EXERCISE 8C: ENGINES, REFRIGERATORS, AND THE GIBBS PARADOX

Objectives:

- Show that the ideal Carnot engine achieves the maximum possible efficiency
- Understand how refrigerators work
- Discuss the Gibbs paradox and the role of indistinguishability in thermodynamics

Useful prior results:

- Maximum efficiency of a heat engine: $\eta \leq 1 - \frac{\tau_1}{\tau_2}$

1. A **Carnot engine** is a reversible heat engine with four stages:

   - Isothermal expansion B
   - Adiabatic expansion C
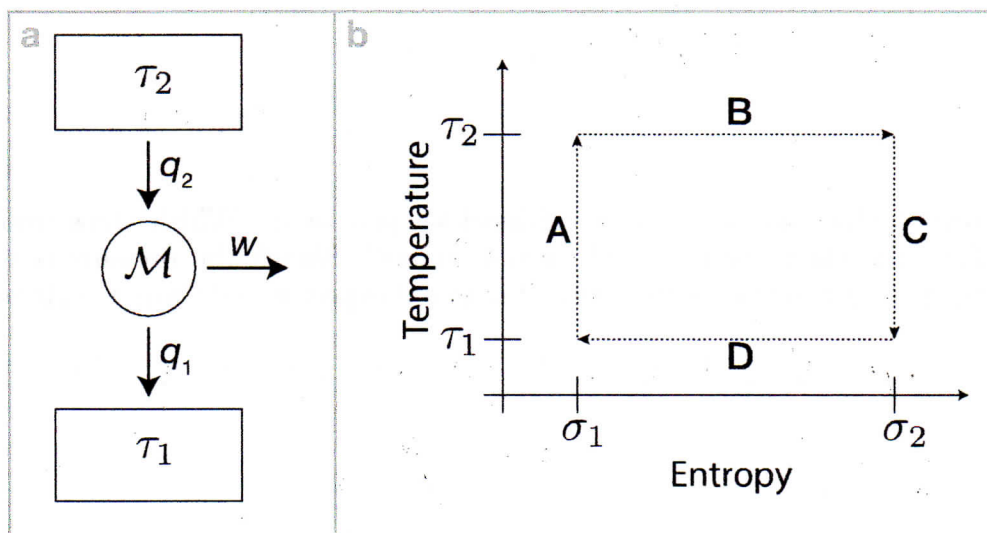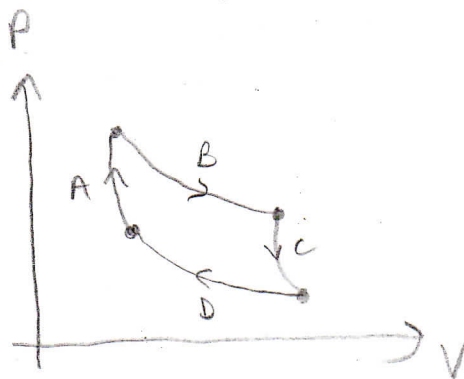   - Isothermal compression D
   - Adiabatic compression A

FIG. 1. **(a)** Schematic diagram of a heat engine. **(b)** Carnot cycle composed of adiabatic and isothermal quasi-static processes.

a. Last time, we showed that the maximum possible efficiency of a heat engine is

$$\eta \equiv \frac{q_2 - q_1}{q_2} \leq 1 - \frac{\tau_1}{\tau_2}.$$

Show that the ideal Carnot engine achieves this efficiency.

- A: $\Delta q_2 = 0, \; \Delta q_1 = 0$
- B: $\Delta q_2 = (\sigma_2 - \sigma_1) \tau_2 \; ; \; \Delta q_1 = 0$
- C: $\Delta q_2 = 0 \; ; \; \Delta q_1 = 0$
- D: $\Delta q_2 = 0 \; ; \; \Delta q_1 = (\sigma_2 - \sigma_1) \tau_1.$

$$q_2 = (\sigma_2 - \sigma_1) \tau_2 \; ; \; q_1 = (\sigma_2 - \sigma_1) \tau_1 \; ;$$

$$\eta = \frac{(\sigma_2 - \sigma_1) \tau_2 - (\sigma_2 - \sigma_1) \tau_1}{(\sigma_2 - \sigma_1) \tau_2} = 1 - \frac{\tau_1}{\tau_2} \checkmark$$

b. Real engines do not achieve efficiencies equal to η. Which steps would most limit the efficiency of a real Carnot engine? Sketch the pressure-volume and temperature-entropy curves that you would expect a real Carnot cycle to follow.

