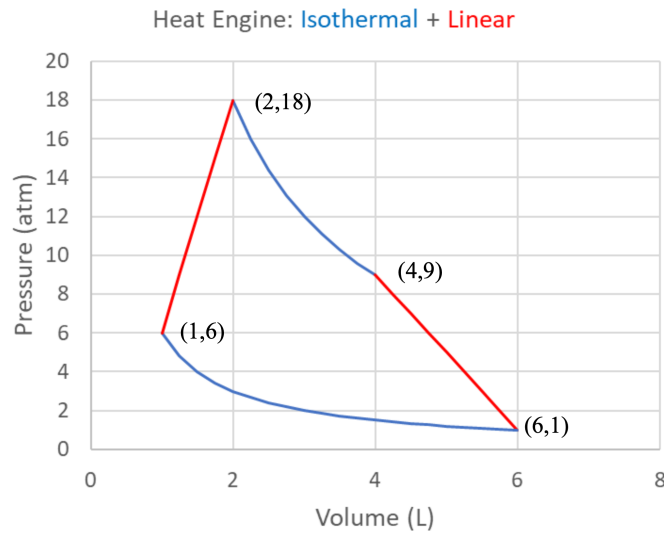


## STATISTICAL MECHANICS ASSIGNMENT 1

J. EMMANUEL FLORES

**Problem 1.** The figure shows the P-V diagram for an unlikely, but conceivable, cyclic process involving two isothermal steps (in blue) and two steps in which pressure varies linearly with volume (in red). Assume that the working medium is a fixed quantity of a monatomic ideal gas, and, of course, that all steps are quasi-static and that they proceed clockwise.



a) For each of the four steps, calculate the work  $W_{\text{on}}$  done on the gas and the heat  $Q$  that flows into the gas. In each case, clearly state whether the gas is doing work or having work done on it, and whether the gas is receiving or releasing heat, and explain why that makes sense physically as well as mathematically. Give numerical values in  $L \text{ atm}$  as well as symbolic expressions.

b) Which of your values would be different if the gas were diatomic instead of monatomic? Would they be larger or smaller?

### SOLUTION

a) Before any calculations, I want to make one assumption, in what follows, I'll be using the first law in the following form

$$\Delta U = Q - W,$$

which corresponds to the Clausius convention or interpretation.

Now, for an ideal gas it is true that  $pV = nRT$ . For this cyclic process, we know that  $n$  is fixed, and furthermore  $R$  is constant. So let's put our attention on the isothermal processes and of these let's focus on the process with the highest temperature. Now, because those processes are done at a fixed temperature, in virtue of the ideal gas equation, we know that  $nRT$  will be a constant, thus we can obtain the functional relationship of  $p$  and  $V$  as follows

$$pV = nRT = \alpha \implies p = \frac{\alpha}{V},$$

where  $\alpha$  is just a constant, as stated previously. Now, with this information, we can calculate the work, which is given by

$$W = \int_{V_i}^{V_f} p dV \implies W = \int_{V_i}^{V_f} \frac{\alpha}{V} dV = \alpha \ln \left( \frac{V_f}{V_i} \right),$$

$$\implies W = \alpha \ln \left( \frac{V_f}{V_i} \right)$$

in this case, the numerical values for the volumes are  $V_f = 2$  and  $V_i = 4$ , then, the work is

$$W = \alpha \ln \left( \frac{2}{4} \right) = \alpha \ln \left( \frac{1}{2} \right),$$

$$\implies W = \alpha \ln \left( \frac{2}{4} \right) = \alpha \ln \left( \frac{1}{2} \right) = -0.693\alpha,$$

$$\therefore W_1 = -0.693\alpha,$$

and moreover, for ideal gases, we know that the internal energy is a function that depends just on the temperature, that is

$$U = U(T),$$

and this relationship is linear, this is  $U = nRT$ , where  $nR$  in this case is just a constant, thus, for an ideal gas and an isothermal process the change in internal energy is zero, thus in virtue of the first law, we have

$$Q_1 = W_1.$$

Now, for the other isothermal process, the procedure and the calculation is the same, the only difference is in the volume initial and final, which in this case are given by  $V_f = 1$  and  $V_i = 6$ , thus

$$W = \alpha \ln \left( \frac{6}{1} \right) = \alpha \ln (6),$$

$$\implies W_2 = 1.792\alpha,$$

and again, in virtue of the first law, we have that

$$Q_2 = W_2.$$

Now, let's move on with the linear process: again, we need a functional relation between  $p$  and  $V$ , but because the process is linear, we can calculate the slope of the line and the intersection with the  $p$ -axis, that is

