Title: Ambiguities in order-theoretic formulations of thermodynamics

Date: Mar 21, 2014 11:30 AM

URL: http://pirsa.org/14030093

Abstract: Since the 1909 work of CarathÃ©odory, an axiomatic approach to thermodynamics has gained ground which highlights the role of the the binary relation of adiabatic accessibility between equilibrium states. A feature of CarathÃ©dory's system is that the version therein of the second law contains an ambiguity about the nature of irreversible adiabatic processes, making it weaker than the traditional Kelvin-Planck statement of the law. This talk attempts first to clarify the nature of this ambiguity, by defining the arrow of time in thermodynamics by way of the Equilibrium Principle (``Minus First Law"). It then examines the extent to which the 1989 axiomatisation of Lieb and Yngvason shares the same ambiguity, despite proposing a very different approach to the second law.

≺ Ambiguities in order-theoretic formulations of thermodynamics

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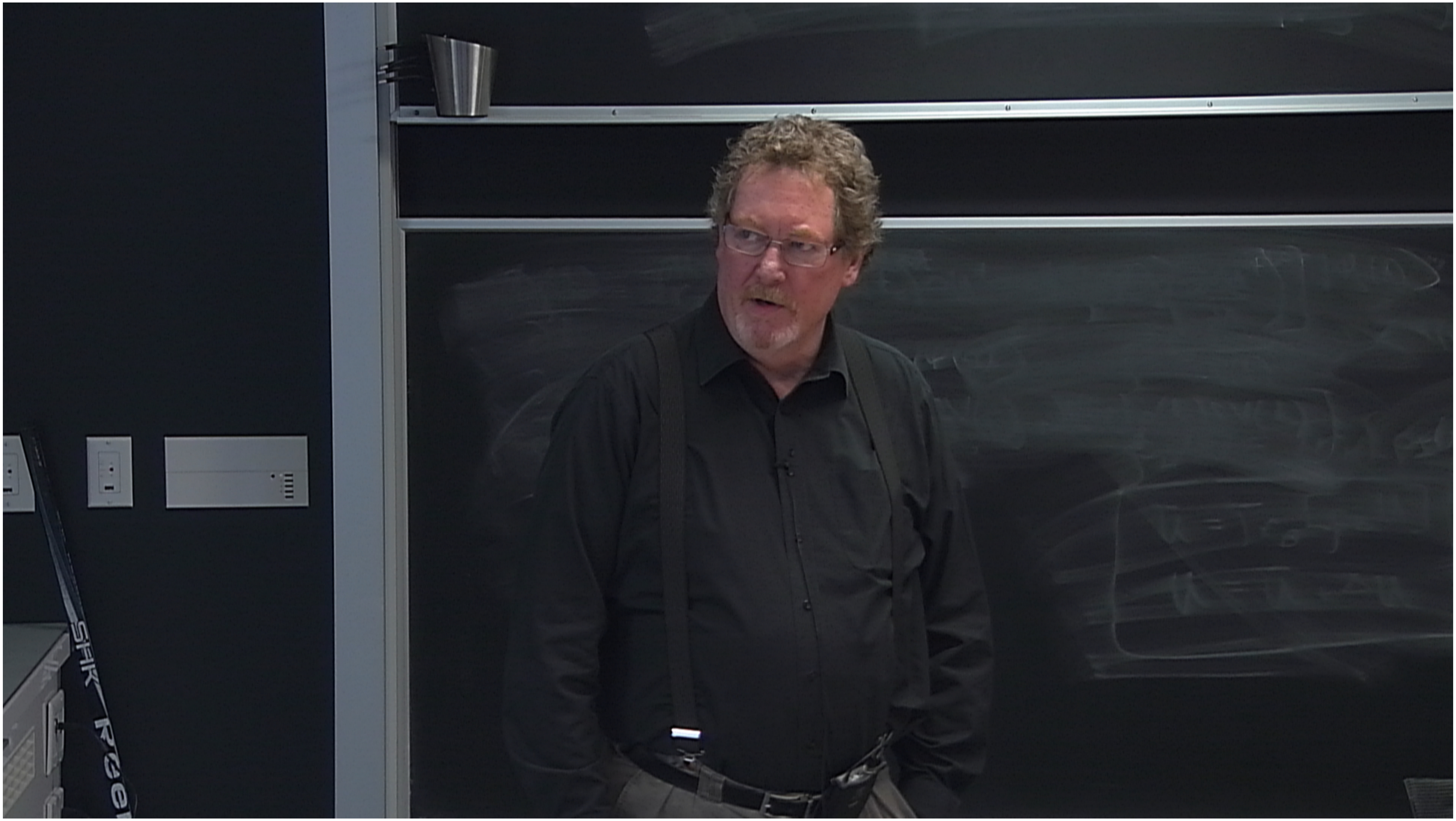