- Steps B and D will not be isothermal (too slow!).
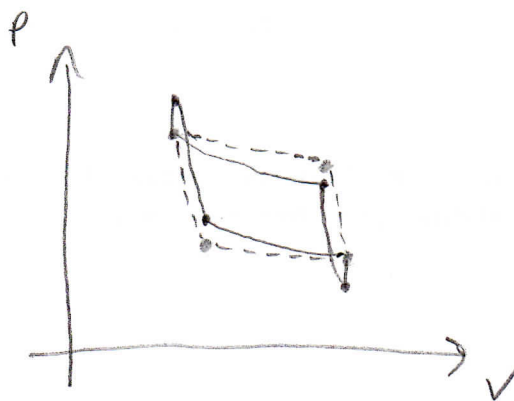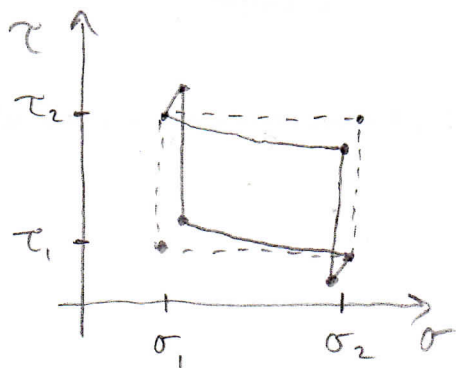
2. A *refrigerator* is a heat engine working in reverse. Refrigerators move heat from a cold reservoir to a hot reservoir at the expense of work.

    a. Draw the temperature-entropy curve of an ideal Carnot refrigerator.
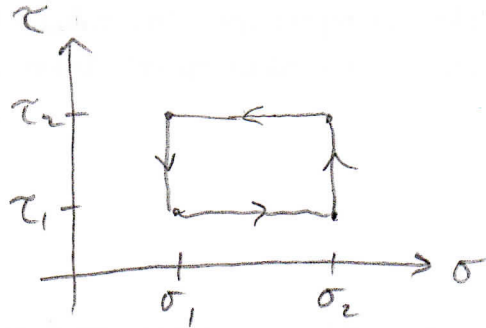
    b. The coefficient of performance C of a refrigerator is given by the heat q_2 added to the hot reservoir per cycle divided by the work W required. Show that C is the inverse of the Carnot efficiency.

$$\eta = \frac{q_2 - q_1}{q_2} \quad ; \quad C = \frac{q_2}{W} = \frac{q_2}{q_2 - q_1} = \frac{1}{\eta}$$

$$C = 1 : \quad \text{no cooling}$$
$$C = \infty : \quad \text{awesome cooling}.$$

    c. Under what reservoir conditions are heat engines most efficient? What about refrigerators?

$$\cdot \text{ Engines}: \quad \eta = 1 - \frac{\tau_1}{\tau_2} \to 1 \implies \tau_1 \ll \tau_2.$$

$$\cdot \text{ Refrigerators}: \quad C = \frac{\tau_2}{\tau_2 - \tau_1} \to \infty \implies \tau_2 = \tau_1$$

3. **The Gibbs paradox.** It is often claimed that the entropy of a classical ideal gas is not extensive. This "paradox" is understood as evidence for the necessity of quantum statistics.

a. At fixed particle number N, compute the entropy $\sigma(\tau, L)$ of a $1D$ classical ideal gas of distinguishable particles at temperature τ in a volume L.

i. What is the dimensionality of the phase space? What is the one-particle Hamiltonian $H(x,p)$?

· N position coordinates, N momentum coordinates $\Rightarrow$ dimensionality $2N$.

