The Condensing Stirling Cycle Heat Engine

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Abstract

The Stirling thermodynamic heat engine cycle is modified, where instead of an ideal gas, a real, monatomic working fluid is used, with the engine designed so that the isothermal compression starts off as a saturated gas, and ends as a mixed-phase fluid. This cycle takes advantage of the attractive intermolecular Van der Waals forces of the working fluid to assist in compressing the working fluid partially into a liquid, reducing the input compression work and increasing the overall heat engine efficiency to exceed that of the Carnot efficiency.

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1. Introduction

From well before recorded human history, man has quested for different sources of energy for survival and comfort. Today, the need for useful energy plays a role in almost all aspects of society. Certainly, there is a benefit to having an efficient source of mechanical energy. When designing an engine, heat pump, or other thermodynamic cycle, one can not get around the laws of thermodynamics. Prevalent is the first law, which stipulates the conservation of energy; no energy can be created or destroyed. The second law is a result of the fact that heat can only flow from hot to cold, and not cold to hot; as a result, heat transfer processes ultimately result in thermodynamic disorder known as entropy throughout the universe. These two natural limitations have to be recognized in the design of a thermodynamic machine to achieve a net mechanical work output.

Under dense, pressurized conditions, a fluid ceases to become an ideal gas, and becomes a real gas following its equation of state. At a certain point, the intermolecular attractive forces of the fluid causes the gas to condense to a liquid, where these forces are too much for the kinetic energy of the fluid molecules to overcome, and the particles converge into a more ordered liquid state. During condensation, the fluid exists at two distinct phases at a constant temperature and pressure until it is a single consistent phase. As the pressure is constant with reduced volume during condensation, the intermolecular forces will reduce the work input during condensation from a saturated gas to a mixed-phase fluid.

The author proposes a closed-loop, internally reversible, piston-cylinder heat engine, not dissimilar to the Stirling cycle. Rather than use an ideal gas, this cycle uses a real fluid that partially condenses during the isothermal compression stage of the cycle. The isothermal compression phase starts off as a saturated gas, and compresses isothermally at the cool temperature until a percentage of the gas has condensed. It then is heated to the hot temperature isochorically, at a temperature greater than the critical temperature. Afterwards, it expands isothermally back to the original saturated gas volume, recovering energy in the process. Finally, the gas is cooled isochorically back to the original stage pressure and temperature, where it is a saturated gas.

The engine takes advantage of the fluid's intermolecular *Van der Waals* attractive forces that enable the fluid to condense into a liquid. The impact of these forces is profound during condensation when the fluid is stable as two distinct phases of liquid and gas, as described by *Maxwell's Construction.* These forces keep the pressure consistent throughout condensation, rather than increasing and decreasing with reduced volume as would be described during the equation of state; this ultimately results in less work input to compress the gas isothermally, and thus greater efficiency of the heat engine.

2. Theory of the Heat Engine

This heat engine is a modification of the Stirling cycle, a heat engine cycle of isothermal compression at the cold temperature sink, followed by isochoric heating up to the high temperature source, followed by isothermal expansion at the high temperature back to the original volume, and ending with isochoric cooling back to the original cold temperature and low pressure. The original Stirling cycle operated under the assumption that the working fluid was constantly an ideal gas, where the equation of state is

$$P{\cdot}v \quad = \quad R{\cdot}T, \tag{1}$$

where P (Pa) is the pressure, v (m^3/kg) is the specific volume, T (K) is the absolute temperature, and R (J/kg·K) is the specific gas constant, where

$$R \quad = \quad \frac{R_u}{M_m}, \tag{2}$$

where M_m (kg/M) is the molar mass, and R_u is the universal gas constant (8.314 J/M·K) defined as

$$R_u \quad = \quad A{\cdot}\kappa, \tag{3}$$

where A is Avogadro's Number $6.02214{\cdot}10^{23}$, and κ is Boltzman's Constant $1.38{\cdot}10^{-23}$ (J/K).

The novel aspect of this engine is that it does not use an ideal gas as the working fluid, but a real fluid that is subjected to condensation and evaporation. The hot temperature of the engine is above the critical temperature T_c (K), whereas the cold temperature of the engine is below the critical temperature, but above the triple point temperature T_{tp} (K). The working fluid is a saturated gas at the initial, low temperature, high volume stage of the engine cycle. The working fluid partially condenses during the isothermal compression, which ends when the working fluid is a liquid-gas mixture. The working fluid is then heated isochorically to the hot temperature, upon which there is isothermal expansion back to the original stage volume, and where mechanical work is recovered. Finally, the working fluid undergoes isochoric cooling back to a saturated gas at the cool temperature, and the cycle repeats itself.

