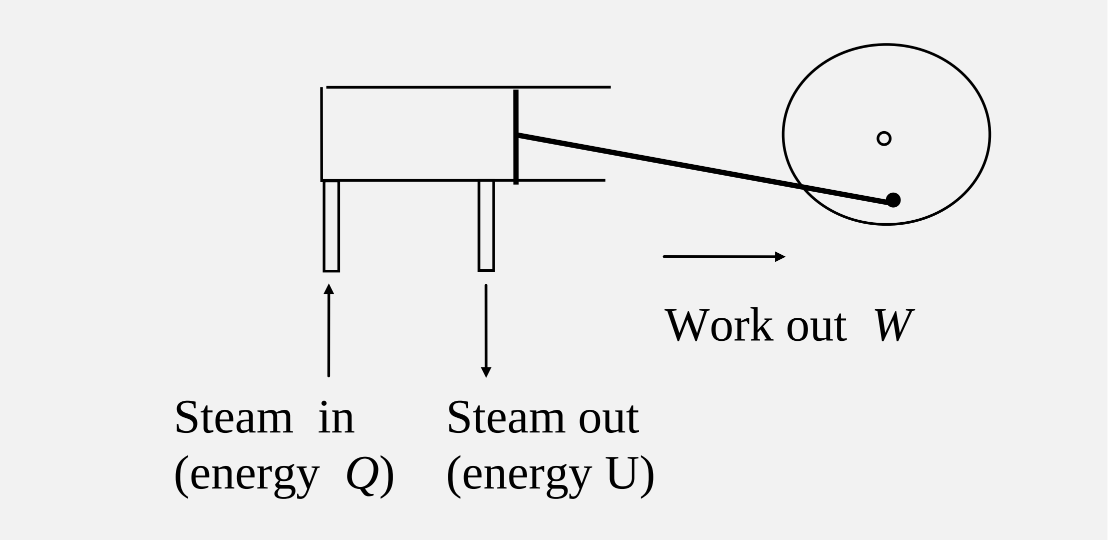
Lecture 11: Thermodynamics

The laws of thermodynamics

The engineers of the industrial revolution were interested in improving the *efficiency* of their steam engines - getting more work out of them for the amount of fuel consumed.



By **conservation of energy**

$$Q = U + W$$

This is **the 1st law of thermodynamics**

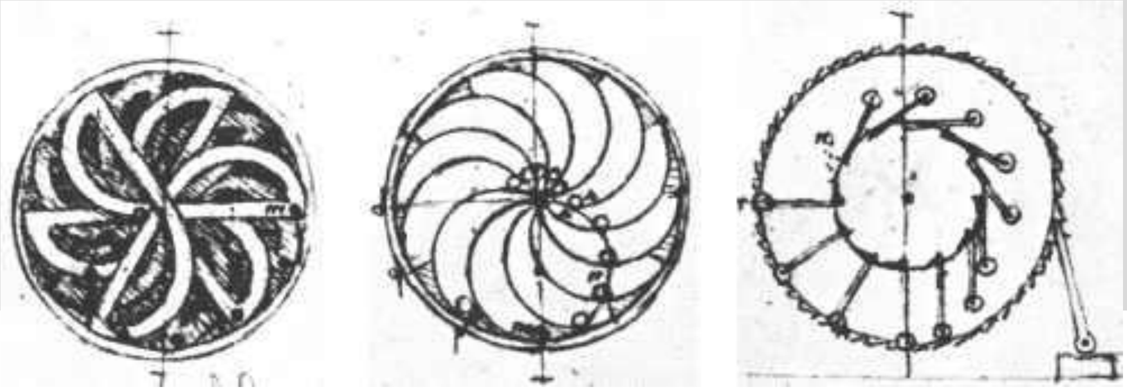
The first law tells us that the **maximum efficiency** of a heat engine, given by:

$$\text{efficiency} = \frac{\text{work out}}{\text{heat in}} = \frac{W}{Q}$$

cannot be greater than 1 (because $U \geq 0$).