Why three laws?

"The first law says you cannot get anything for nothing; the second law says you can get something for nothing, but only at absolute zero; the third law ... implies that you cannot get to absolute zero. The fourth law ... does not fit into this summary. In fact, there cannot really be a fourth law for the following reason.

There were three main personalities whose work led to formulation of the first law: J. R. Mayer, H. von Helmholtz, and J. P. Joule. Two people, Carnot and Clausius, were the main pioneers of the second law, while only one person, Nernst, was involved in the original statement of the third law. Thus nobody can formulate a fourth law. Now the zeroth law does not fit into this scheme, but then everybody knows about that law!"

P.T. Landsberg 1990, p. 10

And what about the minus first law??

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Constantin Carathéodory 1873-1950

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1909 work:

heat not fundamental notion; systems allowed have an arbitrary number of degrees of freedom

thermodynamics itself provides a (pre-0th, -1st, -2nd law) arrow of time:

the equilibrium principle

Uffink (2001):

"… a fundamental presupposition in classical thermodynamics is that isolated systems attain or approach an equilibrium state, and, once they reach equilibrium, they remain there as long as they are left to themselves. In fact, equilibrium is often defined as a state which will not change in the future, if the system is left to itself. Changes in the past, in contrast, are allowed or even explicitly presupposed. This gives a clear time-reversal non-invariant character to thermodynamics. …

Planck (1897) too emphasised that the approach to equilibrium has nothing to do with the second law. This aspect of time-reversal non-invariance is woven much deeper in the theory."