The famous Van der Waals (VDW) equation of state for a real gas is defined as

$$(P + \frac{a}{v^2}) \cdot (v - b) \quad = \quad R \cdot T, \tag{4}$$

where a and b are the gas specifics VDW constants, where

$$\begin{aligned} a &= \frac{27 \cdot R^2 \cdot {T_c}^2}{64 \cdot P_c} = 3 \cdot v_c^2 \cdot P_c, \\ b &= \frac{R \cdot T_c}{8 \cdot P_c} = \frac{v_c}{3}, \end{aligned} \tag{5}$$

where P_c (Pa), T_c (K), and v_c (m^3/kg) are the critical pressure, temperature, and specific volume, where the first and second derivative of the pressure over volume are zero,

$$(\frac{\partial P}{\partial v})_T = (\frac{\partial^2 P}{\partial v^2})_T = 0,$$

and at temperatures greater than T_c, gas is the only possible phase of the fluid. If the specific volume is significantly greater than the critical specific volume ($v >> v_c$), then

$$\begin{aligned} \frac{a}{v^2} &\approx 0, \\ v - b &\approx v, \end{aligned}$$

and thus the VDW equation 4 becomes the ideal gas equation 1.

The critical pressure, temperature, and volume are material-specific, and are determined experimentally. The dimensionless reduced pressure P_R, temperature T_R, and volume v_R are dimensionless ratios of the pressure, temperature, and volume over the critical values

$$\begin{aligned} P_R &= \frac{P}{P_c}, \\ T_R &= \frac{T}{T_c}, \\ v_R &= \frac{v}{v_c}. \end{aligned} \tag{6}$$

The VDW equation of state can be reduced to its dimensionless state, defined as

$$(P_R + \frac{3}{{v_R}^2}) \cdot (v_R - \frac{1}{3}) \quad = \quad \frac{8}{3} \cdot T_R, \tag{7}$$

and equation 7 can be used for an arbitrary fluid.

One limitation of the VDW equation of state is that it cannot be used to represent the change in the fluid from liquid to gas. Following the VDW equation of state, for a constant temperature (Figure 1), the pressure will increase with decreasing volume, but decreasing in the rate of increase until eventually (Figure 1-C) the pressure will *decrease* with decreasing volume, until it reaches an inflection point (Figure 1-D), and eventually the decreasing pressure stops (Figure 1-E), and the pressure increases dramatically with decreasing volume; this fluid is a liquid at this point. It is physically impossible for a stable pressure decrease with decreasing volume, and this is not observed experimentally. Once the gas is compressed isothermally to the point it is saturated, further isothermal compression will maintain a constant pressure, and the fluid will exist as two stable states of liquid and gas. The internal energy u (J/kg), enthalpy h (J/kg), entropy s (J/kg·K), and specific volume v (m^3/kg) are proportional to the quality of the liquid

$$\begin{aligned} u &= (1-\chi)\cdot u_{liquid} + \chi\cdot u_{gas}, \\ h &= (1-\chi)\cdot h_{liquid} + \chi\cdot h_{gas}, \\ s &= (1-\chi)\cdot s_{liquid} + \chi\cdot s_{gas}, \\ v &= (1-\chi)\cdot v_{liquid} + \chi\cdot v_{gas}, \end{aligned} \tag{8}$$

where χ is the *quality*, the mass ratio of the gas in the mixture

$$\chi = \frac{mass_{gas}}{mass_{liquid} + mass_{gas}}.$$

This sudden change in the equation of state at the point of phase change from liquid to gas is explained with *Maxwell's Construction* (Figure 1). For two phases of a fluid to remain stable together, the Gibbs Free energy G (J/kg) remains constant for both the liquid and gas state of the fluid. The Gibbs Free energy is defined as

$$\begin{aligned} G &= u + P\cdot v - T\cdot s, \\ &= A + P\cdot v, \\ &= h - T\cdot s, \end{aligned} \tag{9}$$

where A (J/kg) is the Helmholtz free energy. Another feature of Maxwell's Construction is that the total work applied

$$W = \int P\cdot dv, \tag{10}$$

from the liquid to gas phase equals the value of the VDW equation of state,

$$\int_{v_{liquid}}^{v_{gas}} P_{VDW} \cdot dv = P_R \cdot (v_{gas} - v_{liquid}),$$

where P_{VDW} (Pa) is the pressure found with the VDW equation of state

$$P_{VDW} = \frac{R \cdot T}{(v - b)} - \frac{a}{v^2}, \tag{11}$$

and the reduced pressure following the VDW equation of state is simply

$$P_{R,VDW} = \frac{8 \cdot T_R}{(3 \cdot v_R - 1)} - \frac{3}{{v_R}^2}. \tag{12}$$

The values of P_R, v_{gas}, and v_{liquid} are determined numerically, and some reduced examples are given in Table 1.

