IN SEARCH OF THE HOLY GRAIL: HOW TO REDUCE THE SECOND LAW

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The second law of thermodynamics

"The second law is one of the all-time great laws of science, for it illuminates why anything — anything from the cooling of hot matter to the formulation of a thought — happens at all", or so claims Atkins (2007, preface).

- What is the scope of thermodynamics?
- Can thermodynamics be reduced?

THERMODYNAMICS: THE PARADIGMATIC EXAMPLE OF A REDUCED THEORY?

- Thermodynamics reduces to statistical mechanics: done and dusted?
- But Sklar and Batterman are sceptical: "it is almost surely the case that thermodynamics does not reduce to statistical mechanics according to the received view of the nature of reduction in the philosophical literature" Batterman (2010, p.159).

THERMODYNAMICS: THE PARADIGMATIC EXAMPLE OF A REDUCED THEORY?

- But whether a particular case of reduction is convincing depends on
 - 1 the account of reduction
 - 2) the two theories in question
- The orthodoxy:
 - Nagel
 - Provide the second statistical mechanics (SM)
 Output: The second statistical mechanics (SM)

THERMODYNAMICS: THE PARADIGMATIC EXAMPLE OF A REDUCED THEORY?

- But whether a particular case of reduction is convincing depends on
 - 1) the account of reduction
 - 2) the two theories in question
- In what follows:
 - I'll discuss how functionalism can be helpful for securing reductions.
 - *Gibbsian* SM and I'll emphasise the importance of equilibrium in TD.

Functionalism: to be X is just to play the X-role.

- An archetypal example of a functional property: 'being locked'
- 'Being locked' can be realised by a variety of mechanisms, D-locks, padlocks, combination locks.

FUNCTIONALISM'S RISING POPULAR IN PHILOSOPHY OF PHYSICS

- Knox's Spacetime functionalism
- Lam and Wüthrich: functionalism might help us understand how spacetime emerges from a fundamentally non-spatiotemporal theory of quantum gravity.
- Albert and Ney: functionally recover the 3-dimensional world from 3*N*-dimensional configuration space.
- Wallace: macroscopic patterns in the wavefunction that behave like tigers are tigers.
- Menon and Callender: temperature and entropy are multiply realised functional kinds.

THE FUNCTION OF FUNCTIONALISM

Functionalism is helpful for undertaking inter-theoretic relations:

- Albert and Wallace want to recover the behaviour of macroscopic objects described by classical theory, from the underlying quantum description.
- Spacetime functionalism aims to compare candidate spacetimes across different theories.

THE FUNCTION OF FUNCTIONALISM

Why does functionalism help with reduction?

- If the higher-level concepts are functional role concepts then the realiser just has to play the same role, i.e. have the same *behaviour*.
- Consequently, certain differences won't matter.

$\mathbf{S}\mathbf{K}\mathbf{L}\mathbf{A}\mathbf{R}$

The 'temperature equals mean molecular kinetic energy' bridge law *identifies* a fundamentally non-statistical quantity with a fundamentally *statistical quantity*. How is this supposed to work?' (Sklar, p. 161, as quoted by Batterman).

THE FUNCTION OF FUNCTIONALISM

- Functionalism helps relax certain concerns about property identity: the lower-level details can be conceptually different in certain ways (e.g. it can invoke probabilisitic concepts).
- This allows one to claim the higher-level theory is reduced: a realiser can be found that plays the same role. But nonetheless the two levels can differ in certain ways.
- Of course, in particular case studies, cashing out which differences matter (and which don't) will be very controversial. (Arguably this is part of finding 'functionalism fit for physics').

HATE FUNCTIONALISM? NEVER FEAR....

- Functionalism makes behaviour centre stage, and it is "the behaviour characteristic of the system [that] is the focus of reduction" (Rueger, 2006, p. 343).
- Similarly, Rosaler (2017, p. 4) says: "Fundamentally, the concept of reduction that we investigate here is about showing that all real behaviours that can be accurately modelled in one theory can be modelled at least as accurately in another. Taking limits and deriving one set of laws from another may turn out to be useful *strategies* toward this goal, but neither requirement is regarded from the outset as a *sine qua non* of reduction".
- Provided that real behaviour can be modelled by both theories, other differences may not matter.

HATE FUNCTIONALISM? NEVER FEAR....

- Functionalism helps emphasise that there might be differences between the entity to be reduced T_t and the reducer T_b .
- And this is a standard point in the reduction literature: for example, in the Nagel-Schaffer account only an approximation or 'close cousin', T_t^* , of the original theory T_t , must be deduced from T_b (Butterfield, 2011a,b).
- So if you are allergic to 'functionalist' talk, every time I say 'realiser', think 'reductive basis'.

THE FUNCTIONALIST STRATEGY FOR REDUCING THE SECOND LAW

- 1 Articulate the functional role of the TDSL.
- 2 Search for the realiser of this role in SM.

(Here I am only considering the Second law but in my thesis I considered the Zeroth, First and Third law as well.)

THE PLAN

- Preliminaries: the nature of processes in thermodynamics
- Three types of time-asymmetry
- The second law: how it implicitly defines the thermodynamics entropy and codifies it's behaviour.
- Three important features of the second law
- Articulate the role of the thermodynamic entropy: increasing in non-quasi-static adiabatic processes, but constant in quasi-static adiabatic processes.
- Then I'll emphasise how this role differs from the 'traditional holy grail' (Callender, 2001).
- Search for the realiser in quantum statistical mechanics: Gibbs entropy
- Defend the Gibbs entropy from the 'ensemble' objection.
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Preliminaries

Equilibrium is at the heart of thermodynamics, and it is a presupposition of the theory that systems will end up in equilibrium. That systems will reach such an unique equilibrium state has been dubbed the 'minus first law' of thermodynamics (Brown and Uffink, 2001) — systems will spontaneously reach an equilibrium state, which then, by definition, will not change.



Figure : The equilibrium state-space Ξ appropriate for an ideal gas. The co-ordinates (P_1, V_1) label point x_1 and (P_2, V_2) label point x_2 .

- How to understand curves Ξ? (Recent controversy: Lavis (2017), Valente (2018), Norton (2016)).
- All agree: no system will spontaneously trace out this curve. Tatiana Ehrenfest-Afanassjewa calls these curves 'quasi-processes' to emphasise that they are unphysical, mathematical constructs.
- Interventions are required to change its state by manipulating an external parameter like volume.
- Examples: inserting piston, contact with a heat bath, turning on a magnetic field.
- Two flavours of interventions:
 - **1** *Isothermal:* system's temperature remains constant, since heat flows from a heat bath.
 - 2 Adiabatic: the system is thermally isolated.

- The smaller the intervention, the smaller the deviation from equilibrium.
- The curve delimits the set of processes between two equilibrium states.



Figure : A curve through the above equilibrium state-space Ξ .

THREE TYPES OF IRREVERSIBILITY: QUASI-STATIC



 $\ensuremath{\textit{Figure}}$: Quasi-static processes represented in the p-V plane of equilibrium states.

These 'quasi-static processes' are 'reversible': the arrows can be drawn in either direction on the curves. But travelling in one direction is not straightforwardly the 'time reverse' in the TRI $t \rightarrow -t$ sense: you are performing different interventions. Furthermore, 'quasi-static reversibility' is a property of a sequence of processes, rather than of a single process.

THREE TYPES OF IRREVERSIBILITY: IRRECOVERABILITY

- **Recoverability**: the process in question can be 'fully undone'. The system can be returned to its initial state with no effect in the environment.
- But the system need not retrace its steps it can take a different path to its destination.
- So process P is recoverable if: writing $\langle S_i, E_i \rangle \xrightarrow{P} \langle S_f, E_f \rangle$ there is a process P* such that $\langle S_f, E_f \rangle \xrightarrow{P*} \langle S_i, E_i \rangle$.

THE SECOND LAW INTRODUCED

The Clausius Statement: "It is impossible to perform a cyclic process which has no other result than that heat is absorbed from a reservoir with a low temperature and emitted into a reservoir with a higher temperature." (Clausius (1864) as cited in Uffink, 2001. p. 328).

The Kelvin Statement: "It is impossible to perform a cyclic process with no other result than that heat is absorbed from a reservoir, and work is performed" (Kelvin et al. (1882) as cited in (Uffink, 2001, p.328)).

THE SECOND LAW INTRODUCED

The Carnot Statement: No engine is more efficient than a Carnot engine: $\eta = 1 - \frac{Q_c}{Q_h}$. That is, for engine operating between two reservoirs with temperatures T_h and T_c , a reversible engine is the most efficient.

By considering the heat flow dQ at different temperatures T in a reversible cycle, we can define a new function of state: the thermodynamic entropy, S_{TD} :

$$\int_0^B \frac{dQ}{T} = S_{TD}(B) \tag{1}$$

For an adiabatic process (i.e. a thermally isolated system), $\Delta S \ge 0$, where the equality holds if the process is quasi-static.

THREE KEY FEATURES

- 1 The availability of quasi-static processes
- 2 The importance of the environment
- **3** The Minus First law vs. Second law

THE AVAILABILITY OF QUASI-STATIC PROCESS

- In defining S_{TD} , we relied on quasi-static processes.
- Uffink emphasises their importance: "if such processes did not exist then the entropy difference between these two states would not be defined" (Uffink, 2006, p. 19)¹, adding that "this warning that the increase of entropy is thus conditional on the existence of quasi-static transitions has been pointed out already by Kirchhoff (1894, p. 69)", as cited in (Uffink, 2006, p. 19).

THE AVAILABILITY OF QUASI-STATIC PROCESS

- Since S_{TD} is a state function (a path independent quantity), the entropy change during a non-quasi-static processes is well-defined. But quasi-static processes are required to calculate ΔS_{TD} , and define it in the first place.
- Furthermore, adiabatic quasi-static processes provide the lower bound on the entropy change, $\Delta S_{TD} = 0$.

THE IMPORTANCE OF THE ENVIRONMENT

Sole effect is key: S_{TD} can decrease in isothermal compression.



THE IMPORTANCE OF THE ENVIRONMENT



Irrecoverability and the ravages of time

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THE MINUS FIRST LAW VS. SECOND LAW

- To emphasis the contrast: the Second Law tells us that certain transitions/processes render the initial state irrecoverable, where as the Minus First Law tells us that systems spontaneously reach a state of equilibrium.
- *Approaching* equilibrium, rather than the quasi-static interventions *on* equilibrium states.
- Finding the microphysical 'underpinning' for these two Laws are distinct projects (cf. Luczak (2018)).
- The H-theorem and coarse-graining approaches in SM are concerned with quantitatively describing the approach to equilibrium (minus first law).

THE MINUS FIRST LAW VS. SECOND LAW

- Of course, since equilibrium states are central to TD and the minus first law is baked deep into the nature of quasi-static processes, the two projects are connected (as we will see later).
- Even if we resolve the controversy around the underpinning of the minus first law, there is still a *further* project to find the underpinning of the second law.
- This further project is what I hope to do in this talk....

THE STATE OF PLAY

- We have found the required role:
- For thermally isolated systems, *S*_{TD} increases during non-quasi-static processes, but remains constant in quasi-static processes.
- Having outlined the role in TD, we now need to search for the realiser in SM.
- But first, note that this role differs from the one discussed in much of the literature: what Callender (1999) calls 'The Holy Grail'.

THE TRADITIONAL HOLY GRAIL

- Finding the distinction between heat and work in SM is at best *complicated* (cf. Maroney (2007); Prunkl (2018)) and at worst *'unnatural'* (Knox, 2016, p. 56) or *'anthropocentric'* (Myrvold, 2011).
- Maxwell claimed the distinction between heat and work is one of disordered and ordered motion, which *"is not a property of material things in themselves, but only in relation to the mind which perceives them"* (Maxwell, 1878, p. 221); (Niven, 1965, p. 646) as quoted in Myrvold (2011).

THE TRADITIONAL HOLY GRAIL

- Consequently, the Kelvin formulation does not have an obvious correlate in SM.
- Finding the realiser of the TD entropy in SM seems key to finding the 'image' of the TDSL in SM.
- Callender (1999) calls this the search for 'The Holy Grail': find a SM function to call 'entropy' and establish that it is non-decreasing.

AGAINST THE TRADITIONAL HOLY GRAIL

- Non-decreasing \neq the right role:
 - **1** Not necessary: S_{TD} is only defined at equilibrium, there's no problem is S_{SM} decreases away from equilibrium.
 - 2 Not sufficient: it needs to *increase* in the right situation too!
- The new grail: find a SM realiser which is increasing in non-quasi-static adiabatic processes, but non-increasing in quasi-static adiabatic processes.

FINDING THE NEW GRAIL IN QSM

- I take Gibbsian approach (later I'll defend the Gibbs entropy), but this defence won't involve any criticism of Boltzmann entropy (multiply realised?)
- First, consider how to make interventions on external parameters in QSM.
- Then I show that S_G can play the right role:
 - 1 S_G is constant in quasi-static adiabatic processes but
 - 2 Increases in non-quasi-static processes .
- Then I will connect my claims about S_G back to heat.

FINDING THE NEW GRAIL IN QSM

• In QSM, like CSM, thermal equilibrium is represented by the canonically distributed state:

$$\rho_{can} = \Sigma_i w_i \left| E_i \right\rangle \left\langle E_i \right| \tag{2}$$

where

$$w_i = \frac{e^{-\beta E_i}}{Z},\tag{3}$$

where Z is the partition function.

FINDING THE NEW GRAIL IN QSM

- Whilst in CSM, ρ_{can} is a probability density distribution over the phase space Γ, in QSM ρ_{can} is a density matrix.
- $\hat{\rho_{can}}$ is a statistical mixture of energy eigenstates, where the probability of being a given energy $|E_j\rangle$ depends exponentially on the eigenvalue E_j of that state, and the temperature $\beta = k_B T$.

Maroney (2007) gives an elegant justification for why ρ_{can} represents thermal equilibrium states familiar from thermodynamics, but here are motivating reasons:

The unitary evolution of a density matrix is given by the Liouville-von Neumann equation:

$$i\hbar\frac{\partial\rho}{\partial t} = [H,\rho] \tag{4}$$

Since ρ_{can} commutes with the time-independent H, it is unchanging in time:

$$\frac{d\rho_{can}}{dt} = 0.$$
 (5)

2 The canonical ensemble (at a given total energy and temperature) maximises the Gibbs entropy:

$$S_G = -k_B \operatorname{Tr} \rho \ln \rho \tag{6}$$

which is the quantum analogue of the classical Gibbs entropy:

$$S_G = -k_B \int dq dp \rho(q, p) ln \rho(q, p).$$
(7)

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INTERVENTIONS IN QSM

- At t_0 , let us start with the system in the canonical ensemble, ρ_{can} , where the Hamiltonian, $H(t_0)$ is time-independent.
- When there is an intervention on an external parameter V in the period $t_0 < t < t_1$, the Hamiltonian will be time-dependent.
- At *t*₁, the parameter *V* has a new value *V*₁, and the Hamiltonian is once again time-independent.

CHANGING EXTERNAL PARAMETERS IN QSM

• The external parameter, V, determines the potential energy:

$$U_{box}(x_i, y_i z_i)) = egin{cases} 0 ext{ if } 0 < x_i < x(t), 0 < y_i < L_y, 0 < z_i < L_z \ +\infty ext{ otherwise} \end{cases}$$

- Changing an external parameter, like the volume of the box, changes H(V(t)).
- At the beginning t_0 , $H(V_0)$, and end of the process t_1 , $H(V_1)$, the Hamiltonian is time-independent.
- When $t_0 < t < t_1$, the Hamiltonian is changing.

CHANGING EXTERNAL PARAMETERS IN QSM

- The energy eigenstates $|E_i\rangle$ in the canonical state are eigenstates of the initial Hamiltonian $H(V_0)$, and so are unchanging in time.
- In the period, $t_0 < t < t_1$, each eigenstate $|E_i\rangle$ evolves to a new state $|\Psi(t)\rangle$, which is written in this general form to emphasise that $|\Psi(t)\rangle$ might not be an eigenstate of the new Hamiltonian, and furthermore, is changing in time.

THE GOAL

- show that if the change to the external parameter, is quasi-static, i.e. $t_1 t_0 \rightarrow \infty$, then S_G is constant.
- If the intervention is non-quasi-static, i.e. $t_1 t_0 \approx 0$, then S_G increases.

QUASI-STATIC CHANGE

- Earlier, we saw that a quasi-static process requires that the systems is very close to equilibrium at every stage.
- In QSM, this means that that system is approximately in the canonical distribution.
- Each pure state (which is initially an energy eigenstate of H(t₀)) in the statistical mixture ρ_{can}(t₀) evolves under the time-dependent Schrödinger equation, carrying its original weighting w_i with it.
- ...but why think that $\rho(t)$ will still be canonical?

QUASI-STATIC CHANGE

• For $\rho(t)$ to be canonical, it needs to be

1 a statistical mixture of eigenstates of H(t)

- 2 whose probability depends on the energy eigenstate, E_i .
- **(1)** is ensured by Ehrenfest's principle, also known as the quantum adiabatic theorem.

EHRENFEST'S PRINCIPLE

If the energy eigenstates of H(t) are non degenerate for times $t > t_0$, if $|E_i(t_0)\rangle$ is an energy eigenstate of $H(t_0)$, if $|E_i(t)\rangle$ is the state evolved from $|E_i(t_0)\rangle$ according to the Schrödinger equation, and if the external parameter changes very slowly, then $|E_i(t)\rangle$, for each time $t > t_0$, is very nearly an energy eigenstate of H(t) at the corresponding time. In the mathematical limit of a finite change in the external parameter occurring over an infinite time interval, "is very nearly" becomes "is" (Baierlein, 1971, p. 380).

Why think that Ehrenfest's principle holds?

- Infinite time limits are contentious (cf. Palacios (2018)), and of course, only 'approximately' hold in real life situations.
- But, just like in the thermodynamic situation, an intervention is 'slow enough' if $t_1 t_0$ is large than characteristic timescale.



- If Ehrenfest's principle holds, eigenstates will be taken to new energy eigenstates.
- The distribution is monotonically decreasing... but is it canonically distributed?

QUASI-STATIC CHANGE

- Is the distribution still canonical?
- