

STATISTICAL MECHANICS: MID TERM

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Problem 1. Let's go back to the cyclical heat engine we've analyzed in the last two assignments. In this problem we're going to work out the Clausius integral $\oint \frac{\delta Q}{T}$. We already know from HW #2 how to evaluate the contributions from the isothermal legs. It remains to deal with the linear ones.

- (1) As the system moves along the path, P, V , and T all change. Show that, for a monatomic ideal gas:

$$\int \frac{\delta Q}{T} = \frac{3}{2}nRf(p_A, p_B) + \frac{5}{2}nRf(V_A, V_B),$$

and specify the form of the function $f(a, b)$.

- (2) Using this result, calculate the value of $\oint \frac{\delta Q}{T}$ for the entire cycle.
(3) What does your result imply regarding the reversibility of the cycle.
(4) Compare your conclusion to what we concluded on HW #2 from our analysis of the efficiency of the engine. Do they agree? If not, what do you think might account for the discrepancy?

Solution. Let's start:

- (1) We know that for a monoatomic ideal gas, the internal energy is just a function on the temperature, and even more, we know the functional relation, which is given by

$$U = nC_v T \implies dU = nC_v dT,$$

and even more, in virtue of the second law of thermodynamics, we have that

$$dU = dQ - pdV,$$

$$dQ = dU + pdV.$$

and we also know that for an ideal gas, the following functional relationship (ideal gas equation) holds

$$pV = nRT,$$

and now, we have everything we need to prove the proposition. By definition, we have that

$$\int_A^B \frac{dQ}{T} = \int_A^B \frac{1}{T} (dU + pdV),$$

then, we have

$$\begin{aligned}\int_A^B \frac{dQ}{T} &= \int_A^B \frac{1}{T} (nC_v dT + p dV), \\ \int_A^B \frac{dQ}{T} &= \int_A^B \frac{nC_v dT}{T} + \int_A^B \frac{p dV}{T},\end{aligned}$$

and making use of the ideal gas equation

$$\begin{aligned}\int_A^B \frac{dQ}{T} &= \int_A^B \frac{nC_v dT}{T} + \int_A^B \frac{nR p dV}{pV}, \\ \int_A^B \frac{dQ}{T} &= nC_v \int_A^B \frac{dT}{T} + nR \int_A^B \frac{dV}{V},\end{aligned}$$

and from the previous relation we have, after integration, that

$$\int_A^B \frac{dQ}{T} = nC_v \ln \left(\frac{T_B}{T_A} \right) + nR \ln \left(\frac{V_B}{V_A} \right),$$

and again, making use of the ideal gas equation, we have

$$\int_A^B \frac{dQ}{T} = nC_v \ln \left(\frac{p_B}{p_A} \frac{V_B}{V_A} \right) + nR \ln \left(\frac{V_B}{V_A} \right),$$

and from the properties of the logarithm, $\ln(xy) = \ln x + \ln y$, we have

$$\begin{aligned}\int_A^B \frac{dQ}{T} &= nC_v \ln \left(\frac{p_B}{p_A} \right) + nC_v \ln \left(\frac{V_B}{V_A} \right) + nR \ln \left(\frac{V_B}{V_A} \right), \\ \implies &= nC_v \ln \left(\frac{p_B}{p_A} \right) + (nC_v + nR) \ln \left(\frac{V_B}{V_A} \right),\end{aligned}$$

but for monoatomic gases, we have that $C_v = \frac{3}{2}R$, thus we have

$$\int_A^B \frac{dQ}{T} = \frac{3}{2}nR \ln \left(\frac{p_B}{p_A} \right) + \frac{5}{2}nR \ln \left(\frac{V_B}{V_A} \right),$$

and therefore, the functional form of f is the logarithmic function.