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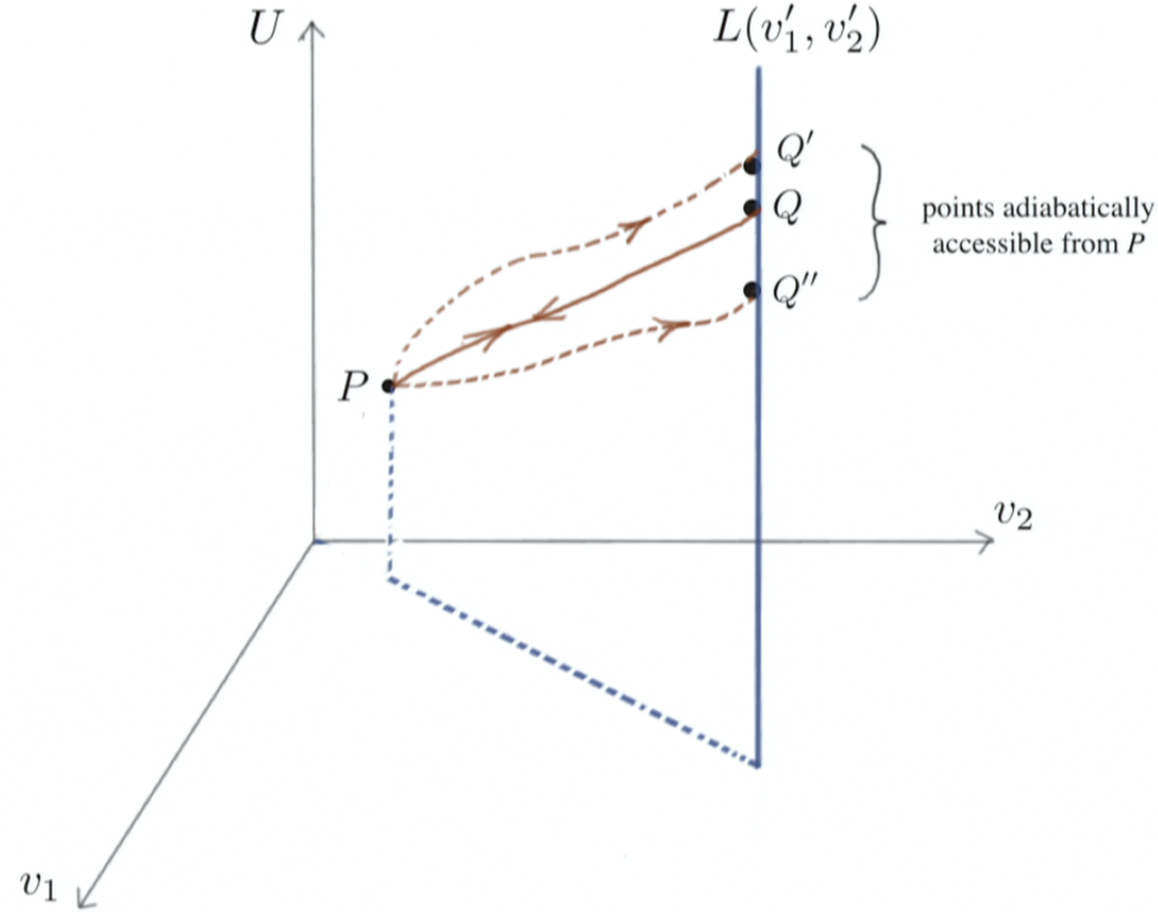
Uhlenbech and Ford (1963): the "zeroth law"

Brown and Uffink (2001): the "minus-first law"

When an isolated system finds itself in a non-equilibrium state within a finite fixed volume, it will spontaneously attain a unique state of equilibrium.

The arrow of time can be chosen to be that relative to which systems equilibrate.

section 9, Carathéodory (1909)



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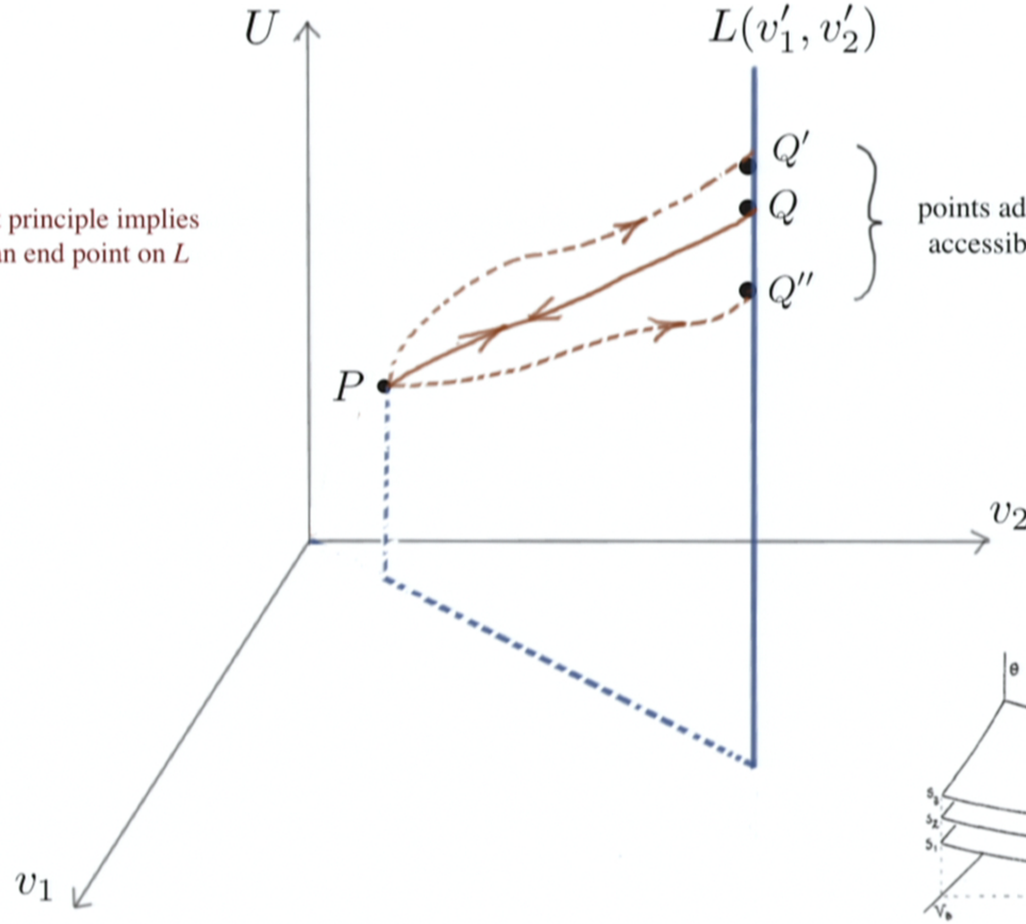
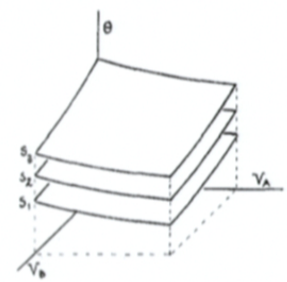
i-point principle implies
Q is an end point on L