In other words, you cannot get more energy out of a machine than you put in. In fact, you will always get *less* because of *entropy (discussed later).*

Perpetual motion machines are devices which supposedly achieve 100% efficiency. Of course they are complete nonsense.



Design by Leonardo da Vinci for a perpetually revolving wheel.
(He wasn't such a genius after all…)

The efficiency limit

The efficiency equation can be rewritten as:

$$\text{efficiency} \leq \frac{W}{Q} = \frac{Q-U}{Q}$$
$$= 1 - \frac{U}{Q}$$

If the inlet gas is at temperature T_1 and the outlet gas is a temperature T_2 , then using the proportionality between kinetic energy and temperature we can write:

$$\text{efficiency} \leq 1 - \frac{T_2}{T_1}$$

In other words, there is another limit imposed on the maximum efficiency of a heat engine, that is stricter than that of the 1st law of thermodynamics.

Practical examples

James Watt's early steam engine

$T_1 = 100°C = 373K$ (steam in)

$T_2 = 40°C = 313K$ (water condensing out)

maximum efficiency = 16%

Modern power station with $T_1 = 600°C = 873K$

maximum efficiency = 65%

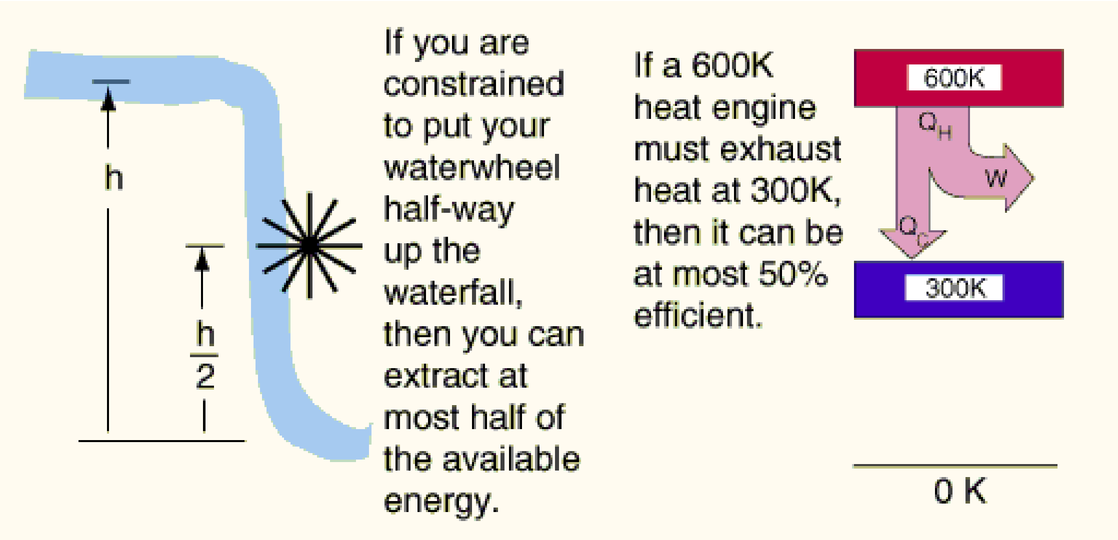
The efficiency of an engine is increased if the difference between the inlet and outlet temperature is increased. In many practical examples, the outlet temperate depends on the ambient temperature, which cannot be lowered. In that case, the only way to increase the efficiency is to **increase the inlet temperature**.

Machines that have a greater efficiency than the thermodynamic limit are referred to as *perpetual motion machines of the second kind*.

Like machines with 100% efficiency (perpetual motion machine of the first kind), they are a physical impossibility.

The 2nd law of thermodynamics

This general principle which places constraints upon the direction of heat transfer and the attainable efficiencies of heat engines. It goes beyond the limitations imposed by the 1st law of thermodynamics. This argument is applicable to any attempt to extract energy from heat, not just to engines with an inlet and an exhaust.



