Table 19: The mean position and RMS velocity, for stage 3-4.
| Trial | $X_{X,STD}$ (m) | $X_{Y,STD}$ (m) | $X_{Z,STD}$ (m) | $V_{X,STD}$ (m/s) | $V_{Y,STD}$ (m/s) | $V_{Z,STD}$ (m/s) |
|-------|----------------|----------------|----------------|------------------|------------------|------------------|
| 41    | 0.00016517     | 4.1502e-05     | 0.00011107     | 12475.365        | 12929.374        | 64158.133        |
| 42    | 0.00021139     | 5.3099e-05     | 0.00014177     | 12434.195        | 12922.285        | 64018.438        |
| 43    | 0.00025288     | 6.3492e-05     | 0.00016912     | 12392.114        | 12914.973        | 63875.223        |
| 44    | 0.00029113     | 7.307e-05      | 0.00019427     | 12357.918        | 12908.773        | 63760.016        |
| 45    | 0.00032697     | 8.205e-05      | 0.00021781     | 12330.242        | 12904.039        | 63667.551        |
| 46    | 0.00036093     | 9.0542e-05     | 0.00024008     | 12308.524        | 12899.748        | 63594.273        |
| 47    | 0.00039335     | 9.8666e-05     | 0.00026135     | 12290.263        | 12896.818        | 63533.746        |
| 48    | 0.00042446     | 0.00010645     | 0.00028176     | 12275.29         | 12894.176        | 63484.234        |
| 49    | 0.00045446     | 0.00011396     | 0.00030143     | 12262.619        | 12891.751        | 63442.59         |
| 50    | 0.00048351     | 0.00012123     | 0.00032047     | 12251.912        | 12889.524        | 63406.324        |
| 51    | 0.00051169     | 0.00012829     | 0.00033895     | 12242.573        | 12888.176        | 63375.582        |
| 52    | 0.0005391      | 0.00013516     | 0.00035694     | 12234.135        | 12886.805        | 63348.426        |
| 53    | 0.00056582     | 0.00014186     | 0.00037448     | 12226.761        | 12885.491        | 63324.754        |
| 54    | 0.00059198     | 0.0001484      | 0.00039162     | 12220.334        | 12884.207        | 63302.836        |
| 55    | 0.00061755     | 0.0001548      | 0.00040838     | 12214.35         | 12883.092        | 63283.516        |
| 56    | 0.00064257     | 0.00016107     | 0.0004248      | 12209.103        | 12882.014        | 63266.578        |
| 57    | 0.00066714     | 0.00016721     | 0.0004409      | 12204.678        | 12881.137        | 63251.363        |
| 58    | 0.00069128     | 0.00017325     | 0.00045672     | 12200.577        | 12880.461        | 63237.582        |
| 59    | 0.00071497     | 0.00017918     | 0.00047226     | 12196.782        | 12879.593        | 63224.891        |
| 60    | 0.00073829     | 0.00018502     | 0.00048756     | 12193.267        | 12878.667        | 63213.461        |
| 61    | 0.00076122     | 0.00019077     | 0.00050262     | 12190.051        | 12878.667        | 63202.711        |

Table 20: The position and velocity standard deviations, for stage 3-4.
| Trial | $V_R$ | $T_R$ | $P_{\text{kin}}$ (MPa) | $P_{\text{PR}}$ (MPa) | $P_{\text{error}}$ (%) | $U$ (kJ) | $S$ (J/K) |
|-------|-------|-------|-------------------------|------------------------|------------------------|----------|----------|
| 61    | 15    | 2     | 2.2151                  | 2.1995                 | 0.07                   | 3.6982   | 189.7445 |
| 62    | 15    | 1.965 | 2.1724                  | 2.1587                 | 0.06                   | 3.632    | 189.5698 |
| 63    | 15    | 1.93  | 2.1298                  | 2.1178                 | 0.06                   | 3.5659   | 189.3951 |
| 64    | 15    | 1.895 | 2.0871                  | 2.077                  | 0.05                   | 3.4998   | 189.2205 |
| 65    | 15    | 1.86  | 2.0442                  | 2.0362                 | 0.04                   | 3.4337   | 189.0457 |
| 66    | 15    | 1.825 | 2.0014                  | 1.9953                 | 0.03                   | 3.3676   | 188.8712 |
| 67    | 15    | 1.79  | 1.9584                  | 1.9544                 | 0.02                   | 3.3015   | 188.6966 |
| 68    | 15    | 1.755 | 1.9156                  | 1.9135                 | 0.01                   | 3.2355   | 188.5222 |
| 69    | 15    | 1.72  | 1.8726                  | 1.8726                 | 0                     | 3.1694   | 188.3478 |
| 70    | 15    | 1.685 | 1.8295                  | 1.8317                 | 0.01                   | 3.1033   | 188.1734 |
| 71    | 15    | 1.65  | 1.7863                  | 1.7907                 | 0.02                   | 3.0373   | 187.9991 |
| 72    | 15    | 1.615 | 1.8693                  | 1.7498                 | 0.68                   | 2.93     | 187.7623 |
| 73    | 15    | 1.58  | 1.8288                  | 1.7088                 | 0.7                    | 2.863    | 187.5864 |
| 74    | 15    | 1.545 | 1.7883                  | 1.6678                 | 0.72                   | 2.796    | 187.4105 |
| 75    | 15    | 1.51  | 1.7478                  | 1.6268                 | 0.74                   | 2.729    | 187.2346 |
| 76    | 15    | 1.475 | 1.7072                  | 1.5857                 | 0.77                   | 2.6619   | 187.0587 |
| 77    | 15    | 1.44  | 1.6667                  | 1.5447                 | 0.79                   | 2.5949   | 186.8828 |
| 78    | 15    | 1.405 | 1.6262                  | 1.5036                 | 0.82                   | 2.5277   | 186.707  |
| 79    | 15    | 1.37  | 1.5857                  | 1.4625                 | 0.84                   | 2.4606   | 186.5311 |
| 80    | 15    | 1.335 | 1.5452                  | 1.4214                 | 0.87                   | 2.3935   | 186.3552 |
| 1     | 15    | 1.3   | 1.5047                  | 1.3803                 | 0.9                    | 2.3263   | 186.1793 |

