

1 The Temperature Dependence on Intermolecular
2 Potential Energy in the Design of a Supercritical Stirling
3 Cycle Heat Engine

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6 **Abstract**

7 The Stirling thermodynamic heat engine cycle is modified, where instead of an ideal gas,
8 a real, supercritical, monatomic working fluid subjected to intermolecular attractive forces
9 is used. The potential energy of real gases is redefined to show it decreasing with tem-
10 perature as a result of the attractive Keesom forces, which are temperature dependent.
11 This new definition of potential energy is used to thermodynamically design a Stirling cycle
12 heat engine with supercritical xenon gas, and an engine efficiency that exceeds the Carnot
13 efficiency is demonstrated. The change in internal energy predicted is compared to ex-
14 perimental measurements of condensing steam, xenon, argon, krypton, nitrogen, methane,
15 ethane, propane, normal butane, and iso-butane, and the close match validates this new def-
16 inition of temperature-dependent real gas potential energy, as well as the thermodynamic
17 feasibility of the modified supercritical Stirling cycle heat engine.

18 **1 Introduction**

19 From well before recorded human history, man has quested for different sources of energy
20 for survival and comfort. Today, the need for useful energy plays a role in almost all aspects
21 of society. Certainly, there is a benefit to having an efficient source of mechanical energy.
22 When designing an engine, heat pump, or other thermodynamic cycle, one can not get
23 around the laws of thermodynamics. Prevalent is the first law [1–4], which stipulates the
24 conservation of energy; no energy can be created or destroyed. The second law is a result
25 of the fact that heat can only flow from hot to cold, and not cold to hot; as a result, heat
26 transfer processes ultimately result in thermodynamic disorder known as entropy throughout
27 the universe [1–4]. These two natural limitations have to be recognized in the design of a
28 thermodynamic machine to achieve a net mechanical work output.

29 **2 Existing Definition of Internal Energy Model**

30 The kinetic model of an ideal gas [3, 5] is a well-established model to predict the kinetic
31 energy of an ideal gas. Internal energy, by definition, is the summation of the kinetic energy
32 from all of the random molecular motion within a fluid, as well as any potential energy from
33 intermolecular forces. In the kinetic model, the gas is assumed to be ideal, where there is
34 no potential energy, and the equation of state is [1–4, 6]

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

35 where P (Pa) is the pressure, v (m³/kg) is the specific volume, T (K) is the absolute
36 temperature, and R (J/kg·K) is the specific gas constant, where

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

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

$$R_u = A \cdot \kappa, \quad (3)$$

39 where A is Avogadro's Number $6.02214 \cdot 10^{23}$, and κ is Boltzman's Constant $1.38 \cdot 10^{-23}$
40 (J/K). For the kinetic model to be applicable, the gas must be ideal, where all of the
41 molecules are moving independent of each other, and there is no interaction between different
42 gas molecules, either by collision or intermolecular forces [3].

43 The internal energy of an ideal gas is comprised solely of the kinetic energy and is *only*
44 affected by the temperature. For a real gas, however, the intermolecular forces affect the
45 behavior of the molecules [1–4, 7]. The impacts of these forces increase as the molecules
46 move closer together, and as the specific volume v (m³/kg) of the fluid decreases. The
47 current equation for the change in specific internal energy u (J/kg) for a real gas is based
48 on the assumptions of entropy [1, 2]

$$\delta u = C_V \cdot \delta T + \left\{ T \cdot \left(\frac{\partial P}{\partial T} \right)_V - P \right\} \cdot \delta v, \quad (4)$$

49 where C_V (J/kg·K) is the specific heat capacity at a constant volume. For a monatomic
50 fluid, the specific heat capacity is

$$C_V = \frac{3}{2} \cdot R.$$

51 The derivation of equation 4 originates from the first law of thermodynamics. The first law
52 of thermodynamics states that energy can not be created or destroyed, and that the change
53 in internal energy equals the heat and work input into the working fluid [1–4]

$$\delta u = q - \delta w, \quad (5)$$

54 where δu (J/kg) is the change in specific internal energy, q (J/kg) is the specific heat

55 transferred, and w (J/kg) is the specific work applied across the boundary [1–4]

$$\delta w = P \cdot \delta v. \quad (6)$$

56 The change in entropy δs (J/kg·K) is defined as [1–4]

$$\delta s = \frac{q}{T}, \quad (7)$$

57 where T (K) is the absolute temperature, and q (J/kg) represent the heat transferred per
58 unit mass. This equation is the basis for the second law of thermodynamics, as it represents
59 the disorder generated by a heat transfer process. It is a fundamental law of the universe
60 that heat always flows from a hot source to a cold sink, and never from the cold to the hot
61 object. The simple reason for this is the fact that due to kinetic theory [2, 3], the square
62 root of the temperature is proportional to average velocity of a particle v_m (m/s)

$$v_m = \sqrt{\frac{3 \cdot \kappa \cdot T}{m_m}}, \quad (8)$$

63 where κ represents the Boltzman's Constant and m_m (kg) is the mass of a molecule. When
64 there is heat transfer, the higher velocity particle from the hotter matter transmits energy
65 when it impacts the lower velocity molecule. The significance of equation 7 is that it defines
66 the idealized Carnot efficiency η_C of a heat engine [2]

$$\eta_C = \frac{W_{out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{T_L}{T_H}, \quad (9)$$