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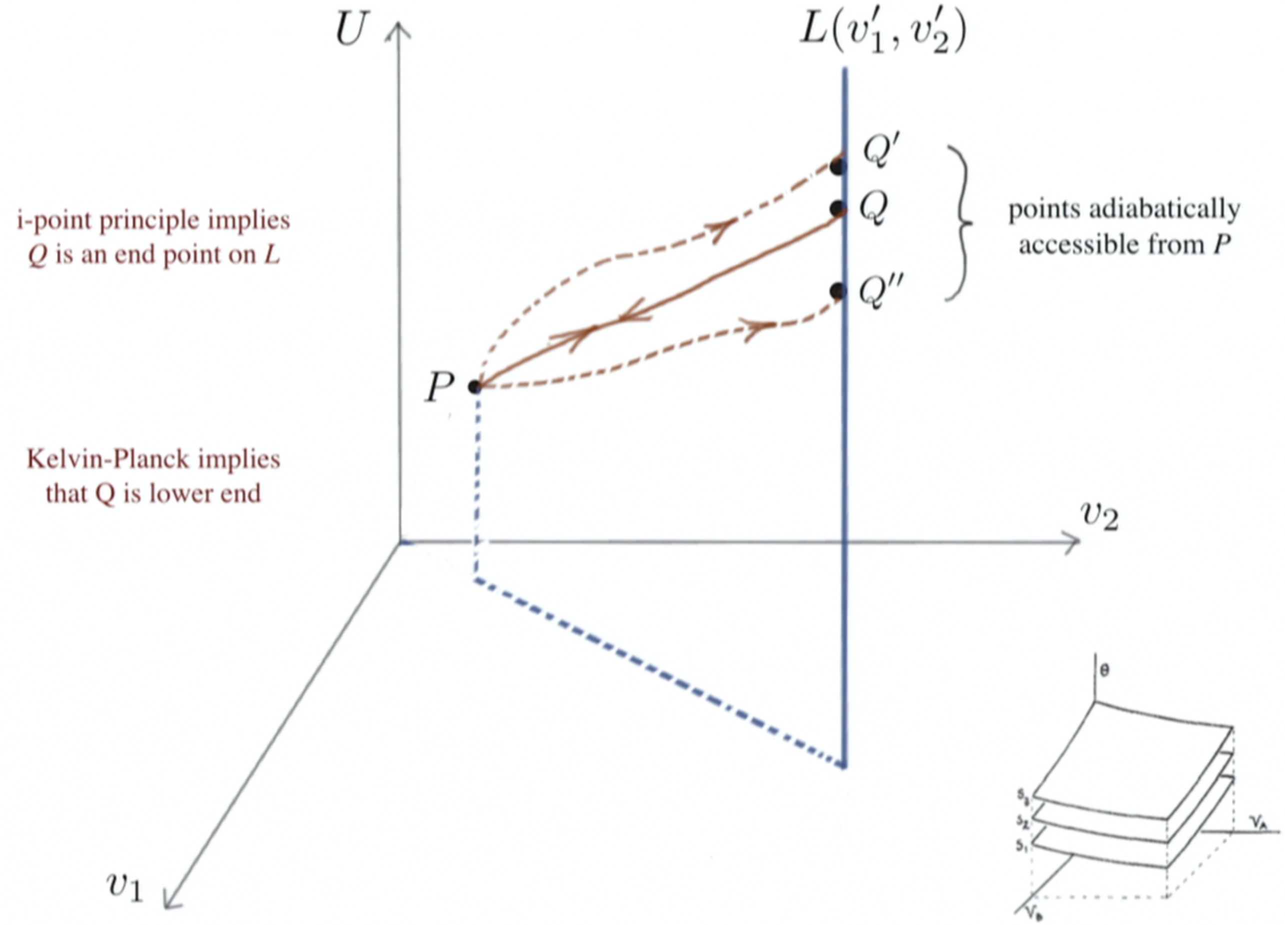