(2) Now, for this second part we have that for both isothermal processes

$$\frac{1}{nR} \int \frac{dQ}{T} = \ln \left(\frac{V_2}{V_3} \right) - \ln \left(\frac{V_1}{V_4} \right),$$

and for the first linear process we have

$$\frac{1}{nR} \int_2^3 \frac{dQ}{T} = \frac{3}{2} \ln \left(\frac{p_3}{p_2} \right) + \frac{5}{2} \ln \left(\frac{V_3}{V_2} \right),$$

and using the ideal gas equation we can write

$$\frac{1}{nR} \int_2^3 \frac{dQ}{T} = \frac{3}{2} \ln \left(\frac{V_2}{V_3} \right) + \frac{5}{2} \ln \left(\frac{V_3}{V_2} \right),$$

and for the other linear process

$$\frac{1}{nR} \int_4^1 \frac{dQ}{T} = \frac{3}{2} \ln \left(\frac{p_4}{p_1} \right) + \frac{5}{2} \ln \left(\frac{V_4}{V_1} \right),$$

and again, making use of the ideal gas equation we have

$$\frac{1}{nR} \int_4^1 \frac{dQ}{T} = \frac{3}{2} \ln \left(\frac{V_1}{V_4} \right) + \frac{5}{2} \ln \left(\frac{V_4}{V_1} \right),$$

thus, the integral over the whole cycle becomes

$$\frac{1}{nR} \oint \frac{dQ}{T} = \ln \left(\frac{V_2}{V_3} \right) - \ln \left(\frac{V_1}{V_4} \right) + \frac{3}{2} \ln \left(\frac{V_2}{V_3} \right) + \frac{5}{2} \ln \left(\frac{V_3}{V_2} \right) + \frac{3}{2} \ln \left(\frac{V_1}{V_4} \right) + \frac{5}{2} \ln \left(\frac{V_4}{V_1} \right),$$

and this implies that

$$\begin{aligned} \frac{1}{nR} \oint \frac{dQ}{T} &= \frac{5}{2} \ln \left(\frac{V_2}{V_3} \right) + \frac{5}{2} \ln \left(\frac{V_3}{V_2} \right) + \frac{1}{2} \ln \left(\frac{V_1}{V_4} \right) + \frac{5}{2} \ln \left(\frac{V_4}{V_1} \right), \\ \frac{1}{nR} \oint \frac{dQ}{T} &= \frac{5}{2} \ln \left(\frac{V_2}{V_3} \right) - \frac{5}{2} \ln \left(\frac{V_2}{V_3} \right) - \frac{1}{2} \ln \left(\frac{V_4}{V_1} \right) + \frac{5}{2} \ln \left(\frac{V_4}{V_1} \right), \end{aligned}$$

and from this, we have

$$\frac{1}{nR} \oint \frac{dQ}{T} = 2 \ln \left(\frac{V_4}{V_1} \right) \neq 0.$$

(3) Now, from the previous equation, we have that

$$\oint \frac{dQ}{T} \neq 0,$$

but we know that if the above closed integral is zero, then the process is reversible, thus, in this case the process is irreversible.

(4) Finally, in the assignment #2, we found that the efficiency of this engine, was lower than a Carnot engine, which by construction is reversible, and even more, we know that all reversible engines share the same efficiency, thus, because the efficiency was lower that implied the process was irreversible, and here, we prove the same statement, but using a different approach.

Problem 2. A typical battery for an internal- combustion-engine vehicle is a 12 Volt lead-acid battery, with a capacity of around 50 Ampere-hours. (Since an Ampere is a Coulomb per second, 50 Ah is a number of Coulombs. It tells you the amount of charge the battery can push through a circuit before it's fully discharged.) The fundamental reaction is:



