

STATISTICAL MECHANICS | ASSIGNMENT 2

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Problem 1. The figure shows the P-V diagram for the same cyclical process that you analyzed on HW1. Now we're going to think of it as an unlikely, but conceivable, cyclic heat engine. Assume that the working medium is a monatomic ideal gas, and, of course, that all steps are quasi-static.

a) What is the efficiency of this engine? Explain your analysis, and, in the end, give a numerical value. You don't have to repeat the calculations of work and heat that you did on HW #1; just use the results.

b) What would be the efficiency of a Carnot engine operating between the same two temperatures? Again, give a numerical value.

c) Could the cycle shown in the figure represent a reversible process? How do you know?

d) If the working medium were a diatomic ideal gas, would the efficiency of the engine be lower, higher, or the same? (You shouldn't need to redo the whole calculation; just look at where that change would make a difference.)

Solution. a) The definition efficiency is given by the following equation

$$\eta = \frac{W}{Q},$$

thus, the efficiency is the ratio of the work out to the heat in. Now, in this particular process the heat and work for each part of the cycle are given by

- Step 1:

$$W_{on,1} = -36 \ln 3, \quad Q_1 = 36 \ln 3,$$

- Step 2:

$$W_{on,2} = -10, \quad \Delta U_2 = -45, \quad Q_2 = -35,$$

- Step 3:

$$W_{on,3} = 6 \ln 6, \quad Q_3 = -6 \ln 6,$$

- Step 4:

$$W_{on,4} = -12, \quad \Delta U_4 = 45, \quad Q_4 = -57,$$

Therefore, for the cycle, the efficiency is given by

$$\eta = 1 - \frac{|Q_1|}{|Q_2 + Q_3 + Q_4|},$$
$$\Rightarrow \eta = 0.615.$$

b) For a Carnot Cycle, the efficiency is given by

$$\eta = 1 - \frac{T_c}{T_h},$$

where T_h and T_c stands for hot and cold, respectively. Thus, in this case, from the diagram, we have $T_h = 36$, and $T_c = 6$, thus

$$\begin{aligned}\eta_{Carnot} &= 1 - \frac{6}{36}, \\ \implies \eta_{Carnot} &= \frac{5}{6}.\end{aligned}$$

c) For this part, we have to remember the definition of a reversible process, which is described as the process where both the system and its surroundings can be returned to their exact starting states without leaving any other changes in the universe. This is an idealization and in nature no process is reversible, however, I think with enough care, we could get close to that ideal process ~ reversible.

d) From the previous assignment we know that in the calculation of the work and heat for each stage of the process, and even more, we know that the heat and the work is changed (higher) for the stages 2 and 4, which means that in our equation for the efficiency, the denominator will be higher, thus, the efficiency lower.

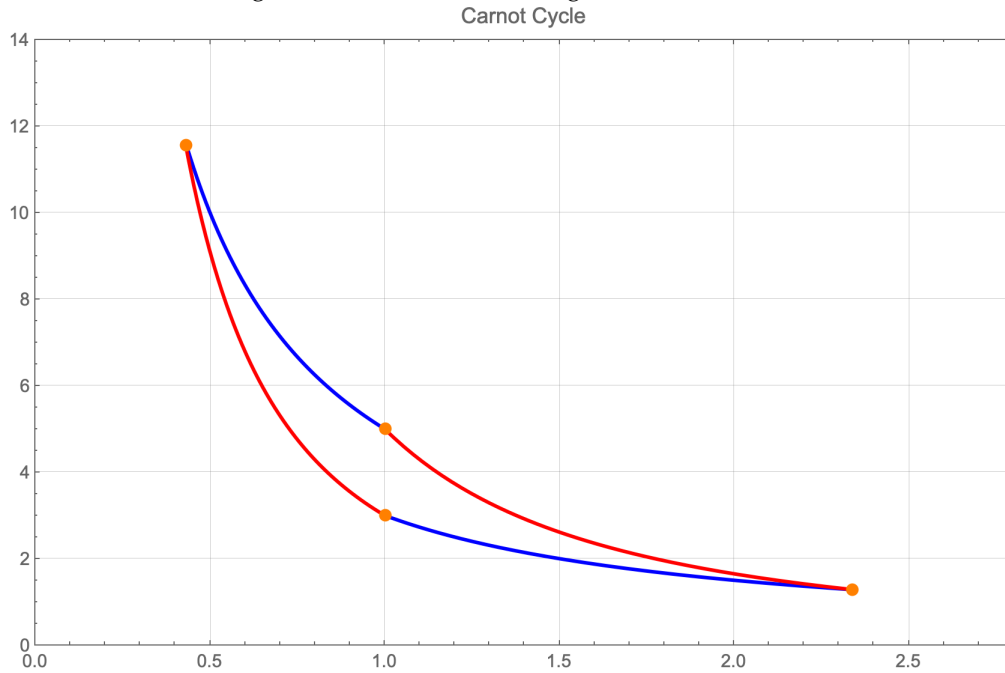
Problem 2. A Carnot engine is defined as one that is reversible. The Carnot cycle is a particular type of ideal-gas engine that uses two isothermal steps joined by two adiabatic steps. But how do we know that the Carnot cycle is in fact reversible (and therefore represents a Carnot engine)?

