

Chapter 20

The Second Law of Thermodynamics

20.1 Thermodynamic Cycles

- 8/23:
- Examples: Engines and pumps.
 - In a thermodynamic cycle, the energy doesn't change, so $W_{\text{on gas}} = -Q$, i.e., $W_{\text{by gas}} = Q_{\text{net}}$.
 - Thus, $W_{\text{by engine}} = Q_{\text{in}} - Q_{\text{out}}$ per cycle.
 - **Otto cycle:** The thermodynamic cycle used in car engines. *Also known as auto cycle.*

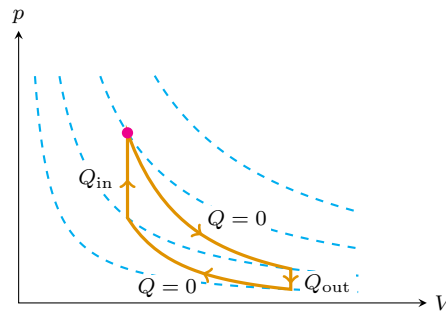


Figure 20.1: Otto cycle.

- Two adiabatic and two isochoric processes.
- **Stirling engine cycle:** The thermodynamic cycle used in steam engines.

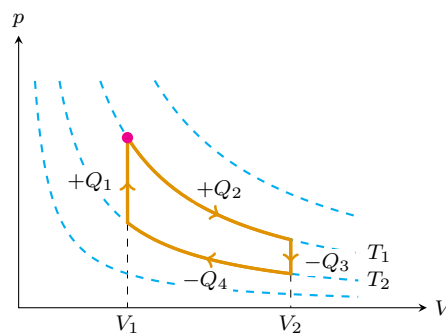


Figure 20.2: Stirling engine cycle.

- Two isothermal and two isochoric processes.
- For the isothermal processes, $\Delta E_{\text{int}} = 0$, so $Q = W_{\text{by gas}} = nRT \ln(V_f/V_i)$.
- For the isochoric process, $Q = nC_V \Delta T$.
- $Q_1 + Q_3 = nC_V(T_1 - T_2) + nC_V(T_2 - T_1) = 0$, so we only have to worry about Q_2 and Q_4 to determine the work done by the gas:

$$\begin{aligned} W_{\text{by gas}} &= Q_2 + Q_4 \\ &= nR \ln\left(\frac{V_2}{V_1}\right) \cdot (T_1 - T_2) \end{aligned}$$

- To get more work, you want the **compression factor** to be as big as possible.
- You also want the difference between the two temperatures to be as big as possible.
- The engine is powered until $T_1 = T_2$, because at that point you can't exchange heat.
- **Compression factor:** The ratio of the final volume to the initial volume, i.e., V_2/V_1 .
- **Efficiency:** The quotient of the work an engine does and the heat you put in per cycle. Denoted by e . Given by

$$\begin{aligned} e &= \frac{W_{\text{engine}}}{Q_{\text{in}}} \\ &= \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} \\ &= 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} \end{aligned}$$

- **Carnot cycle.**

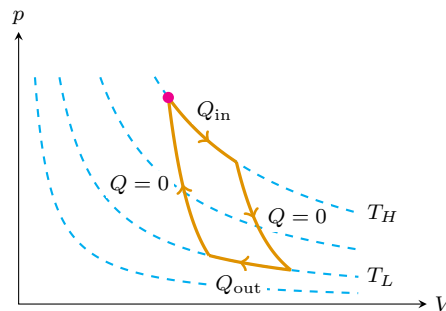


Figure 20.3: Carnot cycle.

- Two isothermal and two adiabatic processes.
- For this engine, $e = 1 - Q_{\text{out}}/Q_{\text{in}} = 1 - T_L/T_H$.
 - Thus, as the temperatures approach each other, efficiency approaches 1.
 - But, you cannot run an engine when the heat bath temperatures are equal to each other.
- Therefore, the Carnot cycle is the most efficient engine you can build, but it's just not physically viable.
 - A car run on the Carnot cycle would have great mileage but wouldn't get you very far.
- Conclusion: The Carnot cycle is interesting, but it does not yield a particularly useful engine.

