PHYS2020 Assignment 2

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Question 1

(21 Marks)

The Ideal Gas Law is an equation of state which describes the relationship between the macroscopic state variables pressure (P), temperature (T) and volume (V) for a gas of non-interacting particles in thermodynamic equilibrium. While detailed knowledge of the underlying microscopic dynamics of the particles is not required to apply the Ideal Gas Law, it does arise out of these dynamics. For this question you will show this numerically by modelling the microscopic dynamics in Matlab.

For all of Question 1, the gas simulated was H_2, with a mass of 3.3471×10^{-24} kg. Velocities were random (and changing each time the code was run), and taken from a normal distribution with a mean of 0 m/s, and a standard deviation of $\sqrt{kT/m}$. The initial positions of the particles (both in the x and y axes) were random and within the dimensions of the box. The box was chosen to be 50×50 metres, where all collisions with the box walls were treated as being perfectly elastic. The temperature of the system was chosen to be 300K.

 a. Develop a Matlab model for the trajectory of a single particle with velocity $v = \{v_x, v_y\}$ in a two dimensional square box. Treat the collisions with the walls of the box as elastic, so that when a particle collides with a wall, the sign of its velocity component in the direction normal to the wall is inverted.

    See Appendix 1 for code for N particles at velocity $\mathbf{v} = \{v_x, v_y\}$.

 b. Calculate and plot the total impulse $J_x(t) = \sum \Delta p_x$ on one of the walls as momentum kicks from the particles build up over time, where Δp_x is the change in momentum of the wall due to one collision. You are free to choose the mass m of the particle as you wish. Use this to estimate the average force $\langle F \rangle = J_x(\Delta t)/\Delta t$ on the wall, where Δt is the total evolution time of the simulation.

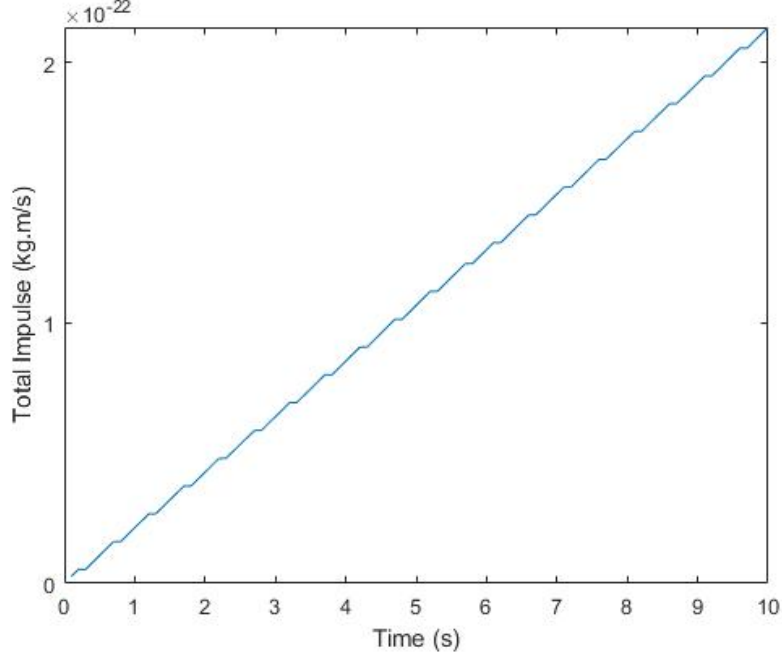   An example of a typical impulse over time graph may be seen in Figure 1 below:

Figure 1: Total Impulse over Time

The properties of this particular simulation are as follows: $\mathbf{v} = \{797.87, 1813.5\}$ m/s, N = 1 particle, and the duration of the simulation, t, was 10 seconds. The calculated (average) force for this simulation was $\langle F \rangle = 2.1364 \times 10^{-23}$N.

c. Extend your code to simulate the trajectories, impulse, and average force for many non-interacting particles in parallel, drawing each velocity component randomly from a Gaussian distribution with standard deviation of $\sqrt{kT/m}$ as dictated by equipartition for thermal equilibrium (the relevant function in Matlab is `randn`).