T_R	P_R	$v_{R,gas}$	$v_{R,x}$	$v_{R,liquid}$
0.70	0.2461	6.0000	1.4528	0.4662
0.75	0.2825	5.6430	1.2814	0.4897
0.80	0.3834	4.1724	1.2083	0.5175
0.85	0.5045	3.1277	1.1454	0.5535
0.90	0.6470	2.3488	1.0904	0.6034
0.95	0.8119	1.7271	1.0426	0.6841
0.99	0.9605	1.2429	1.0083	0.8309
1	1	1	1	1

Table 1: Table of reduced pressures P_R and specific volumes v_R as a function of reduced temperature T_R. The reduced specific volume $v_{R,x}$ is the reduced volume where the reduced VDW pressure is equal to P_R.

The reduced pressure-volume diagram for this heat engine has been generated in Figure 2 for a cold reduced temperature sink of $T_R = 0.8$ and a hot reduced temperature source of $T_R = 1.1$. If the VDW equation of state were constantly applicable, the thin line would be the lower-temperature isotherm, and the total net work of the heat engine would be equal to the area of area A. Due to Maxwell's Construction, however, the pressure is constant when the fluid is two phases, and thus the total work output is equal to the summation of area A and B.

Many of the derivations of traditionally used thermodynamic equations are operating under the assumption that the fluid is an ideal gas. An ideal gas was used to derive the efficiency of the Carnot engine, and the entropy increase during heat transfer

$$\delta s = \frac{Q}{T}, \tag{13}$$

as well as the derivation of the specific internal energy

$$u_{ideal} \quad = \quad (\frac{1}{2} + f)R{\cdot}T, \tag{14}$$

where f is the number of degrees of freedom of the gas particles ($f = 1$ for monatomic gases, $f = 2$ for diatomic gases). Additionally, the assumption of equation 13 is used to predict the internal energy change

$$\delta u \quad = \quad C_V{\cdot}dT + \{T{\cdot}(\frac{\partial P}{\partial T})_V - P\}{\cdot}dv, \tag{15}$$

which can be used when the equation of state is known. It can be easily derived from equation 15 that for isothermal ideal gas compression or expansion, there is no change in internal energy or enthalpy $\delta u = \delta h = 0$.

For this real gas bounded by the VDW equation of state and Maxwell's Construction, these assumptions are not valid; attempts to apply them result in an imbalance in the internal energy after completion of the internally reversible cycle. In any internally reversible cycle the summation of all of the changes in internal energy must be zero,

$$\delta u_{12}^* + \delta u_{23}^* + \delta u_{34}^* + \delta u_{41}^* = 0.$$

In the Stirling Heat Engine Cycle, according to equation 15, assuming the constant volume specific heat C_V remains constant (the assumption that C_V is a constant is only realistic for ideal gases), the isochoric heating and cooling balance

$$\begin{aligned} \delta u_{23}^* &= C_V{\cdot}(T_H - T_L), \\ \delta u_{41}^* &= C_V{\cdot}(T_L - T_H). \end{aligned}$$

If the VDW equation of state defined in equation 11 is plugged into equation 15 for isothermal expansion, the change in internal energy is thus

$$\delta u_{34}^* \quad = \quad \frac{a}{v_3} - \frac{a}{v_4}.$$

If the fluid remained a constant phase, the isothermal compression would balance out perfectly with the isothermal expansion

$$\begin{aligned} \delta u_{12}^* &= \frac{a}{v_1} - \frac{a}{v_2}, \\ &= \frac{a}{v_4} - \frac{a}{v_3}, \\ &= -\delta u_{34}^*, \end{aligned}$$

and thus for a constant phase, equation 15 will balance out for the Stirling Cycle with a real gas following the VDW equation of state.

If there is condensation during the isothermal compression, however, equation 15 will not balance out. The change in internal energy is defined in equation 8, where

$$\delta u_{12}^{MC} = u_l + \frac{v_2 - v_l}{v_g - v_l} \cdot (u_g - u_l),$$

where v_l is the saturated liquid specific volume, and v_g is the saturated gas specific volume, both for the temperature $T_1 = T_2$. As the cycle starts at a saturated gas, $v_1 = v_g$ and $u_1 = u_g$. The specific internal energy of a saturated liquid that follows the VDW equation of state is defined as

$$u_l = u_g + \frac{a}{v_g} - \frac{a}{v_l}.$$

If the isothermal compression were to conclude at a mixed phase fluid, where $v_l < v_2 < v_1$, then due to Maxwell's Construction, the specific internal energy will always be less than the internal energy change for a constant-phase fluid $\delta u_{12}^{*} > \delta u_{12}^{MC}$; this is represented in Figure 3.

