# STATISTICAL MECHANICS ASSIGNMENT 1

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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.

Heat Engine: Isothermal + Linear
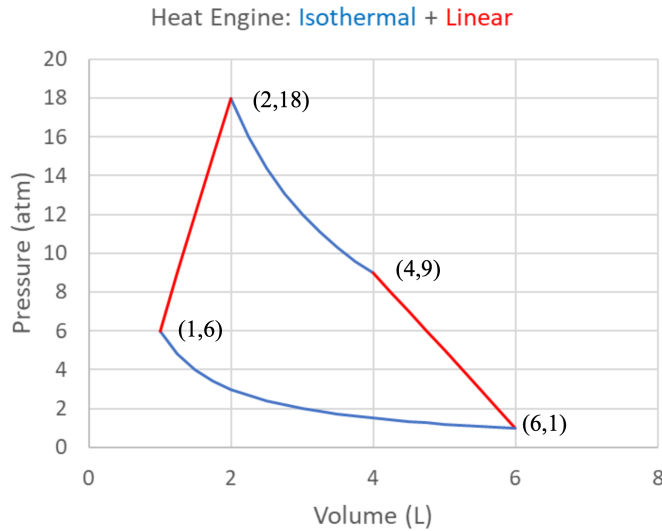
a) For each of the four steps, calculate the work W_{on} done on the gas and the heat Q that flows into the gas. In each case, clearly state whether the gas is doing work or having work done on it, and whether the gas is receiving or releasing heat, and explain why that makes sense physically as well as mathematically. Give numerical values in L 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 α is just a constant, as stated previously. Now, with this information, we can calculate the work, which is given by

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

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

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 funtion 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 isotermal process, the procedure and the calulation 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

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

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

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

$$W = W = -2\left(6^2 - 4^2 \right) + 25(6 - 4),$$

$$\implies W = -2(20) + 25(2) = 10,$$

$$\therefore W_3 = 10.$$

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

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

$$\implies \Delta U = -30,$$

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

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

$$\implies Q = -30 + 10 = -20,$$

$$\therefore Q = -20.$$

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,

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

$$\implies W = 6 \left(V_f^2 - V_i^2 \right) - 6(V_f - V_i),$$

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 prodecure as for the other linear process, we can calculate the change in temperature, anf from that the change in inernal energy, and with that, the heat:

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

thus

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

$$\implies Q = 30 + 12 = 42,$$

$$\therefore Q = 42.$$

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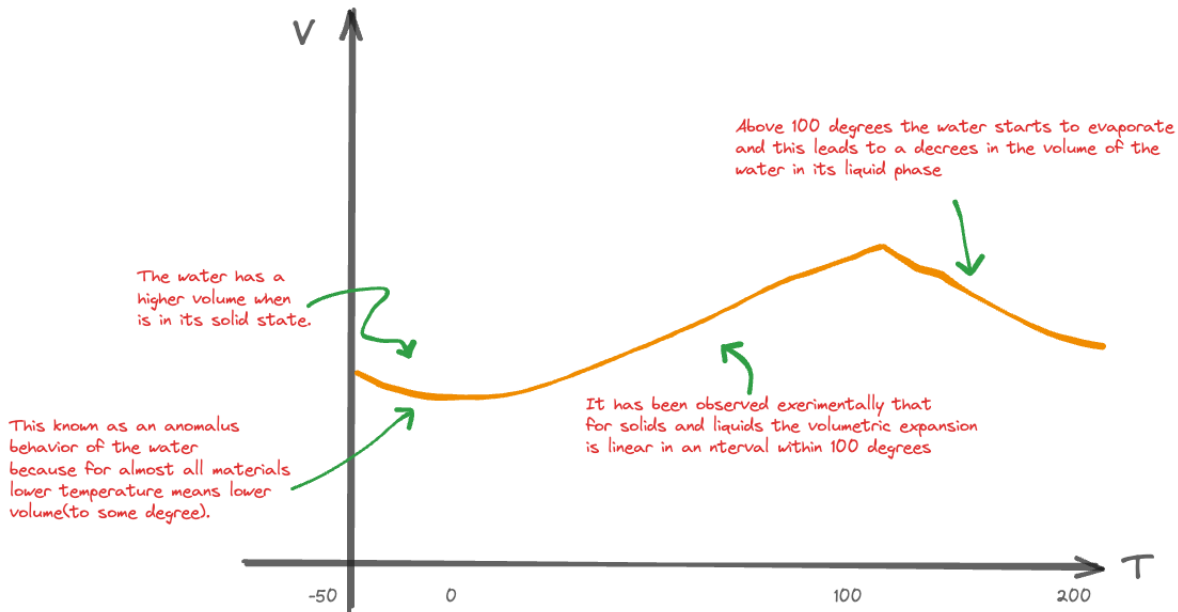
In the following discussion I'm asumming that the pressure is fixed. Now, an increase in the temperature of some system usually also increases the volume liquids and solids. In this case we're interested in a volumetric expansio, but we can first think of a linear expansion, and in this case it has been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

