# Philosophy of Space and Time: Week 10

## Thermodynamics and Statistical Mechanics

Recall from last week that *statistical mechanics* is the constructive theory corresponding to *thermodynamics*, which is a principle theory. Statistical mechanics aims to explain and predict thermodynamic phenomena by starting from classical or quantum microdynamics and deriving statements about the large scale, aggregate behaviour of collection of particles. Some examples of statistical mechanical reductions are:

(a) Temperature in thermodynamics is associated with the mean kinetic energy of particles in statistical mechanics.

(b) Pressure in thermodynamics is associated with the force per unit area exerted by particle collisions on the walls of a container, in statistical mechanics.

(c) An increase in temperature tends to lead to an increase in pressure (a phenomenological result in thermodynamics) because increasing the mean kinetic energy of particles tends to increase the frequency and force of their collisions with the walls of the container.

## Entropy

In the philosophy of thermodynamics and statistical mechanics, there are three key notion of entropy:

1. Thermodynamic entropy, $S_{\mathrm{TD}}$.
2. Boltzmann entropy, $S_{\mathrm{B}}$.
3. Gibbs entropy, $S_{\mathrm{G}}$.

Entropy in thermodynamics, represented by $S_{\mathrm{TD}}$, can only increase with time (this is a consequence of the second law of thermodynamics). This is not true for the statistical mechanical notion of entropy, $S_{\mathrm{B}}$. We won't worry about $S_{\mathrm{G}}$ (another statistical mechanical notion of entropy) here—though it's worth noting that much work has been done recently attempting to make precise the connections between $S_{\mathrm{TD}}$, $S_{\mathrm{B}}$, and $S_{\mathrm{G}}$ (see e.g. papers by David Wallace).

### Boltzmann entropy

The Boltzmann entropy $S_{\mathrm{B}}$ associated with a given distribution of particles can be expressed as

$$S_{\mathrm{B}} = k_B \log \Omega,$$

where $k_B$ is *Boltzmann's constant*, and $\Omega$ is the number of possible particle arrangements (so-called *microstates*) associated with a given macroscopic, thermodynamic configuration of the system in question (a so-called *macrostate*).

- The more ways there are to arrange the particles of the system in question to produce its microstate, the higher that system's Boltzmann entropy.
- Roughly, Boltzmann entropy measures how much (or little) we can know about the microstate of a system, given its macrostate. (High entropy means we know little about the system's exact microstate.)

## Time Asymmetry

Recall our puzzle from last week: How can it be that the laws of thermodynamics are time asymmetric, but the laws of their constructive underpinning—statistical mechanics—are time reversal invariant (i.e., time-symmetric)? Let's now explore two possible answers:

1. Boltzmann's *H-theorem*.
2. Phase space considerations.

## The H-Theorem

Boltzmann claimed to show, in the proof of his so-called *H-theorem*, that given a random distribution of particles interacting with each other, $S_{\mathrm{B}}$ *must* subsequently increase over time.[1]

- But everything in Boltzmann's reasoning depends upon the time-symmetric physics of statistical mechanics! So how does he derive a time-asymmetric law? (This is sometimes known as *Loschmidt's paradox*.)
- In his H-theorem proof, Boltzmann implicitly made use of an assumption now known as the *Stosszahlansatz*: that the initial velocities of colliding particles are uncorrelated (i.e., are not related), but the final (i.e. post-collision) velocities *are* correlated (i.e., are related in some way).
- It's now fairly widely accepted that *this* assumption imported time asymmetry into Boltzmann's proof—and that *this* is what enabled Boltzmann to derive his time-asymmetric result.

These days, most people back off claims to the effect that statistical mechanical entropy $S_{\mathrm{B}}$ *must* increase (in light of e.g. the Poincaré recurrence theorem we saw last week), instead making the weaker claim that $S_{\mathrm{B}}$ is only *highly likely* to increase. Still, many claim that this is sufficient to recover time-asymmetric thermodynamic behaviour from time-symmetric statistical mechanical laws. Below, we'll spell out the details of one argument which is often given here (sometimes called the *neo-Boltzmannian account*).

## Phase Space

The *phase space* for a system of $N$ particles is a $6N$-dimensional space, of all possible particle configurations. (Why $6N$ dimensions? Three dimensions for the position, and three dimensions for the momenta, of all $N$ particles under consideration.) A path through phase space traces one possible *history* of the system under consideration.

[1] Actually, whether Boltzmann was talking about $S_{\mathrm{B}}$ in his proof is a subtle matter; we'll pass over this.

- An alternative explanation for the emergence of time-asymmetric thermodynamic behaviour from time-symmetric statistical mechanical microphysics appeals to the fact that high Boltzmann entropy macroconditions (by definition) correspond to large volumes of phase space, while low Boltzmann entropy conditions correspond to small volumes of phase space.

- If we assume that a system wanders around the phase space in such a way as to spend equal times in all areas (**Question**: Is this assumption reasonable? Doesn't it depend on the details of the dynamics?), then it's overwhelmingly likely, given that it starts in a low entropy region, that it'll enter a higher-entropy region (**Further questions**: Doesn't this require a probability measure over the initial macrostate? How could one be obtained? And doesn't this depend upon the initial state of the system being a low-$S_{\mathrm{B}}$ state?)

We could provide an answer to our first question if we could establish *ergodicity*: that the time a system spends in a phase space region is proportional to its area. We could answer the final further question by appeal to some kind of *past hypothesis* (see below).

## The Past Hypothesis

If we want statistical mechanics to underwrite thermodynamic behaviour *for all time*, then this seems to require pushing the initial low-entropy state *to the start of the universe*—this is Albert's *past hypothesis*.

- The idea is that we account for thermodynamic asymmetries by appeal to an asymmetric boundary condition, even though the micro-laws themselves are symmetric.

- Given a low-$S_{\mathrm{B}}$ initial state, it looks like the Bolzmannian phase space story above will then go through.

But here are some worries:

1. Without specifying the dynamics, there's no guarantee that a system beginning in a low-$S_{\mathrm{B}}$ microstate will transition to higher-$S_{\mathrm{B}}$ states.

2. To claim that systems beginning in low-$S_{\mathrm{B}}$ microstates are *likely* to transition to higher-$S_{\mathrm{B}}$ states seems to require a probability distribution over the initial low-$S_{\mathrm{B}}$ macrostate—where does this come from?
3. Even if we embrace Albert's past hypothesis, does this actually guarantee thermodynamic behaviour?
4. Earman (2006): Can the concept of entropy coherently be applied to the universe as a whole?

Wallace thinks that we should replace this kind of past hypothesis with (what is effectively) a simpler, more direct one: the initial conditions of the universe are such as to guarantee thermodynamic behaviour.