See Appendix 1.

d. Initialise the velocities of the particles multiple times, each time recording the total energy of the ensemble. Assuming thermal equilibrium, calculate the temperature for each initialisation. From the mean temperature, confirm that the code does (on average) produce an ensemble at temperature T.

For 50 particles,

Initialisation	1	2	3	4	5	6	7	Average
Temperature (K)	336.6	301.0	224.6	273.1	302.9	302.9	363.6	300.7

Table 1: Temperature of System over Multiple Initialisations

As Table 1 shows, even for a small sample size of 7 iterations, the simulation produces a system of approximately the desired temperature (300.7K $\approx$ 300K), with particle velocities taken from a normal distribution.

2

e. Determine the mean and standard deviation of the temperature as a function of particle number. By extrapolating this result to a typical thermodynamic particle number, comment on the statistical likelihood of the temperature of an ensemble that is in contact with a thermal reservoir having a temperature that deviates significantly from that of the reservoir temperature.

With a sample size of 50 trials for each mean/SD calculation, the data found was as follows

Number of Particles (N)	10	100	1000	5000	10000	50000	100000	200000	500000
Mean Temperature (K)	321.7	301.5	298.3	299.9	300.1	300.2	299.9	299.9	299.9
Standard Deviation (K)	107.9	28.85	9.056	4.914	3.396	1.48	0.9422	0.6737	0.3362

Table 2: Mean Temperature of Standard Deviation of Gases Consisting of N Particles

Putting the data from Table 2 into a weighted linear regression script developed for the PHYS2020 Linear Regression exercise (with the number of particles being logged), gives the formula for temperature (in Kelvin)

$$T(N) = (-7.2 \times 10^{-2}) \log_{10}(N) + 300$$

and for standard deviation (in Kelvin)

$$\sigma(N) = \frac{346.737}{N^{0.51}}$$

Extrapolating for a particle number of 10^{23}, this gives a temperature of $T = 298.34$K and a standard deviation of $\sigma \approx 6.46 \times 10^{-10}$K. Since one can be 95% confident that the true value of some variable lies within about two standard deviations of the mean, it is incredibly unlikely that the the temperature of a gas consisting of 10^{23} particles will deviate significantly from the 300K thermal reservoir that it is in contact with.

f. Simulate the trajectories of an ensemble of particles over time, calculating the average force $\langle F \rangle$ on one of the walls of the box. Confirm that the pressure on the walls due to particle collisions is as predicted by the Ideal Gas Law.

The calculation of 'pressure' in a two-dimensional simulation may be extrapolated to that of three dimensions, as number of times each particle impacts one wall is identical for each of the 2D and 3D cases. So, the simulation would be valid under the Ideal Gas Law if

$$\frac{F}{L^2} = \frac{NkT}{L^3} \tag{1}$$

The code seen in Appendix 1 was altered to calculate the three-dimensional pressure of the system for $N = 1000$. On one particular example, the average temperature was given as $T = 291.3361$K. The pressure calculated by the code is seen in the LHS of the following equation, showing substitutions into equation (1):

$$P = \frac{NkT}{L^3}$$
$$3.215 \times 10^{-23} \, \text{Pa} = \frac{1000k \times 291.3361}{50^3}$$
$$\approx 3.217 \times 10^{-23} \, \text{Pa}$$

As the LHS and RHS of the above equation are approximately equal, it is reasonable to conclude that the simulation predicts pressure values according to the Ideal Gas Law. The small discrepancy could be explained by the small N of the simulation (compared to typical thermodynamic examples), or even the large time step of the simulation.

g. Use your simulation to investigate an aspect of the Ideal Gas Law (e.g. the relationship between temperature and pressure at fixed number, the dependence of pressure on the size of the box...).