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

where β is the volume expansion coefficient. On the other hand as (bad) first appoximation, 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 temperatureis 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 wate heater, and also a thermometer.

PROBLEM 3.

(Problem 3) Start with the same 1 cm³ 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
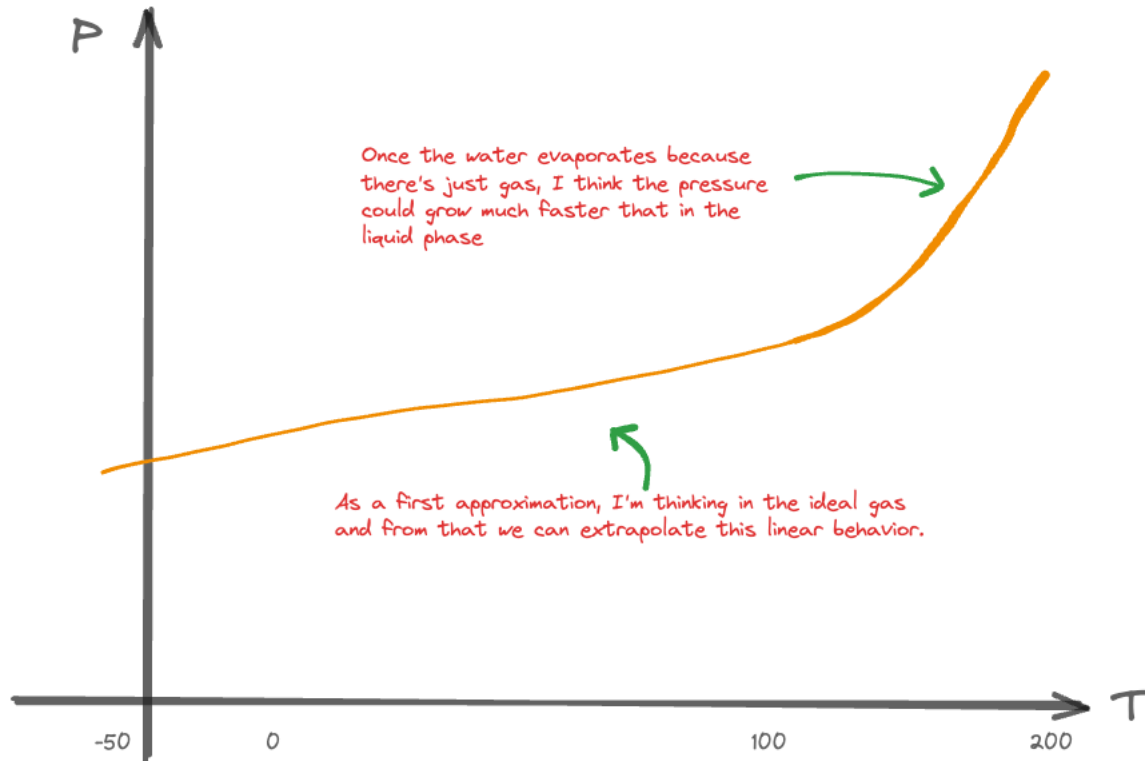
Again, if we start with a (bad) first appoximation, and we think of the system as an ideal gas, maybe we can understant to some degree the system, so, by the ideal gas law, we have

