

Lecture 8

The second law of thermodynamics

Pre-reading: §20.1

Direction of thermodynamic processes

Thermodynamic processes that occur in nature proceed naturally in one direction but not the other.

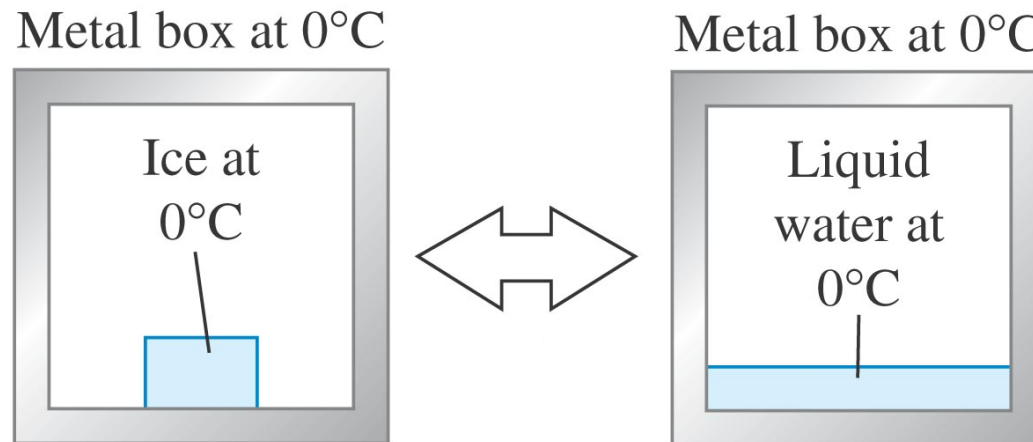
- heat flows from a hot body to a cooler body, not the other way around
- mechanical energy can be converted to heat via friction, but not back again

Why?

Reversible processes

Processes that proceed spontaneously in one direction but not the other are called *irreversible*.

A process is called *reversible* if the system and environment can be restored to their original state, leaving no residual changes anywhere.