67 where W_{out} (J/kg) is the net work output, Q_{in} (J/kg) and Q_{out} (J/kg) are the heat input
68 and output at the hot T_H (K) and cold T_L (K) temperatures, and η_C represents the efficiency
69 of a heat engine where there is no increase in entropy $\delta s = 0$,

$$\begin{aligned} \delta s &= \frac{Q_{in}}{T_H} - \frac{Q_{out}}{T_L} = 0, \\ \frac{Q_{out}}{Q_{in}} &= \frac{T_L}{T_H}, \end{aligned}$$

70 and thus

$$\eta_C = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_L}{T_H}.$$

71 A Carnot heat pump is simply a Carnot heat engine in reverse, and thus the Coefficient of
72 Performance (COP) where $\delta s = 0$ is

$$COP_C = \frac{1}{\eta_C} = \frac{Q_{out}}{W_{in}} = \frac{1}{1 - \frac{T_L}{T_H}}. \quad (10)$$

73 If a heat pump were designed so that the heat output would entirely supply the heat input
74 of a heat engine, and then the work output of the heat engine would supply the work input
75 of a heat pump, this system would run indefinitely provided that

$$\eta_{HE} \geq \frac{1}{COP_{HP}}, \quad (11)$$

76 and if equation 11 does not hold true (as has been consistently observed to date), then a
77 work input will be constantly needed to keep the heat-pump-heat-engine system running.
78 Since heat always flows from hot to cold, for this system to be possible the temperate range
79 of the heat pump must be equal or greater than that of the heat engine

$$T_{H,HE} \leq T_{H,HP},$$

$$T_{L,HE} \geq T_{L,HP},$$

80 and therefore if both the heat pump and heat engine maintained the ideal Carnot COP
81 and efficiency, and the temperature difference was minimized so that $T_{H,HE} = T_{H,HP}$ and
82 $T_{L,HE} = T_{L,HP}$, then $\eta_{HE} = 1/COP_{HP}$. If the heat pump or the heat engine ever exceeded
83 the Carnot efficiency, then $\eta_{HE} > 1/COP_{HP}$ and the system could obtain useful work from
84 the ambient temperature, without the need for a temperature differential. In practice, as
85 the efficiency of all heat engines and the COP of all heat pumps built to date are less than
86 the ideal Carnot, $\eta_{HE} < 1/COP_{HP}$, and a work input is needed to continually operate the

87 system.

88 Using equation 7, the first law can then be written as

$$\delta u = T \cdot \delta s - P \cdot \delta v. \quad (12)$$

89 Expanding the partial derivatives of the entropy yields

$$\delta s = \left(\frac{\partial s}{\partial T}\right)_V \cdot \delta T + \left(\frac{\partial s}{\partial V}\right)_T \cdot \delta v, \quad (13)$$

90 and due to the symmetry of the second derivative of the Helmholtz free energy [2, 3]

$$\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V. \quad (14)$$

91 By plugging equation 14 into equation 13, and then plugging equation 13 into equation 12,

92 and then defining the specific heat capacity

$$T \cdot \left(\frac{\partial s}{\partial T}\right)_V \cdot \delta T = \left(\frac{q}{T}\right)_V \cdot \delta T = C_V \cdot T, \quad (15)$$

93 one can get equation 4.

94 One of the earliest equations of state is Van der Waals (VDW) equation [1–3, 8, 9]

$$\left(P + \frac{a}{v^2}\right) \cdot (v - b) = R \cdot T, \quad (16)$$

95 where P (Pa) is the pressure, v (m^3/kg) is the specific volume, R ($\text{J}/\text{kg}\cdot\text{K}$) is the specific

96 gas constant, T (K) is the absolute temperature, and a ($\text{Pa}\cdot\text{m}^6/\text{kg}^2$) and b (m^3/kg) are the

97 gas specific VDW constants, where

$$\begin{aligned} a &= \frac{27 \cdot R^2 \cdot T_c^2}{64 \cdot P_c} = 3 \cdot v_c^2 \cdot P_c, \\ b &= \frac{R \cdot T_c}{8 \cdot P_c} = \frac{v_c}{3}, \end{aligned} \quad (17)$$

98 where P_c (Pa), T_c (K), and v_c (m^3/kg) are the critical pressure, temperature, and specific

99 volume, where the first and second derivative of the pressure as a function of volume are
100 zero

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

101 and at temperatures greater than T_c , gas is the only possible phase of the fluid.