To get around this limit, the kinetic theory of gas will be used to determine the internal energy of the fluid. For a monatomic gas ($f = 1$), the pressure P (Pa) of a gas is proportional to the average velocity of each gas particle

$$\begin{aligned} P &= \frac{2}{3} \cdot \frac{N \cdot E_{kinetic}}{V}, \\ &= \frac{2}{3 \cdot v} \cdot u, \end{aligned} \tag{16}$$

where N is the total number of particles, $E_{kinetic}$ (J) is the average kinetic energy of each gas particle, V (m^3) and v (m^3/kg) is the volume and specific volume, and u (J/kg) is the specific internal energy. The internal energy U (J), by definition, is related to the average kinetic energy of the gas

$$U = N \cdot E_{kinetic},$$

and the specific internal energy u (J/kg) is simply the total internal energy U divided by the mass. To derive equation 14 to find the specific internal energy of an ideal gas, equation 16 is plugged into the ideal gas equation 1. As this heat engine does not deal with ideal gases, but with real gases that follow the VDW equation of state, the specific internal energy is derived by plugging in the definition of P from equation 11 into equation 16,

$$\begin{aligned} u &= \frac{3}{2}\cdot\{\frac{R\cdot T\cdot v}{(v-b)} - \frac{a}{v}\}, \\ &= \frac{3}{2}\cdot P\cdot v. \end{aligned} \tag{17}$$

The specific heat at a constant volume can thus be easily found as

$$C_V = \frac{3}{2}\cdot\{\frac{R\cdot v}{(v-b)}\}. \tag{18}$$

If one wants to work in terms of dimensionless reduced values, the reduced internal energy, defined as

$$u_R = \frac{u}{P_c\cdot v_c}, \tag{19}$$

can be found with a reduced version of equation 17

$$\begin{aligned} u_R &= \frac{3}{2}\cdot\{\frac{8\cdot T_R\cdot v_R}{3\cdot v_R - 1} - \frac{3}{v_R}\} \\ &= \frac{3}{2}\cdot P_R\cdot v_R. \end{aligned} \tag{20}$$

The reduced specific heat at a constant volume is simply the reduced temperature derivative of equation 20

$$C_{V,R} = \frac{3}{2}\cdot\{\frac{8\cdot v_R}{3\cdot v_R - 1}\}. \tag{21}$$

3. Normalized Heat Engine Cycle

A demonstration was conducted of the condensing Stirling cycle heat engine demonstrated in Figure 2, with a low reduced temperature of $T_R = 0.8$ and a high reduced temperature of $T_R = 1.1$. The working fluid is assumed to be monatomic ($f = 1$), such as Helium, Neon, Argon, Krypton, Xenon, or Radon. According to Table 1, for a reduced temperature of $T_R = 0.8$, the saturated liquid and gas have a reduced volume of 0.5175 and 4.1724, respectively; the reduced pressure is 0.38336. If Maxwell's Construction did not apply, and the VDW equation of state was consistent, a reduced volume of 1.2083 at a quality of 0.1890 would yield the same reduced pressure of 0.38336.

The condensing Stirling cycle heat engine is a moving boundary cycle, as seen in a piston-cylinder system. At Stage 1 and Stage 4, the piston is at Bottom Dead Center (BDC), and the reduced volumes are the saturated gas reduced volume ($v_R = 4.1724$); whereas Stage 2 and Stage 3, the piston is at Top Dead Center (TDC), and the reduced volume is the equivalent volume when the VDW pressure equals the reduced pressure ($v_R = 1.2083$). The reduced temperatures at Stage 1 and 2 are low ($T_R = 0.8$), whereas at Stage 3 and 4 the reduced temperatures are high ($T_R = 1.1$). The reduced pressures P_R are found with equation 12, whereas the reduced internal energy u_R was found with equation 20. The results of the cycle are in Table 2.

Stage	P_R	T_R	v_R	u_R	h_R
1	0.38336	0.8	4.1724	2.3993	3.9989
2	0.38336	0.8	1.2083	0.6936	1.1568
3	1.2977	1.1	1.2083	2.352	3.92
4	0.59175	1.1	4.1724	3.7035	6.1725

Table 2: The reduced pressure P_R, reduced temperature T_R, reduced volume v_R, reduced internal energy u_R, and reduced enthalpy h_R data values of the condensing Stirling cycle heat engine demonstrated in Figure 2, with a low reduced temperature of $T_R = 0.8$ and a high reduced temperature of $T_R = 1.1$.