- (1) Clausius's theorem tells us that for a reversible cycle

$$\oint \frac{dQ}{T} = 0$$

- (2) Our analysis of the Carnot cycle is based on the ideal gas definition of temperature. We also defined a thermodynamic temperature scale based on the requirement that the efficiency of any reversible engine is $\eta_C = 1 - \frac{T_C}{T_H}$. Show, by direct analysis of the heat and work in each stage of the cycle, that the efficiency of the Carnot cycle (calculated using the ideal gas definition of temperature) agrees with this relationship. That result confirms the equivalency of the two temperature scales

Solution. For **a)** we have the following: by definition, the Carnot cycle is given by two isotherms stages and two adiabatic stages, as shown in the next figure:



On the other hand, by definition, the adiabatic stages are processes in which there's no heat exchange with the surroundings, thus, the calculation of

$$\oint \frac{\delta Q}{T},$$

reduces to

$$\oint \frac{\delta Q}{T} = \frac{Q_h}{T_h} + \frac{Q_c}{T_c},$$

now, before jumping into that calculation, let's remember some expressions for each stage in this cyclic process:

- For the isothermal expansion, we have the following equation for the

$$Q_h = RT_h \ln \frac{V_B}{V_A},$$

- For the adiabatic expansion, we have

$$\left(\frac{T_h}{T_c} \right) = \left(\frac{V_C}{V_B} \right)^{\gamma-1},$$

- For the isothermal compression, we have

$$Q_c = -RT_c \ln \frac{V_D}{V_C},$$

- And finally, for the adiabatic compression

$$\left(\frac{T_c}{T_h} \right) = \left(\frac{V_A}{V_D} \right)^{\gamma-1},$$

Now, from the information in the two adiabatic steps, we have that

$$\left(\frac{V_C}{V_B} \right)^{\gamma-1} = \left(\frac{T_h}{T_c} \right) = \left(\frac{V_A}{V_D} \right)^{1-\gamma},$$

then, it follows that

$$\begin{aligned} \left(\frac{V_C}{V_B} \right)^{\gamma-1} &= \left(\frac{V_D}{V_A} \right)^{\gamma-1}, \\ \implies \frac{V_C}{V_B} &= \frac{V_D}{V_A}, \\ \implies \frac{V_C}{V_D} &= \frac{V_B}{V_A}. \end{aligned}$$

Now, if we plug this, into the heat for the isothermal compression, we have that

$$Q_c = -RT_c \ln \frac{V_D}{V_C} = RT_c \ln \frac{V_C}{V_D},$$

then, we have

$$\begin{aligned} Q_c &= RT_c \ln \frac{V_B}{V_A}, \\ \implies \frac{Q_c}{T_c} &= R \ln \frac{V_B}{V_A}. \end{aligned}$$

Now, for the isothermal expansion we have a similar expression, this is

$$\frac{Q_h}{T_h} = R \ln \frac{V_B}{V_A},$$

then, it follows that

$$\begin{aligned} \frac{Q_c}{T_c} &= \frac{Q_h}{T_h} \\ \implies \frac{Q_c}{T_c} - \frac{Q_h}{T_h} &= 0, \\ \therefore \oint \frac{\delta Q}{T} &= 0, \end{aligned}$$

just as we wanted to prove.