The simulation was used to analyse the relationship between temperature and pressure. Table 3 shows the data collected from multiple iterations of the code, with $N = 1000$,

Mean Temperature (K)	28.13	49.81	103.32	157.74	244.49	355.07	439.44	552.02
Pressure ($\times 10^{-23}$ Pa)	0.339	0.527	1.09	1.66	2.75	3.91	4.86	6.03
Ratio ($\times 10^{23}$ K/Pa)	82.9	94.5	94.8	95.0	88.9	90.8	90.4	91.5

Table 3: Ratio of a Range of Temperatures to Observed Pressure

The Ideal Gas Law (with $V = (50\text{m})^3$, and $N = 1000$) produces a constant T/P ratio of ≈ 90.547. As Table 3 shows, this ratio is approximated reasonably consistently for $T \geq 255$K. This data shows that the Ideal Gas Law becomes increasingly valid for typical real-world temperatures. That is, it becomes more accurate for the range of temperatures typically observed and used today. With a larger particle number and smaller time step, the observed pressure would become increasingly accurate, however this was limited due to computational constraints.

Question 2

(7 Marks)

a. Starting from the thermodynamic identity in a relevant form, derive the following expression for the internal pressure of a gas:
$$\pi_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

The thermodynamic identity, for a system where N is held fixed, is given by
$$dU = TdS - PdV \tag{2}$$

Assuming constant temperature for the system, dividing both sides of equation (2) by dV gives
$$\left(\frac{\partial U}{\partial V} \right)_T = \left(\frac{T\partial S}{\partial V} \right)_T - P$$
$$= T \left(\frac{\partial S}{\partial V} \right)_T - P \tag{3}$$

Using the Maxwell Relation
$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$
and substituting it into equation (3) gives
$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \tag{4}$$

Since the internal pressure of a gas is described as the change in internal energy of a gas as it changes volume at a constant temperature,
$$\left(\frac{\partial U}{\partial V} \right)_T = \pi_T \tag{5}$$

Substituting equation (5) into equation (4) gives the desired equation:
$$\pi_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \tag{6}$$

b. Determine the expression for the internal pressure of a real gas described by the Van der Waals equation. Give a physical explanation of the result and the implications for the sign of the internal pressure.
A convenient form of the Van der Waals equation is given in the following equation:
$$P = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2 \tag{7}$$

Substituting equation (7) into equation (6) gives an expression of internal pressure described by the Van der Waals equation:
$$\pi_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$
$$= T \left(\frac{\partial \left(\frac{nRT}{V-nb} - a \left(\frac{n}{V} \right)^2 \right)}{\partial T} \right)_V - \left(\frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2 \right)$$
$$= T \left(\frac{nR}{V - nb} \right) - \frac{nRT}{V - nb} + a \left(\frac{n}{V} \right)^2$$
$$= a \left(\frac{n}{V} \right)^2 \tag{8}$$

However, n may be expressed in terms of N by $n = N/N_A$. Substituting this into equation (8) gives:

$$\pi_T = a \left(\frac{N}{N_A V} \right)^2 \tag{9}$$

Equations (8) and (9) effectively describe the internal pressure of a gas to be proportional to the square of it's density. Alternatively, equating equation (9) to equation (5) gives

$$\left(\frac{\partial U}{\partial V} \right)_T = a \left(\frac{N}{N_A V} \right)^2 \tag{10}$$

Equation (10) implies that the sign of the internal pressure, π_T, or more specifically the constant a, will be negative if the internal energy of a gas is reduced as it's volume increases. The contrapositive of this is also true.

Question 3

(7 Marks)

a. Show that when the volume and temperature of an ideal gas are modified at constant chemical potential μ and particle number N, the resulting change in entropy is

$$\Delta S = \frac{f}{2} Nk \ln \frac{T_2}{T_1} + Nk \ln \frac{V_2}{V_1}$$

where f is the number of degrees of freedom of each gas molecule, and the subscripts 1 and 2 respectively label the initial and final states of the gas. Assess this result. *Hint: use the thermodynamic identity.*

Beginning with the thermodynamic identity of the form

$$dU = TdS - PdV + \mu dN$$

The identity may be rearranged to give

$$dS = \frac{dU + PdV - \mu dN}{T} \tag{11}$$

The two equations $U = \frac{f}{2} NkT$ and $P = \frac{NkT}{V}$ may be substituted into equation (11). This gives

$$dS = \frac{d \left(\frac{f}{2} NkT \right) + \left(\frac{NkT}{V} \right) dV - \mu N}{T}$$

$$= \frac{f}{2} Nk \frac{1}{T} dT + Nk \frac{1}{V} dV + \frac{1}{T} \mu N \tag{12}$$