102 If the VDW equation of state were plugged into equation 4 to find the change in internal
103 energy [1,2]

$$\delta u = C_V \cdot \delta T + \frac{a}{v^2} \cdot \delta v. \quad (18)$$

104 This equation represents the change in kinetic energy as a function of temperature $C_V \cdot \delta T$,
105 and potential energy as a function of volume $\frac{a}{v^2} \cdot \delta v$, for the total change in internal energy
106 Δu (J/kg)

$$\begin{aligned} \Delta u &= \int_{T_1}^{T_2} C_V \cdot \delta T + \int_{v_1}^{v_2} \frac{a}{v^2} \cdot \delta v., \\ &= C_V \cdot (T_2 - T_1) + a \cdot \left(\frac{1}{v_1} - \frac{1}{v_2}\right). \end{aligned} \quad (19)$$

107 The first term represents the kinetic portion of the internal energy, whereas the second term
108 represents the potential energy.

109 3 Supercritical Stirling Cycle Heat Engine

110 The ideal Stirling heat engine, with an ideal gas as its working fluid, is as efficient as
111 the Carnot efficiency. A Stirling engine cycle is defined by isothermal compression at the
112 cold sink (stage 1-2), isochoric heating from the cold to the hot temperature (stage 2-3),
113 isothermal expansion at the hot source (stage 3-4), and isochoric cooling back from the hot
114 temperature to the cold temperature (stage 4-1). In order that the ideal gas Stirling Engine
115 achieve the same efficiency as the Carnot efficiency, there must be perfect regeneration from
116 the isochoric cooling to the isochoric heating. This is thermodynamically possible (though

117 difficult in practice) as the specific heat of an ideal gas is constant regardless of volume,
 118 and thus $Q_{23} = Q_{41}$ over the same temperature range. Provided there is this perfect
 119 regeneration, $Q_{in} = Q_{34}$ and $Q_{out} = Q_{12}$. For an ideal gas subject to the equation of state
 120 defined in equation 1 undergoing isothermal expansion [2], the heat input $q_{\delta T=0}$ (J/kg)

$$q_{\delta T=0} = R \cdot T \cdot \log\left(\frac{V_2}{V_1}\right), \quad (20)$$

121 and thus the efficiency of an ideal gas Stirling Engine is

$$\eta = 1 - \left(\frac{Q_{out}}{Q_{in}}\right) = 1 - \left(\frac{Q_{12}}{Q_{34}}\right) = 1 - \left(\frac{R \cdot T_L \cdot \log\left(\frac{V_2}{V_1}\right)}{R \cdot T_H \cdot \log\left(\frac{V_2}{V_1}\right)}\right) = 1 - \left(\frac{T_L}{T_H}\right),$$

122 which is the Carnot efficiency defined in equation 9.

123 Equation 20 no longer applies when a working fluid is no longer an ideal gas (equation
 124 1) but a real fluid subjected to intermolecular forces such as the Van der Waal forces. In
 125 addition to the Van der Waal equation of state (equation 16), there are several empirical
 126 equations of states for real gases that are far more accurate, including the Redlich-Kwong
 127 [10], Peng–Robinson [11, 12], and Benedict–Webb–Rubin [2, 13, 14]. One of these equations
 128 of state, or preferably direct experimental measurements, is necessary in order to properly
 129 design a real-life heat engine utilizing a real working fluid subjected to intermolecular forces.

130 The author proposes a hypothetical, novel definition of the change in internal energy
 131 for a real fluid undergoing isothermal compression and expansion, very different from the
 132 currently accepted definition defined in equation 4, and applied to the Van der Waal equation
 133 of state in equation 18-19. One contribution to the Van der Waal intermolecular forces is due
 134 to electrostatic interactions between charges in molecular ions, dipoles for polar molecules,
 135 quadrupoles for all molecules with symmetry lower than cubic, and permanent multipoles [7].
 136 These forces are referred to as the Keesom force, named after Willem Hendrik Keesom [15].
 137 These forces are inversely proportional to the temperature of the fluid, and thus it stands
 138 to reason that the total attractive component of the intermolecular forces can be defined as

$$a \approx \frac{a'}{\sqrt{T}}. \quad (21)$$

139 If equation 21 were plugged into equation 19 for the change in internal energy, for isothermal
 140 ($\Delta T = 0$) compression and expansion

$$\begin{aligned}\Delta u &= \frac{a'}{\sqrt{T}} \cdot \left(\frac{1}{v_1} - \frac{1}{v_2} \right), \\ a' &= \frac{R^2 \cdot T_c^{2.5}}{9 \cdot (2^{\frac{1}{3}} - 1) \cdot P_c}.\end{aligned}\tag{22}$$

141 It must be noted that a' is the exact same equation for the attractive component of the
 142 intermolecular forces defined with the Redlich-Kwong [10] equation of state. Just like gravity
 143 has been observed to be an entropic force [16–21], it can be expected that this temperature-
 144 sensitive attractive intermolecular force can impact the entropy generated as a result of
 145 thermodynamic processes involving real working fluids, and possibly improve the efficiency
 146 of a thermodynamic cycle.

