Lecture 36 - Entropy and the second law

What's important:
- entropy
- second law of thermodynamics
- heat engines

Demonstrations:

Entropy

The laws of mechanics tell us about the motion of particles and the behavior of energy and momentum. Thermodynamics tells us about the "flow" of heat - how the energy of collective systems behaves. We have introduced two of these laws before, and will briefly recap them momentarily. But first, we introduce the concept of entropy.

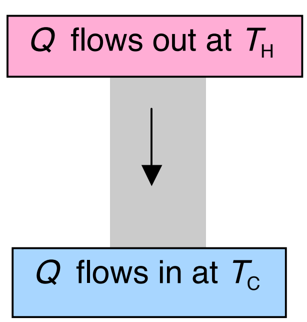
In mechanics, we talked about a change in the direction of motion of an object as following the change in the potential energy - work was done by a system when its potential energy was lowered. What is the analog for thermodynamics? What law says that heat flows from a hot system to a cold one, and not the reverse - assuming that total energy can be conserved in both cases?

Clausius introduced a quantity called the entropy for reversible processes by

$$\Delta S = Q_{rev} / T$$

where we have added a "rev" to the heat Q just for the time being to remind us that the process must be reversible. We know as well from statistical mechanics that S can be related to the disorder of a system.

How does this apply to the simple problem of two systems at different temperatures in thermal contact?



At T_H, there is an entropy decrease of

$$\Delta S_H = -Q / T_H$$

associated with the "outflow" of heat. At T_C, there is an entropy increase of

$$\Delta S_C = +Q / T_C$$

associated with the "inflow" of heat.

By conservation of energy, Q is the same at the hot and cold ends. Along the thermal path between them, there is no entropy change because the heat entering and leaving a given position is the same.

The total entropy change is thus

$$\Delta S_{TOT} = +Q / T_C - Q / T_H$$
$$= Q\,(1/T_C - 1/T_H)$$

By assumption, $T_H > T_C$, so $\Delta S_{TOT} > 0$. That is, heat flows from hot to cold if entropy increases.

We now formalize this result as the second law of thermodynamics.

Laws of thermodynamics

Zeroth Law: If object **A** is in thermal equilibrium with object **B**, and object **B** is separately in thermal equilibrium with object **C**, then objects **A** and **B** will be in thermal equilibrium if they are placed in thermal contact.

First Law: The change in a systems internal energy ΔE is related to the heat Q and work W in a process by

$$\Delta E = Q - W_{\text{by system}}.$$

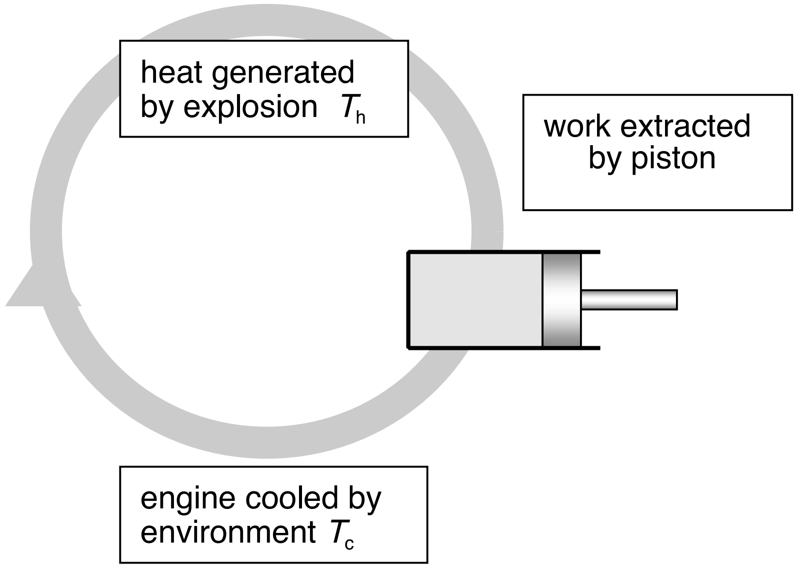
Second Law: When objects of different temperatures are brought into thermal contact, heat flows spontaneously from the higher temperature object to the lower temperature one. The entropy of an irreversible process always increases.

