

PHYS 427 - Thermal and Statistical Physics - Discussion 05

Feb 25, 2025

-
1. **Carnot's theorem:** A heat engine is a device that turns heat into mechanical work. More precisely, it takes energy from a large high-temperature reservoir in the form of heat, converts some of that energy into useful mechanical work, and deposits the rest into a large low-temperature reservoir as heat.

A "good" heat engine is one that converts a lot of the input energy into work. Therefore, the efficiency η of a heat engine is defined as the amount of work it produces divided by the amount of heat it takes in.

In this problem, you will prove Carnot's theorem, which places a fundamental maximum limit on η , *no matter what the heat engine is made of*.

Without losing any generality, we can assume that the heat engine operates *cyclically*. During one cycle of the engine, it extracts an amount of energy Q_H from the hot reservoir in the form of heat, produces an amount W of mechanical work, and deposits energy Q_C into the cold reservoir as heat. At the end of the cycle, the engine itself returns to its exact initial state. The reservoirs are very large, so that their temperatures T_H and T_C do not change.

- (a) Apply the first law of thermodynamics ($dU = Q + W$) to the engine itself (not including the reservoirs). Integrate over a full cycle to show that $\eta \leq 1$. This is sometimes summarized by saying "you can't win" in the game of thermodynamics. (This isn't Carnot's theorem yet, keep going!)
- (b) Assume that the number of particles in the hot reservoir is fixed¹, but allow for the possibility that it can expand and contract. Suppose for now that when the engine extracts heat from the hot reservoir, it does so *quasistatically*, i.e. slowly enough that the system remains in equilibrium at all times. Use the fundamental thermodynamic relation and the first law of thermodynamics to show $\Delta S_H = -\frac{Q_H}{T_H}$ during one cycle of the engine.
- (c) Similarly, argue that $\Delta S_C = \frac{Q_C}{T_C}$ is the smallest possible change in entropy of the cold reservoir during one cycle of the engine.
- (d) The second law of thermodynamics says that $\Delta S \geq 0$ for any process in a *closed* system. Use this to show $\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}$.
- (e) Using the definition of the efficiency and your result from part (d), show that $\eta \leq 1 - \frac{T_C}{T_H}$. This is Carnot's theorem. It's sometimes summarized by saying "you can't even break even" in the game of thermodynamics.

¹We could be more general and allow for particle flow, but let's keep it simple

- (f) Argue that ΔS_H would be larger if the same amount of heat Q_H were extracted non-quasistatically. Therefore, Carnot's theorem also holds for non-quasistatic engines. In fact, non-quasistatic engines can't achieve the maximum efficiency.
 - (g) What are some other ways that a heat engine can fail to achieve the maximum efficiency?
-

2. Quasistatic adiabatic processes in an ideal gas:

The goal of this problem is to understand and prove the following statement:

"Consider a non-monatomic ideal gas with f classical quadratic degrees of freedom, translations included. When such a gas undergoes a quasistatic, adiabatic process, the combination pV^γ stays constant, where $\gamma = 1 + \frac{2}{f}$."

This is a useful fact to know. For example, a quasistatic adiabatic process occurs in two of the four steps of a Carnot engine. If the working substance of the Carnot engine is an ideal gas, this fact lets us relate the pressure to the volume during the process. Plus, the derivation is interesting!

- (a) First, run through the regular proof to understand what goes into it. Prove that pV^γ is a constant for an isentropic (adiabatic) process of an ideal gas. Here, $\gamma = 1 + 2/f$, where f is the number of quadratic degrees of freedom of the gas. Do not assume any particular value of f .
- (b) Now let's think about what this means. Consider a non-monatomic ideal gas with N particles, volume V and temperature T . Show that the partition function for the whole N -particle system can be factorized as

$$Z = Z_{\text{monatomic}} Z_{\text{internal}}^N, \quad (1)$$

where $Z_{\text{monatomic}}$ is the partition function of a *monatomic* ideal gas with the same N , V and T , and

$$Z_{\text{internal}} = \sum_i e^{-\beta \varepsilon_i} \quad (2)$$

where i label the different internal states of motion of a single gas particle, i.e. the different states of rotation and vibration, and ε_i are the corresponding energies. (In other words, Z_{internal} would be the partition function of a single gas particle if it weren't allowed to move around the box).

- (c) In certain simple cases, the sum in (2) can be evaluated exactly. For example, this was done in Lecture 6 for the vibrational and rotational states of an idealized CO molecule.

For gases with more complicated internal degrees of freedom, we can still say something useful if we assume that the spacing between the internal energy levels ε_i is small compared to $k_B T$. This can be considered the high-temperature limit, and it happens to be a very good approximation in many cases of practical interest.

Then the energy levels can be treated as a continuum and (2) can be replaced by an integral. We have seen explicit examples of this limit in the lecture notes and homework 3. In general, though, there is a prescription for dealing with

systems for which the energy levels can be treated as a continuum—classical mechanics! In the previous discussion, we wrote down the partition function for a system which can be treated with classical mechanics. Adapted to the present context, we have

$$Z_{\text{internal}} = \int \frac{d^D q d^D p}{(2\pi\hbar)^D} e^{-\beta H(q,p)}. \quad (3)$$

In this expression, the q_1, \dots, q_D are the generalized coordinates (from classical mechanics) needed to describe the internal degrees of freedom of the system.

We know that the different quadratic degrees of freedom go into the Hamiltonian, and we can obtain the internal energy of the gas from the partition function. Having done the proof in part (a), do you see how the number of quadratic degrees of freedom shows up in pV^γ ?
