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**.
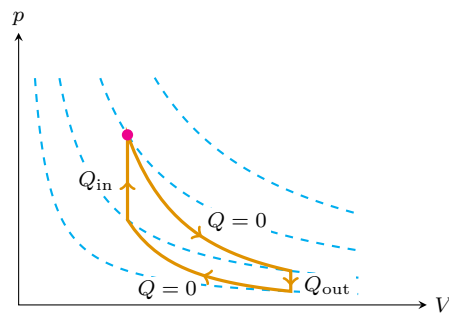

Figure 20.1: Otto cycle.

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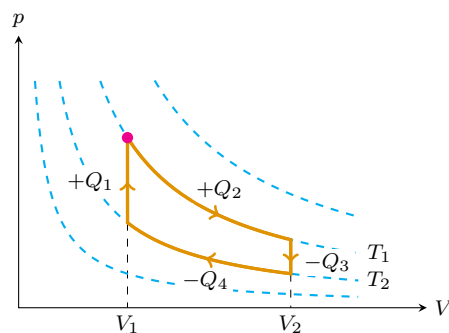

Figure 20.2: Stirling engine cycle.

- 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:

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

- 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*

$$e = \frac{W_{\text{engine}}}{Q_{\text{in}}}$$
$$= \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}}$$
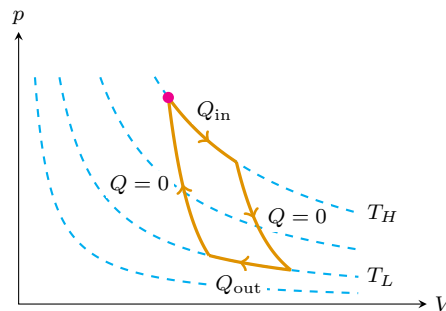$$= 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}}$$

• **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, $\mathrm{d}E_{\text{int}} = \mathrm{d}Q - p\,\mathrm{d}V = 0 - 0\,\mathrm{d}V = 0$.
    - 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 molecules 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* $\mathbf{\Omega_{macro}}$.

- 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 $\Omega_{N_A/2,N_A/2} = \frac{N_A!}{(N_A!)^2} \approx 10^{N_A/3} \approx 10^{2\times10^{23}}$, 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.