features of Carathéodory's argument

argument presupposes $\prec$ is (locally) a preorder (reflexive and transitive)

role of continuity assumptions: Landsberg (1961) and Turner (1966)

temporal metric issue

Kelvin-Planck implies Carathéodory (Crawford-Oppenheim (1961) and Landsberg (1964))
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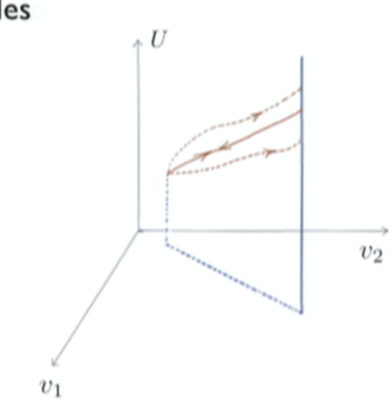
Landsberg (1956), Dunning-Durning (1965), Sears (1966)

Carathéodory's principle implies:

- in adiabatic processes taking a given state to a final configuration, the final internal energy is
  either greater for irreversible processes than for reversible ones,
  or less for irreversible processes than for reversible ones

- *either* it is impossible to create a cyclic process that converts heat entirely into work,
  or it is impossible to create a cyclic process that converts work entirely into heat

- the efficiency of a Carnot cycle is $\eta = 1 - \frac{T_2}{T_1}$ and all other cycles
  either have lower efficiency,
  or have greater efficiency



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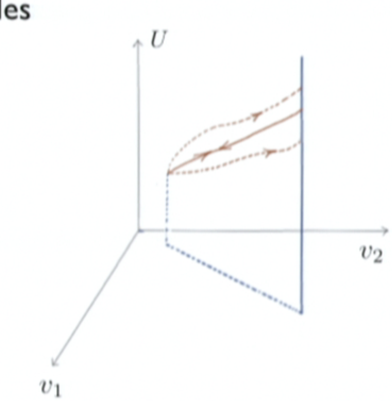

resolving the ambiguity: appeal to experience

"which needs to be ascertained in relation to a single experiment only" (1909) See also (1925)

relative to the arrow of time defined by the Equilibrium Principle

the 1999 Lieb-Yngvason formulation

principal motivations:

radical rejection of heat "No one has ever seen heat, nor will it ever be seen, smelled or touched."