b) For this part, we're going to make use of one of the relationships previously proved, that is

$$\frac{Q_c}{T_c} = \frac{Q_h}{T_h},$$

now, in general the efficiency is given by

$$\eta = \frac{W}{Q},$$

but given the setup of the system, this equations can be expressed as follows

$$\eta = \frac{Q_h - Q_c}{Q_h},$$

therefore, we have that

$$\eta = 1 - \frac{Q_c}{Q_h},$$

but using the relationship stated at the beginning of the problem, we have that

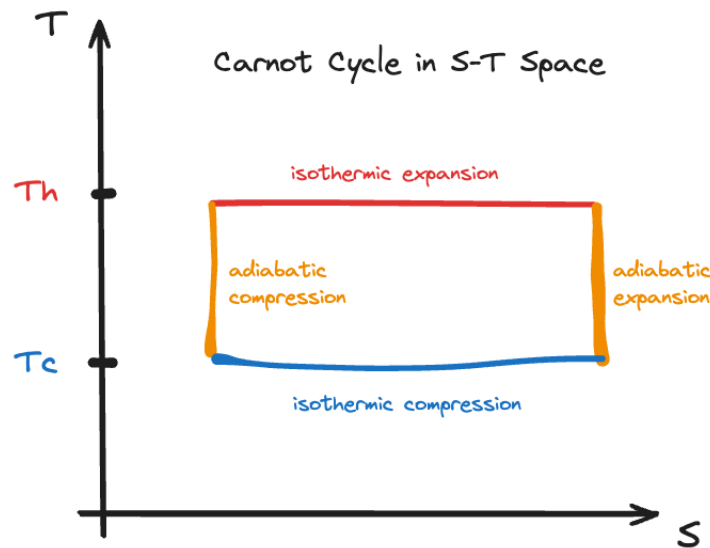
$$\eta = 1 - \frac{T_c}{T_h},$$

which corresponds to the efficiency to any reversible engine, and thus, the efficiency of Carnot's engine agrees with this expression.

Problem 3. We customarily show ideal gas processes in a $P - V$ diagram. In such a diagram you can read changes in internal energy and work directly from the diagram, but you have to infer heat from those values and the First Law. Isobaric and isochoric processes are represented by horizontal and vertical lines, while isothermal and adiabatic processes are represented by curves. For reversible processes, it's also possible to use an $S - T$ diagram, with entropy S on the horizontal axis and T on the vertical axis.

- (1) Sketch a Carnot cycle in an $S - T$ diagram, clearly labeling each of the steps (e.g. "isothermal expansion," "adiabatic compression," etc.)
- (2) Find the heat Q and work W_{by} from this diagram. Which can you read off directly, and which do you need to infer from the First Law?
- (3) Use your results to find the efficiency of the engine.

Solution. a) Here is my sketch of the cycle in the $S - T$ space



b) The work will be the the sum of the area under the curve for each step in the cycle,. which in this case will correspond to

$$W = (T_h - T_c) (S_h - S_c),$$

now for the heat, we need to make use the of the first law, and in this case, because the process is cyclic, the change in internal energy is zero, thus

$$Q = -W.$$

c) Finally, for the efficiency, we have, in virtue of the second law

$$dQ_1 = T_h dS \implies Q_1 = T_h (S_B - S_A),$$

$$dQ_3 = T_c dS \implies Q_3 = T_c (S_D - S_C) = T_c (S_A - S_B),$$

now, with this at hand, we can obtain η , thus

$$\eta = \frac{W}{Q_h} = \frac{T_h (S_B - S_A) + T_c (S_A - S_B)}{T_h (S_B - S_A)} = \frac{(T_h - T_c) (S_B - S_A)}{T_h (S_B - S_A)},$$

$$\implies \eta = 1 - \frac{T_c}{T_h},$$

which corresponds to our known definition.

Problem 4. There is great interest these days in heat pumps for heating buildings, as alternatives to burning fossil fuels. A heat pump is essentially a refrigerator (or air conditioner) in which an electrical motor provides the work required to pump heat from a cold reservoir (the outside air) into a hot reservoir (the warm air inside the building).