Taking equation (12) over the range $T_1 \to T_2$ and $V_1 \to V_2$ gives

$$\Delta S = \frac{f}{2} Nk \int_{T_1}^{T_2} \frac{1}{T} dT + Nk \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$= \frac{f}{2} Nk \ln \left(\frac{T_2}{T_1} \right) + Nk \ln \left(\frac{V_2}{V_1} \right) \tag{13}$$

This equation takes into account the change in entropy of both the change in temperature and the change in volume, with the temperature component of the equation factoring in the degrees of freedom of the ideal gas. This equation, however, doesn't account for a change in pressure of the system. Consequently, it is only valid for systems in which the pressure remains constant.

b. Consider air in a rigid container with volume of 0.1 m³, temperature of 300 K, and pressure of 15 kPa. Assuming that the air is an ideal gas, calculate the change in entropy when 10 kJ of heat is added.

Firstly, the molarity of the ideal gas must be calculated.

$$PV = nRT \Rightarrow n = \frac{PV}{RT}$$

$$= \frac{15000\,\text{J} \times 0.1\,\text{m}^3}{8.3145\,(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \times 300\,\text{K}}$$

$$\approx 0.60136\,\text{mol}$$

Next, the change in temperature of the system may be represented by

$$\Delta U = \frac{f}{2}nR\Delta T$$

$$\Delta T = \frac{2\Delta U}{fnR} \tag{14}$$

Substituting $\Delta U = Q = 10\text{kJ}$ into equation (14), and approximating air as a diatomic gas (namely N_2 and O_2) with 5 degrees of freedom at room temperature:

$$\Delta T = \frac{2 \times 10000\,\text{J}}{5 \times 0.60136\,\text{mol} \times 8.3145\,(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})}$$

$$= 800\text{K}$$

Since $T_2 = T_1 + \Delta T$, $T_2 = 1100\text{K}$. Substituting this into equation (13) gives

$$\Delta S = \frac{f}{2}Nk\ln\left(\frac{1100}{300}\right) + Nk\ln\left(\frac{V_2}{V_1}\right)$$

Since $nR = Nk$, $f = 5$, and $V_2 = V_1$ (as the box is rigid),

$$\Delta S = \frac{5}{2}nR\ln\left(\frac{1100}{300}\right) + nR\ln\left(\frac{V_1}{V_1}\right)$$

$$= \frac{5}{2}0.60136\,\text{mol} \times 8.3145\,(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})\ln\left(\frac{1100}{300}\right)$$

$$\approx 16.241\,\text{J} \cdot \text{K}^{-1}$$

Therefore, after 10kJ of heat is added to the system, the entropy is increased by approximately $16.421\text{J} \cdot \text{K}^{-1}$.
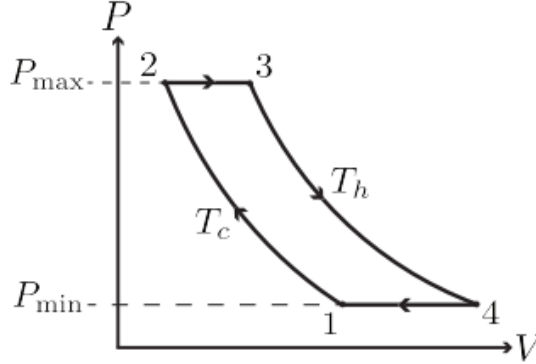
Question 4

(14 Marks)

Figure 2: Ericsson Cycle PV diagram

   Figure 2 shows the Ericsson cycle, consisting of two isobaric processes and two isothermal processes. The cycle operates between hot and cold reservoirs with temperatures of T_h and T_c, and between maximum and minimum pressures of P_{max} and P_{min}, respectively. Assume that the working fluid is an ideal gas.

a. Identify the processes in the cycle for which the engine does positive work on its environment, and for which the environment does positive work on the engine.