147 The author proposes a Stirling engine, using supercritical xenon gas as the working
 148 fluid. The reduced specific volume at top and bottom dead center are $V_R = 0.83701$ and
 149 $V_R = 8.3701$, whereas the reduced specific temperatures are $T_R = 1.029$ and $T_R = 1.7193$
 150 at the low and hot temperature range. Xenon has a molar mass of 131.3 g/mole, a critical
 151 pressure of 5.84 MPa, a critical temperature of 289.734 K, and a critical specific volume
 152 of 0.91 cm³/g [22]; therefore the temperature of this Stirling engine ranges between 25°C
 153 and 225°C, and the specific volume ranges between 0.76161 cm³/g and 7.6161 cm³/g. The
 154 intermolecular attractive parameter a' defined in equation 22 (and also in the Redlich-
 155 Kwong [10] equation of state) is thus 419.3652 Pa·K^{0.5}·m⁶·kg⁻² for xenon. Using referenced
 156 experimental $P \cdot v \cdot T$ data from 1951 tabulated in Table 1 [22, 23], the pressures can be
 157 obtained, and are both plotted on Figure 1 and the values at each stage is tabulated in
 158 Table 2.

159 By integrating the pressure and the change in volume during the isothermal stage 1-2
 160 and stage 3-4, the work (equation 6) input W_{in} (J/kg) and output W_{out} (J/kg) can be

161 determined

$$W_{in} = 27,135,$$

$$W_{out} = 67,152,$$

162 and by using the proposed equation 22 for the change in internal energy during isothermal
163 compression δu_{12} (J/kg) and isothermal expansion δu_{34} (J/kg)

$$\delta u_{12} = 28,700,$$

$$\delta u_{34} = 22,203,$$

164 the isothermal heat output Q_{12} (J/kg) and input Q_{34} (J/kg) can be determined

$$Q_{12} = W_{in} + \delta u_{12} = 55,835,$$

$$Q_{34} = W_{out} + \delta u_{34} = 89,355,$$

165 This engine assumes perfect regeneration, where all of the heat output from isochoric cooling
166 Q_{41} (J/kg) is used for isochoric heating Q_{23} (J/kg). This is extremely difficult to practically
167 implement, but absolutely possible thermodynamically. For an ideal gas $Q_{23} = Q_{41}$; for a
168 real gas this is not the case. In order to determine the difference in heat needed from the
169 hot source

$$\delta Q_{23} = Q_{23} - Q_{41} = Q_{12} - Q_{34} + W_{out} - W_{in} = 6,497,$$

170 and this additional heating requirement can be used to find the heat input Q_{in} (J/kg) and
171 output Q_{out} (J/kg) of this engine

$$Q_{in} = Q_{34} + \delta Q_{23} = 95,852,$$

$$Q_{out} = Q_{12} = 55,835.$$

172 The heat input and output can be used to find the thermodynamic efficiency of this heat
173 engine

$$\eta_{HE} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{55,835}{95,852} = 41.749\%,$$

174 which exceeds by 4% the theoretical Carnot efficiency defined in equation 9

$$\eta_C = 1 - \frac{T_L}{T_H} = 1 - \frac{1.029}{1.7193} = 40.149\%.$$

175 This Stirling cycle example demonstrates that, provided the theoretical description for
176 the change in internal energy of a real fluid during isothermal compression or expansion
177 defined in equation 22 is valid, a heat engine that exceeds the Carnot efficiency defined in
178 equation 9 is possible. An engine that exceeds the Carnot efficiency would, by definition,
179 reduce the net entropy of the universe $\delta s_u < 0$. If equation 22 held true, it would mean that
180 the intermolecular Van der Waal forces, in-particular the temperature-sensitive attractive
181 Keesom forces [7, 15] can reduce the net global thermodynamic entropy.