In addition to these, there is a third law, that we won't be concerned with, but include for completeness:

Third Law: One cannot attain the absolute zero of temperature in a finite number of steps.

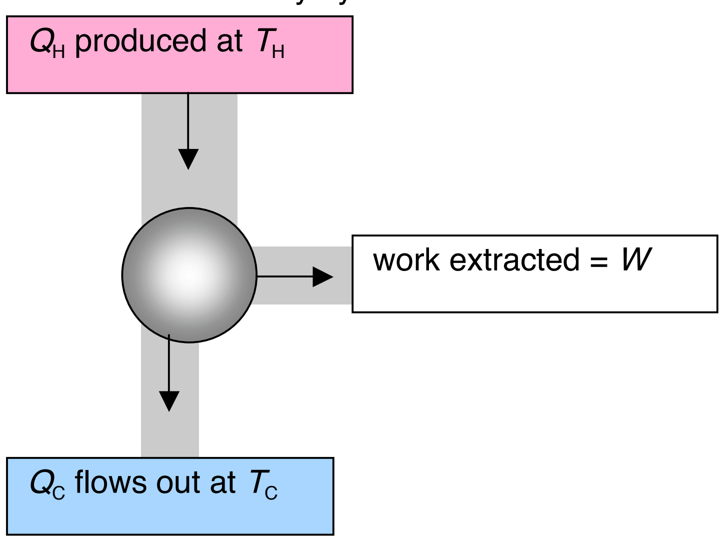
Heat engines

Car engines, refrigerators, steam engines...are all examples of heat engines. A schematic representation of how a car engine works might be



- At the top of the circle, the gas - air mixture in the engine explodes, producing heat Q_H at a temperature T_H
- The piston moves as the gas expands, producing a work W
- At the bottom of the circle, the radiator and moving air removes heat Q_C at temperature T_C.
- The hot temperature T_H is higher than the cold temperature T_C.

We can represent the heat flow schematically by



We can apply the first law of thermodynamics to the heat engine. The internal energy of the engine doesn't change, so

$$\Delta E_{\text{engine}} = 0$$

and the first law says

$$-W_{\text{by engine}} + (Q_H - Q_C) = \Delta E_{\text{engine}} = 0.$$

So

$$W_{\text{by engine}} = Q_H - Q_C.$$

Now, the thermal efficiency e of the engine is defined as the ratio of the amount of work extracted compared to the amount of heat produced; that is

$$e = W_{\text{by engine}} / Q_H$$

That is, the more heat "wasted", the lower the efficiency. Using our expression for W_{engine}, we can write

$$e = (Q_H - Q_C) / Q_H = 1 - Q_C/Q_H.$$

What does the second law say about this? If entropy never decreases spontaneously, then

$$Q_H/T_H \geq Q_C/T_C$$

or

$$T_C/T_H \geq Q_C/Q_H.$$

Thus, the efficiency is governed by

$$e \leq 1 - T_C/T_H.$$

The maximum efficiency occurs for reversible engines, and is called the Carnot efficiency. Clearly, the efficiency increase with the ratio of the temperatures.

Example

What is the maximum efficiency of a steam engine with a boiler temperature of 177 C which exhausts its heat to a condenser at 27 C?

$$e_{\text{Carnot}} = 1 - T_C/T_H = 1 - (27 + 273)/(177 + 273) = 1 - 300/450$$

or

$$e_{\text{Carnot}} = 1 - 2/3 = 33\%$$

This may not look too impressive, but typical thermal efficiencies are even lower, closer to 20%.

In this hypothetical example, the boiler temperature is much above 100 C, perhaps by being pressurized.