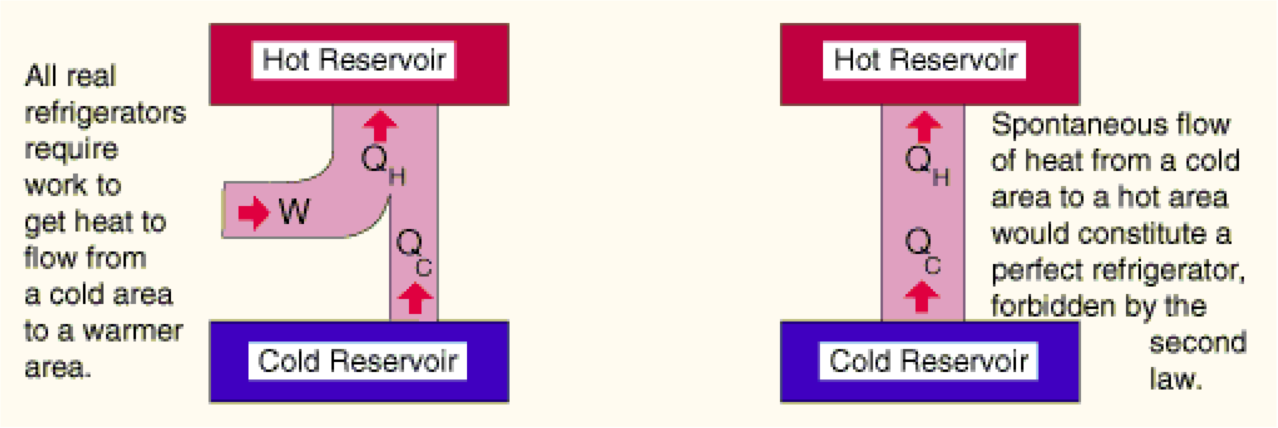
Therefore, work is only extracted as a **difference** when heat flows from a hot reservoir to a cold one. In other words,

It is not possible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow.

This is the Kelvin-Planck statement of the 2nd law of thermodynamics.

Entropy

Basically, the 2nd law says that heat flows from hot to cold.



It implies a **non-reversibility** on a macroscopic scale, even though the laws governing the motion of atoms on a microscopic scale are reversible in time (Newton's equations do not distinguish between *t* and *–t.*

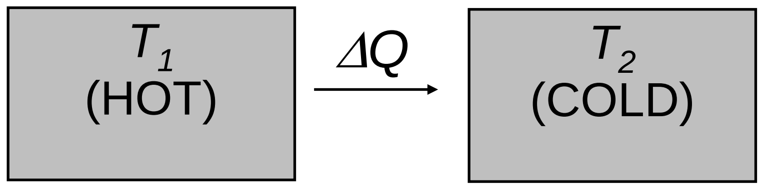
A movie of the motion of single atoms in a gas would be indistinguishable from a copy run backwards.

BUT

A movie of two objects at different temperatures being brought together and reaching the same temperature **is distinguishable** from its time-reversed copy, since it would show one object getting hotter and the other colder.

The concept of *entropy* provides a mathematical description of this irreversibility.

Suppose a quantity of heat ΔQ moves from a high temperature reservoir to one at a lower temperature.



Clearly, since $T_1 > T_2$, the quantity:

$$S = \left(\frac{\Delta Q}{T} \right)$$

is greater than zero.

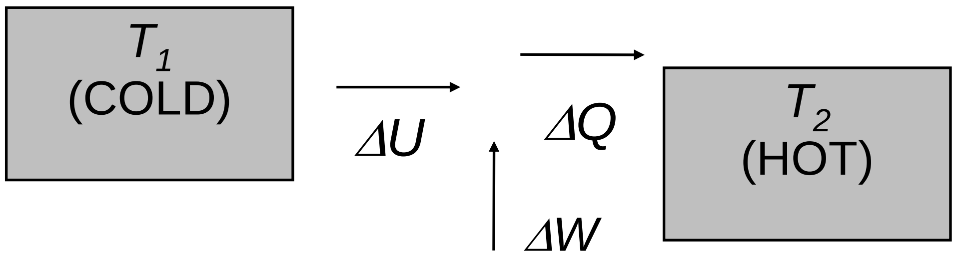
Thus, the *entropy*

$$\Delta S = \left(\frac{\Delta Q}{T_2} \right) - \left(\frac{\Delta Q}{T_1} \right)$$

always increases.
If a movie of the process is run backwards, then the entropy would decrease rather than increase. This is physically impossible.

