140a Lecture 7, 1/29/19

⋆ Week 4 reading: Blundell+Blundell, chapters 13, 14

• Our topic this week is entropy. By continuing our discussion of engines and $\eta = |W|/|Q_H|$ we will argue that $dS = đQ_R/T$ is a state variable, where the R stands for reversible. As an appetizer, and to recall things from last week, let us compute the various ΔS's for the Carnot cycle. On the T_H isotherm where the gas expands from $V_1 \to V_2$, we have $\Delta S_{1\to 2} = Q_H/T_H = Nk_B \ln(V_2/V_1)$ (note that it is extensive, and has the same units as k_B). On the adiabatic segments, we have $\Delta S_{2\to 3} = \Delta S_{4\to 1} = 0$. On the T_C isotherm we have $\Delta S_{3\to 4} = Q_C/T_H = Nk_B \ln(V_4/V_3)$, which is negative since Q_C is negative, since $V_4/V_3 < 1$. Using $TV^{\gamma-1}$ on the adiabats, it follows that $V_2/V_1 = V_3/V_4$, so $\oint dS = 0$, consistent with it being a state variable.

Integrating $dU = TdS - pdV$ around the cycle, the work that the engine does is $|W| = \oint pdV = \oint TdS$. Evaluating it for the Carnot cycle with an ideal gas gives $|W| = (T_H - T_C)\Delta S_{1\to 2}$ and we recover $\eta_{Carnot} = |W|/|Q_H| = (1 - \frac{T_C}{T_H})$.

$$\text{Carnot reversible engine} : \eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H} \leftrightarrow \qquad \frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C}.$$

• Summary. A system undergoes a cyclic process: absorbs heat Q_1 from reservoir at temperature T_1 and Q_2 from one at temperature T_2. Carnot says $(1+Q_1/Q_2) \leq (1-T_1/T_2)$. E.g. $T_1 = T_C$, $T_2 = T_H$, and $Q_1 = -|Q_C| < 0$, $Q_2 = Q_H > 0$. So $(Q_1/T_1) + (Q_2/T_2) \leq 0$, with equality holding iff the cycle is reversible. Recall from last time the argument: let X be an engine that takes heat Q_2' from the T_2 bath and deposit heat Q_1' to the T_1 bath, doing work $W' = Q_2' - Q_1'$, and couple it to a Carnot engine running in reverse, so $W = Q_2 - Q_1$ and Q_2 and Q_1 are negative, chosen such that $Q_2^{total} = Q_2 + Q_2' = 0$. The upshot is that heat $-Q_1^{total} = -(Q_1' + Q_1)$ is taken from the bath at temperature T_1 and converted into work $W^{total} = -Q_1^{total}$. By Kelvin's statement, $W^{total} = -Q_1^{total} < 0$. So $|Q_1'| \geq |Q_1|$ with $|Q_2| = |Q_2'|$ so $\eta = (1 - \frac{|Q_1|}{|Q_2|}) \geq \eta'$.

• Emphasize how powerful a statement it is that something is a state variable. E.g. $dU = đQ + đW = đQ_R + đW_R$, with $đW_R = -pdV$. Can compute $\Delta U = \int_i^f dU$ by considering any path between the initial and final states, even for irreversible processes, e.g. free expansion of an ideal gas. Also, can compute ΔV for any process, even irreversible, via $\Delta V = -\int_i^f đW_R/p$ for a reversible path with the same endpoints. Emphasizing this because similar statements will apply to $\Delta S = \int đQ_R/T$.

• Discussing temperature with extraterrestrials (ETs). Use Carnot engine to define temperature Θ, via lots of Carnot engines in series, each extracting work W independent of n, with $\eta \equiv 1 - \frac{Q_{n-1}}{Q_n} \equiv 1 - \Theta_{n-1}/\Theta_n$ is independent of n. So $Q_n/\Theta_n \equiv x$ is independent of n. So $\Theta_n - \Theta_{n-1} = W/x$ is independent of n, and can be used to define a temperature scale. Comparing to $\eta_{Carnot} = 1 - \frac{T_C}{T_H}$, we get $\Theta = (const)T$. Agrees with previous definition, $\Theta = T$, with overall scale of the constant dependent on our conventions (earthlings define the constant by choosing the triple point of water, which is chosen by convention to be at some $T_{t.p.} \equiv 273.1600K$ for historical reasons; it occurs with pressure $0.00603659atm$; aside, mention also the critical point, which is at around $647K \approx 705F$ and $218atm.$).

• Consider an arbitrary system $\mathcal{O}$ undergoing an arbitrary cyclic process. Divide into N infinitesimal steps during which the temperature is constant, $T_1 \dots T_N$ and let Q_i be the heat absorbed by the system while at temperature T_i. Now couple to N tiny Carnot engines / refrigerators C_i, whose heat output is chosen to be $\mathcal{O}$'s input on the i-th step. The Carnot engines output is heat Q_i and temperature T_i and their input is heat $Q_i^* = T_* Q_i / T_i$ at temperature $T_* > T_i$. The Carnot engines have input $W_i = Q_i - Q_i^*$. The system $\mathcal{O}$ does work $W_{\mathcal{O}} = \sum_i Q_i$ and the total work done by combining the system and the attached Carnot engines is $W_{\mathcal{O}} - \sum_i W_i = \sum_i Q_i^*$, which is the total heat taken from a reservoir at T^*. The combined system, would violate Kelvin's statement unless this "work" is actually negative, i.e. the arrows are reversed and energy is being wasted into heat:

$$\sum_i Q_i^* \leq 0, \qquad \text{i.e.} \qquad \sum_i \frac{Q_i}{T_i} \leq 0, \qquad \text{i.e.} \qquad \oint \frac{đQ}{T} \leq 0.$$