   The engine does net work on the environment during processes in which there is an enclosed area beneath the process in the PV diagram. Using this method, the processes $2 \to 3$ and $3 \to 4$ produce work. The contrapositive of this is also true, in that the environment does work on the engine during processes in which there is no enclosed area beneath it on the PV diagram. This means processes $4 \to 1$ and $1 \to 2$ involve the environment doing work on the engine.

b. Identify the processes in the cycle for which heat is transferred into the engine, and for which it is transferred out.

   Firstly, looking at the isobaric process $2 \to 3$, the process involves going from $V_2 \to V_3$. As the change in pressure is 0 across this process, the heat can be expressed as the difference in enthalpies between points 3 and 2: $Q = H_3 - H_2$. Expanding on this gives

$$
\begin{aligned}
Q_{2\to3} &= H_3 - H_2 \\
&= U_3 + P_{max}V_3 - (U_2 + P_{max}V_2) \\
&= (U_3 - U_2) + P_{max}(V_3 - V_2) \\
&= \Delta U_{2\to3} + P_{max}\Delta V_{2\to3}
\end{aligned}
$$

As both $\Delta U_{2\to3}$ and $\Delta V_{2\to3}$ are positive (since $T_3 > T_2$ and $V_3 > V_2$), $Q_{2\to3}$ is also positive, so heat is transferred into the system. The same method may be applied to the process $4 \to 1$ and it may be seen that $Q_{4\to1}$ is negative (or heat is being transferred out of the system).

Heat in an isothermal process is calculated by $Q = -W$, where $W = NkT \ln(\frac{V_f}{V_i})$. From process $1 \to 2$, the volume is decreasing, so the ratio of $V_2/V_1 < 1$. This means that the work done by the system is negative, and the heat transferred out of the system, $Q_{1\to2}$, is positive. The same method may be applied to the isothermal process $3 \to 4$, and it may be shown that $Q_{3\to4}$ is negative, meaning heat is transferred into the system.

8

c. Show that the isobaric processes $2 \to 3$ and $4 \to 1$, together, transfer zero net heat (i.e. $Q_{2\to3} + Q_{4\to1} = 0$).

Firstly, take the relations

$$\Delta U_{i\to f} = U_f - U_i = \frac{f}{2}Nk(T_f - T_i)$$

and, (for an isobaric process),

$$\Delta V_{i\to f} = V_f - V_i = \frac{Nk}{P}(T_f - T_i)$$

For an isobaric process,

$$
\begin{aligned}
\Delta U_{i\to f} &= Q_{i\to f} + W_{i\to f} \\
Q_{i\to f} &= \Delta U_{i\to f} - P\Delta V_{i\to f} \\
&= \frac{f}{2}Nk(T_f - T_i) - P\frac{Nk}{P}(T_f - T_i) \\
&= Nk(T_f - T_i)\left(\frac{f}{2} - 1\right)
\end{aligned}
\tag{15}
$$

Worth noting is that, due to the isothermal processes $3 \to 4$ and $1 \to 2$ in the Ericsson Cycle, $T_1 = T_2$, and $T_3 = T_4$. Taking this into account, and summing the heat from processes $2 \to 3$ and $4 \to 1$, gives

$$
\begin{aligned}
Q_{2\to3} + Q_{4\to1} &= Nk(T_3 - T_2)\left(\frac{f}{2} - 1\right) + Nk(T_1 - T_4)\left(\frac{f}{2} - 1\right) \\
&= Nk\left(\frac{f}{2} - 1\right)(T_1 - T_4 + T_3 - T_2) \\
&= Nk\left(\frac{f}{2} - 1\right)(T_2 - T_4 + T_4 - T_2) \\
&= 0
\end{aligned}
$$

Therefore, the two isobaric processes in the Ericsson Cycle, in conjunction, produce no net heat.

Given that no net heat is transferred during the isobaric processes, Ericsson's idea was to incorporate a regenerator into the engine, storing the heat transferred out of the engine during one isobaric process to provide the heat required for the other isobaric process. The efficiency of the engine is then given by

$$\epsilon = \frac{W}{Q_{3\to4}}$$

where W is the total work done during a cycle, and $Q_{3\to4}$ is the heat transferred during the isothermal process $3 \to 4$.

d. Justify why this is the appropriate definition of efficiency.