· $H(x,p) = \frac{p^2}{2m}$.

ii. Write the partition function Z of the gas as an integral over phase space and perform the integral over the spatial coordinates.

· In general, $Z = \frac{1}{\xi^N} \int dx_1 \cdots \int dx_N \int dp_1 \cdots \int dp_N \, e^{-\beta H(\vec{x}, \vec{p})}$

· Here $Z = \frac{1}{\xi^N} \int_0^L dx_1 \cdots \int_0^L dx_N \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_N \, e^{-\beta/2m \sum_{i=1}^{N} p_i^2}$

$= \frac{L^N}{\xi^N} \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_N \, e^{-\frac{\beta}{2m} \sum_{i=1}^{N} p_i^2}$

iii. Using the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-\alpha u^2} \, du = \sqrt{\frac{\pi}{\alpha}}$$

perform the integral over momentum coordinates.

$\alpha = \frac{\beta}{2m} = \frac{1}{2m\tau}$, so

$Z = \frac{L^N}{\xi^N} \left(\sqrt{2m\tau\pi} \right)^N$

iv. Find $\sigma(\tau, L)$. At fixed density $n \equiv N/L$, how does σ scale with N? This is the Gibbs paradox.

$$F = -\tau \ln Z = -N\tau \ln \frac{L}{\xi} \cdot \sqrt{2m\tau\pi} .$$

$$= -N\tau \ln L + N\tau \ln \xi - \frac{N\tau}{2} \ln 2\pi m \tau$$

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = +N\ln L - N\ln \xi + \frac{N}{2}\ln 2\pi m\tau + \frac{N}{2}$$

$$= N \ln \left(\frac{L}{\xi} \cdot \sqrt{2\pi m \tau}\right) + \frac{N}{2} - N\ln N + N\ln N$$

$$= N \ln \left(\frac{1}{n} \cdot \frac{\sqrt{2\pi m \tau}}{\xi}\right) + N\ln N.$$

b. How does quantum mechanics resolve the Gibbs paradox? How could it be resolved within classical physics?

- QM: $\xi \to h$; divide by $N!$ originally because the particles are indistinguishable.

- Classical: make ξ a function of N. Choose $\xi(N) = Nh$. Then

$$\sigma = N \ln \left(\frac{1}{n} \cdot \frac{\sqrt{2\pi m \tau}}{h}\right) + \frac{N}{2} .$$

$$N_A = N, \quad N_B = N$$

4. *Entropy of mixing.* Suppose we have two containers A and B, each with volume V and temperature τ, containing respectively N_A and N_B particles of an ideal gas. All gas particles have mass m. The containers are connected by an initially closed valve.

   a. If the particles in container A are *distinguishable* from the particles in container B, what is the entropy of the system before the valve is opened?
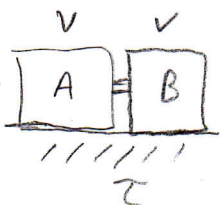
$$\cdot \text{3D ideal gas:} \quad \sigma = N \ln\left(\frac{V}{N} \cdot \frac{1}{\lambda_\tau^3}\right) + \frac{5}{2}N$$

$$\cdot \text{Before:} \quad \sigma_i = \sigma_A + \sigma_B = N_A \ln\left(\frac{V}{N_A} \cdot \frac{1}{\lambda_\tau^3}\right) + \frac{5}{2}N_A$$

$$+ N_A \ln\left(\frac{V}{N_A} \cdot \frac{1}{\lambda_\tau^3}\right) + \frac{5}{2}N_B$$

$$= 2N \ln\left(\frac{V}{N} \cdot \frac{1}{\lambda_\tau^3}\right) + 5N.$$

   b. What is the entropy of the system after the valve is opened and equilibrium is reestablished?

$$\sigma_f = \sigma_A + \sigma_B = N_A \ln\left(\frac{2V}{N_A} \cdot \frac{1}{\lambda_\tau^3}\right) + N_B \cdot \ln\left(\frac{2V}{N_B} \cdot \frac{1}{\lambda_\tau^3}\right) + \frac{5}{2}N_A + \frac{5}{2}N_B$$

$$= \sigma_i + 2N \ln 2.$$

   c. Now suppose the particles in container A are *indistinguishable* from the particles in container B. What is the entropy before the valve is opened? What about after the valve is opened?