Something to think over: Does a refrigerator violate the 2nd law?

A refrigerator moves heat from a cold space (making it colder) to a warmer space (making it hotter).



However, to do so it requires the input of energy.

To extract heat ΔU from the low temperature T_1, *additional energy* ΔW is needed.

Thus the heat flow into the high temperature T_2 is $\Delta Q = \Delta U + \Delta W$.

The higher temperature T_2 is balanced by the higher heat flow so that 2nd law is not violated.

How much energy is required?

Entropy decrease in cold chamber is $\Delta U / T_1$

Entropy increase in hot chamber is $(\Delta U + \Delta W) / T_2$

Hence,

$$\frac{\Delta U + \Delta W}{T_2} - \frac{\Delta U}{T_1} \geq 0$$

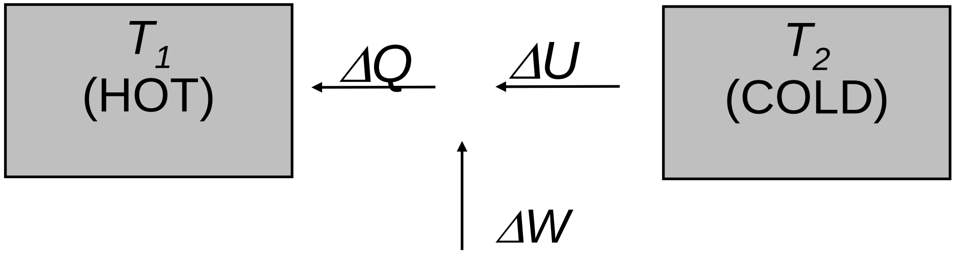
$$T_1 \Delta U + T_1 \Delta W - T_2 \Delta U \geq 0$$

$$\Delta W \geq \left(\frac{T_2 - T_1}{T_1} \right) \Delta U = \left(\frac{T_2}{T_1} - 1 \right) \Delta U$$

So the energy required depends on:
the amount of heat to be moved from cold to hot
and
the temperature difference between the two chambers.

Notice that for small differences in temperature, a small amount of work can move a large amount of heat from cold to hot.   This makes refrigerators extremely efficient machines.

The same principle can be applied in reverse for heating instead of cooling. It is then called a “heat pump”.



$$\Delta W \geq \left(1 - \frac{T_2}{T_1}\right) \Delta Q$$

Again, a small amount of work can move a large amount of heat from cold to hot. Heat pumps are more efficient than heaters.

Further notes on entropy

The laws of thermodynamics introduce us to two fundamental quantities:

Energy , which is always conserved (reversible)

Entropy , which always increases (irreversible)

Is the concept of entropy restricted to heat engines or can it be applied to other irreversible situations in physics, where temperature is not directly involved ?

Recall our example:

T_1
(HOT)
high average KE

$\xrightarrow{\Delta Q}$

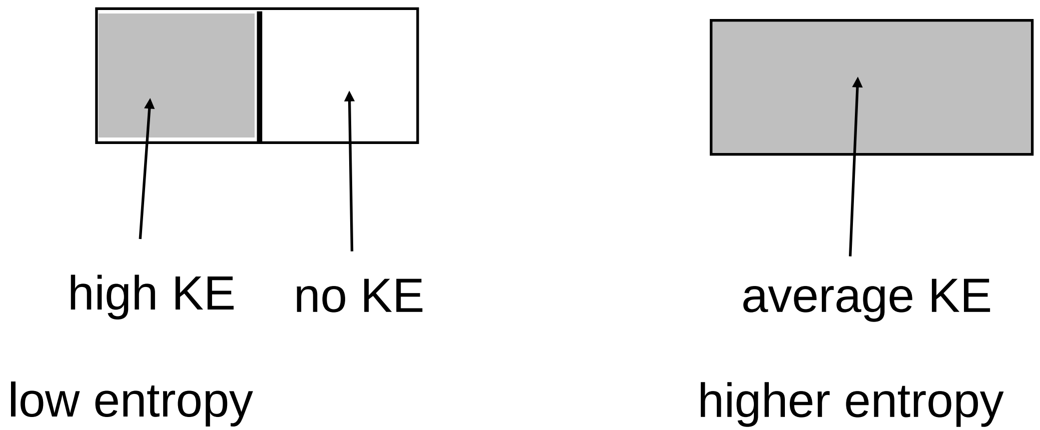
T_2
(COLD)
low average KE

Resulting in:

$T_1 > T > T_2$
WARM
intermediate average KE

- Thus, an increase in entropy corresponds to a balancing out of the kinetic energy.
- The total amount of energy remains the same, but it is distributed over more particles.
- **Entropy can thus be regarded as a measure of the *uniformity* of the distribution of energy.**

Example: Diffusion



The statistical nature of entropy

From the above examples, it can be seen that entropy is statistical in nature.

Ludwig Boltzmann (1890) showed that the thermodynamic definition of entropy

$$S = \left(\frac{\Delta Q}{T} \right)$$

is equivalent to the statistical description:

$$\boxed{S = k \ln \Omega}$$

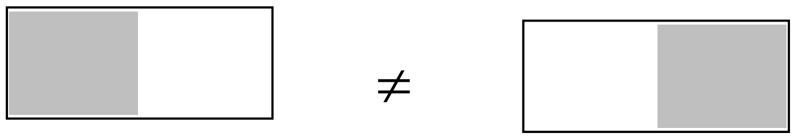
where Ω is a measure of the *disorder* of the system.

2nd law implies that disorder increases

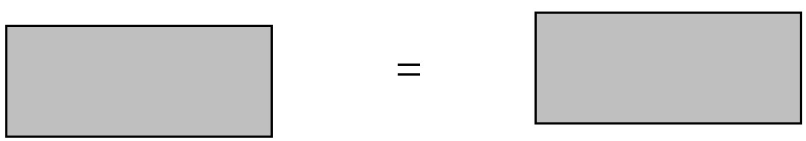
What do we mean by Ω ?

Ω is the number of ways a system can be rearranged so that it still looks the same.

Consider our example of the diffusing gas:



But



So Ω is larger in the second case.

Some questions to think over:

- Does Friction involve a change in entropy?
- Does a change of state (freezing, boiling) involve a change in entropy?
- Does writing in a computer memory involve a change in entropy?

The emergence of order (and the relation between physics, chemistry and biology)

The 2nd law of thermodynamics states that entropy (and hence disorder) can only increase.

However, the emergence of ordered systems (crystals, life, solar systems…) implies that disorder can increase locally.

The problem is similar to that of the refrigerator, which decreases entropy in the cold chamber - at the expense of increasing it in the hot chamber. Globally, entropy can only increase.

Locally decreasing entropy (increasing order) requires energy.

The “heat death” of the universe

The Universe originated in a state of extremely high temperature and small volume.

In its current state, it is still highly ordered with significant temperature differentials (stars compared to empty space).

Eventually, it must reach a state of uniform temperature (maximum disorder).

The arrow of time

Irreversible processes are associated with increasing entropy.

“Future” means more entropy than “past”

The 2nd law of thermodynamics defines the **direction of time**.

Clocks distinguish between before and after

Therefore, a clock **must** involve some irreversible process

Do clocks measure entropy?

What does this tell us about the nature of time?

There's no escaping entropy