20.2 The Second Law

- **Second Law of Thermodynamics:** It is not possible to remove heat at a high temperature and convert it entirely to work done by the engine. In other words, some heat is always exhausted to the low temperature.
- Maximizing engine efficiency:
 - You want to maximize the temperature difference.
 - You could technically run an engine between air temperature and ice, but it's hard to lug around a bunch of ice.
 - Additionally, you can't have T_H be too high because hotter engines emit nastier exhaust (specifically, exhaust that contributes more to acid rain).
 - Recall that the area on a pV -graph encompassed by the cycle is equal to the work done by the gas.
- If you run a heat engine backwards, you get a **heat pump**.
- **Heat pump:** A device that removes heat from low temperature sinks and exhausts it into high temperature sinks.
 - This is an air conditioner.
 - The second law of thermodynamics asserts that you can't remove heat at a low temperature and move it to a high temperature without doing work on the gas. Thus, you have to plug in the air conditioner and provide power — heat won't magically flow from cold to hot.

20.3 Statistical Mechanics

- Free expansion.
 - Imagine you have gas on one side of a thermally insulated container separated from the rest of the container by a partition.
 - If you remove the partition, the gas will expand out to fill the entire container.
 - However, the gas is not working against a force ($p = 0$) and heat is not flowing in ($Q = 0$).
 - Therefore, $dE_{\text{int}} = dQ - p dV = 0 - 0 dV = 0$.
 - From this, we can conclude that $\Delta T = 0$.
 - Note that this is an **irreversible process**.
- **Irreversible process:** A process that looks like it could occur on a microscopic level but could not on a macroscopic level.
 - Imagine a video of the milk molecules moving in a cup of coffee (which would look normal forwards and backwards) vs. a video of milk spreading out in a cup of coffee (which most certainly would not look normal backwards).
- **Macrostate:** A set of thermal variables (n, p, V, T) defining a system at an instant in time.
- **Microstate:** A way of arranging the molecules in a system that produces a macrostate.
 - Multiple microstates can correspond to the same macrostate.
- Consider a box with 10 molecules inside.
 - Each molecule has a 50/50 chance of being on the left *or* right side of the box.
 - We want to achieve the macrostate defined by 10 molecules on the left side and 0 on the right.

- There is only 1 corresponding microstate (namely that just described).
 - We want to achieve the macrostate defined by 3 molecules on the left side and 7 on the right.
 - There are $\frac{10!}{7!3!} = 120$ corresponding microstates.
 - For the even 5/5 split, there are $\binom{10}{5} = 252$ corresponding microstates.
- If there are N molecules and we want m on the left and $N - m$ on the right, the number of microstates that will realize this macrostate is $\frac{N!}{m!(N-m)!}$.
 - This corresponds to a binomial distribution.
- **Fundamental Assumption of Statistical Physics:** All microstates of a system are equally probable.
- **Number of microstates of a macrostate:** Denoted by Ω_{macro} .
- It follows from the fundamental assumption that

$$P_{\text{macro}} \propto \Omega_{\text{macro}}$$

- Relating this back to our example, since $P_{m,N-m} \propto \Omega_{m,N-m}$ we have that (5,5) is approximately twice as likely as (3,7).
- If we have N_A of molecules, it is going to be much more likely that the molecules are evenly (or almost evenly) distributed on both sides of the box than anything else.
 - $\Omega_{N_A,0} = 1$ still, but $\Omega_{N_A/2,N_A/2} = \frac{N_A!}{(N_A/2)!^2} \approx 10^{N_A/3} \approx 10^{2 \times 10^{23}}$, which is a huge number.
- If you make N and m continuous rather than integer quantities, the binomial distribution becomes a Gaussian distribution.
 - Thus, Gaussian distributions describe the probability distribution corresponding to the number of molecules on the left and the right.
 - The standard deviation of the Gaussian distribution of N_A macrostates is $\sigma \approx \sqrt{N_A}$.
 - Thus, the fraction of the width of the central peak to all states is $\sigma/N_A \approx 10^{-12}$.
 - Therefore, the width of the spike is approximately one-trillionth the width of the whole distribution, meaning that although you won't typically see a perfect 50/50 split, you won't see very large fluctuations (even 49/51 is very unlikely).
- It's not that you *can't* have all of the air molecules move to one side of the room; it's that you *won't* have this happen.