$$m = \frac{\Delta p}{\Delta v} = \frac{1-9}{6-4} = -\frac{8}{2} = -4 \implies p = -4V + b,$$

but because we know that the point  $(4,9)$  is an element of the line, we can determine the  $b$  constant by direct evaluation, this is

$$9 = -4(4) + b \implies b = 25,$$

and thus, the functional relation between  $p$  and  $V$  is given by

$$p = -4V + 25,$$

and with this, we can compute the work as follows

$$W = \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} (-4V + 25) dV = -4 \frac{V^2}{2} \Big|_{V_i}^{V_f} + 25V \Big|_{V_i}^{V_f},$$

$$\implies W = -2(V_f^2 - V_i^2) + 25(V_f - V_i),$$

in this case is important to notice that the slope  $m$  has dimensions, otherwise our equation will be wrong, and the volumes for this part of the cycle are  $V_f = 6$  and  $V_i = 4$ , then, the work is

$$\begin{aligned} W &= W = -2(6^2 - 4^2) + 25(6 - 4), \\ \implies W &= -2(20) + 25(2) = 10, \\ \therefore W_3 &= 10. \end{aligned}$$

Now, for the heat, the approach is to calculate the change in internal energy and from that, use the first law to calculate the heat. Indeed, using the equation for the internal energy of an ideal gas, we have that

$$U = \alpha T \implies \Delta U = \alpha \Delta T,$$

and the temperature can be calculated for each one of the isotherms using the ideal gas equation, thus, in general we have

$$pV = \alpha T \implies T = \frac{pV}{\alpha},$$

and for the first isotherm, we have

$$T = \frac{36}{\alpha},$$

whereas for the second isotherm

$$T = \frac{6}{\alpha},$$

thus, the change in internal energy is given by

$$\begin{aligned} \Delta U &= \alpha \Delta T = \alpha \left( \frac{6}{\alpha} - \frac{36}{\alpha} \right) = -30 \\ \implies \Delta U &= -30, \end{aligned}$$

and with this at hand, in virtue of the first law, the heat is given by

$$\begin{aligned} Q &= \Delta U + W, \\ \implies Q &= -30 + 10 = -20, \\ \therefore Q &= -20. \end{aligned}$$

And again, for the other linear process, we proceed in the same way:

$$m = \frac{\Delta p}{\Delta v} = \frac{18 - 6}{2 - 1} = \frac{12}{1} = 12 \implies p = 12V + b,$$

but because we know that the point  $(1, 6)$  is an element of the line, we can determine the  $b$  constant by direct evaluation, this is

$$6 = 12(1) + b \implies b = -6,$$

and thus, the functional relation between  $p$  and  $V$  is given by

$$p = 12V - 6,$$

and with this in mind we can also calculate the work. Indeed,

$$\begin{aligned} W &= \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} (12V - 6) dV = 12 \frac{V^2}{2} \Big|_{V_i}^{V_f} - 6V \Big|_{V_i}^{V_f}, \\ \implies W &= 6(V_f^2 - V_i^2) - 6(V_f - V_i), \end{aligned}$$

now, in this case the volumes are given by  $V_f = 2$  and  $V_i = 1$ , then, the work is

$$W = 6(4 - 1) - 6(2 - 1) = 12,$$

$$\implies W = 12,$$

and again, using the same procedure as for the other linear process, we can calculate the change in temperature, and from that the change in internal energy, and with that, the heat:

$$\Delta U = \alpha \Delta T = \alpha \left( \frac{36}{\alpha} - \frac{6}{\alpha} \right) = 30,$$

thus

$$\begin{aligned} Q &= \Delta U + W, \\ \implies Q &= 30 + 12 = 42, \\ \therefore Q &= 42. \end{aligned}$$

**Remark 1.** There are some issues with the development of my solution. Here I will like to elaborate a little more on that:

- First, I'm not sure on the integration limits that are provided in the solution of the problem, in particular for the  $W_{on,1}$  on the integral  $\int dV/V$ , from given figure the integration limits should be  $V_f = 4$  and the  $V_i = 2$ , not sure if I'm misreading the plot, and the same applies for  $W_{on,2}$ .
- Because I used a different convention, it makes sense that the work changes sign, but overall, I think that the physics is well interpreted.
- For the linear processes, I used an analytical method, and my numbers match with the solution provided, which was done following another approach.
- I didn't put the results in the correct units, however, the reasoning was OK, overall, but the units are a great deal of this theory, I understand that.
- **Score: 8/10**

## PROBLEM 2.

As mentioned in class, not everything is well approximated by an ideal gas. The next three problems ask about behaviors of a familiar material under different conditions. You are not expected to produce quantitatively accurate results, and the reasoning is more important than the answer. Get as far as you can using your store of knowledge about the world and water (more than you may realize!) Use Google only when your own knowledge base is exhausted and you need something more.

