Thermodynamics, Part 2

Last time

Energy

First law of thermodynamics

Today

Entropy

Second law of thermodynamics

Next time

Open systems

Free energy

Spontaneity

Last time

- We started deriving classical thermodynamics from the more fundamental statistical mechanics
- The first law imposes the conservation of energy
- Energy flows into or out of a system are either work or heat:
  - Work is macroscopic movement in the direction of a macroscopic force
  - Heat is everything else

Today: Thermodynamics

Today, we will derive the remaining laws of thermodynamics—the second and the third—from statistical mechanics

In particular, we will find a more satisfactory notion of heat, and show that it flows from systems of higher temperature to those of lower temperature

Second law

While the first law says which processes are possible, the second law determines which ones occur spontaneously.

Version 1: **Entropy of an isolated system always increases, $\Delta S \geq 0$.**

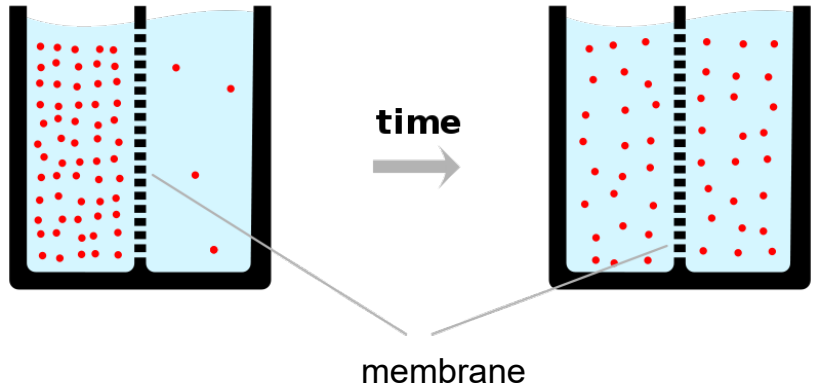
Version 2: **Heat can never pass from a colder body to a hotter one without some other change occurring.**

Version 3: **An engine cannot extract heat from a reservoir and convert it completely into work.**

Spontaneous processes: The arrow of time

Systems will spontaneously tend towards configurations with more microstates.

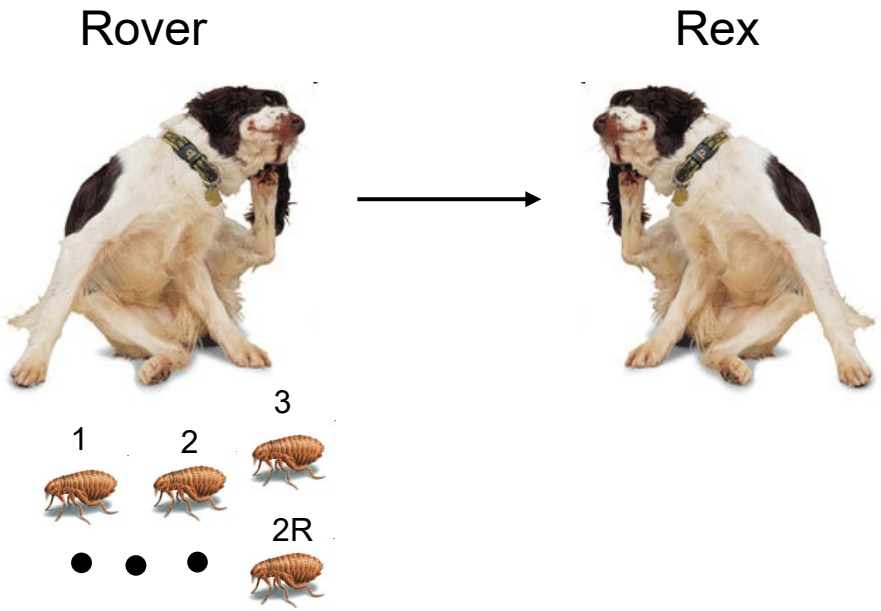
The end point of this process is equilibrium, the state of maximum microstate number.