With the change of each stage in this cycle, there is some heat exchanged with the ambient universe, as well as a work applied when there is a moving boundary. The first law of thermodynamics states that energy can not be created or destroyed, and that the change in internal energy equals the heat and work input into the working fluid,

$$\delta u_{ij} = Q_{ij} - W_{ij}, \tag{22}$$

where δu_{ij} (J/kg) is the change in internal energy, Q_{ij} (J/kg) is the heat transfered, and W_{ij} (J/kg) is the work applied across the boundary, from stage i to j. As the pressure is constant during the isothermal compression with partial condensation, the reduced work input from Stage 1 to 2 is simply

$$\begin{aligned} W_{R,12} &= P_R \cdot (v_{R,gas} - v_{R,x}), \\ &= 0.38336 \cdot (4.1724 - 1.2083) = 1.1363, \end{aligned}$$

where reduced work is defined as the work W (J/kg) divided by the product of the critical pressure and critical temperature, similar to equation 19

$$W_R = \frac{W}{P_c \cdot v_c}. \tag{23}$$

The reduced work applied across the boundary during isothermal expansion can be found by integrating the VDW pressure, defined in equation 12, plugged into equation 10,

$$\begin{aligned} W_{R,34} &= \int_{v_{R3}}^{v_{R4}} \{\frac{8 \cdot T_R}{(3 \cdot v_R - 1)} - \frac{3}{{v_R}^2}\} dv_R, \\ &= \{\frac{8}{3} \cdot T_R \cdot log(v_R - \frac{1}{3}) + \frac{3}{v_R}\}_{v_{R3}}^{v_{R4}}, \\ &= -2.5740. \end{aligned}$$

The change in reduced internal energy is found by taking the difference in internal energy at each stage, determined with equation 20. Finally, the value of the heat transfered during each stage is found with the first law of thermodynamics equation 22. These results are tabulated in Table 3. It can be noted that the summation of the heat and work changes is equal to zero, as this is an internally reversible cycle.

Stage	12	23	34	41
Q	-2.8420	1.6584	3.9255	-1.3042
W	1.1363	0	-2.5740	0

Table 3: Heat and work changes between each stage during the condensing Stirling cyle heat engine demonstrated in Figure 2, with a low reduced temperature of $T_R = 0.8$ and a high reduced temperature of $T_R = 1.1$. The summation of the heat and work changes in this table is equal to zero.

What is interesting about this engine cycle is the entropy change of the universe (Table 4) for each phase of the cycle, when entropy is determined with equation 13, which was determined for the ideal Carnot cycle, which assumes an ideal gas equation of state (equation 1). For the isothermal compression and expansion stages, these are easily determined

$$\delta s_{12} = -\frac{Q_{12}}{T_{12}} = \frac{2.8420}{0.8} = 3.5526,$$

$$\delta s_{34} = -\frac{Q_{34}}{T_{34}} = -\frac{3.9255}{1.1} = -3.5686.$$

The reduced constant specifc heat of a constant volume is determined with equation 21

$$C_{V,41} = \frac{3}{2} \cdot \{\frac{8 \cdot v_{R,gas}}{3 \cdot v_{R,gas} - 1}\} = \frac{3}{2} \cdot (\frac{8 \cdot 4.1724}{3 \cdot 4.1724 - 1}) = 4.3473,$$

and $C_{V,41}$ can be used to find the equivalent entropy change out of the universe during stage 41,

$$\delta s_{41} = -\int_{T_4}^{T_1} \frac{C_V \cdot dT}{T} = C_V \cdot log(\frac{T_4}{T_1}) = 4.3473 \cdot log(\frac{1.1}{0.8}) = 1.3844.$$

Because of Maxwell's Construction, the entropy change during stage 2-3 had to be determined numerically until the fluid was a single-phase super-heated gas. At each subsequent reduced temperature increment, the saturated liquid and gas reduced volumes are found numerically with Maxwell's Construction, the quality is determined as the volume is held constant during the heating, and then the cumulative internal energy is found as the summation of the liquid and gas reduced internal energies (equation 8). The gas becomes super-heated after $T_R = 0.9930$, and then the reduced internal energy increase is found the same way as δs_{41}. The change in entropy is determined by finding the change in internal energy for each temperature increment, and dividing by the reduced temperature. When heating a two-phase fluid from $T_R = 0.8$ to a super-critical gas at $T_R = 1.1$ at a constant reduced volume of $v_R = 1.2083$, the entropy increase is demonstrated in Figure 4, and the total reduced entropy increase is $\delta s_{23} = 1.7487$.

S12	S23	S34	S41	Snet
3.5526	-1.7487	-3.5686	1.3844	-0.3803

Table 4: The change in reduced entropy to the universe, calculated with equation 13, for each stage of the condensing Stirling cycle heat engine demonstrated in Figure 2, with a low reduced temperature of $T_R = 0.8$ and a high reduced temperature of $T_R = 1.1$. The entropy in Stage 23 cannot be calculated analytically; it was solved numerically, and the reduced entropy increase as a function of reduced temperature can be found in Figure 4.