- (1) How much electrical work can the battery provide before it's fully discharged?
- (2) If you want to know how much electrical work can be provided per mole of reactants, which thermodynamic parameter should you look at?
- (3) If you want to know how much total energy is released per mole of reactants, which thermodynamic parameter should you look at?
- (4) Using the table, what are the values of the quantities mentioned in 2 and 3? Are they the same? If not, where does the energy go or come from to account for the difference?
- (5) Based on your answer to 4, is the entropy of the products higher or lower than the entropy of the reactants? By how much (per mole)? Does your answer agree with what you find in the table?
- (6) Each time the reaction occurs, two electrons are released by the reactants, flow through the external circuit, and then recombine with the products. Knowing this, what is the voltage provided by one such battery cell? A 12 V battery has multiple cells arranged in series to give the full voltage. How many?
- (7) How many moles of SO_4^{2-} would you expect the battery to contain? Does the order of magnitude of your answer seem reasonable? Why?

Solution. Let's begin:

- (1) We know that the voltage of the battery is given by $V = 12$ Volt, and the capacity of the battery is 50 Ah, thus the energy or electrical work will be

$$W_e = 12 \times 50 [\text{VAh}],$$

$$W_e = 600 [\text{Wh}],$$

thus the battery could provide a maximum amount of electrical work given by 600 Watts-hours

- (2) For this we know that ΔG is associated with the spontaneity of a physical or chemical change, and this, is also associated with the amount of work that a system can perform on the surroundings, but let's elaborate a little more on this; by definition, we have

$$G = H - TS,$$

thus, under constant pressure and temperature

$$\Delta G = \Delta H - T\Delta S,$$

and from the above expression we can see that the first term on the RHS, under some conditions, could be interpreted as energy released to the environment, and therefore used to work. On the other hand, the second term in the RHS is interpreted as increasing the entropy, thus, if we consider a process in which the system is always in equilibrium, in such a way that $\Delta S \rightarrow 0$, we can associate ΔG with the maximum amount of possible work. Therefore, I will look up for the change in Gibbs free energy.

- (3) We should look for the change in enthalpy; H is the total amount of thermal energy at a constant pressure, thus we can associate ΔH as the difference in enthalpy between the products and reactants of a chemical reaction.
- (4) Here's the full reaction and a table with the information provided for this problem



Substance	ΔH (kJ/mol)	ΔG (kJ/mol)	S (J/(mol K))
Pb	195	162.2	175.4
PbO ₂	-277.4	-217.3	68.6
H ⁺	0	0	0
SO ₄ ²⁻	-909.3	-744.5	18.5
PbSO ₄	-920.0	-813.0	148.5
H ₂ O	-285.8	-237.1	70.0

TABLE 1. Standard enthalpy of formation and the standard Gibbs free energy of formation for the species present in the chemical reaction.

As we can see, the values are different, but as stated in 2 and 3, Gibbs free energy is associated with the maximum amount of possible work, whereas the enthalpy is associated with the total amount of energy at constant pressure. Thus they are related but they not necessarily coincide, and even more, in the discussion for the work and the Gibbs free energy we assume $\Delta S \rightarrow 0$, thus, the discrepancies are related to the entropy change.

Problem 3. 3. At atmospheric pressure, water melts at 0°C with a latent heat of 334 J/g . In the process of melting, the volume decreases by about 10% (ice is less dense than water; otherwise the Titanic would have reached New York). The heat capacity of liquid water is $4.184 \text{ J/g } ^\circ\text{C}$ and is nearly independent of temperature. The molecular weight of water is 18 g/mol

- (1) Is the difference in internal energy ΔU between the liquid and solid states of water at 0°C larger or smaller than the difference in enthalpy ΔH ? By what percentage?
- (2) What is the difference in Gibbs free energy, ΔG , between the liquid and solid states of water at the melting point?
- (3) What is the difference in entropy (per mole) between the liquid and solid states of water at the melting point?
- (4) What is the difference in entropy between a mole of liquid water at 100°C and at 0°C ?