The efficiency of an engine cycle is traditionally given by

$$\epsilon = \frac{\text{Benefit}}{\text{Cost}} = \frac{W}{Q_h}$$

Where Q_h is the heat transferred from the hot reservoir into the system. Since heat is transferred into the system from the isobaric process $Q_{2\to3}$ and the isothermal process $Q_{3\to4}$ (as determined in part b. the cost is the sum of these two heats. However, the cost of the process $Q_{2\to3}$ is now 0J due to the presence of the regenerator that takes the heat from the process $Q_{4\to1}$ to power it. This now means that the total cost is just the heat from the process $3 \to 4$, and the stated equation to determine the efficiency of the Ericsson Cycle is valid.

9

e. Calculate the efficiency and compare it to the Carnot efficiency. Interpret your result. *Hint: you may use, without proof, the result that the isobaric processes* $2 \to 3$ *and* $4 \to 1$, *together, do zero net work (i.e.* $W_{2\to3} + W_{4\to1} = 0$).

Since the two isobaric processes do no net work, the total work of the system may be found by

$$W_{total} = W_{3\to4} - W_{1\to2}$$

The work from process $1 \to 2$ is negated because, as was determined in part a., this process involves the environment doing work on the system (so the system produces negative work for this process). The efficiency equation given in part d. can then be written as

$$\epsilon = \frac{W_{3\to4} - W_{1\to2}}{Q_{3\to4}}$$

Worth noting is that $W_{3\to4}$ is the work done by the *engine*, whereas $Q_{3\to4}$ is the heat transferred from the *environment*. Since $Q = -W$, the work done by the environment is negative, and so $Q_{env} = W_{eng}$. This means that

$$\epsilon = 1 - \frac{W_{1\to2}}{W_{3\to4}} \tag{16}$$

As was stated in part b., the work expended by the system over an isothermal process is equal to $NkT \ln(\frac{V_f}{V_i})$. Substituting this into equation (16) gives

$$\epsilon = 1 - \frac{NkT_2 \ln(\frac{V_2}{V_1})}{NkT_3 \ln(\frac{V_3}{V_4})}$$

$$= 1 - \frac{T_2 \ln(\frac{V_2}{V_1})}{T_3 \ln(\frac{V_3}{V_4})}$$

Taking $T_2 = T_c$, $T_3 = T_h$, and $V_2/V_1 = V_3/V_4$ (due to the like isotherms),

$$\epsilon = 1 - \frac{T_c}{T_h} \tag{17}$$

Equation (17) is equal to the Carnot Efficiency equation, meaning that the Ericsson Cycle is just as efficient as the Carnot Cycle. Worth noting is that this may only be the case with the use of a perfectly efficient regenerator that solely powers one of the two isobaric processes.

Question 5

(14 Marks)
Design your own heat engine or refrigerator, different than those considered in the lectures, labs, tutorials, text and assignments. Draw its cycle on the PV and/or TS diagram. Calculate its ideal efficiency and compare to Carnot. Discuss the advantages and disadvantages of this engine, and how you might build it.

Take the imaginary engine cycle shown in Figure 3, aptly named "B-Grade Engine Cycle", or "Benjin Cycle" for short.
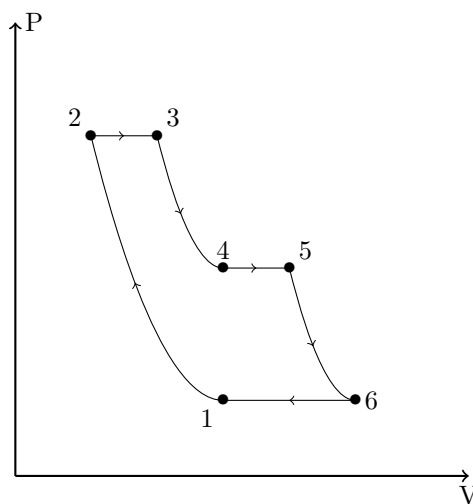