Before: $2N$ particles occupy volume $2V$

$$\sigma_i = 2N \ln\left(\frac{2V}{2N} \cdot \frac{1}{\lambda_\tau^3}\right) + 5N = 2N \ln\left(\frac{V}{N} \cdot \frac{1}{\lambda_\tau^3}\right) + 5N.$$

After: Nothing happens.

$$\sigma_f = \sigma_i.$$

   Note that the above result does not depend on *how* distinguishable the particles are.

- What if some particles that we consider to be indistinguishable are actually distinguishable?

5. *Example 1: breaking the Second Law.* Suppose I show you an apparatus that violates the Second Law of Thermodynamics (or so I claim). The apparatus consists of two containers A and B as above, each containing N gas particles. The valve between the containers is initiallly closed, and the containers are at thermal equilibrium at temperature τ. A pressure gauge on container A reads $P_A = P$; likewise, a pressure gauge on container B reads $P_B = P$.

   a. When I open the valve, the pressure in container A drops to $P/2$, and the pressure in container B rises to $3P/2$.

      i. How does the apparatus work? Does it really violate the laws of thermodynamics?
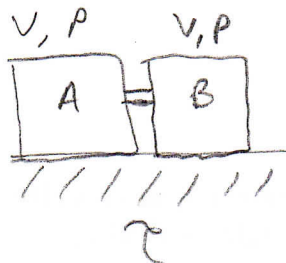
- why it appears to violate 2nd law: could use the pressure difference to do work. Have I extracted useful work from a system in equilibrium?

- The two containers contain two different gases A and B.
- There is a barrier between the containers that is selectively permeable. Gas A can diffuse through it, but not gas B.
- Opening the valve causes the partial pressure of gas A to be the same on both sides. But gas B is still stuck in container B.
- The system was not in chemical equilibrium initially.

6. *Example 2: the pedantic lab partner.* You are taking a chemistry lab course. One of the pre-lab exercises asks you to derive the heat capacity of air from the entropy of an ideal gas at constant temperature.
      ^volume V

   a. Do this for a gas of N particles.

$$\sigma(N, V, \tau) = N \ln\left(\frac{V}{N} \cdot \frac{1}{\lambda_\tau^3}\right) + \frac{5}{2} N$$

$$C_V = \tau \frac{\partial \sigma}{\partial \tau} = \frac{3}{2} N.$$

b. Your lab partner, noticing your calculation, complains that you are treating all of the air molecules as being indistinguishable, when in fact they are microscopically distinguishable. He calculates the entropy by treating the gas as being composed of fraction f_1 of N_2 gas and fraction f_2 of O_2 gas.

  i. Will your partner's entropy function be the same as yours, or different?

$$\sigma(N_A, N_B, V, \tau) = N_A \ln\left(\frac{V}{N_A} \cdot \frac{1}{\lambda_\tau^3}\right) + \frac{5}{2} N_A$$
$$+ N_B \ln\left(\frac{V}{N_B} \cdot \frac{1}{\lambda_\tau^3}\right) + \frac{5}{2} N_B.$$

Different!

  ii. Will you and your partner predict the same heat capacity for a system of N air molecules? If not, which of you is right, and why?

Partner computes $C_V = \tau \frac{\partial \sigma}{\partial \tau} = \frac{3}{2}(N_A + N_B)$

$\Rightarrow$ same if $N = N_A + N_B$.

So although the entropy functions were different, there was no consequence in this experiment.
The system didn't distinguish between N_2 and O_2, so we don't have to distinguish between them either.

Lessons:
- Entropy is not defined by the microstates of a system, but by the macrostates.

$\Rightarrow$ Entropy is in the eye of the beholder.
  We want to use enough macrostate variables to describe the system, but we don't need to use too many.
  Let the system guide your choice of macrostate variables.