Solution. In order to solve all of these questions we need going to remember the definition of the thermodynamical potentials, thus, it's a good idea to write the definitions;

$$dU = TdS - pdV \leftarrow (\text{Internal Energy}),$$

$$dH = TdS + Vdp \leftarrow (\text{Enthalpy}),$$

$$dF = -SdT - pdV, \leftarrow (\text{Free Energy}),$$

$$dG = -SdT + Vdp \leftarrow (\text{Gibbs}),$$

now, let's move on to the questions.

- (1) We know that the internal energy is a function of the entropy and the volume, this is $U = U(T, p)$. On the other hand, for the Enthalpy, we have a contribution from the entropy and the pressure, but because in this case there's no variation in the former, we have just one contribution, this is,

$$dU = TdS - pdV \implies \Delta U = T\Delta S - p\Delta V,$$

$$dH = TdS \implies \Delta H = T\Delta S,$$

now, if we compare the above expressions we have that

$$\Delta U = \Delta H - p\Delta V,$$

and from we can use the information given un the statement of the problem about the fact that ice decreases it's volume by about 10% when melting, and this implies that $\Delta V = -10\%$, and this is negative because we're seeing a reduction in the volume, then

$$\Delta U = \Delta H + \alpha, \quad \alpha = p\Delta V > 0,$$

and from this we have that the change in internal energy is 10% higher than the change in enthalpy.

- (2) For this part we have that the Gibbs free energy is function of the change in temperature and the change in pressure, but both of those state variables are kept constant during the phase transition, therefore, this implies that the change in Gibbs free energy is zero. Now, in math

terms, what we have is the following

$$dG = -SdT + Vdp,$$

and for a finite change, not a differential change, we need to integrate the previous expression

$$\Delta G = - \int S(T)dT + \int V(p)dp,$$

but in this case, there's no variation in the temperature nor in the pressure, because of the physical constraints of the system, thus

$$\Delta G = 0.$$

Now, for the following two problems, we have to remember that in a first order phase transition there are some parameters which are discontinuous, and we can associate a latent heat to the transition, in this case we're talking about melting and vaporization of water. Now, for we can associate the change in entropy and the latent heat as follows

$$L = \Delta Q = T_c (S_2 - S_1),$$

where L is the latent heat, T_c is the transition temperature and S_2, S_1 are the entropies at the phases 2 and 1, respectively.

- (3) Thus, going from ice to liquid we have that the change in entropy is given by

$$\begin{aligned} \Delta S &= \frac{L}{T_c} = \frac{6.01 \times 10^3}{273.15} \left[\frac{\text{J/mol}}{\text{K}} \right], \\ \implies \Delta S &= 22.0 \frac{\text{J/mol}}{\text{K}}. \end{aligned}$$

- (4) On the other hand, going from liquid to gas, we have

$$\begin{aligned} \Delta S &= \frac{L}{T_c} = \frac{40.7 \times 10^3}{373.15} \left[\frac{\text{J/mol}}{\text{K}} \right], \\ \Delta S &= 109.1 \frac{\text{J/mol}}{\text{K}}. \end{aligned}$$

Problem 4.

- (1) Suppose a warm stone, at temperature T_s^0 , is placed in a container of cool water, at temperature T_w^0 . As the combined system comes to thermal equilibrium, at some final temperature T_f , heat flows between the stone and the water. Assuming that the combined system does not exchange energy with its surroundings, show that the total change of entropy of the combined system as it approaches equilibrium, $\Delta S_s + \Delta S_w$ is necessarily positive. Would the result be different if the stone were initially cooler than the water?
- (2) Suppose a fixed amount of gas is enclosed in a sealed container with a freely moving piston, so its volume can change and it can exchange heat with its surroundings. It is placed inside a much larger bath, which is at temperature T and pressure p , and allowed to come (quasi-statically) to equilibrium. In the process, the gas transfers an amount of heat Q_{bath} (which may be positive or negative) into the bath. Relate Q_{bath} to the change in enthalpy of the gas, and use that relationship to show that maximizing the total entropy change of the combined system corresponds to minimizing the Gibbs free energy G of the gas. (Because the bath is large, we can assume T and p do not change.)