- (1) A heat pump can deliver several times as much heat energy as the amount of electrical energy it uses (unlike, for example, an electric space heater, where the heat delivered is exactly equal to the electrical energy used.) A friend of yours, who has never studied thermal physics, wants to know how that can possibly be true. Provide an accurate but accessible explanation.
- (2) When the outside temperature is moderate, the COP of a heat pump (the ratio of the heat delivered to the building to the electrical energy used) can be on the order of 5 or 6, but as the outside temperature drops, so does the COP, as shown in the figure. Explain, in terms of fundamental thermodynamics, why such a drop in COP is unavoidable. (You're not expected to account quantitatively for the values, just for the qualitative trend.)

Solution. a) For this part I think the main issue relies on the fact that a heat pump is moving heat, instead of generating it, and it turns out that it's easier to "move heat" than generate, or at least in the majority of the cases, it could be possible to make a heat pump very inefficient. Again, the principal thing here is that there are many ways in which you can transport heat, and for that process the amount of work is lower than in the generation process.

b) For this part we have to remember the first law, which in broad terms states that we can't have a machine with 100% efficiency, thus this drop in the COP when the temperature is lower outside is a consequence of this fact.

Problem 5. You may be aware that the temperature at which water boils decreases with decreasing atmospheric pressure, so it is lower in Denver, for example, than in Boston. The Clausius-Clapeyron equation describes the change of the boiling point of a liquid with pressure.

$$\frac{dP}{dT} = \frac{L_{vap}}{T\Delta V}.$$

Where L_{vap} is the latent heat of vaporization and ΔV is the change in volume between the liquid and gas phases.

- (1) Using this relation, estimate the difference in boiling point for water between Boston and Denver. Look up whatever you need to, but specify what you looked up and why. Be careful about units. Does your answer seem reasonable? Why?
- (2) Imagine a Carnot steam engine that uses 1 mole of water as its working medium. It takes heat $Q_h = L$ from the hot reservoir at T boiling, converting the water at pressure P into water vapor, increasing its volume by ΔV . The vapor then expands adiabatically, reducing its pressure to $P-dP$, and its temperature to $T-dT$. (The volume also increases, but the change is very small compared to the change between liquid and vapor, so the work done in this step can be neglected.) The vapor then condenses back into liquid water, decreasing its volume by ΔV . To complete the cycle, the liquid water is brought back to its original state (P, T) with essentially no change in volume. Make a rough sketch of the $P - V$ diagram for this process. (Remember, this is NOT an ideal gas!)
- (3) Show that the net work done by the engine in the cycle is by $W_{by} = \Delta V dP$ and the Carnot efficiency is $\eta_C = \frac{dT}{T}$. From these results, derive the Clausius-Clapeyron equation given above.
- (4) A hurricane can be thought of as a heat engine that operates something like the idealized steam engine described above (see this article from Physics Today). The primary source of work is the evaporation and condensation of water. The high- temperature reservoir is the ocean surface, at a temperature of about 300 K. The low-temperature reservoir is the upper atmosphere, at a temperature of about 200 K. Water evaporates from the ocean surface. The water vapor, mixed with air, undergoes adiabatic expansion as it rises and cools, and condenses into clouds in the upper atmosphere. (In real hurricanes it isn't the same air/water mixture that cycles back to close the loop, but that doesn't really matter to the analysis.) The work drives the hurricane's winds – in steady state the kinetic energy of the winds is dissipated by surface friction. To be self-sustaining, a hurricane needs to vaporize and condense about 10^{11} kg/hour of water. Estimate the maximum power output of such a hurricane, in watts. Compare that value to something that allows you to place it in some kind of meaningful context.