Figure 3: Benjin Cycle PV diagram

The Benjin Cycle features the following processes:

$$1 \rightarrow 2 - \text{Isothermal Compression}$$
$$2 \rightarrow 3 - \text{Isobaric Expansion}$$
$$3 \rightarrow 4 - \text{Isothermal Expansion}$$
$$4 \rightarrow 5 - \text{Isobaric Expansion}$$
$$5 \rightarrow 6 - \text{Isothermal Expansion}$$
$$6 \rightarrow 1 - \text{Isobaric Compression}$$

In more detail, the engine, specifically designed for use in cheap tanks, operates via the following processes. Firstly, at point 1, the weight of one of the engine's many pistons compresses air in a sealed container (the combustion chamber). While this isothermal process occurs, the gas transfers heat into the combustion chamber walls. Once maximum pressure is achieved, low-purity kerosene fuel is injected into the chamber and immediately ignites, reaching an idealised maximum temperature of about 1263K. The rapid combustion forces the piston to move outward, resulting in an isobaric process seen from points 2 to 3. While this occurs, a significant amount of heat is transferred into the chamber walls and the piston. At point 3, the piston hits the first of two rusty springs and an opening is revealed via the form of a valve. The spring dampens the upward movement of the piston, slowing the rate of volume expansion, while exhaust (and a significant volume of unreacted fuel) is released out of the valve. This results in the isothermal compression seen between points 3 and 4. The net temperature change in this process is zero, as the fuel is still in the process of combustion, while the hottest exhaust is ejected, and intake air is brought in. As the spring is of low quality, it soon breaks and the isobaric expansion resumes, albeit at a slower pace. This

results in the process between points 4 and 5. As the piston reaches the second spring, the cycle reaches another isothermal process between the points 5 and 1. This process is more or less identical to the process from 3 to 4, both in terms of thermodynamics and mechanics. When the system reaches point 6 on the PV diagram, it undergoes isobaric compression from $6 \rightarrow 1$. During this time, a significant amount of heat is transferred into the chamber walls, and pressurised intake air is injected into the combustion chamber at the same rate exhaust is vented out - further reducing the temperature inside the combustion chamber.

This engine has many disadvantages and few advantages. Firstly, as it is designed to run with sub-par materials, the isothermal expansions are put in place to ease temperature loads on the combustion chamber walls, preventing (likely) melting or even sublimation. The engine jettisons much of it's fuel to reduce internal pressure from the combustion, further accommodating for poor manufacturing processes. A major disadvantage of this engine (despite the extreme wastage of cheap fuel) is the fact that the two key springs that dampen the piston must be replaced on each cycle, creating a very avoidable and hazardous operation process for anyone that decides to use this engine.

The Carnot Efficiency for an engine running between the thermal reservoirs of $T_h = 1263$K and $T_c = 298$K (room temperature) is calculated as

$$
\begin{aligned}
e_{max} &\leq 1 - \frac{T_c}{T_h} \\
&= 1 - \frac{298}{1263} \\
&\approx 0.764
\end{aligned}
$$

The efficiency of the Benjin Cycle isn't so simple, however. Firstly, the efficiency of an engine may be found by

$$
e = 1 - \frac{Q_c}{Q_h}
$$

Using equation (15) for the isobaric processes, and $Q = -W$ for the isothermal processes,

$$
\begin{aligned}
Q_c &= Q_{6 \rightarrow 1} + Q_{1 \rightarrow 2} \\
&= Nk \left(\left(\frac{f}{2} - 1 \right) (T_5 - T_2) + T_2 \ln \left(\frac{V_2}{V_1} \right) \right)
\end{aligned}
$$

and,

$$
\begin{aligned}
Q_h &= Q_{2 \rightarrow 3} + Q_{3 \rightarrow 4} + Q_{4 \rightarrow 5} + Q_{5 \rightarrow 6} \\
&= Nk \left(\left(\frac{f}{2} - 1 \right) (T_5 - T_2) \right) + Nk \left(T_4 \ln \left(\frac{V_4}{V_3} \right) + T_5 \ln \left(\frac{V_6}{V_5} \right) \right) \\
&= Nk \left(\left(\frac{f}{2} - 1 \right) (T_5 - T_2) + T_4 \ln \left(\frac{V_4}{V_3} \right) + T_5 \ln \left(\frac{V_6}{V_5} \right) \right)
\end{aligned}
$$