Solution. Let's begin:

- (1) For this we have that

$$\Delta S_i = \int \frac{dQ_i}{T},$$

where $i = 1, 2$ refers to the stone and the water in the container. Now, we know that once in thermal contact, after some time, they will be in thermodynamical equilibrium at some temperature T_f , and in the following I'm going to use the following notation

$$T_s^0 \rightarrow T_1, \quad T_w^0 \rightarrow T_2,$$

then, we have that

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{dQ_1}{T}, \quad \Delta S_2 = \int_{T_2}^{T_f} \frac{dQ_2}{T},$$

and, even more, for a reversible heat transfer we have $dQ_i = C_i dT$, where in general C_i is a function of T and $C_i > 0$, thus

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{C_1(T) dT}{T}, \quad \Delta S_2 = \int_{T_2}^{T_f} \frac{C_2(T) dT}{T},$$

then, it follows that

$$\Delta S = \Delta S_1 + \Delta S_2 = \int_{T_1}^{T_f} \frac{C_1(T) dT}{T} + \int_{T_2}^{T_f} \frac{C_2(T) dT}{T},$$

but for the first integral we have that $T_f < T_1$ and the integrand is an increasing function, thus

$$\Delta S_1 < 0,$$

on the other hand, for the second integral $T_f > T_2$, and again, for being an increasing function, we have that

$$\Delta S_2 > 0,$$

now we must show that even with one of the ΔS_i negative, the ΔS (i.e, the sum) is still positive. And for this we're going to simplify a little our model, we're going to consider that C_1, C_2 are constants, thus

$$\Delta S_1 = C_1 \ln \left(\frac{T_f}{T_1} \right), \quad \Delta S_2 = C_2 \ln \left(\frac{T_f}{T_2} \right),$$

and from this, we have

$$\Delta S = C_1 \ln \left(\frac{T_f}{T_1} \right) + C_2 \ln \left(\frac{T_f}{T_2} \right),$$

and in order to find T_f we have

$$Q_1 + Q_2 = 0 \iff C_1 (T_f - T_1) + C_2 (T_f - T_2) = 0,$$

and from this, we have

$$\begin{aligned} T_f (C_1 + C_2) - (C_1 T_1 + C_2 T_2) &= 0, \\ \implies T_f &= \frac{(C_1 T_1 + C_2 T_2)}{(C_1 + C_2)} = \frac{C_1}{C_1 + C_2} T_1 + \frac{C_2}{C_1 + C_2} T_2, \\ \therefore T_f &= \frac{C_1}{C_1 + C_2} T_1 + \frac{C_2}{C_1 + C_2} T_2, \end{aligned}$$

and now, if we define

$$\alpha = \frac{C_1}{C_1 + C_2},$$

we have that

$$\begin{aligned} \alpha - 1 &= \frac{C_1}{C_1 + C_2} - 1 = \frac{C_1 - (C_1 + C_2)}{C_1 + C_2} = -\frac{C_2}{C_1 + C_2}, \\ \implies \frac{C_2}{C_1 + C_2} &= 1 - \alpha, \end{aligned}$$

and then T_f is given by

$$T_f = \alpha T_1 + (1 - \alpha) T_2,$$

now, let's use this relation in the total change in entropy

$$\begin{aligned} \Delta S &= C_1 \ln \left(\frac{T_f}{T_1} \right) + C_2 \ln \left(\frac{T_f}{T_2} \right), \\ &= C_1 \ln \left(\frac{\alpha T_1 + (1 - \alpha) T_2}{T_1} \right) + C_2 \ln \left(\frac{\alpha T_1 + (1 - \alpha) T_2}{T_2} \right), \\ &= (C_1 + C_2) \ln (\alpha T_1 + (1 - \alpha) T_2) - C_1 \ln T_1 - C_2 \ln T_2, \end{aligned}$$