Solution. a) For this part of the problem let's start with the Clausius-Clapeyron equation,

$$\frac{dP}{dT} = \frac{L}{T\Delta V},$$

now, in our case ΔV corresponds to the change of the vapor water and the volume of the liquid water, thus, if we consider that $V_{gas} \gg V_{liq}$, then we have

$$\frac{dP}{dT} = \frac{L}{TV'}$$

and if we also consider the vapor water as an ideal gas, we have that

$$\begin{aligned} \frac{dP}{dT} &= \frac{L}{\frac{RT^2}{P}}, \\ \Rightarrow \frac{dP}{dT} &= \frac{LP}{RT^2} \\ \Rightarrow \frac{dP}{P} &= \frac{LdT}{RT^2}, \end{aligned}$$

and the solution for this differential equation is given by

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{L}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

now if we assume that $P_1 = 1$ atm, and $T_1 = 373$ K, and (digging) in the web I found that pressure in Denver is 0.85 atm, thus

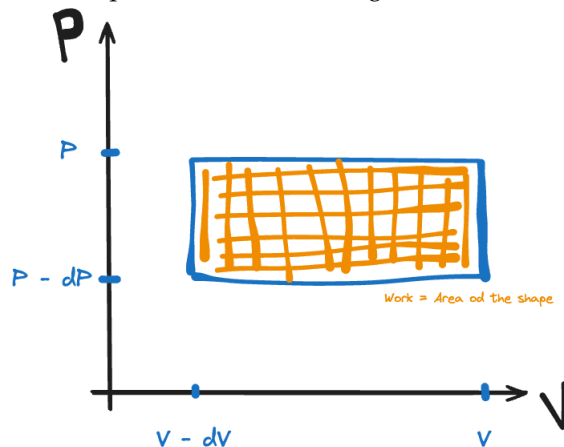
$$\ln(0.85) = \frac{L}{R} \left(\frac{1}{T_2} - \frac{1}{373}\right),$$

now, in this case $\frac{L}{R} = 5092$ K, thus

$$\begin{aligned} \frac{\ln(0.85)}{-592} &= \frac{1}{T_2} - \frac{1}{373}, \\ \frac{1}{T_2} &= 0.000036592 + \frac{1}{373}, \\ \Rightarrow \frac{1}{T_2} &= 0.0027175, \\ \Rightarrow T_2 &= \frac{1}{0.0027175}, \\ \therefore T_2 &= 367.985 \text{ K}, \end{aligned}$$

and this results is lower, as expected.

b) For b, here's the sketch of the process in a $P - V$ diagram:



c) First let's focus on the work, we know that in a $P - V$ diagram, the work corresponds to the area of the cycle, thus, in this case, the area is simply

$$w_{by} = \Delta V dP.$$

Now, with this results at hand, we can prove the Clausius-Clapeyron equation as follows: by definition, the efficiency is given by

$$\eta = \frac{W}{Q_h},$$

but in our case we have the following relations

$$\eta = \frac{dT}{T}, \quad W = \Delta V dP, \quad Q_h = L,$$

thus

$$\begin{aligned} \frac{dT}{T} &= \frac{\Delta V dP}{L} \\ \Rightarrow \frac{dP}{dT} &= \frac{L}{T \Delta V}, \end{aligned}$$

just as we wanted.

d) For this problem, we know that the latent heat of vaporization of water is about 2,260 kJ/kg, thus

$$\text{Power} = 2260 \left[\frac{\text{kJ}}{\text{kg}} \right] \times 10^{11} \left[\frac{\text{kg}}{\text{hour}} \right] = 2.63 \times 10^{17} \left[\frac{\text{J}}{\text{hour}} \right]$$

Final questions

You'll be asked these same questions at the end of every homework assignment. You don't have to put each of them on a new page.

Final Reflection: Looking back on the problem set as a whole:

a) What is something specific you understand better than you did before? I think I've seen much of this material in the past, except for the Clausius-Clapeyron, I think I used that equation ages ago, so I think it was a good thing for me to do some exercises on that, and remember how those things operate.

b) What is something specific that surprised, confused, or intrigued you, or that you struggled with? Heat flow and the sign of work is always a little difficult to me, mainly because of the conventions, I still have a hard time getting used to the convention that we're using. On the other hand I feel more comfortable with the math behind, so, I always try to think on those terms.

c) What is something that this problem set made you want to know more about? I think this problem set required a little bit more maths than the previous one, so I really like that part, and because of that I really want to start doing things in statistical mechanics, ensembles, probability distributions, and maybe work a little bit more with the computer.

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."

AI: I used Gemini (similar to ChatGPT but from google) to easily find some constants and to convert some units.

For the textbook, I've been using: Blundell, Stephen J., and Katherine M. Blundell. Concepts in thermal physics. Oup Oxford, 2010, which I think it's quite a good book.