This fact about the direction of spontaneous change determines the forward direction of time.

These statements are strictly true only in the thermodynamic limit. For small systems, there can be fluctuations away from equilibrium.

Dynamics of equilibration



Imagine the dog-flea system, starting with $2R$ fleas all on Rover.

Every second, a random flea jumps to the other dog.

Each second, the probability of a flea jumping from Rover to Rex is

$$P_{+}(N_{\text{Rover}}) = N_{\text{Rover}}/2R$$

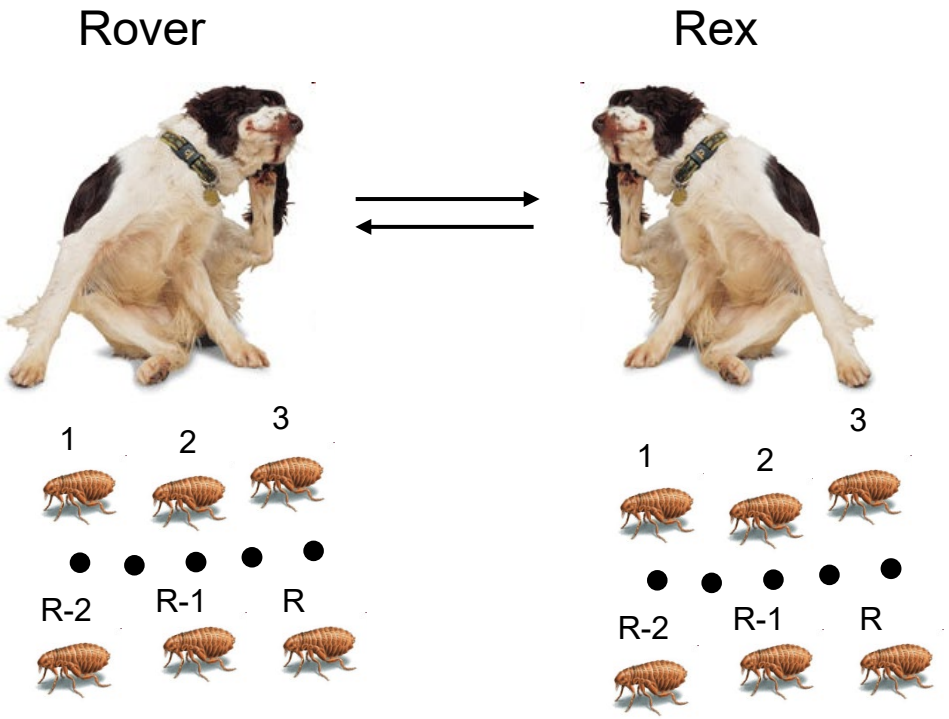
The probability of a flea jumping from Rex to Rover is

$$P_{-}(N_{\text{Rover}}) = 1\text{-}P_{+}(N_{\text{Rover}})$$

This is a system with $2R$ particles (the fleas) and two degenerate energy levels (Rover and Rex).

Dynamics of equilibration

The configuration with the maximum number of microstates—equilibrium—is that for which $N_{Rover} = N_{Rex} = R$.