In ideal heat transfer, where the difference in temperature is kept to a minimum, the summation of the entropy changes out of the known universe

$$\begin{aligned} -(\delta s_{12} + \delta s_{23} + \delta s_{34} + \delta s_{41})_R &= \delta s_{net} \\ 3.5526 - 1.7487 - 3.5686 + 1.3844 &= -0.3803. \end{aligned}$$

is observed to be negative. This phenomenon is observed for real gases; when the specific volume is expanded significantly (reducing the influence of intermolecular attractive forces) to simulate ideal gases, the net-total entropy goes to zero. This phenomenon can be observed by the fact that the heat engine efficiency, assuming perfect regeneration between isochoric heating and cooling,

$$\begin{aligned} \eta &= \frac{W_{net}}{Q_{in}}, \qquad (24) \\ &= \frac{W_{12} + W_{34}}{Q_{34} + Q_{23} - Q_{41}} = 0.3359, \end{aligned}$$

exceeds the ideal-gas Carnot efficiency,

$$\begin{aligned}\eta_C &= 1-\frac{T_L}{T_H}, \\ &= 1-\frac{0.8}{1.1}=0.2727,\end{aligned} \tag{25}$$

This reduction in ideal-gas entropy is increased due to Maxwell's Construction and mixed-phase condensation; the reduced pressure and work input to compress the gas results in less heat transfer out and thus less entropy generated to the surrounding universe. Of course, this does not encompass the real losses, as heat transfer has to have a temperature gradient, and there is some irreversible loss from friction. Nevertheless, under ideal conditions, the condensing Stirling cycle heat engine demonstrated in Figure 2, with a low reduced temperature of $T_R = 0.8$ and a high reduced temperature of $T_R = 1.1$, can have a theoretical reduction in total entropy within the universe; all the while heat transfer flows consistently from hot to cold, consistent with the second law of thermodynamics.

4. Conclusions

The first law of thermodynamics, described in equation 22, is consistently observed, as energy can never be created or destroyed (disregarding relativistic physics). The second law of thermodynamics has multiple definitions, but at its most fundamental level the second law can be ascribed as the fact that heat can only flow from hot to cold, thus increasing the overall disorder during heat transfer. The fact that in a natural process heat transfer only flows from hot to cold has consistently been observed, and is therefore a fundamental law of nature.

How can this condensing Stirling cycle heat engine be reconciled with the second law of thermodynamics? This can be explained by the fact that the reduction in overall entropy is only observed near the point of condensation, when the intermolecular attractive VDW forces are profound due to the fluid molecules being in close proximity. During the isothermal compression, these intermolecular forces pull the gas molecules together, in effect generating order with less work input by the boundary piston. By removing the intermolecular force component a from the equation of state, which effectively happens when the specific volume is increased and the fluid becomes an ideal gas, there is no reduction in net entropy. For this reason, this condensing Stirling cycle heat engine can have a theoretical thermodynamic efficiency greater than the Carnot efficiency, and reduce the net overall entropy in the universe without violating the first and the second law of thermodynamics.

References

[1] Yunus A. Çengel and Michael A. Boles. *Thermodynamics, An Engineering Approach*, McGraw Hill Higher Education, Columbus, OH, (2008), 6th Edition.

[2] Enrico Fermi. *Thermodynamics*, Dover Publications Inc, New York, NY, (1936).