Combining these gives the efficiency,

$$
\begin{aligned}
e &= 1 - \frac{Q_c}{Q_h} \\
&= 1 - \frac{Nk \left(\left(\frac{f}{2} - 1 \right) (T_5 - T_2) + T_2 \ln \left(\frac{V_2}{V_1} \right) \right)}{Nk \left(\left(\frac{f}{2} - 1 \right) (T_5 - T_2) + T_4 \ln \left(\frac{V_4}{V_3} \right) + T_5 \ln \left(\frac{V_6}{V_5} \right) \right)} \\
&= 1 - \frac{\left(\frac{f}{2} - 1 \right) (T_5 - T_2) + T_2 \ln \left(\frac{V_2}{V_1} \right)}{\left(\frac{f}{2} - 1 \right) (T_5 - T_2) + T_4 \ln \left(\frac{V_4}{V_3} \right) + T_5 \ln \left(\frac{V_6}{V_5} \right)}
\end{aligned}
$$

Appendices

Appendix 1: Matlab Code for Particle Simulation

```matlab
clear all;
%following statements are initialising propeties of gas
m = 2 * 1.6735575 * 10^(-27);    %Mass of each particle, value is for H2
k = 1.38064852 * 10^(-23);       %Boltzmann's Constant
Temp = 550;                      %Temperature of gas
SD = sqrt((k * Temp) / m);       %Standard deviation of gas speed
N = 1000;                        %total number of particles
Particles = zeros(4, N);

%initialise box dimensions, time
dt = 10^(-3);                    %Time step for particle trajectories
t = 1;                           %Total time to simulate particles
Box_Size = 50;
[x_min, y_min, elapsed, hits] = deal(0);
[x_max, y_max] = deal(Box_Size);

%create impulse (J) and time arrays for graphing
[J, Time] = deal(zeros(t / dt, 1));

%following for loop determines values for particle variables
for n = 1:N
    Particles(1, n) = 50 .* rand(1);    %x_ini
    Particles(2, n) = 50 .* rand(1);    %y_ini
    Particles(3, n) = SD .* randn(1);   %vx
    Particles(4, n) = SD .* randn(1);   %vy
end

%particle simulation:
for i = 1:length(Time)
    for n = 1:N
        %initialise properties for particle calculation
        x_ini = Particles(1, n);
        y_ini = Particles(2, n);
        vx = Particles(3, n);
        vy = Particles(4, n);
        x_new = x_ini + vx * dt;
        y_new = y_ini + vy * dt;
        %following if statements check if particle collides with wall
        if x_new > x_max
            x_new = x_max - (x_new - x_max);
            J(i) = max(J) + (2 * abs(m * vx));
            hits = hits + 1;
            vx = -1 * vx;
        else
            J(i) = max(J);
        end
        if y_new > y_max
            y_new = y_max - (y_new - y_max);
            vy = -1 * vy;
        end
        if x_new < x_min
```

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            x_new = x_min + (x_min - x_new);
            vx = -1 * vx;
        end
        if y_new < y_min
            y_new = y_min + (y_min - y_new);
            vy = -1 * vy;
        end

        %assign new properties for next iteration
        Particles(1, n) = x_new;
        Particles(2, n) = y_new;
        Particles(3, n) = vx;
        Particles(4, n) = vy;
    end
    %uncomment following lines for movie
%    plot(Particles(1,:), Particles(2,:), '.');
%    axis([0 50 0 50]);
%    M(i) = getframe;

    elapsed = elapsed + dt;
    Time(i) = elapsed;
end

Force = J(end) / t;                     %average force on wall
Pressure = Force / (Box_Size^2)         %average pressure of gas

%following calculations used to find apparent temperature
vrms = sqrt(mean(Particles(3, 1:N).^2 + Particles(4, 1:N).^2));
apparent_temp = (m / (2 * k)) * vrms^2

%plot impulse graph. comment out if opting for movie
plot(Time, J);                          %plot of impulse v time
axis([0, t, 0, inf]);
xlabel('Time (s)');
ylabel('Total Impulse (kg.m/s)');
% movie(M, 1, 1 / dt);                  %uncomment for movie
```