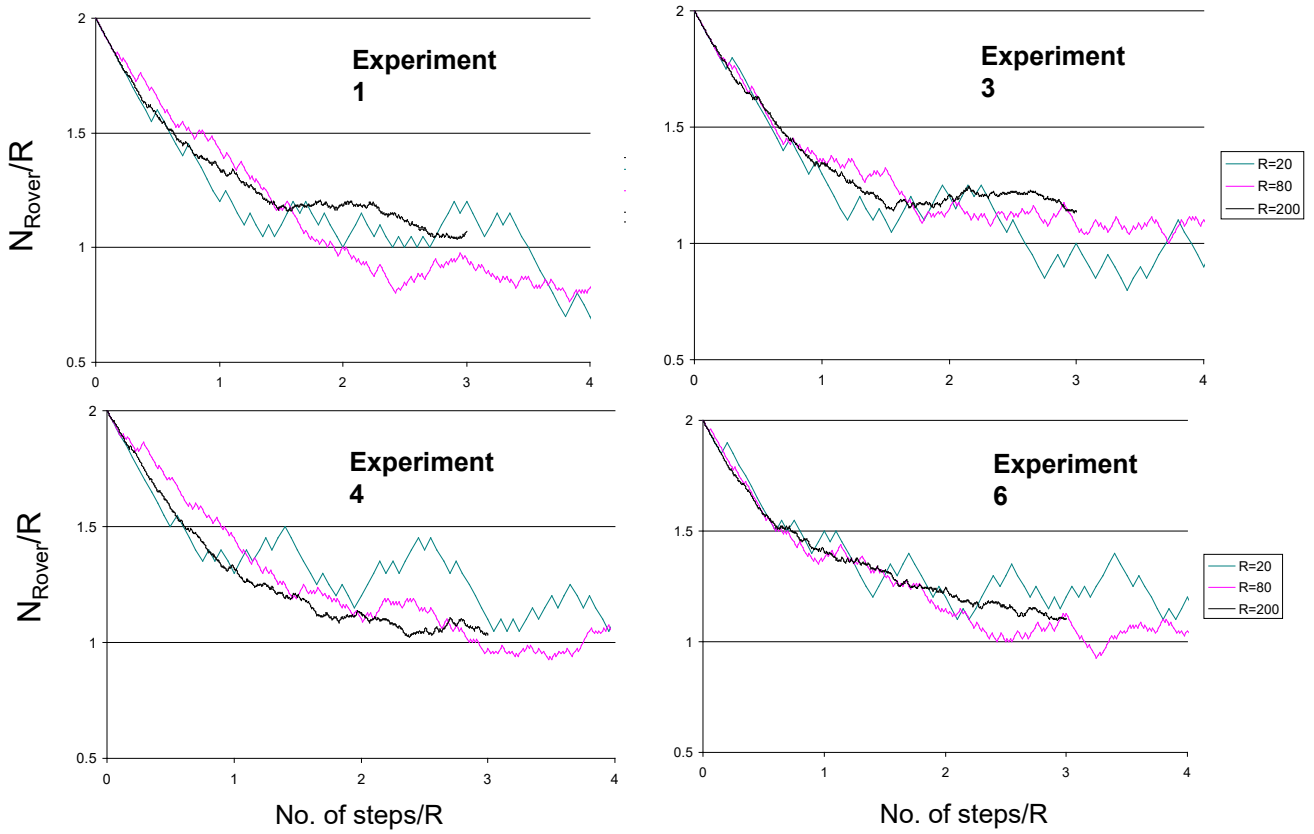


At equilibrium, the system is no longer changing measurably, but microscopic events are still occurring.

The probability of a flea jumping *off* Rover must equal the probability of one jumping *onto* Rover, i.e.,

$$N_{Rover} = N_{Rex} = R \text{ at equilibrium}$$

Dynamics of equilibration



The larger the number of fleas, the smaller the random fluctuations in N_{Rover}

Each experiment differs in the nature of the random fluctuations

N_{Rover}, averaged over the different experiments, decays to R, the equilibrium value

The direction of change by counting microstates

At constant *N* and *E*, systems spontaneously move to configurations with more microstates.