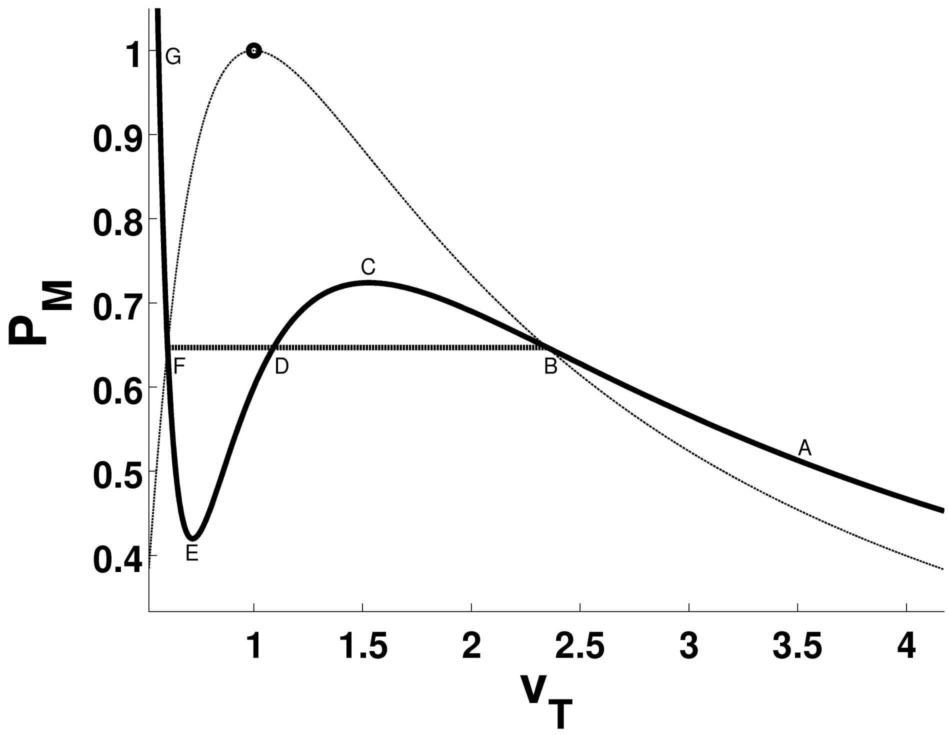

Figure 1: The labile Van der Waal isotherm (solid line), and the stable Maxwell's Construction (thick dashed curve), for a reduced temperature $T_R = 0.90$. The thin line represents the phase change as determined with Maxwell's construction for a reduced VDW equation of state.

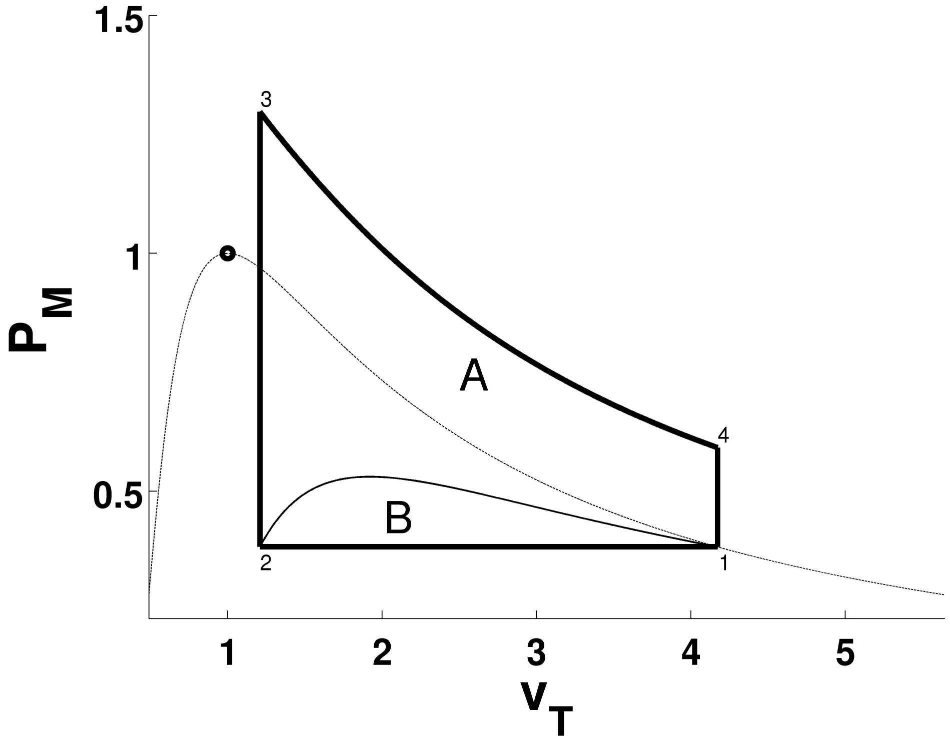

Figure 2: The Pv diagram of this modified Stirling cycle heat engine, for a low reduced temperature of $T_R = 0.8$, and a high reduced temperature of $T_R = 1.1$. The thin line represents the phase change as determined with Maxwell's construction for a reduced VDW equation of state.