182 4 Experimental Verification

183 The author claims that equation 22 is in fact a valid description of the change in internal
184 energy of a real fluid during isothermal compression or expansion, based on an abundance
185 of experimental data available within the literature, specifically due to experimental mea-
186 surements of the enthalpy of vaporization for a variety of fluids. One limitation of all of the
187 existing equation of state functions are that they cannot be used to represent the change in
188 the fluid from liquid to gas. For example, following the van der waal equation of state, for
189 a constant temperature, the pressure will increase with decreasing volume, but decreasing
190 in the rate of increase until eventually the pressure will *decrease* with decreasing volume,
191 until it reaches an inflection point, and eventually the decreasing pressure stops, and the
192 pressure increases dramatically with decreasing volume; this fluid is a liquid at this point.
193 It is physically impossible for a stable pressure decrease with decreasing volume, and this

194 is not observed experimentally. Once the gas is compressed isothermally to the point it is
 195 saturated, further isothermal compression will maintain a constant pressure, and the fluid
 196 will exist as two stable states of liquid and gas. The internal energy u (J/kg), enthalpy h
 197 (J/kg), entropy s (J/kg·K), and specific volume v (m³/kg) are proportional to the quality
 198 of the liquid [1,2]

$$u = (1 - \chi) \cdot u_{liquid} + \chi \cdot u_{gas}, \quad (23)$$

$$h = (1 - \chi) \cdot h_{liquid} + \chi \cdot h_{gas},$$

$$s = (1 - \chi) \cdot s_{liquid} + \chi \cdot s_{gas},$$

$$v = (1 - \chi) \cdot v_{liquid} + \chi \cdot v_{gas},$$

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

$$\chi = \frac{mass_{gas}}{mass_{liquid} + mass_{gas}}. \quad (24)$$

200 This sudden change in the equation of state at the point of phase change from liquid to
 201 gas is explained with *Maxwell's Construction*. For two phases of a fluid to remain stable
 202 together, the Gibbs Free energy G (J/kg) remains constant for both the liquid and gas state
 203 of the fluid. The Gibbs Free energy is defined as [1–4]

$$G = u + P \cdot v - T \cdot s, \quad (25)$$

$$= A + P \cdot v,$$

$$= h - T \cdot s,$$

204 where A (J/kg) is the Helmholtz free energy. Another feature of Maxwell's Construction is
 205 that the total work applied from the liquid to gas phase equals the value of the equation of
 206 state [1,2]

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

207 where P_{EoS} (Pa) is the pressure as defined by the equation of state of the fluid, and P_V (Pa)
 208 is the constant pressure of condensation and vaporization, and therefore measurements of
 209 the enthalpy of vaporization can be used as a valid measurement for the change in internal
 210 energy of a real fluid, simply by subtracting the work applied on the fluid

$$\delta u = H_V - P_V \cdot (v_{gas} - v_{liquid}) \quad (26)$$

211 In 1938, an effort by the National Bureau of Standards was made to experimentally
 212 measure the enthalpy of vaporization of water, ranging from 0°C to 200°C [24]

$$\begin{aligned} H_V &= 2500.5 - 2.3233 \cdot (T - 273.15) - 10^\chi, \\ \chi &= 5.1463 - 1540/T. \end{aligned} \quad (27)$$

213 The saturated pressure was obtained with the Goff Gratch equation from 1946 [25], and
 214 specific volumes for saturated liquid water and saturated gaseous steam were obtained by
 215 using published data [26–28].

216 Steam has a critical pressure of 22.064 MPa, a critical temperature of 647.14 K, a molar
 217 mass of 18.02 g/mole, and a critical density of 322 kg/m³ [29]. The intermolecular attractive
 218 parameter a' defined in equation 22 (and also in the Redlich-Kwong [10] equation of state) is
 219 thus $4.3971 \cdot 10^4 \text{ Pa} \cdot \text{K}^{0.5} \cdot \text{m}^6 \cdot \text{kg}^{-2}$. The functions of both the experimental change in specific
 220 internal energy from equation 26 utilizing the empirical equation 27 for the value of H_V , and
 221 the calculated change in specific internal energy defined in equation 22, is plotted in Figure
 222 2. The mean error between these two data functions is 4.6472%; the maximum error of all
 223 the data points is 10.7343%. The coefficient of determination value of these two functions
 224 is $R^2 = 0.99691$, demonstrating that these two functions match remarkably, and providing
 225 experimental validation to equation 22.

226 In addition to water, experimental measurements of the enthalpy of vaporization for
 227 argon, krypton, and xenon [30,31] have been published, along with the pressure and specific
 228 volumes measured during evaporation. Utilizing the published critical properties for these

229 noble gases [2, 14, 32–34] to solve equation 22, the results have been tabulated in Table
230 3, and a remarkable match has been observed for all three noble gases, providing further
231 experimental validation to demonstrate that equation 22 is applicable for real fluids in
232 general, and not just steam.