but

$$C_1 = \alpha (C_1 + C_2) \text{ \& } C_2 = (1 - \alpha) (C_1 + C_2),$$

then naming $\beta = -C_1 \ln T_1 - C_2 \ln T_2$, we have

$$\beta = -\alpha (C_1 + C_2) \ln T_1 - (1 - \alpha) (C_1 + C_2) \ln T_2,$$

$$\beta = - (C_1 + C_2) (\alpha \ln T_1 + (1 - \alpha) \ln T_2),$$

$$\beta = - (C_1 + C_2) \left(\ln T_1^\alpha + \ln T_2^{1-\alpha} \right),$$

then, finally

$$\beta = - (C_1 + C_2) \left(\ln T_1^\alpha T_2^{1-\alpha} \right),$$

and from this, we have that the total change in entropy is given by

$$\Delta S = (C_1 + C_2) \ln (\alpha T_1 + (1 - \alpha) T_2) - (C_1 + C_2) \left(\ln T_1^\alpha T_2^{1-\alpha} \right)$$

$$\Delta S = (C_1 + C_2) \ln \left(\frac{\alpha T_1 + (1 - \alpha) T_2}{T_1^\alpha T_2^{1-\alpha}} \right),$$

now, in order to prove that $\Delta S > 0$, we have to prove that the function is increasing, and the logarithm is an increasing function, as long as the value inside the function is increasing, and indeed, this is the case because α is bounded to live between $[0, 1]$, and this comes purely from its definition, thus

$$\alpha T_1 + (1 - \alpha) T_2 > 0,$$

and therefore

$$\Delta S > 0,$$

and finally, if we take into consideration the other case in which the stone were colder instead of hotter, the same reasoning applies, and therefore in that case the total change in entropy also increases.

- (2) Now for this part, when we transfer energy dU and volume dV from the surroundings, to the system we have that the internal energy of the surrounding changes by an amount dU_0 which is given by

$$dU_0 = -dU = T_0 dS_0 - p_0 (dV),$$

where the minus sign reflect the fact that the energy and volume is decreasing. Then, from the previous expression we have that

$$dS_0 = -\frac{dU + p_0 dV}{T_0},$$

now, if the entropy of the system changes by dS , then the total change in the entropy dS_0 is given by

$$dS_{\text{tot}} = dS_0 + dS,$$

and using the second law, we have

$$T_0 dS_{\text{tot}} = -[dU + p_0 dV - T_0 dS] \geq 0,$$

and therefore, we have that

$$dU + p_0 dV - T_0 dS \leq 0.$$

And now, if we assume that the system can be approximated as a system with constant pressure and temperature, we can use the definition of the Gibbs free energy, as follows

$$dG = dU + p_0 dV + V dp - T_0 dS - S dT = dU - T_0 dS + p_0 dV,$$

since $dp = dT = 0$, and from the condition for the previous equation, we have

$$dG \leq 0,$$

and from this we have that maximizing the total entropy change of the combined system corresponds to minimizing the Gibbs free energy G of the gas.

Problem 5. This problem explores the thermodynamics of a stretched rubber band. Because a stretched rubber band exerts a force f , changing the length L of the band does work on the band, which must be reflected in our expression for changes in the band's internal energy

$$dU = TdS - pdV + fdL,$$

- (1) The dV and dL terms both represent work. Explain why they have opposite signs.
- (2) Write the comparable expression for dG .
- (3) Use appropriate second derivatives of G to derive a Maxwell relation between

$$\left(\frac{\partial S}{\partial L}\right)_{T,p} \text{ and } \left(\frac{\partial f}{\partial T}\right)_{L,p}.$$

- (4) This relationship means that you can determine the variation of entropy with length by measuring something completely different, and very accessible experimentally: the variation of force with temperature. The graph at right shows f (actually it shows something called the "storage modulus," which has pressure units, but for a given rubber band, f is proportional to this quantity.). Based on these data and your result in (c), does the entropy of the rubber increase or decrease when it is stretched?

Solution. Let's begin:

- (1) As the problem says, both dV and dL represent a form of work, but in one of those we found that the system is doing the work over the surroundings, while in the other, we have that the surroundings are doing work over the system.
- (2) Let's move on with the calculation of dG , and we know that

$$G = H - TS; \quad H = U + pV,$$

thus we have

$$G = U + pV - TS,$$

and its differential becomes

$$dG = dU + Vdp + pdV - SdT - TdS,$$

$$\implies dG = (TdS - pdV + fdL) + Vdp + pdV - SdT - TdS,$$

and as we can observe, some terms cancel, with each other, leaving us with

$$dG = Vdp - SdT + fdL.$$

- (3) Now, we're going to make use of the previous relation, but before jumping with the math, let's remember the property under which base the Maxwell relations, this is

$$\partial_{xy}\square = \partial_{yx}\square,$$

or in words; we are assuming that the mixed derivatives commute with each other for any of this functions. Now, with this in mind, from the Gibbs free energy, we have that

$$\left(\frac{\partial G}{\partial L}\right)_{p,V} = f, \quad -\left(\frac{\partial G}{\partial T}\right)_{p,L} = S,$$

thus, from the two previous equations, making use of the commutativity of the mixed partial derivatives, we have

$$\left(\frac{\partial f}{\partial T}\right)_x = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial L}\right)_x = \frac{\partial}{\partial L} \left(\frac{\partial G}{\partial T}\right)_x = -\left(\frac{\partial S}{\partial L}\right)_x,$$

where the subscript means keeping the appropriate variables constant. And with this we end up with the following Maxwell relation

$$\left(\frac{\partial f}{\partial T}\right)_{L,p} = -\left(\frac{\partial S}{\partial L}\right)_{T,p}.$$

- (4) Now, from the figure we can see that we have a linear relation between the f and T variables, thus we can write

$$f(T) = mT + b,$$

and even more, from the figure(experimental data) we can see that $m > 0$ as well as $b > 0$, thus, in virtue of the derived Maxwell equation, previously derived, we have that

$$\begin{aligned} \frac{\partial S}{\partial L} &= -\frac{\partial f}{\partial T} = -\frac{\partial}{\partial T} (mT + b) = -m, \\ \implies \frac{dS}{dL} &= \alpha, \end{aligned}$$

where $\alpha = -m < 0$, thus, from the previous equation, we have that

$$dS = \alpha dL \implies \Delta S = \alpha \Delta L,$$

now, is we assume that we go from “lower” stretch to “higher” stretch, we can see that $\Delta L > 0$, and this implies that

$$\Delta S < 0,$$

thus, the entropy decrease when we stretch the rubber.

Resources. List any resources, aside from course materials, that you consulted in doing this assignment, and describe how you used them and for which problem(s). This could include web sites, videos, computational tools (e.g. Desmos), or AI tools (e.g. ChatGPT). If you didn't use any such resources, write "None."

For the chemistry problem I used the following resource:

[https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_\(Brown_et_al.\)/19%3A_Chemical_Thermodynamics/19.05%3A_Gibbs_Free_Energy?readerView#mjb-eqn-Eq2](https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/19%3A_Chemical_Thermodynamics/19.05%3A_Gibbs_Free_Energy?readerView#mjb-eqn-Eq2)

I'm not very good at chemistry, and although I think it's amazing and very difficult, and because I'm not very interested in that discipline, it was quite difficult for me to map the knowledge that I have from thermal physics, and I needed some help with that.

Other than that I used the following books for help with some definitions: Blundell, Stephen J., and Katherine M. Blundell. Concepts in thermal physics. Oup Oxford, 2010