$$\Delta W \geq 0$$

For convenience, we will consider ln *W*, so the direction of spontaneous change is

$$d \ln W \geq 0$$

At equilibrium,

$$d \ln W = 0$$

Entropy

We *define*

$$S = k \ln W$$

Then, we get the first statement of the second law of thermodynamics:
In an isolated system,

$$dS \geq 0$$

Mentimeter

Macroscopic entropy

Recall that we can express the weight of a configuration as

$$W\left(n_0, n_1, n_2, \ldots\right) = \frac{N!}{n_0! n_1! n_2! \cdots}$$

Stirling's approximation gives

$$\ln W = N \ln N - \sum_i n_i \ln n_i$$

We can take the total differential dW, noting that N is constant (dN = 0):

$$d \ln W = -\sum_i \ln n_i \, dn_i$$

Macroscopic entropy

$$d \ln W = -\sum_i \ln n_i \, dn_i$$

At equilibrium, $n_i = n_0 e^{-\beta \varepsilon_i}$, so

$$\ln n_i = \ln n_0 - \beta \varepsilon_i$$

$$\begin{aligned} d \ln W &= -\sum_i (\ln n_0 - \beta \varepsilon_i) \, dn_i \\ &= -\ln n_0 \sum_i dn_i + \beta \sum_i \varepsilon_i \, dn_i \\ &= \beta dQ_{\text{rev}} \end{aligned}$$

Therefore, we get

$$dS = \frac{dQ_{\text{rev}}}{T}$$

which is the original, thermodynamic definition of entropy in terms of macroscopic variables

A reversible process is one that is always at equilibrium, i.e., infinitesimally slow

Reversible and irreversible processes

For reversible processes,

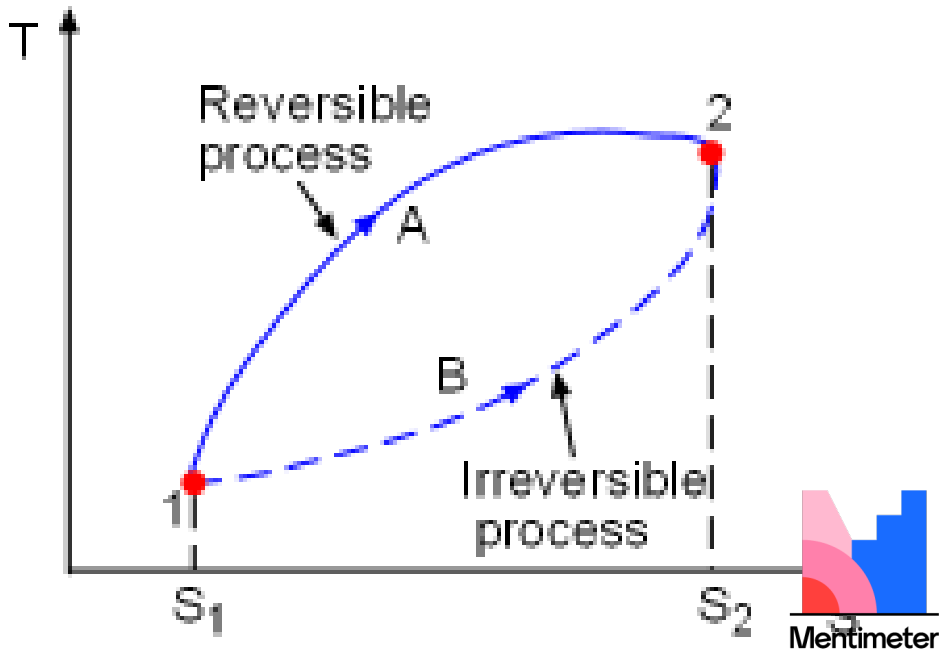
$$dS = \frac{dQ_{\text{rev}}}{T}$$

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} \geq 0$$

What about irreversible processes?