$$pV = nRT,$$

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 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.
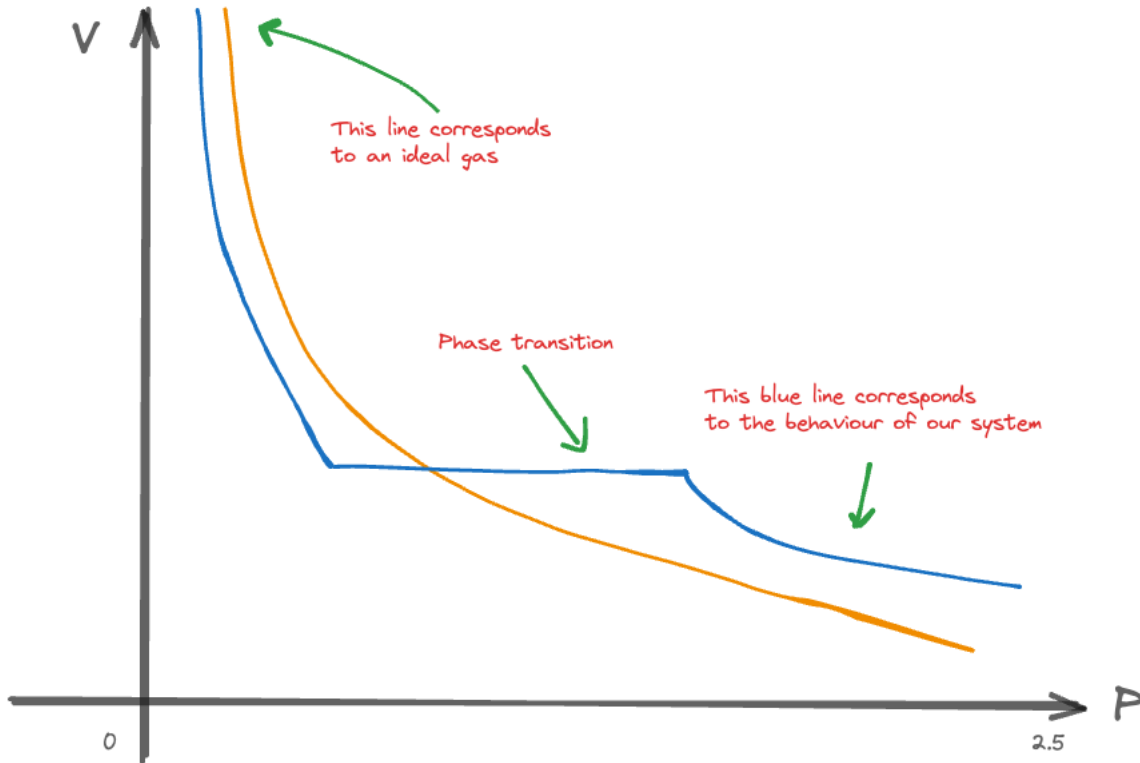
PROBLEM 4.

(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 somethign 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

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

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

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.

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 $4k_BT$, but in fact, for normal conditions, it's $(5/2)k_BT$. This problem explores that discrepancy.

a) At room temperature, what is the value of k_BT, 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 l).

d) The vibrational frequency of N_2 is 2560cm^{-1}. (In infrared spectroscopy, frequencies are usually given in units of cm^{-1}. What this really means is that $1 1 2560\text{cm} \lambda - =$ where λ 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_BT 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 $(5/2)k_BT$ at temperatures not too far from room temperature.

SOLUTION

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

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

$$\therefore k_BT = 0.025ev.$$

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.

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 Universitary Physics by Sears and Zemansky, and I think my favorite book in thermodynamics: Termodinamica, by Eduardo Piña Garza.