formulation deals with *possible* processes, not *impossible* processes

a "simple" definition of entropy, which requires no real analysis

> "…entropy and its essential properties can best be described by maximum principles instead of equations among derivatives"

and which is based on an exact numerical representation of the adiabatic accessibility relation $\prec$ (subject to certain axioms) and no more.

not all thermodynamic parameters are assumed to be differentiable

the 1999 Lieb-Yngvason formulation

principal motivations:

$\prec$

Initial assumptions related to $\prec$

A1) Reflexivity. *$X \stackrel{A}{\sim} X$.*
A2) Transitivity. *$X \prec Y$ and $Y \prec Z$ implies $X \prec Z$.*
A3) Consistency. *$X \prec X'$ and $Y \prec Y'$ implies $(X, Y) \prec (X', Y')$.*
A4) Scaling invariance. *If $X \prec Y$, then $tX \prec tY$ for all $t > 0$.*
A5) Splitting and recombination. *For $0 < t < 1$*

$$X \stackrel{A}{\sim} (tX, (1-t)X).$$

(If $X \in \Gamma$, then the right side is in the scaled product $\Gamma^{(t)} \times \Gamma^{(1-t)}$, of course.)
A6) Stability. *If, for some pair of states, X and Y,*

$$(X, \varepsilon Z_0) \prec (Y, \varepsilon Z_1)$$

holds for a sequence of ε's tending to zero and some states Z_0, Z_1, then

$$X \prec Y.$$

CH) Definition: *We say the* **comparison hypothesis** *(CH) holds for a state space if any two states X and Y in the space are comparable, i.e., $X \prec Y$ or $Y \prec X$.*

Entropy principle: *There is a real-valued function on all states of all systems (including compound systems), called* **entropy** *and denoted by S such that*

a) Monotonicity: *When X and Y are comparable states then*

$$X \prec Y \quad \text{if and only if} \quad S(X) \leq S(Y). \tag{2.3}$$

(See (2.6) below.)

b) Additivity and extensivity: *If X and Y are states of some (possibly different) systems and if (X, Y) denotes the corresponding state in the composition of the two systems, then the entropy is additive for these states, i.e.,*

$$S((X, Y)) = S(X) + S(Y). \tag{2.4}$$

S is also extensive, i.e., for each $t > 0$ and each state X and its scaled copy tX,

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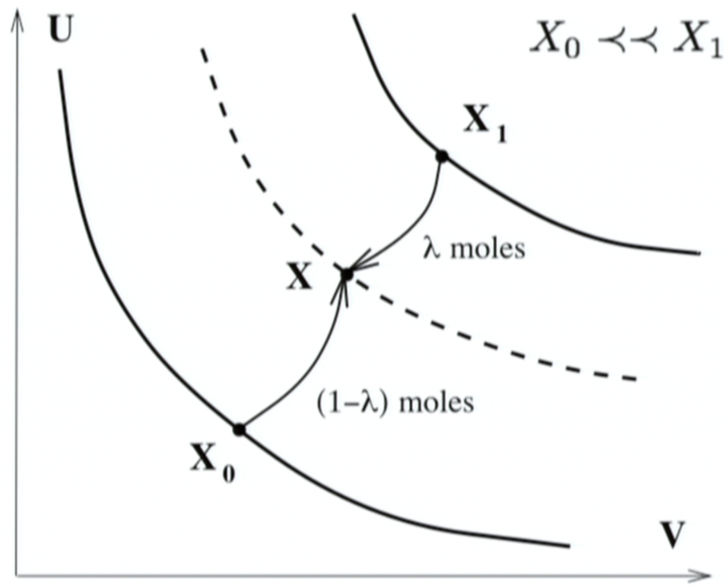
"[An] important point about entropy, which is often overlooked, is that entropy … tells us exactly which processes are adiabatically possible in any given system; states of high entropy in a system are always accessible from states of lower entropy." Lieb-Yngvason (1999) p. 12.