Entropy is a *state function*, i.e., depends only on the configuration. Therefore,

$$\Delta S_{\text{rev}} = S_2 - S_1 = \Delta S_{\text{irrev}}$$



Mentimeter

Entropy from the partition function

It is also possible to show that the total entropy can be calculated from the partition function (derivation in textbook):

$$S = \frac{U}{T} + Nk \ln q$$

$$S = NkT \frac{\partial \ln q}{\partial T} + Nk \ln q$$

$$S = Nk \frac{\partial}{\partial T} (T \ln q)$$

The point here is to illustrate the fact, which we saw before, that derivatives of the partition function contain vital macroscopic information. There is no need to memorise this formula, which is not particularly useful.

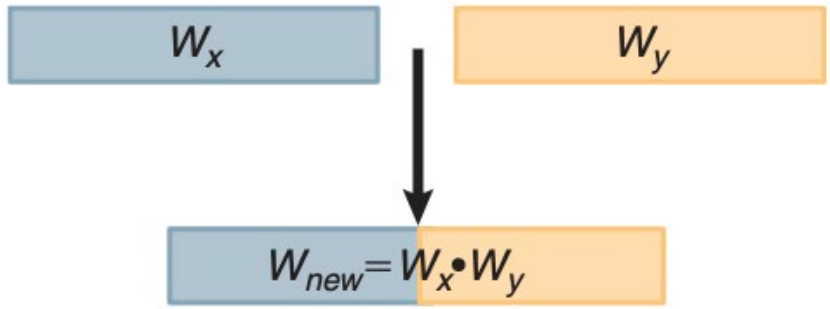
Entropy is additive (extensive)

For two independent, isolated systems:

$$W_{\text{total}} = W_x \cdot W_y$$

$$\ln W_{\text{total}} = \ln W_x + \ln W_y$$

$$S_{\text{total}} = S_x + S_y$$



Which way does heat flow?

If we bring two isolated systems into thermal contact, while keeping them isolated from the rest of the universe:

$$dS_{\text{total}} = dS_x + dS_y \geq 0$$

$$\frac{dQ_x}{T_x} + \frac{dQ_y}{T_y} \geq 0$$

$$dQ_x \left(\frac{1}{T_x} - \frac{1}{T_y} \right) \geq 0$$

Heat flows into x ($dQ_x > 0$) if

$$T_x < T_y$$

Another formulation of the second law: Heat flows spontaneously from hot to cold

Mentimeter

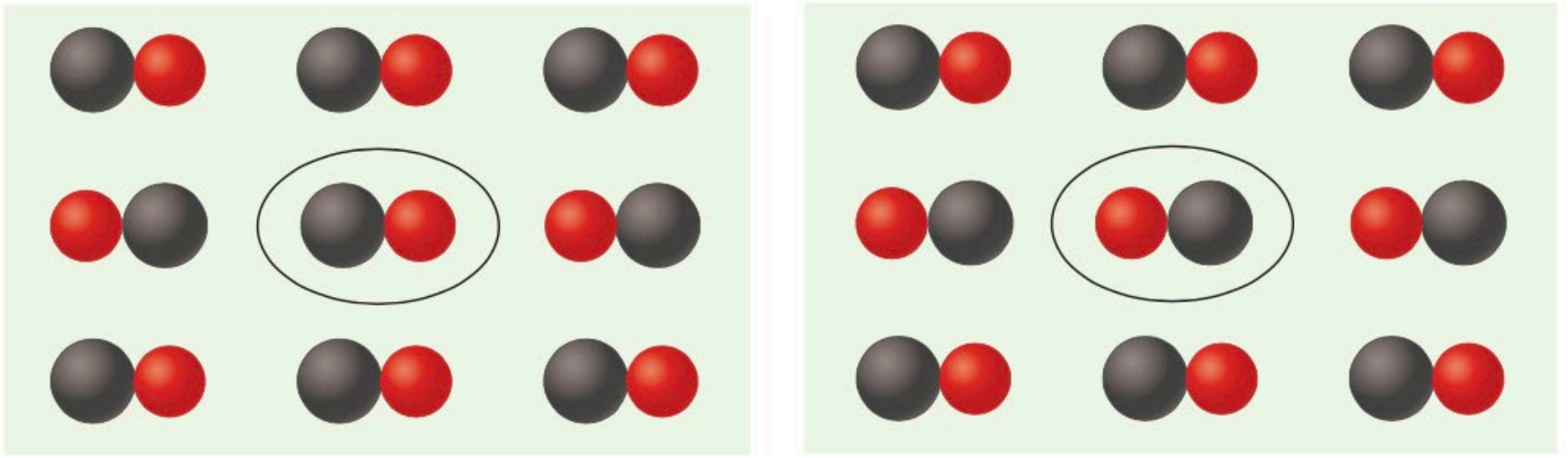
Third law

Entropy of a system approaches a constant value as $T \longrightarrow 0$.

For a perfect crystal of any pure substance, there is only one possible microstate (the ground state) at $T = 0$, so $S(0) = k \ln(1) = 0$.

A system such as a glass (we'll return to it in a few lectures) can have more than one minimum microscopically distinct energy state. The resulting non-zero entropy at $T = 0$ is called the "residual entropy".

Residual entropy



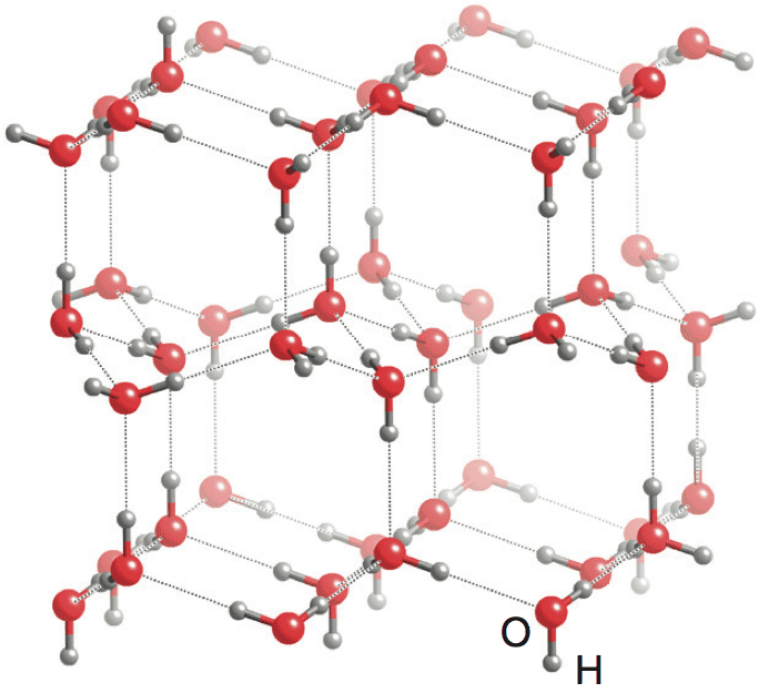
In CO, each molecule can assume one of two orientations, giving