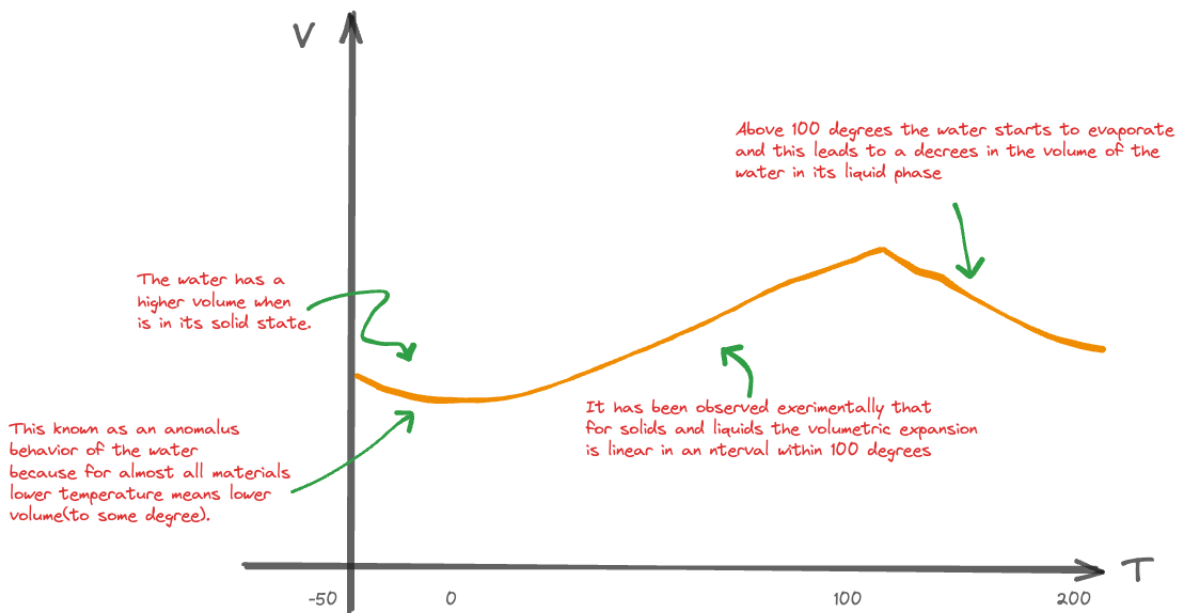
**(Problem 2)** Suppose you have  $1 \text{ cm}^3$  of pure water at room temperature and atmospheric pressure. Imagine you keep the pressure constant and vary the temperature slowly so that the water is always in internal equilibrium.

a) Sketch on the graph below qualitatively how you think the volume will vary as the temperature is changed over the range shown. Explain the important features of your sketch.

b) What kind of apparatus would be needed to carry out such a measurement?

## SOLUTION

a) Here's a sketch of the graph



In the following discussion I'm assuming that the pressure is fixed. Now, an increase in the temperature of some system usually also increases the volume liquids and solids. In this case we're interested in a volumetric expansion, but we can first think of a linear expansion, and in this case it has been seen experimentally that, if the change in the temperature is not very large (around  $100^\circ\text{C}$ ), then the increase in volume is proportional to the temperature change, and this proportionality is, to a very good approximation, linear, and follows the equation

$$\Delta V = \beta V_0 \Delta T,$$

where  $\beta$  is the volume expansion coefficient. On the other hand as (bad) first approximation, maybe we could think of this problem as an ideal gas, in which, by the ideal gas law, we have

$$pV = nRT,$$

and if we fix the pressure, then

$$V = \frac{nR}{p} T,$$

$$\implies V = \alpha_1 T,$$

which gives us also a linear dependence, however, as I argued before this is valid if the change in the temperature is not very large, but still, it could be us a picture in mind of what's happening in the system.

b) Because the pressure is fixed, we can put the water in a scale with an electric resistance water heater, and also a thermometer.