"In a sense it is amazing that much of the second law follows from certain abstract properties of the relation among states, independent of physical details (and hence of concepts such as Carnot cycles)." Lieb-Yngvason (1999) p. 14.

"It is remarkable that the theorem is obtained without appealing to anything remotely resembling Carathéodory's principle." Uffink (2001).

"[W]e define the entropy of a state by letting a system interact with a copy of itself. …

[W]e construct the entropy function for a single system in terms of the amount of substance in a reference state of 'high entropy' that can be converted into the state under investigation with the help of a reference state of 'low entropy'."



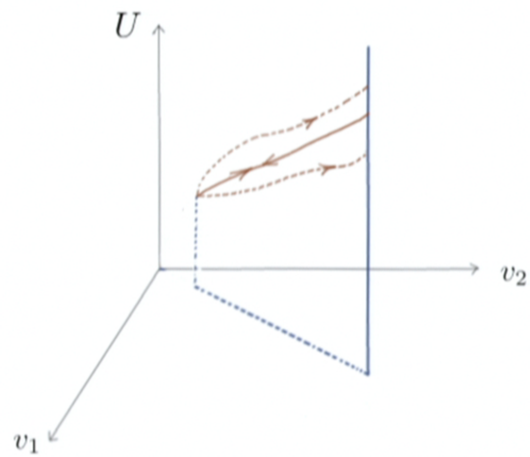
$$S_\Gamma(X) := \sup\{\lambda : \ ((1-\lambda)X_0, \lambda X_1) \prec X\}.$$

no reference to work/energy
no d/d*t*'s
no differentiability assumptions
no restriction to simple systems
no need for ubiquitous irreversibility

return to energy considerations for simple systems

recall that for Carathéodory, in the case of adiabatic processes involving no change in the work (deformation) coordinates:

either the internal energy always increases, or it always decreases

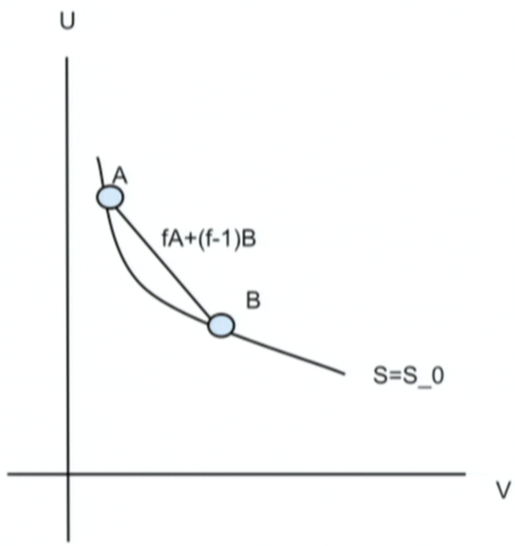


Back to L-Y: When is a convention not a convention?

"As far as our axiomatic framework is concerned the direction of the energy coordinate and hence of the forward sectors is purely conventional, except for the proviso that once it has been set for one system it is set for all systems. …

We shall adopt the convention that they are on the positive energy side. From a physical point of view there is more at stake, however. In fact, our operational interpretation of adiabatic processes … involves either the raising or lowering of a weight in a gravitational field and these two cases are physically distinct. Our convention, together with the usual convention for the sign of energy for mechanical systems and energy conservation, means that we are concerned with a world where adiabatic process at fixed work coordinate can never result in the raising of a weight, only in the lowering of a weight. The opposite possibility differs from the former in a mathematically trivial way, namely by an overall sign of the energy, but given the physical interpretation of the energy direction in terms of raising and lowering of weights, such a world would be different from the one we are used to." (p. 44)

Axiom 7 (Convexity)



conclusions

the Equilibrium Principle can be used to define an arrow of time

the L-Y axioms are both weaker and stronger than Carathéodory's, but both formulations share the same ambiguity/incompleteness

The L-Y entropy principle does not alter this fact; the issue has more to do with the relationship between adiabatic accessibility and energy