20.4 Office Hours (Gazes)

- Preference for sine vs. cosine when describing harmonic waves?
 - No preference.
 - Gazes tends to start with sines, but it really doesn't matter; there is no canonical preference.
- We say that the open end of a pipe is a node and we often say that closed ends are antinodes. However, on the midterm, there was a question with a tuning fork at one end of a pipe with water at the bottom, and we were supposed to infer that the open end with the tuning fork was an antinode and the end with water was a node. As such, I'm wondering if there's any unambiguous way we can identify open and closed ends of pipes.
 - We do assume the end with the tuning fork to be a pressure node and the water to be a pressure antinode.

- It's a *pressure* node at the end of the tube, but a displacement antinode.
- Some transmission does occur at the end of a tube.
- Flaring the ends of instruments cuts down on reflection and increases transmission.
- How do we know that even rays with not so well understood geometry converge on the image?
 - A computer can just brute force the problem and come to this conclusion.
- When refracting an object through multiple lenses, the side the *original* object is on is always the $+s$ and $-s'$ side, even when the first image may be on the other side of the next lens?
 - Yes.
 - Because the rays just continue on through the second lens. Those *rays* act as the object and effectively determine the sign.
- Plano-convex lens on top of a mirror?
 - You can make the contraption image the same way as a concave mirror.
 - Allows analogy of concave mirrors to regular lenses.
 - Also helps define our sign convention: flips what defines positive image distance.
- When do we make use of vibration? In Problem 19.43, shouldn't we have needed to use $\frac{7}{2}nR\Delta T$ for every degree Kelvin above 1000 K?
 - Didn't quite cross over the threshold.
 - Won't have to account for this on the final.
 - Everything is monoatomic on the final!

20.5 Entropy

- 8/24: • **Entropy** (of a macrostate): The following quantity, where k is the Boltzmann constant. Denoted by S_{macro} .

$$S_{\text{macro}} = k \ln \Omega_{\text{macro}}$$

- $\Delta S > 0$ (i.e., entropy increases) for an irreversible process.
- Entropies of multiple systems:
 - Consider 2 systems in macrostates A and B , respectively.
 - The number of microstates pertaining to each macrostate is Ω_A and Ω_B , respectively.
 - We know that $P_A \propto \Omega_A$ and $P_B \propto \Omega_B$.
 - Moreover, the probability P_{AB} that the combination of the two systems is in microstate AB is equal to $P_A P_B$ by fundamental probability laws, and the total number of microstates for the combination is equal to $\Omega_A \Omega_B$.
 - It follows that

$$\begin{aligned} S_{AB} &= k \ln(\Omega_A \Omega_B) \\ &= k \ln \Omega_A + k \ln \Omega_B \\ &= S_A + S_B \end{aligned}$$

i.e., that entropies are additive.

- Primary consequences of the second law of thermodynamics:

- Wrt heat engines: You will never see gas taking in Q_{in} and converting entirely to $W_{\text{by gas}}$ (i.e., there will always be some Q_{out}).
- Wrt heat pumps: You will never see Q extracted from T_L and exhausted to T_H without some $W_{\text{on gas}}$.
- Wrt entropy: You will never see a decrease in entropy.
- Change in entropy for a reversible process:
 - Consider the Carnot cycle (Figure 20.3).
 - For the cycle, $\Delta S_{\text{gas}} = 0$.
 - If we add or subtract Q of heat at a constant T ,

$$\Delta S = \frac{Q}{T}$$

- Thus,

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{Q_{\text{in}}} + \Delta S_{Q_{\text{out}}} \\ &= \frac{Q_{\text{in}}}{T_H} - \frac{Q_{\text{out}}}{T_L}\end{aligned}$$

The above is true for any thermodynamic cycle. But since $Q_{\text{in}}/Q_{\text{out}} = T_H/T_L$ for a Carnot cycle...

$$\begin{aligned}&= \frac{Q_{\text{out}} T_H / T_L}{T_H} - \frac{Q_{\text{out}}}{T_L} \\ &= 0\end{aligned}$$

for a Carnot cycle.

- Thus, overall, $\Delta S = 0$. This is actually true of any reversible process.
- Thus, since every process is either reversible or irreversible, $\Delta S_{\text{univ}} \geq 0$ for every process in this universe.