Lecture: Frolov Thermo of SM – Therm Procs (Norton & Valente) 19 Dec 2017
(1)

Start: exs of irreversible procs (stirring water enough to heat it; wiping whiteboard eraser vigorously to friction-heat it) not rep'd on equil space of states as thermo process, b/c intermediate states are manifestly nonequil on timescales comparable to relaxation to equil scales

- irreversible procs rep'd on equil space of states? Slow friction-heating? No – all curves reversible on equil space of states ~~[struck out]~~

and ΔQ > 0 for whole sys when the sys is isolated ⇓ need a composite system SoS for irreversible proc – irrevers: heat flows by conduction from A to B; then no forces in whole universe, w/ same init conds, happens (when no other changes occur anywhere)

role of time for curves on equil SoS
- prima facie, none: the only thing distinguish 'directions' of curves are signs of ΔQ & ΔW

→ first, sketch "naive meaning" of curve on equil SoS, draw pic
- isochore
- isothermal
- isentropic
- adiabatic (reversible, no heat exchange)
- cycle – returns to beginning, though env may change

"textbook" view of thermo procs

an equil curve on SoS represents a 'thermo proc' does so as one can envisage it as a "series of steps" of infinitesimally small changes occurring infinitely slowly; one needs tiny driving forces to push one out of equil, Minus-First Law to 'push one' back to equil ⇒ no real reversible procs in nature, but excellent approx to treat 'slow' ones, w/ delicately changing parameters, as such – in limit of no small changes, total proc takes so long

Norton
- his diagnosis of problem:

Paradox:

1) thermo rev procs have non-equil imbalance of driving forces, otherwise no change of state
2) they are sets of equil states in each of which ~∃ imbalance of forces

usual resolutions fail:
- ∞ slow proc never progresses
- 'insensibly small' diff from equil is still not equil

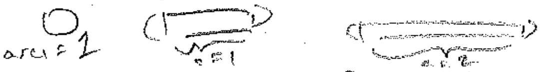
⇒ either sys changes or it doesn't!

# Lecture: Fndns Thermo of SM – Thermo Procs (Norton & Valente)

19 Dec 2017 (2)

## Norton on ideal vs approx (as limit)

- consider 'limit' of systems $S_1, S_2, \ldots$ that "approach" (in some sense) limit sys $S_\infty$, w/ corresponding properties $p_1, p_2, \ldots$ that also 'approach' some limit property $p_\infty$
  1) it may happen that $\neg\exists$ well defined $S_\infty$, when though $p_\infty$ may still 'exist'
  2) even if so, $\neg\exists$ may no well defined property $p_\infty$, or it may not "behave properly"
- if $\exists$ well defined $S_\infty$, that is idealization = "real or fictitious sys, distinct from target, some of whose properties provide inexact desc of some aspects of target sys", e.g., sequence of capsules starting from unit sphere




– – – ⇒ ∞ cylinder

ratio of surf area/vol = $(2\pi a + 4\pi)/(\pi a + 4\pi/3)$

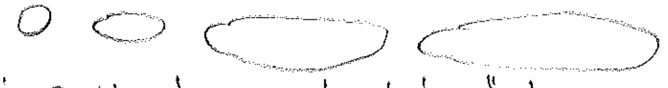
$\Rightarrow 2$ as $a \Rightarrow \infty$

agrees with simple limit of ∞ cylinder

- if one takes limit of spheres w/ rad $a = 1, 2, 3$, one gets no limit sys

- $\exists$ may limit sys w/ 'wrong' limit prop

unit sphere growing into ellipsoids w/ semi major axis $a = 2, 3, 4, \ldots$ (unit semi-minor axis)



"grows to cylinder", but now surf area/vol ratio is $(\pi^2 a)/(4\pi a/3) = 3\pi/4$ as $a \Rightarrow \infty$

⇒ approx = "an inexact desc of target system, proposition stating properties that approximate those of target system"

- also, approxs w/ no limit system – e.g., "∞ box of gas" w/ ratio N/V (particle #/vol) held constant in ∞ limit

Lecture: Fdns Thermo & SM – Thermo Procs (Norton, Valente) 19 Dec 2017 (3)

∃ resolution to paradox: thermo rev procs are approximations not idealizations

"inexact propositional descriptions of systems of interest"

- construction

rep revers proc by "continuous sequence" of irrevers procs

→ "limiting" "bounding" set of equil states is rev proc (curve on SOS) of sequence

→ properties of "rev procs" recovered by limits of props of ∃ in sequence of irrev procs