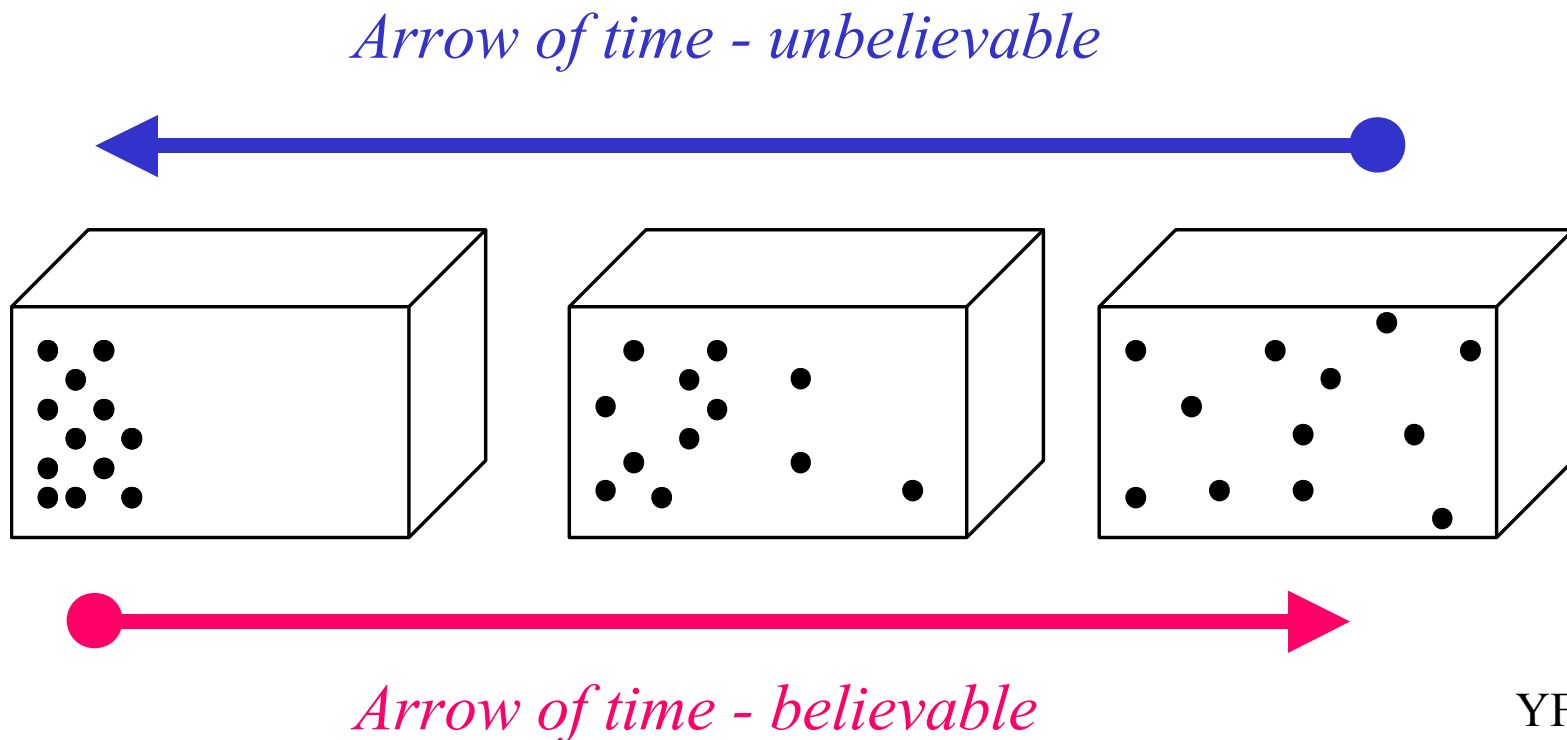
Reversible processes

A system that undergoes such a idealized reversible process is always very close to being in thermodynamic equilibrium within itself and with its surroundings.

Reversible processes are thus *equilibrium* processes, with the system always being in thermodynamic equilibrium.

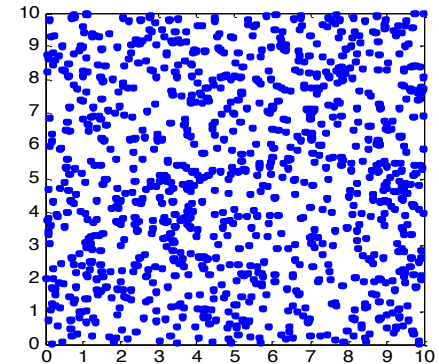
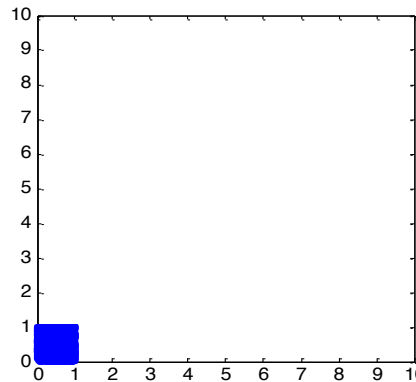
Disorder

There is a relationship between the direction of a process and the *disorder* or *randomness* of the resulting state.



Disorder

Free expansion of gas leads to more disorder.



Sliding a book across a table converts bulk kinetic energy of the book into the random motion of many molecules.

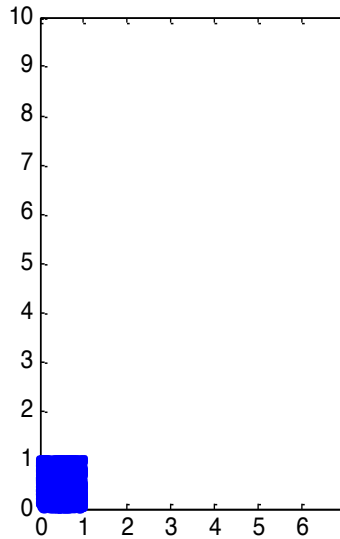
2nd law of thermodynamics

For an isolated system, the direction of spontaneous change is from

- a situation of lesser randomness (probability) to a situation of greater randomness (probability)
- order to disorder

We need a quantitative measure of disorder: we call this *entropy*.

