Irreversibility and the Second Law in Thermodynamics and Statistical Mechanics

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The law that entropy always increases,—the second law of thermodynamics—holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much the worse for Maxwell's equations. If it is found to be contradicted by observation—well, these experimentalists bungle things some times. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

A. Eddington
The Nature of the Physical World

Outline

Varieties of Irreversibility

The Second Law in Thermodynamics

The Second Law in Statistical Mechanics

(Atemporal) Gibbsian Thermodynamics

5 kinds (at least)

1. failure of time-reversal invariance (semi-group dynamics, ...)
2. constraints on initial conditions (Past Hypothesis, ...)
3. system coupled to coarse-grained environment (Zwanzig coarse-graining, master equations, ...)
4. constraints from physical geometry (balancing a perfect die, ...—not recognized in literature)
5. irrecoverability (friction, ...)

- some systems manifest several: Lindblad equation has semi-group dynamics, coarse-grained coupling
- quasi-static thermodynamical processes, sometimes called “reversible”, are irrelevant
- entropy increase *per se* is irrelevant (though perhaps not *per accidens*)

Minus-First Law

spontaneous approach to equilibrium enters into classical thermodynamics in characterizing admissible thermodynamical processes (on standard view)

quasi-static sequence: knock system "infinitesimally" out of equilibrium; allow it to settle into a neighboring equilibrium

Minus-First Law versus Second Law

spontaneous approach to equilibrium

is not equivalent to

Clausius/Kelvin Postulates (irrecoverability)

Minus-First Law has nothing to do with irreversibility (in the relevant sense)

Varieties of Irreversibility

The Second Law in Thermodynamics

The Second Law in Statistical Mechanics

(Atemporal) Gibbsian Thermodynamics

irrecoverability

system + (relevant) environment transition

$$\langle \sigma_i,\, w_i \rangle \xrightarrow{T} \langle \sigma_f,\, w_f \rangle$$

is *recoverable* if and only if

there exists T^* such that

$$\langle \sigma_f,\, w_f \rangle \xrightarrow{T^*} \langle \sigma_i,\, w_i \rangle$$

no other constraints on T *or* T^*

- T can be non-quasi-static, non-adiabatic, entropy increasing or decreasing, cyclic, whatever
- don't require entire rest of world to return to initial state (radiation emitted by star in M80), only what "directly interacts with system"
- T^* need not be the "reverse" of T in any sense other than returning system $+$ environment to initial states
- nothing is said or implied about a "direction of time"

The Second Law

The Clausius Postulate

A recoverable transformation whose only final result is to transfer heat from a source at a lower temperature thoughout to one at a higher throughout is impossible.

The Kelvin Postulate

A recoverable transformation whose only final result is to transform into work heat extracted from a source that is at the same temperature throughout is impossible.

- all physically equivalent (ignoring possibility of “negative temperature”)
- delimitation of class of physically possible transformations
- *possible* here means: realizable in the actual world (not: solution to equations of motion or field equations for some initial conditions or boundary conditions, whether consistent with actual world or not)

fundamental irreversibility is irrecoverability

grounded in asymmetry of possibility of transforming work into heat and vice-versa

N.b.: not the impossibility of transforming heat entirely into work *simpliciter*—allow a gas-filled piston coupled to a heat bath to slowly expand isothermally. Rather, there is no *recoverable* engine whose sole result is that heat is transformed entirely into work, but there is one whose sole result is that work is transformed entirely into heat.

fundamental irreversibility is not entropy non-decrease:

- derivable from CK, but not conversely
- not used to prove any other propositions of interest
- CK implies many other propositions of interest (Carnot's Theorem, definition of absolute temperature, definition of entropy, ...)

fundamental asymmetry is not temporal

The Anti-Second Law

The Anti-Clausius Postulate

A recoverable transformation whose only final result is to transfer heat from a source at a higher temperature thoughout to one at a lower throughout is impossible.

The Anti-Kelvin Postulate

A recoverable transformation whose only final result is to add heat to a body after work is performed by a system whose potential energy is constant throughout is impossible.

- ACK is not the time-reverse of CK in any sense
- ACK implies entropy non-increase
- ACK is the contrariety, not contradiction, of CK (can both be false, but not both true)

some philosophers have argued that the irreversibility intrinsic to some versions of the Second Law are not temporal; they base their arguments on one (or both) of the two following claims:

1. there are atemporal axiomatizations of thermodynamics
2. it more fruitful to think of the irreversibility as atemporal

I find these arguments inadequate:

1. one cannot formulate, much less derive, CK in such axiomatizations, only entropy non-decrease
2. fruitfulness is irrelevant here: it's simply the case that the fundamental asymmetry is atemporal

Boltzmann's Law

Consider an arbitrary instant of time $t = t_1$ and assume that the Boltzmann entropy of the system at that time, $S(t_1)$, is far below its maximum value. It is then highly probable that at any later time $t_2 > t_1$ we have $S(t_2) \geq S(t_1)$.

the irreversibility is fundamentally and intrinsically temporal

(I don't know how to do this for Gibbs)

the fundamental irreversibility of thermodynamics cannot be reduced to that of statistical mechanics *simpliciter*

a proposition containing no temporal concepts cannot be reduced to one containing them, without introducing by hand extrinsic bridging principles that "de-temporalize" the latter

Varieties of Irreversibility

The Second Law in Thermodynamics

The Second Law in Statistical Mechanics

(Atemporal) Gibbsian Thermodynamics

why is thermodynamics atemporal?

Uffink (2001): thermodynamics has no equations of motion because "thermodynamical processes only take place after an external intervention on the system" $\Rightarrow$ *non sequitur*

Rather: thermodynamics is intrinsically atemporal because it admits an atemporal interpretation (*not*: axiomatization); thus, any temporal interpretation must import temporal concepts extrinsic to the theory itself

equilibrium (quasi-static) processes

fix a continuous curve γ on equilibrium space of states of a given system ("quasi-static"); approximate γ as follows:

1. step 0: label endpoints 'σ_0' and 'σ_1'
2. step 1: pick point in the middle of γ, label it '$\sigma_{\frac{1}{2}}$'
3. step 2: pick points between σ_0 and $\sigma_{\frac{1}{2}}$ and between $\sigma_{\frac{1}{2}}$ and σ_1, labeled respectively '$\sigma_{\frac{1}{4}}$' and '$\sigma_{\frac{3}{4}}$'
4. ...
5. step n: pick points between σ_0 and $\sigma_{\frac{1}{2^{n-1}}}$, ..., labeled respectively '$\sigma_{\frac{1}{2^n}}$', ...
6. we construct the limit so that $2^n \Delta Q(\sigma_i, \sigma_{i+1})$ goes to zero uniformly (and the same for work performed)

in the limit, we have a dense collection of points, *i.e.*, they uniquely determine γ

interpretation

not: temporally successive states of numerically the same system

rather:

1. at each step, we imagine there are $2^n + 1$ copies of the same system, each in a different state, labeled appropriately so that the i^{th} system is in the state σ_i
2. we calculate the transformations that would take σ_i to σ_{i+1}
3. in the limit, we obtain an "infinite sequence" of copies of the same system, each in a state "infinitesimally differing from the next", with changes in heat and work vanishing to first-order between successive states

explicitly atemporal

by the way: resolves Norton's "paradox" of infinite-time processes; the idealization here is no worse than the thermodynamic limit in statistical mechanics

non-quasi-static processes

do the same, except don't require that $2^n \Delta Q(\sigma_i, \sigma_{i+1})$ goes to zero in the limit