*Remark 2. I think my solution is not right but it was on the right path, and here I like to elaborate a little more:*

- First, I totally agree with your graph, and I understand what you're trying to say.
- However, the main issue here is that I considered the volume of the water and the volume of the gas as two different things. In my mind I was thinking that above at 100 degrees Celsius water evaporates, which means that the volume of water is less. However in the problem you stated to draw the diagram for the whole system, and I misread that.
- **Score: 8/10**

## PROBLEM 3.

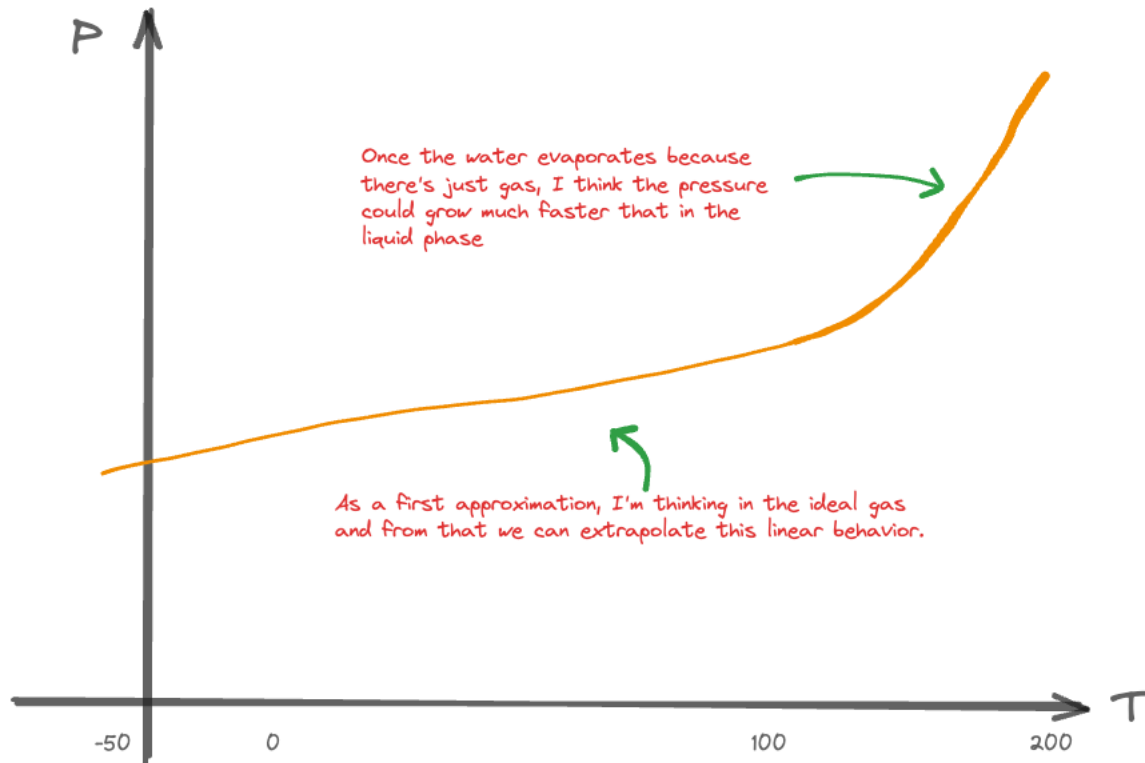
**(Problem 3)** Start with the same  $1 \text{ cm}^3$  of water at room temperature and atmospheric pressure. Now assume that the volume is kept constant as the temperature is slowly changed.

a) Sketch on the graph below how you think the pressure of the water will vary as the temperature is changed over the range shown. Explain the important features of your sketch

b) What kind of apparatus would be needed to carry out such a measurement?

## SOLUTION

a) Here's a sketch of the graph



Again, if we start with a (bad) first approximation, and we think of the system as an ideal gas, maybe we can understand to some degree the system, so, by the ideal gas law, we have

$$pV = nRT,$$

and if we fix the volume, then

$$p = \frac{nR}{V}T,$$

$$\implies p = \alpha_2 T,$$

which gives us also a linear dependence, however, I think that after the water evaporates, because we just have gas, I think the pressure is more easy to increment, that's why I don't expect a linear behavior beyond  $100^\circ \text{C}$ .

b) For this experiment we could try to couple a thermometer with a barometer inside some container, something like a pressure cooker such that we can fix the volume and we have some control over the temperature and the pressure.