$$S_{\text{residual}} = Nk \ln 2$$

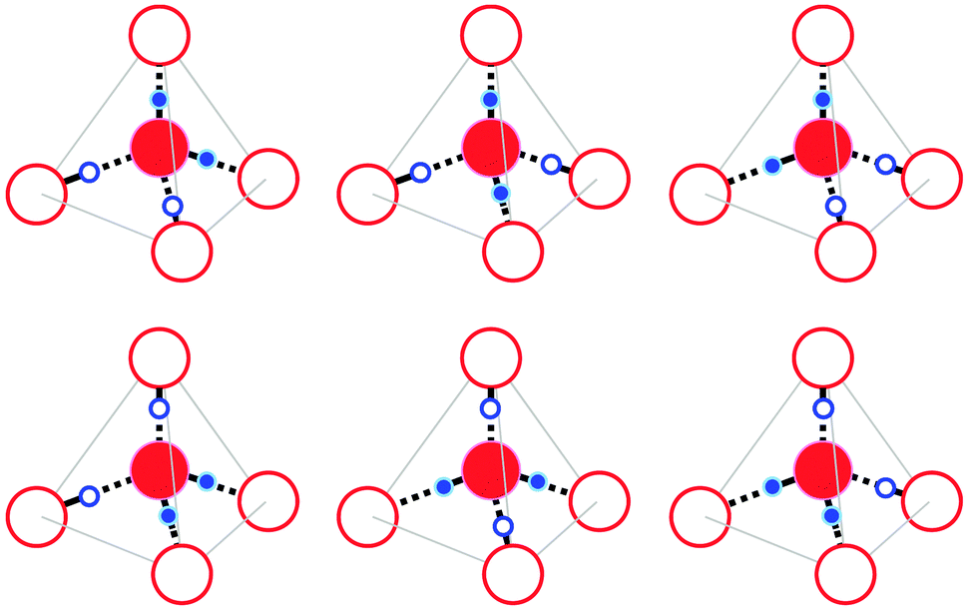
Mentimeter

Residual entropy in ice

Water ice has residual entropy because of the many ways of arranging the covalent and hydrogen bonds



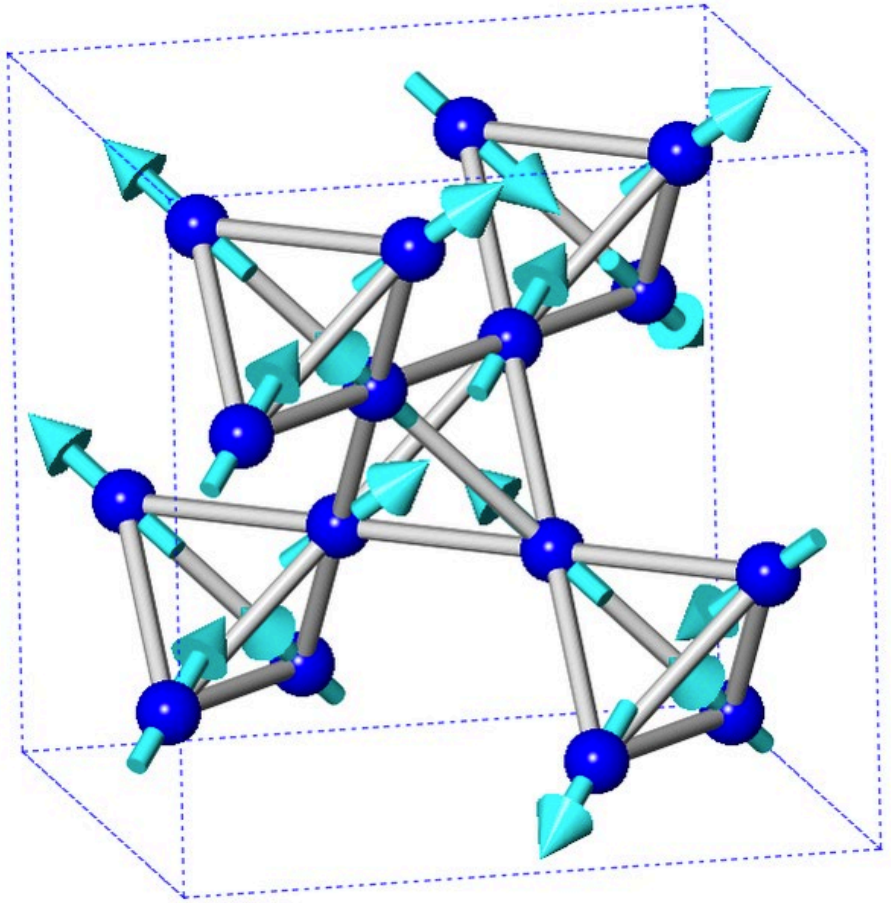
Out of the four hydrogens around each oxygen, two are close and two are far