233 Finally, thermodynamic tables based on existing experimental measurements were previ-
234 ously published for xenon [22], argon [14], nitrogen [35], methane, ethane, propane, normal
235 butane, and iso-butane [36], to realize the equation of state and enthalpy of vaporization of
236 these fluids. In all of these fluids, the change in internal energy closely matches with the
237 predicted change in internal energy for isothermal expansion as defined by equation 22. The
238 results are plotted in figure 3, and tabulated in Table 4. All of the results show little error,
239 and the error is overwhelmingly near the triple point when the fluid is about to solidify.
240 The error is close to negligible for hotter temperatures. This demonstration experimentally
241 validated equation 22 as an accurate representation of the isothermal change in internal
242 energy for ten different fluids.

243 5 Conclusion

244 This effort has demonstrated that the change in internal energy of a real fluid undergo-
245 ing isothermal compression or expansion will be inverse proportional to the square root
246 of the temperature, as defined in equation 22. This is validated by significant experimen-
247 tal data available in the literature regarding the enthalpy of vaporization of ten different
248 fluids, including steam, xenon, argon, krypton, nitrogen, methane, ethane, propane, and
249 both normal and iso-butane. It can reasonably be assumed that equation 22 is applicable
250 for super-critical fluids, and it was used to find the change in internal energy during the
251 isothermal compression and expansion of a Stirling cycle heat engine utilizing supercritical
252 xenon gas as a working fluid. This heat engine, which used actual experimental measure-
253 ments for the pressure, rather than an equation of state, was predicted to have a theoretical
254 efficiency that exceeded the Carnot efficiency by 4%. With this redefined change in internal
255 energy, it can be inferred that the temperature-dependent Keesom intermolecular attrac-

256 tive force can have the effect of limiting the random possible states of fluid molecules and
257 reducing the net thermodynamic entropy in the universe.

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v (cm ³ /g)	25°C	225°C
7.6161	2.1727	3.9934
5.0774	3.0438	5.8897
3.8081	3.7861	7.7319
3.0465	4.4114	9.5302
2.5387	4.9315	11.295
2.1760	5.3573	13.0388
1.9040	5.7028	14.7664
1.6925	5.9782	16.4967
1.5232	6.195	18.2369
1.2694	6.497	21.8082
1.0880	6.6844	25.5886
0.9520	6.8212	29.7186
0.8462	6.9509	34.3188
0.7616	7.1313	39.7052

Table 1: Experimental pressure data (in MPa) of supercritical xenon gas as a function of specific volume v (cm³/g), for both a constant temperatures of 25°C and 225°C collected in 1951 [22, 23].

Stage	P (MPa)	v (cm ³ /g)	T (°C)	P_R	v_R	T_R
1	2.1727	7.6161	25	0.37204	8.3701	1.029
2	7.1313	0.76161	25	1.2211	0.83701	1.029
3	39.7052	0.76161	225	6.7988	0.83701	1.7193
4	3.9934	7.6161	225	0.6838	8.3701	1.7193

Table 2: Pressure, Specific Volume, and Temperature for the Stirling cycle heat engine utilizing supercritical xenon gas as the working fluid, and the referenced experimental $P \cdot v \cdot T$ data from 1951 [22, 23] tabulated in Table 1.

Fluid	Argon	Argon	Argon	Argon	Krypton	Xenon
T (K)	129.4	139.833	145.372	87.29	119.93	165.13
P (bar)	19.68	31.44	39.28	1.01	1.03	0.39
V_l (cm ³ /g)	0.93	1.06	1.18	0.72	0.41	0.34
V_g (cm ³ /g)	9.97	5.65	3.99	173.42	113.51	100.05
Exp Hv (kJ/kg)	110.55	85.27	64.08	163.126	107.748	96.24
P^*dV (kJ/kg)	17.79	14.43	11.07	17.475	11.609	3.852
Exp δu (kJ/kg)	92.765	70.84	53.01	145.65	96.14	92.39
Theory δu (kJ/kg)	90.95	69.07	52.43	157.98	106.66	95.67
Error (%)	1.99	2.56	1.10	7.80	9.86	3.43
Reference	[30]	[30]	[30]	[31]	[31]	[31]

Table 3: Comparison of the predicted change in internal energy δu (kJ/kg) with equation 22 with the experimentally measured enthalpy of vaporization of monatomic fluids argon, krypton, and xenon [30, 31].

Fluid	Mean % Error	Max % Error	R^2	Reference
Steam	4.6471	10.7326	0.99692	[24, 26]
Xenon	3.2529	10.767	0.98877	[22]
Argon	3.2749	10.4469	0.98952	[14]
Nitrogen	4.9127	9.1253	0.98538	[35]
Methane	4.9672	16.3029	0.97713	[36]
Ethane	7.9522	20.4914	0.95352	[36]
Propane	8.8375	16.0174	0.96625	[36]
Iso-Butane	10.9058	16.8838	0.96608	[36]
Normal Butane	10.9574	17.111	0.96377	[36]

Table 4: Tabulated percent error and coefficient of determination R^2 between the predicted change in internal energy δu (kJ/kg) with equation 22 with the empirically derived thermodynamic tables to determine the enthalpy of vaporization of ten different fluids [22, 24, 26, 35, 36].