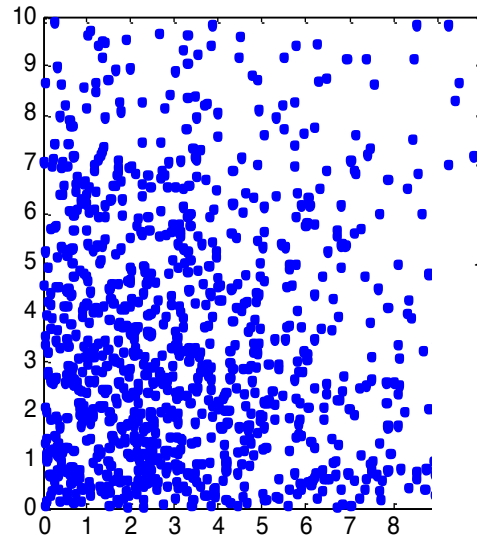
1000 particles moving
randomly in a box



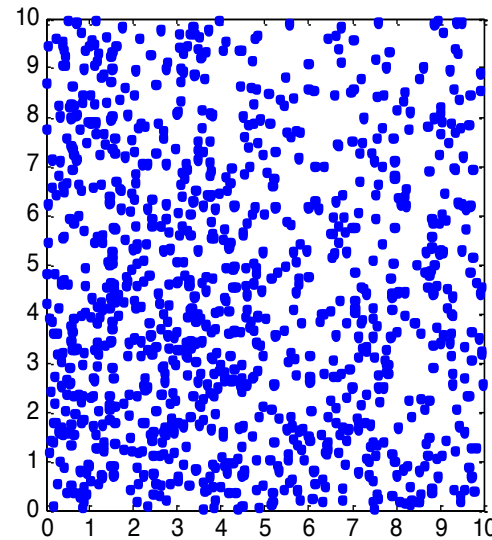
$t = 0$

**Perfume
released**

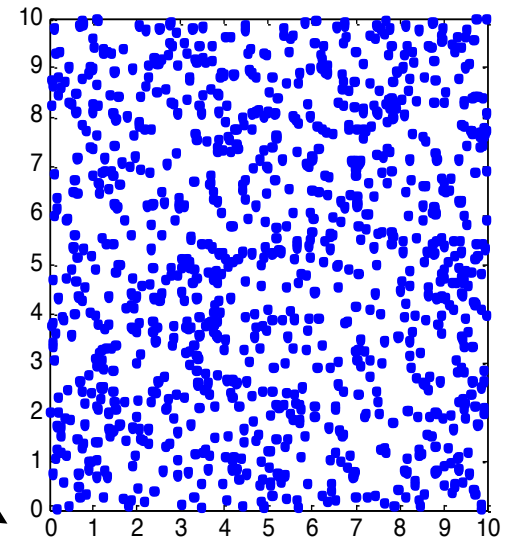
**How does it
spread?**



$t = 20$



$t = 200$



$t = 400$

Entropy



ice cube
(crystal structure)

minimum entropy
maximum order



puddle of water
(no structure)

maximum entropy
minimum order

Entropy and disorder

Consider the isothermal expansion of an ideal gas.