Table 21: The reduced temperature $T_R$, reduced specific volume $V_R$, pressure (obtained with the model) $P_{\text{kin}}$ (MPa), pressure obtained with the Peng-Robinson equation of state defined in equation $30$ $P_{\text{PR}}$ (MPa), the % errors between the numerical and empirical pressure, the internal energy $U$ (kJ) obtained with equation $48$ utilizing the RMS velocities tabulated in Table 22, and the entropy $S$ (J/K) as defined with empirical equation $47$ for stage 4-1.
Table 22: The mean position and RMS velocity, for stage 4-1.

| Trial | Avg X (m) | Avg Y (m) | Avg Z (m) | RMS V$_X$ (m/s) | RMS V$_Y$ (m/s) | RMS V$_Z$ (m/s) |
|-------|-----------|-----------|-----------|-----------------|----------------|----------------|
| 61    | -0.0355   | 0.014428  | -1.4688e-09 | 291.4971        | 204.5832       | 251.4015       |
| 62    | -0.035496 | 0.014429  | -1.4685e-09 | 289.0241        | 202.7886       | 249.2124       |
| 63    | -0.035493 | 0.01443   | -1.4682e-09 | 286.5298        | 200.9805       | 247.0038       |
| 64    | -0.035489 | 0.014431  | -1.4679e-09 | 284.0149        | 199.1556       | 244.776        |
| 65    | -0.035485 | 0.014433  | 6.7697e-09  | 281.4797        | 197.3137       | 242.5276       |
| 66    | -0.035481 | 0.014434  | -1.4672e-09 | 278.9223        | 195.4551       | 240.2589       |
| 67    | -0.035477 | 0.014436  | -1.4669e-09 | 276.3444        | 193.5779       | 237.9677       |
| 68    | -0.035472 | 0.014437  | -1.4665e-09 | 273.7418        | 191.6822       | 235.6573       |
| 69    | -0.035468 | 0.014439  | 2.6397e-09  | 271.1165        | 189.7692       | 233.3229       |
| 70    | -0.035462 | 0.014441  | -1.4657e-09 | 268.4683        | 187.8354       | 230.9655       |
| 71    | -0.035458 | 0.014443  | 5.5553e-10  | 265.7936        | 185.8824       | 228.5862       |
| 72    | -0.035578 | 0.014398  | -1.476e-09  | 259.9124        | 183.72         | 225.4507       |
| 73    | -0.035578 | 0.014398  | -1.476e-09  | 257.0806        | 181.7183       | 222.9943       |
| 74    | -0.035578 | 0.014398  | -1.476e-09  | 254.2173        | 179.6944       | 220.5106       |
| 75    | -0.035578 | 0.014398  | -1.476e-09  | 251.3213        | 177.6473       | 217.9986       |
| 76    | -0.035578 | 0.014398  | -1.476e-09  | 248.3916        | 175.5764       | 215.4574       |
| 77    | -0.035578 | 0.014398  | -1.476e-09  | 245.4269        | 173.4808       | 212.8857       |
| 78    | -0.035578 | 0.014398  | -1.476e-09  | 242.4259        | 171.3596       | 210.2827       |
| 79    | -0.035578 | 0.014398  | -1.476e-09  | 239.3873        | 169.2118       | 207.647        |
| 80    | -0.035587 | 0.014398  | -1.476e-09  | 236.3097        | 167.0363       | 204.9774       |

1 -0.035587 | 0.014398 | -1.476e-09 | 233.1914 | 164.8321 | 202.2726
Table 23: The position and velocity standard deviations, for stage 4-1.