*Remark 3.* Here are my thought on this problem:

- I agree 100 %, this was a really tricky problem to think about. I knew that it was really hard to comprise but the discussion that you made in terms of the partial derivatives was really helpful.
- I found really interesting all the discussion you made in order to justify the drop in the pressure, while true (it seems to me) I find really hard to think or visualize the process at that stage.
- However, I think we agree on the behavior after that drop in the pressure.
- Score: 8/10.



## PROBLEM 4.

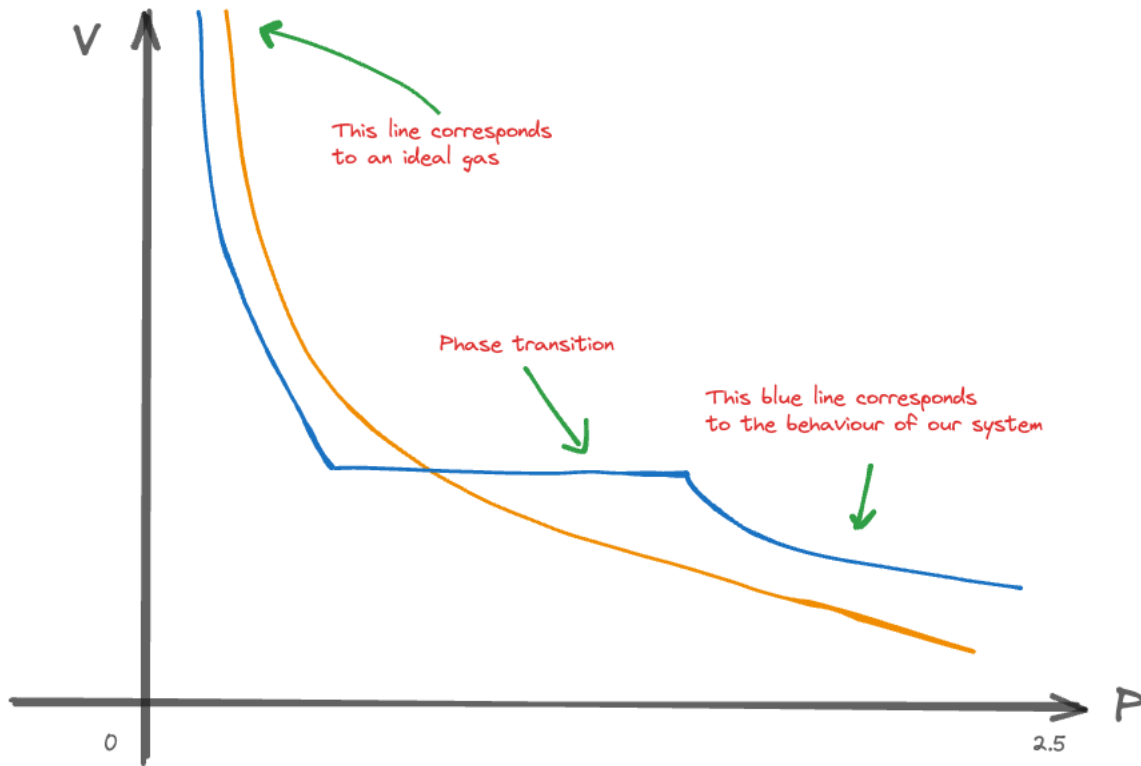
**(Problem 4)** You can probably guess the next question. Now we will keep the temperature of the water constant.

a) Sketch on the graph below how the volume of the water will vary as the pressure is changed. Explain the important features of your sketch.

b) What kind of apparatus would be needed to carry out such a measurement?

## SOLUTION

a) Here's a sketch of the graph



Here I tried something different, I draw two graphics, one for an ideal gas and another for our actual system, and for the later, in virtue of the ideal gas law, we have

$$pV = nRT,$$

and if we fix the temperature, then

$$V = \frac{nRT}{p},$$

$$\Rightarrow V = \frac{\alpha_3}{p},$$

which gives us also a dependence of  $1/p$ , however, that doesn't take into account the fact that we can see a change of phase, thus I think that a more realistic picture would be the orange line, in which the region parallel to the pressure corresponds to a phase change in the water.

b) Maybe we can try to connect a piston, a barometer and a heat reservoir such that we can have control over the pressure via de piston, and the heat reservoir to fix the temperature.