Residual entropy in spin ice

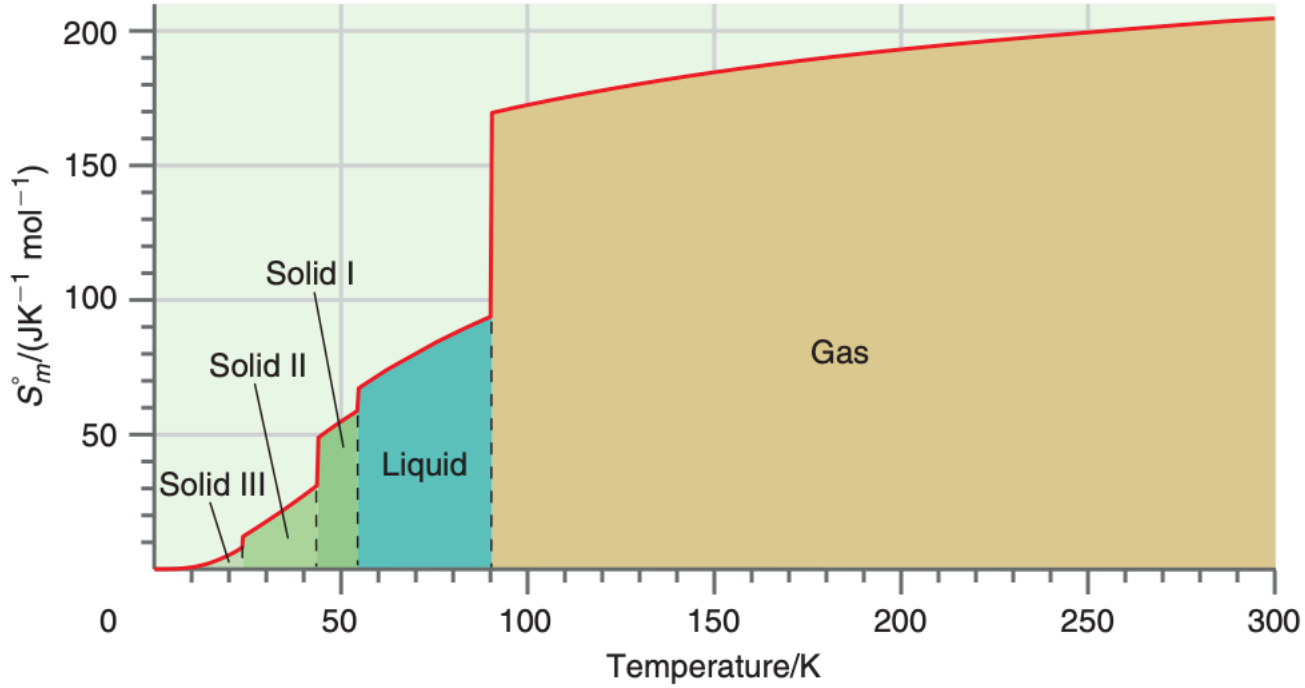
An analogous situation—spin ice—arises in some magnetic materials, where the spins cannot all align, a phenomenon called frustration

The first spin-ice materials to be discovered were the pyrochlores $Dy_2Ti_2O_7$ (dysprosium titanate) and $Ho_2Ti_2O_7$ (holmium titanate)



Absolute entropy

The third law allows the evaluation of absolute entropies relative to the reference at $T = 0$.



Summary

Key points:

- Entropy measures the statistical weight of the configuration and always increases in an isolated system
- Heat flows from higher temperature to lower
- Residual entropy at absolute zero is possible in glassy or frustrated systems

Next time

Next time, we will consider what governs spontaneity in systems that are *not* isolated, using the concept of free energy.

Reading:

E&R *Phys. Chem.* 32.6, 6.1

or E&R *Thermo.* 15.6, 6.1