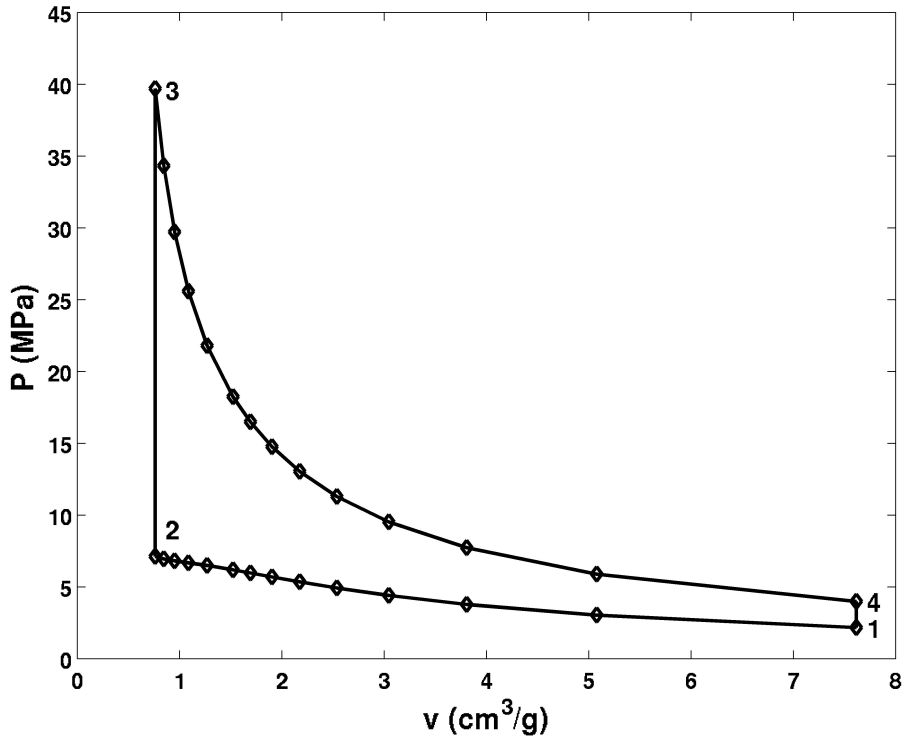


Figure 1: Pressure vs Specific Volume for the Stirling cycle heat engine utilizing supercritical xenon gas as the working fluid, and the referenced experimental $P \cdot v \cdot T$ data from 1951 [22, 23]. The diamonds represent experimental data points tabulated in Table 1.

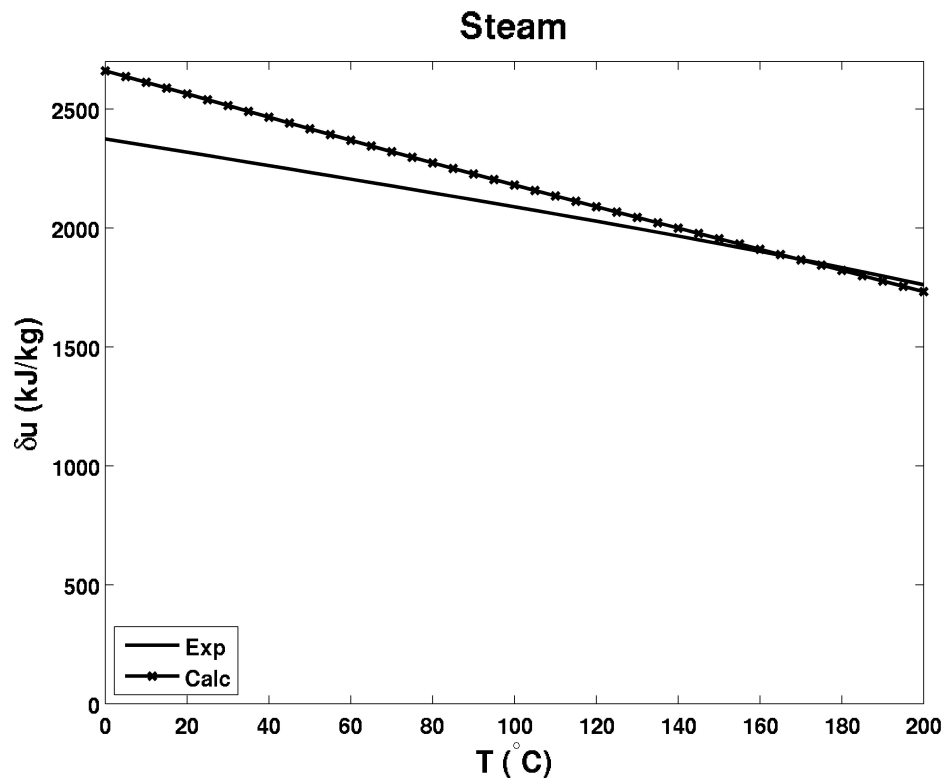


Figure 2: Change in internal energy δu (kJ/kg) during vaporization of steam, both the calculated internal energy change with equation 22, as well as the experimental data that forms the basis of empirical equation 27. The change in internal energy was found from the enthalpy using equation 26.