→ provides properties only, not a system/proc bearing them, since ~∃ such a limiting proc as "real, target proc"

→ ∴ approx, not an ideal

- properties characterizing sequence [ignoring ~~stuff about forward vs reverse process, irrelevant for our purposes~~]

1) each proc may exchange heat / work w/ env, coz of ∃ of imbalanced forces

2) procs either 'forward' or 'reverse' depending on signs of ΔQ and ΔW

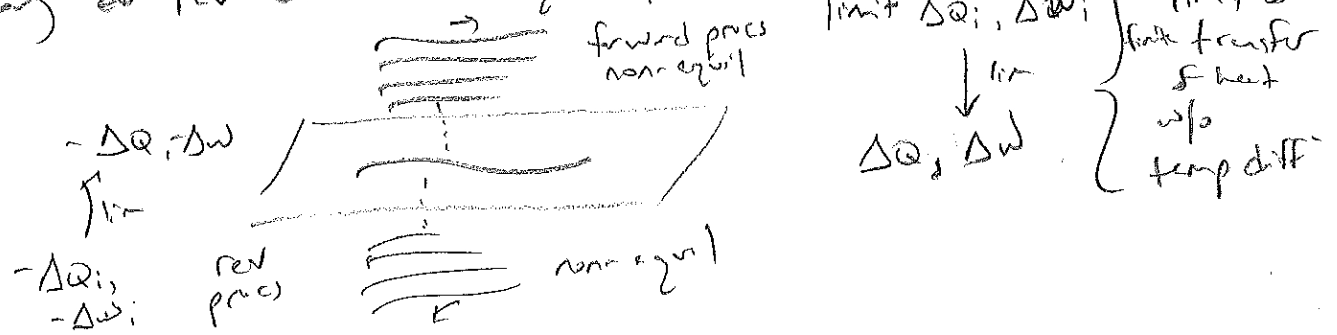
3) in each sequence, ∃ procs in which driving forces are as small as one pleases

4) s.th. in limit, driving forces → 0

5) limiting values of ΔQ and ΔW are equal of opposite sign for reverse procs

6) limiting ΣS of ΔQ & ΔW at any stage of proc = those computed along ~~the~~ rev curve in equil space

Picture



Lecture: Found Thermo, SM ~ Thermo Proc (Norton, Valente)

## Valente

- 2 ways out of paradox
  1) either admit rev proc can pass through non-equil states, but deviations from equil curves are in some sense negligible
  2) deny any rev proc as equil curve is thermo proc

Norton takes 2 and Valente (à la Afriat-Sjamna) takes 2

- for 2 one needs: a) show that rev proc can be constructed as equil curve in 'quasi-static' limit
  b) connect construction to 'real' thermo proc

## Criticism of Norton

- must be careful: ∞-time limit of non-equil curves doesn't always yield rev proc ($P_\infty$ has no heat exchange, $P_{eq}$ does); depends on how one takes limit
- just coz ∞-time lim has contradictory properties, it doesn't follow that rev proc does
  → $P_{eq}$ has $\Delta Q \neq 0$ and $\Delta T = 0$, so it *is* an ideal in Norton's sense! (no contradictory/impossible properties) it's just not an actual process (cf. ∞ cylinder)
  ⇒ saying rev proc is "approx" not "ideal" does no real work
- how to define "close enough to equil"? No topology on sequence of non-equil curves, coz no larger space in which they and equil states are embedded, not in classical thermo
  ⇒ Giovanni grants Norton too much on bottom of 2nd page of §4.1 – can't define "continuous sequence of curves" and can't integrate along them, coz no space, and so no topology and no differential and no affine structure (needed for integration)

- Norton's account leaves out procs that start and end in equil states (as real thermo procs often do), since all non-equil curves in his sequence contain no equil states
  → this seems to me easy to rectify

## My criticism of Norton

- whence comes fix non-equil curves?
  → imports external machinery from outside class thermo, no account of how they relate to, fit w/, thermo theory struct
  - there may be no ~~____~~ such coms or may not be unique; in latter case, how to decide? (thermo can't tell us!)
  - thus, physical significance of limit is not clear
  - ~~defin of~~ thermo props out of equil not well defined, and contra Norton (p. 49) this is not a problem for 'standard accounts'
- ∃ assumption (cont. set of non-equil curves w/ rev proc as limit) holds only in 'fictitious world in which ordinary thermo holds at all scales' (p. 50) ⇒ unsatisfactory for analyzing empirical content of classical thermo