| Trial | $X_{X,STD}$ (m) | $X_{Y,STD}$ (m) | $X_{Z,STD}$ (m) | $V_{X,STD}$ (m/s) | $V_{Y,STD}$ (m/s) | $V_{Z,STD}$ (m/s) |
|-------|-----------------|-----------------|-----------------|-------------------|------------------|-------------------|
| 61    | 0.00076122      | 0.00019077      | 0.00050262      | 12190.051         | 12878.667        | 63202.711         |
| 62    | 0.0007613       | 0.00019078      | 0.00050275      | 11979.74          | 12653.573        | 62106.824         |
| 63    | 0.00076137      | 0.0001908       | 0.00050289      | 11769.589         | 12428.755        | 61010.902         |
| 64    | 0.00076143      | 0.00019083      | 0.00050305      | 11559.307         | 12204.073        | 59915.305         |
| 65    | 0.00076147      | 0.00019085      | 0.00050321      | 11349.042         | 11979.267        | 58819.648         |
| 66    | 0.00076155      | 0.00019088      | 0.00050338      | 11138.983         | 11754.545        | 57724.32          |
| 67    | 0.00076164      | 0.00019091      | 0.00050356      | 10928.737         | 11529.713        | 56628.637         |
| 68    | 0.00076172      | 0.00019094      | 0.00050376      | 10718.919         | 11305.094        | 55534.383         |
| 69    | 0.0007618       | 0.00019097      | 0.00050395      | 10509.233         | 11080.416        | 54439.594         |
| 70    | 0.00076188      | 0.00019101      | 0.00050417      | 10299.312         | 10855.646        | 53345.043         |
| 71    | 0.00076194      | 0.00019104      | 0.00050438      | 10089.736         | 10631.023        | 52251.656         |
| 72    | 0.00075956      | 0.00019024      | 0.00049914      | 9779.6768         | 10388.283        | 50828.02          |
| 73    | 0.00075956      | 0.00019024      | 0.00049914      | 9567.7334         | 10163.149        | 49726.48          |
| 74    | 0.00075956      | 0.00019024      | 0.00049914      | 9355.79           | 9938.0166        | 48624.945         |
| 75    | 0.00075956      | 0.00019024      | 0.00049914      | 9143.8467         | 9712.8838        | 47523.41          |
| 76    | 0.00075956      | 0.00019024      | 0.00049914      | 8931.9033         | 9487.751         | 46421.875         |
| 77    | 0.00075956      | 0.00019024      | 0.00049914      | 8719.96           | 9262.6182        | 45320.34          |
| 78    | 0.00075956      | 0.00019024      | 0.00049914      | 8508.0166         | 9037.4844        | 44218.801         |
| 79    | 0.00075956      | 0.00019024      | 0.00049914      | 8296.0732         | 8812.3516        | 43117.266         |
| 80    | 0.00075956      | 0.00019024      | 0.00049914      | 8084.1299         | 8587.2188        | 42015.73          |
| 1     | 0.00075956      | 0.00019024      | 0.00049914      | 7872.1855         | 8362.085         | 40914.195         |
| Trial | $\delta s_0$ (J/K) | $\delta s_1$ (J/K) | Trial | $\delta s_0$ (J/K) | $\delta s_1$ (J/K) |
|-------|------------------|------------------|-------|------------------|------------------|
| 1     | -0.17588         | 0.33839          | 41    | 0.16867          | -0.23228         |
| 2     | -0.056728        | 0.42342          | 42    | 0.092491         | -3.4944          |
| 3     | -0.057627        | 0.44536          | 43    | 0.079956         | -2.3947          |
| 4     | -0.058585        | 0.46965          | 44    | 0.076307         | -1.8376          |
| 5     | -0.05961         | 0.49672          | 45    | 0.073902         | -1.4966          |
| 6     | -0.060591        | 0.52711          | 46    | 0.072242         | -1.2648          |
| 7     | -0.062019        | 0.56142          | 47    | 0.070494         | -1.0965          |
| 8     | -0.063185        | 0.60048          | 48    | 0.068976         | -0.96845         |
| 9     | -0.064585        | 0.64529          | 49    | 0.067472         | -0.86758         |
| 10    | -0.066118        | 0.67925          | 50    | 0.065975         | -0.78599         |
| 11    | -0.067808        | 0.75818          | 51    | 0.064727         | -0.71862         |
| 12    | -0.069685        | 0.8306           | 52    | 0.063836         | -0.66198         |
| 13    | -0.071789        | 0.91806          | 53    | 0.06224          | -0.6137          |
| 14    | 0.084935         | 0.36012          | 54    | 0.061105         | -0.5203          |
| 15    | -0.062444        | 0.87445          | 55    | 0.060064         | -0.53568         |
| 16    | -0.062554        | 0.97989          | 56    | 0.059098         | -0.50373         |
| 17    | -0.061862        | 1.116            | 57    | 0.058254         | -0.4754          |
| 18    | -0.059979        | 1.2997           | 58    | 0.057407         | -0.45012         |
| 19    | -0.056355        | 1.5642           | 59    | 0.056482         | -0.4274          |
| 20    | -0.049502        | 1.9871           | 60    | 0.055765         | -0.40687         |
| 21    | -0.039792        | 2.8138           | 61    | 0.054953         | -0.38825         |
| 22    | 0.16088          | -0.34252         | 62    | -0.17472         | 0.22131          |
| 23    | 0.16136          | -0.33451         | 63    | -0.17472         | 0.22528          |
| 24    | 0.16227          | -0.32676         | 64    | -0.17464         | 0.22939          |
| 25    | 0.16293          | -0.31935         | 65    | -0.17471         | 0.23364          |
| 26    | 0.16329          | -0.31222         | 66    | -0.17456         | 0.23806          |
| 27    | 0.164            | -0.30538         | 67    | -0.17461         | 0.24265          |
| 28    | 0.16445          | -0.29881         | 68    | -0.17436         | 0.24742          |
| 29    | 0.16504          | -0.29248         | 69    | -0.17446         | 0.25237          |
| 30    | 0.16527          | -0.2864          | 70    | -0.17438         | 0.25754          |
| 31    | 0.16563          | -0.28055         | 71    | -0.17425         | 0.2629           |
| 32    | 0.16619          | -0.2749          | 72    | -0.23686         | 0.43587          |
| 33    | 0.1663           | -0.26947         | 73    | -0.17588         | 0.2783           |
| 34    | 0.16668          | -0.26424         | 74    | -0.17588         | 0.28462          |
| 35    | 0.16731          | -0.25915         | 75    | -0.17588         | 0.29124          |
| 36    | 0.16741          | -0.2543          | 76    | -0.17588         | 0.29816          |
| 37    | 0.16783          | -0.24958         | 77    | -0.17588         | 0.30543          |
| 38    | 0.16778          | -0.24504         | 78    | -0.17588         | 0.31305          |
| 39    | 0.16816          | -0.24064         | 79    | -0.17588         | 0.32107          |
| 40    | 0.16834          | -0.23639         | 80    | -0.17588         | 0.3295           |

Table 24: Change in the entropy, including the difference in entropy $\delta s_0$ (J/K) due to standard deviation of the molecule location and velocity as determined with empirical equation [47] as well as the change in entropy $\delta s_1$ (J/K) to the universe from the heat input and output as determined by equation [4].
| Trial | $\int \delta s_0$ (J/K) | $\int \delta s_1$ (J/K) | $\int \delta s_0 + \int \delta s_1$ (J/K) | Trial | $\int \delta s_0$ (J/K) | $\int \delta s_1$ (J/K) | $\int \delta s_0 + \int \delta s_1$ (J/K) |
|-------|----------------------|----------------------|---------------------------------|-------|----------------------|----------------------|---------------------------------|
| 1     | -0.17588             | 0.33839              | 0.16251                         | 41    | 2.068                | 13.0822              | 15.1502                         |
| 2     | -0.23261             | 0.79181              | 0.5292                          | 42    | 2.1605               | 9.5878               | 11.7483                         |
| 3     | -0.29024             | 1.2072               | 0.91693                         | 43    | 2.2405               | 7.1931               | 9.4336                          |
| 4     | -0.34882             | 1.6768               | 1.328                           | 44    | 2.3168               | 5.3555               | 7.6723                          |
| 5     | -0.40843             | 2.1735               | 1.7651                          | 45    | 2.3907               | 3.8589               | 6.2496                          |
| 6     | -0.46902             | 2.7007               | 2.2316                          | 46    | 2.4629               | 2.5941               | 5.057                           |
| 7     | -0.53104             | 3.2621               | 2.731                           | 47    | 2.5334               | 1.4976               | 4.031                           |
| 8     | -0.59423             | 3.8626               | 3.2683                          | 48    | 2.6024               | 0.52915              | 3.1316                          |
| 9     | -0.65881             | 4.5079               | 3.849                           | 49    | 2.6699               | -0.33843             | 2.3314                          |
| 10    | -0.72493             | 5.2051               | 4.4802                          | 50    | 2.7359               | -1.1244              | 1.6114                          |
| 11    | -0.79274             | 5.9633               | 5.1705                          | 51    | 2.8006               | -1.843               | 0.95754                         |
| 12    | -0.86242             | 6.7939               | 5.9315                          | 52    | 2.864                | -2.505               | 0.35894                         |
| 13    | -0.93421             | 7.7119               | 6.7777                          | 53    | 2.9262               | -3.1187              | -0.19251                       |
| 14    | -0.84928             | 8.0721               | 7.2228                          | 54    | 2.9873               | -3.6907              | -0.70344                       |
| 15    | -0.91172             | 8.9465               | 8.0348                          | 55    | 3.0474               | -4.2264              | -1.1791                        |
| 16    | -0.97427             | 9.9264               | 8.9521                          | 56    | 3.1065               | -4.7302              | -1.6237                        |
| 17    | -1.0361              | 11.0424              | 10.0062                         | 57    | 3.1647               | -5.2056              | -2.0408                        |
| 18    | -1.0961              | 12.3421              | 11.246                          | 58    | 3.2221               | -5.6557              | -2.4336                        |
| 19    | -1.1525              | 13.9063              | 12.7538                         | 59    | 3.2786               | -6.0831              | -2.8045                        |
| 20    | -1.202               | 15.8933              | 14.6914                         | 60    | 3.3344               | -6.49                | -3.1556                        |
| 21    | -1.2418              | 18.7072              | 17.4654                         | 61    | 3.3893               | -6.8782              | -3.4889                        |
| 22    | -1.0899              | 18.3646              | 17.2838                         | 62    | 3.2146               | -6.6569              | -3.4423                        |
| 23    | -0.91952             | 18.0301              | 17.1106                         | 63    | 3.0399               | -6.4316              | -3.3917                        |
| 24    | -0.75725             | 17.7034              | 16.9461                         | 64    | 2.8653               | -6.2022              | -3.337                         |
| 25    | -0.59432             | 17.384               | 16.7897                         | 65    | 2.6905               | -5.9686              | -3.278                         |
| 26    | -0.43103             | 17.0718              | 16.6408                         | 66    | 2.516                | -5.7305              | -3.2145                        |
| 27    | -0.26703             | 16.7664              | 16.4994                         | 67    | 2.3414               | -5.4879              | -3.1465                        |
| 28    | -0.10258             | 16.4676              | 16.365                          | 68    | 2.167                | -5.2405              | -3.0734                        |
| 29    | 0.062455             | 16.1751              | 16.2376                         | 69    | 1.9926               | -4.9881              | -2.9955                        |
| 30    | 0.22773              | 15.8887              | 16.1165                         | 70    | 1.8182               | -4.7305              | -2.9124                        |
| 31    | 0.39336              | 15.6082              | 16.0015                         | 71    | 1.6439               | -4.4676              | -2.8237                        |
| 32    | 0.55955              | 15.3333              | 15.8928                         | 72    | 1.4071               | -4.0318              | -2.6247                        |
| 33    | 0.72585              | 15.0638              | 15.7897                         | 73    | 1.2312               | -3.7355              | -2.5223                        |
| 34    | 0.89253              | 14.7996              | 15.6921                         | 74    | 1.0553               | -3.4688              | -2.4136                        |
| 35    | 1.0598               | 14.5404              | 15.6003                         | 75    | 0.87941              | -3.1776              | -2.2982                        |
| 36    | 1.2273               | 14.2861              | 15.5134                         | 76    | 0.70353              | -2.8794              | -2.1759                        |
| 37    | 1.3951               | 14.0365              | 15.4316                         | 77    | 0.52765              | -2.574               | -2.0464                        |
| 38    | 1.5629               | 13.7915              | 15.3544                         | 78    | 0.35176              | -2.261               | -1.9092                        |
| 39    | 1.731                | 13.5508              | 15.2819                         | 79    | 0.17588              | -1.9399              | -1.764                         |
| 40    | 1.8994               | 13.3145              | 15.2138                         | 80    | 0                 | -1.6104              | -1.6104                        |

Table 25: Cumulative change in the entropy, including the cumulative difference in entropy $\int \delta s_0$ (J/K) due to standard deviation of the molecule location and velocity as determined with empirical equation 47, as well as the cumulative change in entropy $\int \delta s_1$ (J/K) to the universe from the heat input and output as determined by equation 4.
7 Conclusion

The change in entropy to the surrounding $\delta s_1$ assumes heat transfer occurs at a virtually identical temperature between the surrounding and the argon. As expected, it is clear looking at Table 24 and 25 that while the entropy of the fluid increases, the entropy of the surrounding universe is decreasing (and vice versa); it is observed, however, that the magnitude in the change in entropy is consistently different despite the fact that identical heat transfer occurs at identical temperatures. The net change in entropy at the conclusion of this cycle $(\int \delta s_1 + \int \delta s_0) = \int \delta s_1$ is -1.6104 J/K, suggesting a net reduction of entropy to the universe for each revolution of one mole of high-pressure argon throughout this cycle, due to the intermolecular attractive Van der Waal force [16], in violation of Clausius' Theorem [1] described in equation [3]. In addition, the net entropy of the high-pressure argon working fluid $\int \delta s_0$ is 0 J/K as this cycle is internally reversible.

One observation is that the total entropy of the real-fluid argon, when utilizing the empirical equation [47] and the numerically obtained standard deviations for the molecule position and velocity, is consistently greater than for a mole of ideal gas argon of comparable temperature (equation 22). The intermolecular attractive forces add to the RMS velocities (typically 10% increase), and require the molecules to travel (on average) a longer spatial distance to move throughout the spherical container. In an ideal gas, the increase in entropy (equation 4) for a given quantity of heat energy input is reduced for higher entropy fluids (i.e. hotter temperatures). The same holds true for fluids of identical temperatures, but differences in entropy; the entropy of the real fluid is higher, but the increase in entropy for a given heat input is less than the decrease in entropy (defined equation [22]) of the ideal-gas surrounding universe. This characteristics of entropy, and the increase in disorder and entropy as a result of intermolecular attractive Van der Waal force, demonstrates how Clausius’s Theorem (equation [3]) can be violated with this macroscopic, high pressure Stirling cycle heat engine, where the intermolecular attractive Van der Waal forces affect the entropy of the working fluid, and the cycle results in a net decrease in total entropy to the surrounding universe.
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program MakeInput
implicit none
real Vr,Tr
real U,S_entropy,P_kinetic,P_PR
double precision pi,Kb,Av
real t1,t2,Rat(100),outputdat(22)
integer fooint,ct,ii,jj,kk,ppnum
character(len=16) filenameSV

call CPU_Time(t1)

pi=3.1415926535897932384626
Kb=1.38064852e-23
Av=6.02214086e23

open(unit=1000,file='param_output_data_run1_run2_stirling.txt')
ppnum=0

Vr=100
do ii=1,21
    ppnum=ppnum+1
    Tr=2.+((ii-1)*0.05)
call ThermoCalc(Vr,Tr,ppnum,outputdat)
call CPU_Time(t2)

if (ppnum<10) then
    write(filenameSV,'("Save_0",I1,".txt")')ppnum
elseif (ppnum<100) then
    write(filenameSV,'("Save_",I2,".txt")')ppnum
endif
open(unit=ppnum,file=filenameSV)
write(ppnum,*) ppnum,Vr,Tr,outputdat,'t (s) = ',(t2-t1)
close(ppnum)

write(1000,*) ppnum,Vr,Tr,outputdat,'t (s) = ',(t2-t1)
print *,ppnum,'/122, t (s) = ',t2
enddo

Tr=2
do ii=1,21
    ppnum=ppnum+1
    Vr=100.+((ii-1)*20.)
call ThermoCalc(Vr,Tr,ppnum,outputdat)
call CPU_Time(t2)

if (ppnum<10) then
    write(filenameSV,'("Save_0",I1,".txt")')ppnum
elseif (ppnum<100) then
    write(filenameSV,'("Save_",I2,".txt")')ppnum
endif

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endif

open(unit=ppnum,file=filenameSV)
write(ppnum,*) ppnum,Vr,Tr,outputdat,'t (s) = ','(t2-t1)
close(ppnum)

write(1000,*),ppnum,Vr,Tr,outputdat,'t (s) = ','(t2-t1)
print *,ppnum,'/122, t (s) = ',t2
endo
Vr=1.5

do ii=1,20
  ppnum=ppnum+1
  Tr=1.3+((ii-1)*0.0350)
call ThermoCalc(Vr,Tr,ppnum,outputdat)
call CPU_Time(t2)

  if (ppnum<10) then
    write(filenameSV,'("Save_0",I1,".txt")')ppnum
  elseif (ppnum<100) then
    write(filenameSV,'("Save_",I2,".txt")')ppnum
  endif
  open(unit=ppnum,file=filenameSV)
  write(ppnum,*) ppnum,Vr,Tr,outputdat,'t (s) = ',(t2-t1)
  close(ppnum)

  write(1000,* )ppnum,Vr,Tr,outputdat,'t (s) = ',(t2-t1)
  print *,ppnum,'/122, t (s) = ',t2
endo
do

Tr=2.0

do ii=1,20
  ppnum=ppnum+1
  Vr=1.5+((ii-1)*0.675)
call ThermoCalc(Vr,Tr,ppnum,outputdat)
call CPU_Time(t2)
if (ppnum<10) then
    write(filenameSV,'("Save_0",I1,".txt")')ppnum
elseif (ppnum<100) then
    write(filenameSV,'("Save_",I2,".txt")')ppnum
endif
open(unit=ppnum,file=filenameSV)
write(ppnum,*) ppnum,Vr,Tr,outputdat,'t (s) = ',(t2-t1)
close(ppnum)
write(1000,*) ppnum,Vr,Tr,outputdat,'t (s) = ',(t2-t1)
print *,ppnum,'/122, t (s) = ',t2
enddo

Vr=15
do ii=1,20
    ppnum=ppnum+1
    Tr=2.0-((ii-1)*0.0350)
call ThermoCalc(Vr,Tr,ppnum,outputdat)
call CPU_Time(t2)
if (ppnum<10) then
    write(filenameSV,'("Save_0",I1,".txt")')ppnum
elseif (ppnum<100) then
    write(filenameSV,'("Save_",I2,".txt")')ppnum
endif
open(unit=ppnum,file=filenameSV)
write(ppnum,*) ppnum,Vr,Tr,outputdat,'t (s) = ',(t2-t1)
close(ppnum)

write(1000,*), ppnum, Vr, Tr, outputdat, 't (s) = ', (t2-t1)
print *, ppnum, '/122, t (s) = ', t2
enddo

close(1000)

end program

c ------------------------------- Make Source -------------------------------

subroutine ThermoCalc(Vr, Tr, ppnum, outputdat)

real, intent(in) :: Vr, Tr
integer, intent(in) :: ppnum
real, intent(out) :: outputdat(22)

real U, S_entropy, P_kinetic, P_PR
real t1, t2
double precision MM, Pc, Tc, Vc, ecc, V, T, Rg, a, b, R, AreaS, minVr
double precision  kappa, a_PR, xx(3), Vx(3), Vx0(3), RMS3(3)
double precision  Coeff
double precision  dP_VWD, F_VDW_m, phi, theta, Vel, dP_VDW, V_rms_0, V_avg_0
double precision  drX, Vel_travel(3), Vel_xx
double precision  VelF, Vrat(3), Xrat(3)
double precision  VXdot, dP_Pauli, P_IG, U KE, U PE
double precision  Read6(6), Avg6(6), StDev6(6), V_rms_calc, V_avg_calc

c character (len=200) output

integer ii, ii0, jj, jj0, kk, ct, dir(3)
integer dx0, Nx, Ny, Np, Total_CT
double precision bp, aa
double precision  pi, Kb, Av, m_m, dt, Fx(3), fooV(2)
double precision, allocatable :: phi_fct(:), theta_fct(:), rrX(:, :)
double precision, allocatable :: VXrat(:, :), F_dat(:, :), VelFdat(:, :)
double precision, allocatable :: Vel_travelDat(:, :), Vel_fct(:, :)
double precision, allocatable :: Xstore(:, :), Vstore(:, :)
double precision, allocatable :: Fx_Stored(:, :)
double precision, allocatable :: foocrap(:, :), randnum(:, :)
integer, allocatable :: Tct(:)

c character(len=16) filenameSV

filenameSV = 'BigData_XV_3.txt'

call CPU_Time(t1)

c  ------------------------------------------------------------- Make Source  -------------------------------------------------------------

57
\[ \pi = 3.1415926535897932384626 \]
\[ K_b = 1.38064852 \times 10^{-23} \]
\[ A_v = 6.02214086 \times 10^{23} \]

\[ c \quad dx_0 = 300 \quad ! \text{Estimated time steps per bounce} \]
\[ c \quad Nx = 361 \quad ! \text{Number of steps in each degree (square it in theta and phi)} \]
\[ c \quad Ny = 101 \quad ! \text{Number of steps at each degree increment, varying speed randomly} \]

\[ dx_0 = 300 \quad ! \text{Estimated time steps per bounce} \]
\[ Nx = 361 \quad ! \text{Number of steps in each degree (square it in theta and phi)} \]
\[ Ny = 1 \quad ! \text{Number of steps at each degree increment, varying speed randomly} \]

\[ c \quad \text{Argon} \]
\[ \text{MM} = 0.0399 \quad ! \text{Molar Mass (kg/mole)} \]
\[ Pc = 4.863 \times 10^6 \quad ! \text{Critical Pressure (Pa)} \]
\[ Tc = 150.687 \quad ! \text{Critical Temperature (K)} \]
\[ Vc = 1./535 \quad ! \text{Critical Volume (m}^3/\text{kg)} \]
\[ ecc = 0 \quad ! \text{Eccentricity factor} \]

\[ \text{-----------------------------------------------} \]
\[ Np = (Nx**2) * Ny \]

\[ \text{ALLOCATE}(rrX(Np,3)) \]
\[ \text{ALLOCATE}(Tct(Np)) \]
ALLOCATE(VXrat(Np))
ALLOCATE(F_dat(Np))
ALLOCATE(VeLFdat(Np))
ALLOCATE(Vel_travelDat(Np))
ALLOCATE(Vel_fct(Np))
ALLOCATE(Xstore((dx0*10),3))
ALLOCATE(Vstore((dx0*10),3))
ALLOCATE(Fx_Stored((dx0*10),3))
ALLOCATE(randnum(Ny))

ALLOCATE(foocrap(Np))

V=Vr*Vc*MM
T=Tr*Tc

m_m=MM/Av
Rg=Av*Kb/MM
a=0.45724*(Rg**2)*(Tc**2)/Pc
b=0.07780*Rg*Tc/Pc

minVr=1./100
if (Vr<((1+minVr)*b/Vc)) then
    V=((1+minVr)*b/Vc)*Vc*MM
endif

bp=(2.**(1./3))-1.
aa=(1/(9*bp))*(Rg**2)*(Tc**2.5)/Pc
59
\[
R = (V \times (3./(4\pi)))^{**(1./3)} \\
Rb = ((V-(b*MM))\times(3./(4\pi)))^{**(1./3)} \\
\text{AreaS} = 4\pi \times (R^{**2}) \\
\]

\[
V_{rms_0} = \sqrt{3*KB*T/m_m} \\
V_{avg_0} = V_{rms_0} \times (sqrt(8/(3*pi))) \\
\]

\[
kappa = 0.37464 + (1.54226*ecc) - (0.26992*(ecc**2)) \\
a_{PR} = (1. + (kappa \times (1-(sqrt(T/Tc)))))*2 \\
P_{PR} = ((Rg*T)/((V/MM)-b)) \\
P_{PR} = P_{PR} - ((a_{PR}*a)/(((V/MM)**2)+(2*b*(V/MM)-(b**2)))) \\
\]

\[
dt = (2*R/V_{avg_0})/dx0 \\
\]

\[
ct = 0 \\
do \ jj = 1,Nx \\
\phi = (pi/2)*((jj-1.)/(Nx-1.)) \\
do \ ii = 1,Nx \\
\]

\[
ct = ct+1 \\
\theta = (pi)*((ii-1.)/(Nx-1.)) \\
xx(1) = (sin(\theta)) \times (cos(\phi)) \\
xx(2) = (sin(\theta)) \times (sin(\phi)) \\
xx(3) = cos(\theta) \\
\]

\[
do \ kk = 1,Ny \\
rrX(((ct-1)*Ny)+kk,1) = xx(1) \\
rrX(((ct-1)*Ny)+kk,2) = xx(2) \\
\]

60
\[
rrX(((ct-1)\times Ny)+kk,3)=xx(3)
\]
enddo
enddo
enddo

call make_rand_fct(Ny,randnum)

\[
V_{rms\_calc}=0
\]
\[
V_{avg\_calc}=0
\]
do ii=1,Ny
\[
V_{avg\_calc}=V_{avg\_calc}+(randnum(ii)\times V_{avg\_0}/Ny)
\]
\[
V_{rms\_calc}=V_{rms\_calc}+((randnum(ii)\times V_{avg\_0})^{2}/Ny)
\]
enddo
\[
V_{rms\_calc}=\sqrt{V_{rms\_calc}}
\]

do ii=1,(Nx**2)
do jj=1,Ny
\[
ii0=((ii-1)\times Ny)+jj
\]
if (Ny==1) then
\[
Vel\_fct(ii0)=V_{rms\_0}
\]
else
\[
Vel\_fct(ii0)=(randnum(jj))\times V_{avg\_0}
\]
endif
enddo
enddo
Total_CT=0
open(unit=ppnum,file=filenameSV)
do ii=1,Np
  if ((mod(ii,Nx*Nx))==0) then
    call CPU_Time(t2)
    print *,(ii/(Nx*Nx)),'/',Ny,' ','t=',NINT(t2-t1)
    print *,'Vr=',Vr,'Tr=',Tr,ppnum,'/122'
  endif
  call Get_dP_VDW(Vel_fct(ii),Vr,dP_VDW)
  F_VDW_m=dP_VDW*AreaS/Av
  Vx0=(Vel_fct(ii))*(rrX(ii,:))
  Vx=Vx0
  xx=xx*0
  xx(1)=-R
  drX=(sqrt(sum(xx**2)))*(0.99)
  Xstore=Xstore*0
  Vstore=Vstore*0
  Fx_Stored=Fx_Stored*0
  ct=0
  do while ((abs(drX/R))<1.0)
    ct=ct+1
    xx=xx+(Vx*dt)
    drX=(sqrt(sum(xx**2)))
do jj=1,3
   if (xx(jj)==0) then
      dir(jj)=0
   else
      dir(jj)=-(xx(jj)/(abs(xx(jj))))
   endif
endo
Fx=(abs(F_VDW_m*((xx/R)**3)))*dir
do jj=1,3
   Vx(jj)=Vx(jj)+(Fx(jj)*dt/m_m)
endo
write(ppnum,*) xx,Vx

dojj=1,3
   Xstore(ct,jj)=xx(jj)
   Vstore(ct,jj)=Vx(jj)
   Fx_Stored(ct,jj)=Fx(jj)
endo
if (ct>(dx0*10)) then
   drX=10*R
   print *,’PROBLEM!!!’,ct,dx0
endif
endo
Tct(ii)=ct
Total_CT=Total_CT+ct
Vel_travel=Vel_travel*0
do jj=1,3
    fooreal1=0
    do kk=1,ct
        fooreal1=fooreal1+(Vstore(kk,jj)/ct)
    enddo
    Vel_travel(jj)=fooreal1
enddo

do jj=1,3
    Vel_travelDat(ii)=Vel_travelDat(ii)+(Vel_travel(jj)**2)
enddo
Vel_travelDat(ii)=sqrt(Vel_travelDat(ii))

VelF=0
do jj=1,3
    VelF=VelF+(Vstore(ct,jj)**2)
enddo
VelF=sqrt(VelF)
VelFdat(ii)=VelF

Vrat=Vstore(ct,:)/VelF
Xrat=xx/R

VXdot=0
do jj=1,3
    VXdot=VXdot+(Xrat(jj)*Vrat(jj))
enddo
VXrat(ii)=VXdot

F_dat(ii)=((2*m_m*VXdot)*VelF/(ct*dt))-F_VDW_m

enddo
close(ppnum)

Avg6=Avg6*0.
RMS3=RMS3*0.
StDev6=StDev6*0.

open(unit=ppnum,file=filenameSV)
do ii=1,Total_CT
   read(ppnum,*) Read6(:)
   Avg6=Avg6+Read6
   RMS3=RMS3+(Read6(4:6)**2.)
endo
dAvg6=Avg6/Total_CT
RMS3=snrt(RMS3/Total_CT)
close(ppnum)

open(unit=ppnum,file=filenameSV)
do ii=1,Total_CT
   read(ppnum,*) Read6(:)
   StDev6=StDev6+((Read6-Avg6)**2)
endo
StDev6=StDev6/Total_CT
close(ppnum)
\[ P_{\text{kinetic}} = 0 \]
\[ U_{\text{KE}} = 0 \]
\[ S_{\text{entropy}} = 0 \]
do ii=1,Np
\[ P_{\text{kinetic}} = P_{\text{kinetic}} + (F_{\text{dat}}(ii)) \]
\[ U_{\text{KE}} = U_{\text{KE}} + (V_{\text{elFdat}}(ii)^{**2}) \]
\[ S_{\text{entropy}} = S_{\text{entropy}} + (V_{\text{el_travelDat}}(ii)) \]
enddo

\[ P_{\text{kinetic}} = ((P_{\text{kinetic}}/Np)*(Av/AreaS))*(R/Rb) \]
\[ P_{\text{IG}} = Av*Kb*T/V \]

\[ U_{\text{KE}} = ((U_{\text{KE}}/Np))*(0.5*Av*m_m) \]
\[ U_{\text{PE}} = -dP_{\text{VDW}}*V \]
\[ U = U_{\text{KE}} + U_{\text{PE}} \]
\[ S_{\text{entropy}} = ((3*log(S_{\text{entropy}}/Np))+(log(V-(b*MM))))*Av*Kb \]

outputdat(1)=U
outputdat(2)=S_{\text{entropy}}
outputdat(3)=P_{\text{kinetic}}
outputdat(4)=P_{\text{PR}}
outputdat(5:10)=Avg6
outputdat(11:16)=StDev6
outputdat(17:19)=RMS3
outputdat(20)=Total_CT
outputdat(21)=V_rms_calc
outputdat(22)=V_avg_calc

end subroutine

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subroutine linspace(start,stop,ct,out)

real, intent(in) :: start,stop
integer, intent(in) :: ct
real, intent(out) :: out(ct)
real dx,foo
integer ii

dx=(stop-start)/(ct-1.)
foo=start

do ii=1,ct
    out(ii)=foo
    foo=foo+dx
enddo

end subroutine
subroutine Get_dP_VDW(Vel,Vr,dP_VDW)

real, intent(in) :: Vr
double precision, intent(in) :: Vel
double precision, intent(out) :: dP_VDW
double precision pi,Kb,Av,m_m,T_eff,Tr,Pc
double precision MM,Tc,Vc,V,R,Coeff,Rb,bp,aa
integer ii

pi=3.1415926535897932384626
Kb=1.38064852e-23
Av=6.02214086e23

Argon

MM=.0399 ! Molar Mass (kg/mole)
Pc=4.863e6 ! Critical Pressure (Pa)
Tc=150.687 ! Critical Temperature (K)
Vc=1./535 ! Critical Volume (m^3/kg)

V=Vr*Vc*MM

m_m=MM/Av
Rg=Av*Kb/MM

bp=(2.**(1./3))-1.
aa=(1/(9*bp))*(Rg**2)*(Tc**2.5)/Pc
\[ T_{\text{eff}} = (\text{Vel}^2) \frac{m_m}{(3Kb)} \]
\[ Tr = \frac{T_{\text{eff}}}{T_c} \]

if (Tr<1.) then
  \[ \text{Coeff} = (2.3246 + (-0.8441/(\sqrt{Vr})) + (-0.8670)) \times Tr \]
else
  \[ \text{Coeff} = 2.3246 + (-0.8441/(\sqrt{Vr})) + (-0.8670 \times \sqrt{Tr}) \]
endif
if (Coeff>1) then
  \[ \text{Coeff} = 0 \]
endif

\[ dP_{\text{VDW}} = \frac{(aa/(\sqrt{T_{\text{eff}}}))}{((V/MM)^2)} \]
\[ dP_{\text{VDW}} = dP_{\text{VDW}} \times \text{Coeff} \]

end subroutine

c
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subroutine make_rand_fct(NN, randdat)
integer, intent(in) :: NN

double precision, intent(out) :: randdat(NN)

double precision, allocatable :: NormFct(:,), Xfct(:)

double precision, allocatable :: NormFct0(:)

double precision ctX, x, MinX, stdev0, dx, foo

integer ii

ALLOCATE(Xfct(NN))
ALLOCATE(NormFct0(NN))
ALLOCATE(NormFct(NN))

MinX=0.200
stdev0=0.71

dx=((1.-MinX)*2.)/(NN-1)

tX0=0.0

do ii=1,NN
  x=MinX+((ii-1)*dx)
  Xfct(ii)=x
  NormFct(ii)=(exp(-0.5*(((x-1)/stdev0)**2)))
  ctX=ctX+(1./(exp(-0.5*(((x-1)/stdev0)**2))))
endo

randdat(1)=MinX

do ii=2,NN
  foo=(((1.-MinX)*2.)*(1./NormFct(ii))/ctX)
  randdat(ii)=randdat(ii-1)+foo

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end do

end subroutine

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