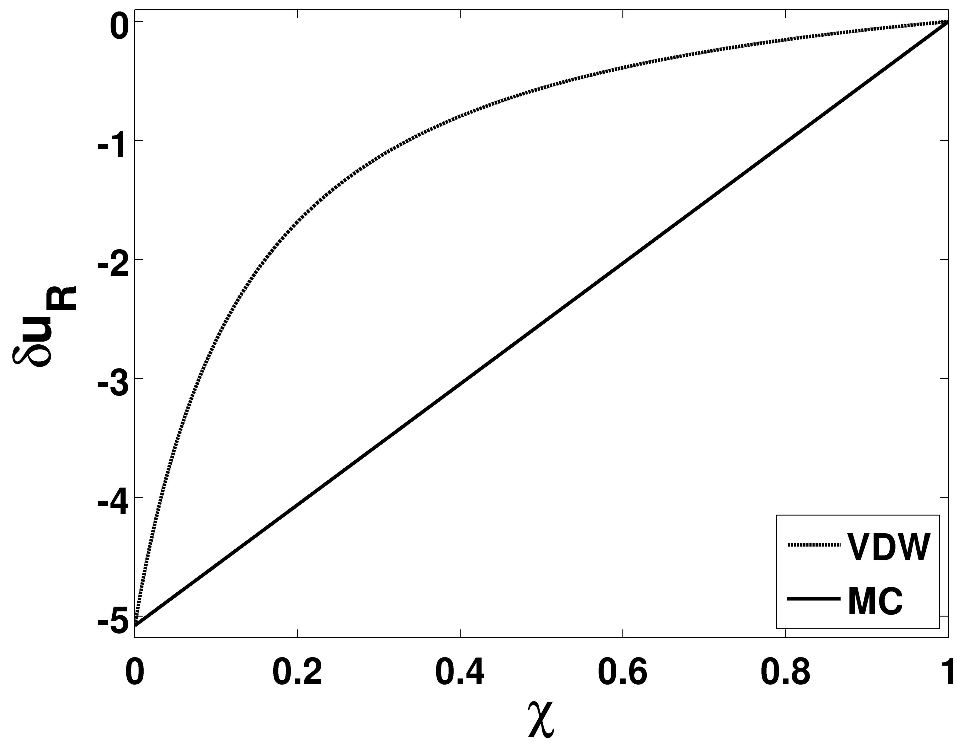

Figure 3: The comparison of the change in reduced specific internal energy during isothermal compression from a saturated gas to a saturated liquid, following equation 15, at a reduced temperature of $T_R = 0.8$.

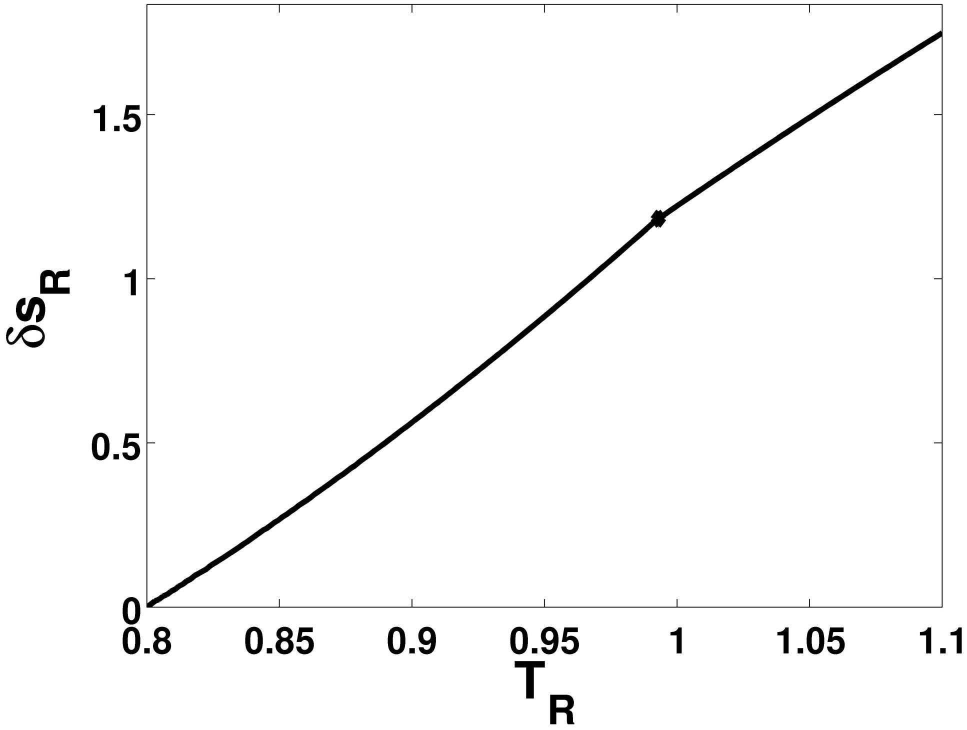

Figure 4: The entropy increase, determined numerically, from heating the mixed phase fluid at a reduced temperature of $T_R = 0.8$ and a quality $\chi = 0.1890$, to a super-critical gas at a reduced temperature of $T_R = 1.1$. The diamond marker points out the point, determined to be at $T_R = 0.9930$, when the fluid is entirely a super-heated gas, before it becomes super-critical past $T_R = 1$. The total reduced entropy is $\delta s_R = 1.7487$ at $T_R = 1.1$.