## Valente's positive account

- following Afanassjewa, deny rev procs are thermo procs at all but rather only a 'mere mathematical construction useful for calculations* using diff calculus'

- Call, rev proc 'quasi-proc' in so far as not realizable in any real proc – just oriented curve on equil sos – pure math
- need now to show connection to real thermo procs

⇒ quasi-static proc – a sys can be made to assume any equil state by external forces, and such can be used to "approx" quasi-process by a dense, discrete sequence of equil states (part of quasi-proc) such that during proc connecting any two equil states, state of sys is "close to" equil state

⇒ "iterated equilibria", passing through intermediary non-equil states, an elementary quasi-static proc

- when driving forces go to zero, dense discrete seq of equil states goes to quasi-process (curve on equil sos)

to make connect w/ real therm procs

- "∞ time limit" means 'sufficiently slowly that in each state we may neglect deviation from equil' : "∞ slow ≠ quasi-static"
  ⇒ so quasi-static complete in finite time
- init and final states are equil states

defense

- "close enough to" equil states? ⇒ 'falls beneath perceptible errors'

My criticism

- same problem as w/ Norton re: topology, space, diff struc
  ⇒ quasi-static procs are not in equil sos, so what does "close enough" mean precisely? how to rep it in machinery of pure classical therm?

# Thermodynamical Processes as Equilibrium Processes

Erik Curiel†

December 22, 2017

## Contents

1. recent controversy: Norton (2016) (wrong, along with Duhen 1903 that Norton cites, for several reasons) versus Valente (2017) (better than Norton, but still faces problems: in what space do the "elementary quasi-static processes" live? what topology defines "closeness" to reversible paths in equilibrium space of states?)

2. I propose an analysis that is consistent with the orthodoxy (*e.g.*, Fermi (1956)) that I think Norton rightly draws attention to as potentially inconsistent, whereas mine has not even the whiff of inconsistency, and has no need for resources external to classical thermodynamics (*e.g.*, non-equilibrium states):

   a. "equilibrium" is a concept that is always relative to a time scale (*e.g.*, the evaporation of the glass of water—the water is in equilibrium over scales of a few minutes but not several hours), and to an acuity of proposed types of measurement relevant to envisaged experiments

   b. choose a small enough time scale that the system is essentially in equilibrium over it, say $\tau$ units of time

   c. for the process at issue, determine the equilibrium states at discrete intervals of $\tau$ units of time

   d. this gives a discrete set of points in the equilibrium space of states, labeled by instants of time every $\tau$ units

   e. now, construct an interpolated continuous limit curve between the discrete points, as follows: just as equilibrium is relative to time scale, and so sets lower bounds on the admissible acuity of temporal measurements, so the same holds for the admissible acuity of the measurements of all thermodynamical quantities. For the pragmatic purposes of the proposed experiment, therefore, given two equilibrium states between which all relevant quantities differ by at most the admissible acuities, those two states for all intents and purpores "differ by an infinitesimal", and so a linear interpolation ("tangent vector" on the space of states) between them is justified.

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f. label the points of the full curve by the appropriate instants of time (these labels are not part of the curve in the equilibrium space of states *per se*, but an externally imposed device), *viz.*, by a parametrization with respect to the changes of the relavant physical quantities are linear—the integrated time of the complete curve will be finite

g. one can now integrate quantities (total heat exchanged, total work performed, *etc.*) along the curve in the usual way

One fundamental question for may account: does its pragmatic aspect, in which each curve must be treated differently depending on what experiment one envisages (and so what the time-scale for equilibrium is, and what acuities are admissible in differences of quantities), suffice for a foundational (or "philosophical") explication? I think so. The only reason it could not is because one holds to the idea that the empirical meaning of theoretical terms and structures in a theory is exhausted by their "ontological" import, irrespective of how they are instantiated in particular experiments. The goal, however, after all, is to tease out, analyze, and characterize the *empirical* content of the theory by an explication of the theoretical structures in a way consonant with their possible experimental applications, and indeed so as to be able to model and explain the possible experimental applications. Such an explication must also be capable of explaining the possibilities of our broader, general "experience" of the kinds of physical systems the theory treats, *e.g.*, to explain why fluids do not maintain shape without external constraint. That one can do this in isolation from consideration of how the theory is applied in practice to actual experiments is a highly non-trivial assumption, though one endemic to contemporary philosophy of science in general, and philosophy of physics in particular—but one which I deplore and reject. (See, *e.g.*, Curiel 2014, 2017a, 2017b.)

## References

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