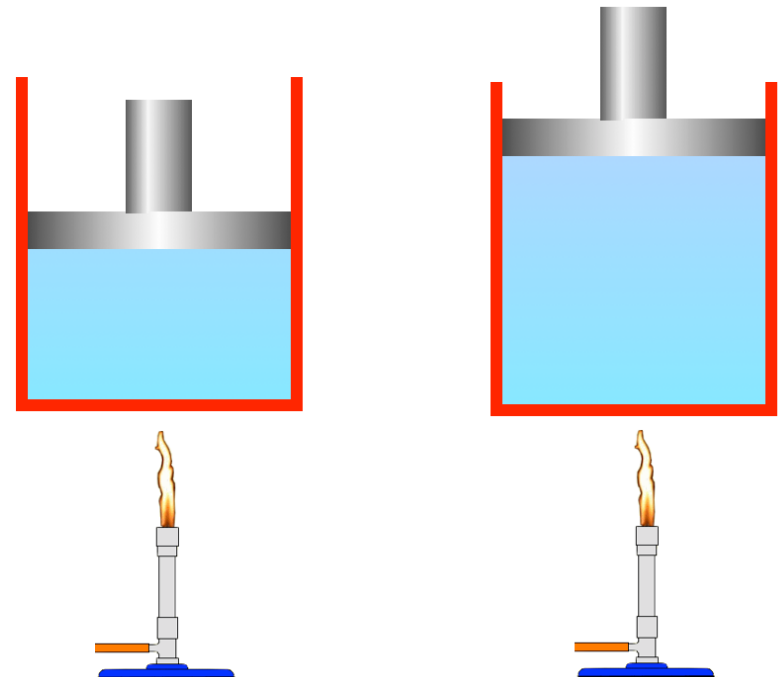
We add heat dQ and let the gas expand isothermally.

Since $\Delta T = 0$, $\Delta U = 0$, and so

$$dQ = dW = p dV = \frac{nRT}{V} dV$$

or

$$\frac{dV}{V} = \frac{dQ}{nRT}$$



Entropy and disorder

dV/V is the fractional volume change, and is a measure of the increase in disorder. dV/V is proportional to dQ/T .

We introduce the symbol S for the entropy of the system, and we define the entropy change as

$$dS = \frac{dQ}{T} \quad (\text{infinitesimal reversible process})$$

Units: J.K^{-1} **NOTE:** T must be in K!

Entropy and reversible processes

If the process is *isothermal*, then T is constant, so

$$\Delta S = S_2 - S_1 = \frac{Q}{T} \text{ (reversible isothermal process)}$$

In general, if we have a reversible change from state 1 to state 2, then

$$\Delta S = \int_1^2 \frac{dQ}{T}$$

The entropy change depends only on the initial and final states, not on the path.

Entropy in irreversible processes

Entropy is a measure of the disorder of a system, so it depends only on the current state of the system. If a system is changing from state 1 with entropy S_1 , to state 2 with entropy S_2 , the entropy change ΔS is the same for *all possible processes* between the two states.

This means we can compute entropy change for an *irreversible* process: compute the entropy change for a *reversible* process between the two states, and ΔS will be the same.

Entropy and phase change

1.0 kg of ice at 0 °C is melted to water at 0 °C.
Compute its change in entropy.

Take $L_f = 3.34 \times 10^5 \text{ J.kg}^{-1}$.



Entropy and temperature change

1.0 kg of water at 0 °C is heated to 100 °C.

Compute its change in entropy.

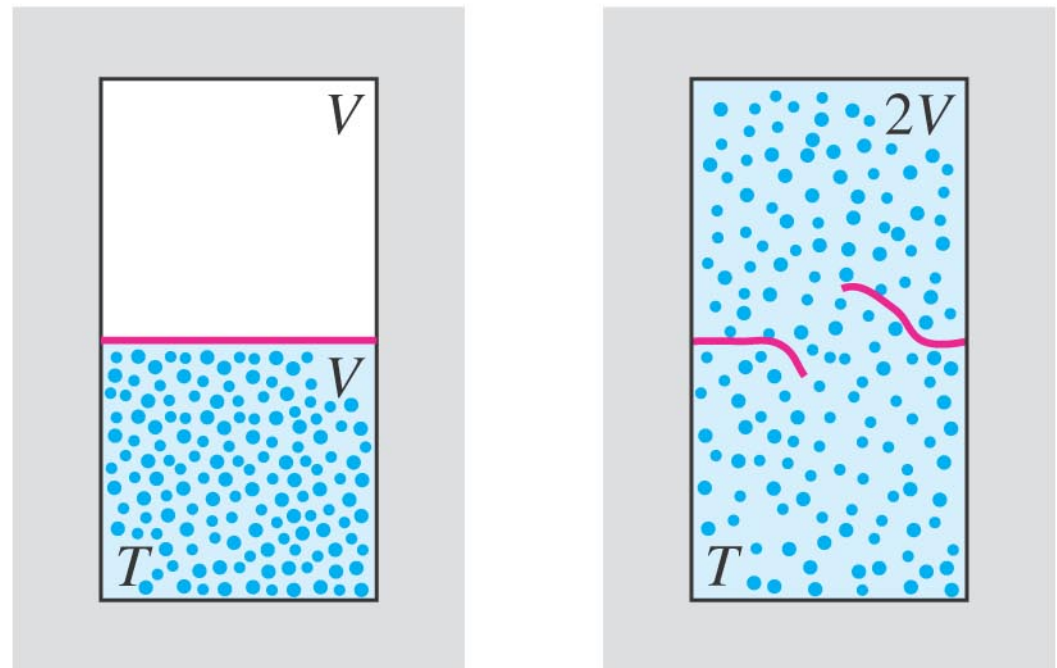
Take $c = 4190 \text{ J.kg}^{-1}.\text{K}^{-1}$.



Entropy in free expansion

A thermally insulated box is divided into two halves of volume V , one half containing n moles of an ideal gas at temperature T . The partition separating them breaks and the gas expands.

What is the entropy change?



Entropy in isothermal expansion

Consider an isothermal expansion from V to $2V$.

$$p = \frac{nRT}{V}$$

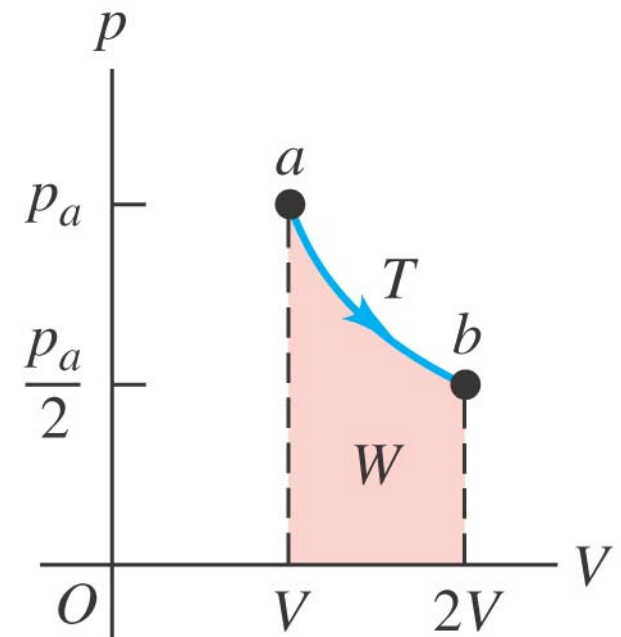
$$\begin{aligned}\text{so } W &= \int_{V_1}^{V_2} p \, dV = \int_{V_1}^{V_2} \frac{nRT \, dV}{V} \\ &= nRT \ln \frac{V_2}{V_1}\end{aligned}$$

So

$$Q = W = nRT \ln \frac{2V}{V} = nRT \ln 2$$

and

$$\Delta S = \frac{Q}{T} = nR \ln 2$$



2nd law of thermodynamics

General statement of the second law:

When all systems taking part in a process are included, the entropy remains constant or increases.

There is *no process* where the total entropy decreases, when all systems taking part in the process are included.

2nd law of thermodynamics

Note: All irreversible processes have $\Delta S > 0$
→ entropy is not a conserved quantity

For *all* processes, $\Delta S \geq 0$

Isothermal process: $\Delta S = nR \ln \frac{V_2}{V_1}$

Adiabatic process: $Q = 0$ so $\Delta S = 0$
(constant entropy)

Problem

A mug of coffee cools from $100\text{ }^{\circ}\text{C}$ to room temperature, $20\text{ }^{\circ}\text{C}$. The mass of the coffee is $m = 0.25\text{ kg}$ and its specific heat capacity may be assumed to be equal to that of water, $c = 4190\text{ J.kg}^{-1}.\text{K}^{-1}$.

Calculate the change in entropy

- (i) of the coffee
- (ii) of the surroundings



Next lecture

Heat engines

Read: YF §20.2