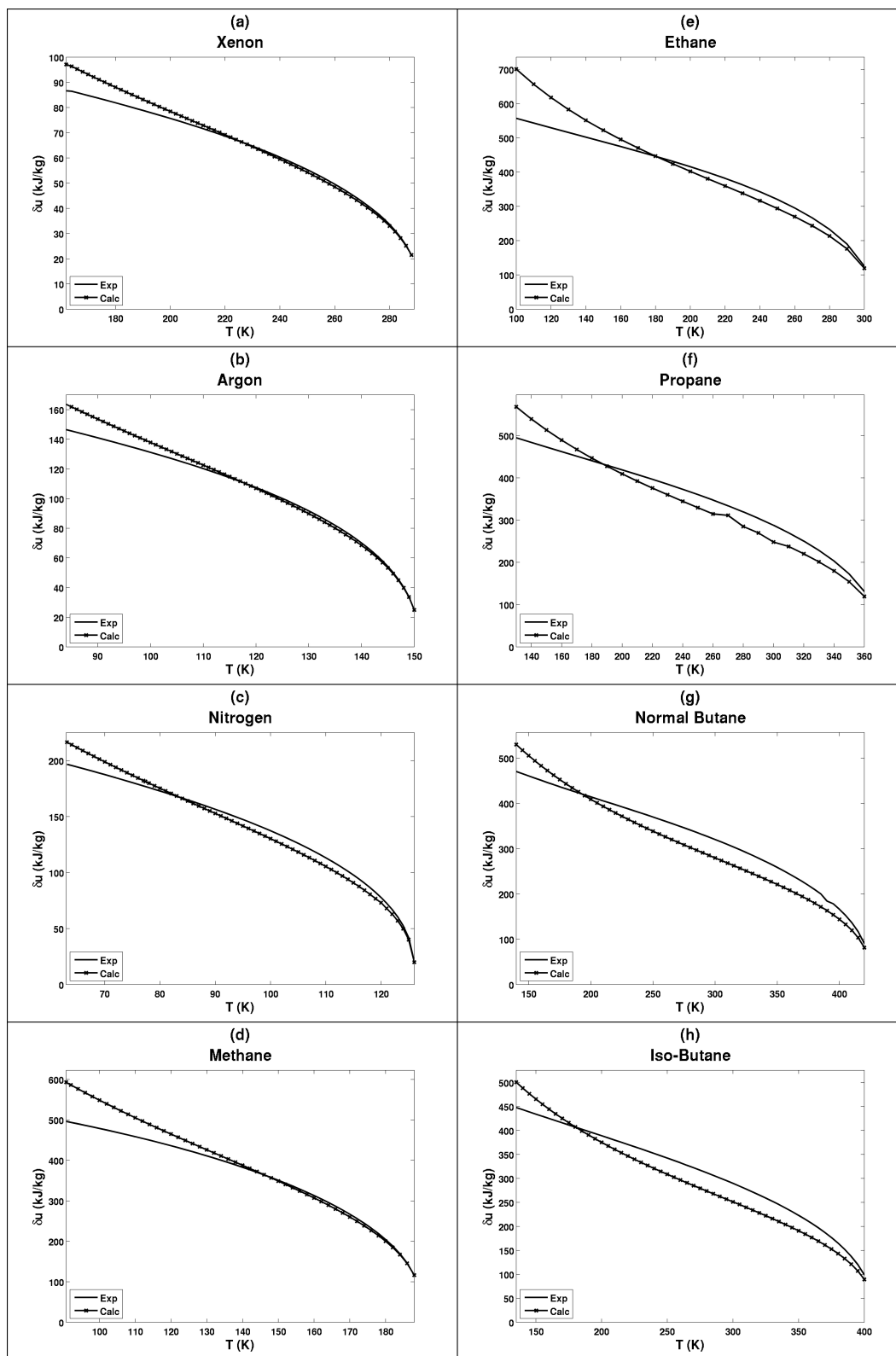


Figure 3: Change in internal energy δu (kJ/kg) of (a) xenon [22], (b) argon [14], (c) nitrogen [35], (d) methane, (e) ethane, (f) propane, (g) normal butane, and (h) iso-butane [36], during vaporization, both the calculated internal energy change with equation 22, as well as published empirical equations for the enthalpy of vaporization.