**Remark 4. Here are my thought on this process:**

- In my discussion (line of thought) I used as a base an ideal gas, I think it was biases since the beginning, and that lead me to a wrong understanding of the system, at least in the middle of the diagram.

- However, we agreed on the asymptotical behavior which makes me think that it was a “good thing” to use the ideal gas as an example, however, I need to take more care with my analogies and have a better understanding of the physics involved.
- **Score: 8/10**

PROBLEM 5.

**(Problem 5)** Classically, a diatomic molecule has three degrees of freedom associated with center-of-mass motion, two degrees of freedom associated with rotational motion around axes perpendicular to the interatomic bond, one degree of freedom associated with rotational motion around the interatomic bond (see the figure), and two degrees of freedom (KE and PE) associated with the interatomic vibration. That's 8 degrees of freedom. So the equipartition theorem says that the average internal energy per molecule should be  $4k_B T$ , but in fact, for normal conditions, it's  $(5/2)k_B T$ . This problem explores that discrepancy.

a) At room temperature, what is the value of  $k_B T$ , in eV? (This is a good number to memorize.)

b) For a nitrogen molecule,  $N_2$ , estimate the moment of inertia  $I$  for rotation about axes perpendicular and parallel to the molecular axis, that is, the line joining the nuclei. Remember that virtually all of the mass is contained in the nuclei, which have radii  $\sim 10 - 15$  m, but there is also an electron cloud, which has much less mass, but a much larger radius. You don't need to do any complicated calculations with the parallel axis theorem; we're just trying to get the right order of magnitude.

c) Quantum mechanically, we know that the angular momentum is quantized. Using this fact, estimate, in eV, the spacing between rotational energy levels, for rotations perpendicular and parallel to the molecular axis. (The levels are not evenly spaced, but we're just looking for the order of magnitude, for relatively small  $I$ ).

d) The vibrational frequency of  $N_2$  is  $2560\text{cm}^{-1}$ . (In infrared spectroscopy, frequencies are usually given in units of  $\text{cm}^{-1}$ . What this really means is that  $1/\lambda = 2560\text{cm}^{-1}$  where  $\lambda$  is the wavelength of light at that frequency.) To a very good approximation, we can model the vibration as a harmonic oscillator. What is the spacing of energy levels, in eV?

e) Classical thermodynamics generally works as long as  $k_B T$  is much greater than the energy spacing between quantum mechanical energy levels. Using this insight, explain which degrees of freedom can be described classically, and, thus, why the average energy is  $(5/2)k_B T$  at temperatures not too far from room temperature.

SOLUTION

a) Room temperature is around  $20^\circ\text{C}$  which is to a good approximation  $293\text{ K}$ ,  $k_B = 1.381 \times 10^{-23}\text{J/K}$ , and we have the following conversion  $1\text{eV} = 1.602 \times 10^{-19}\text{J}$ , thus

$$k_B T = 293 \times 1.381 \times 10^{-23} \times \frac{1\text{eV}}{1.602 \times 10^{-19}} [\text{K}] \left[ \frac{\text{J}}{\text{K}} \right] \left[ \frac{\text{eV}}{\text{J}} \right],$$

$$\therefore k_B T = 0.025\text{eV}.$$

*Remark 5. Here are my thoughts on this problem:*

- As stated in the final reflexion due to my lack of organization I couldn't finish this problem, however, the first part of my problem was right.
- Score: **2/10**

## FINAL REFLEXION:

Looking back on the problem set as a whole:

a) What is something specific you understand better than you did before?

I think it is important to take into account the limitations of the models I am working with, that is, knowing their conditions of applicability. I believe the problems served as a reminder of the topics I covered and learned in undergrad.

b) What is something specific that surprised, confused, or intrigued you, or that you struggled with?

Conventions have always been difficult for me, or the point of reference, whether the heat is positive or negative, for me it is clear that the work is the integral under the curve, but even so, every time I solve an exercise I tend to review the book and the notation it uses, just to know exactly what your reference point is like.

c) What is something that this problem set made you want to know more about?

Due to my lack of organization I was not able to finish the last exercise, but I would like to explore more. The area in which I have the most experience is doing molecular dynamics, and I am curious how I could model that specific system. Honestly, I would like to explore this a little more.

*Remark 6. Total Score: 40/50*

## RESOURCES:

List any resources, aside from course materials and fellow students, 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 books I used another material, in particular University Physics by Sears and Zemansky, and I think my favorite book in thermodynamics: Termodinamica, by Eduardo Piña Garza.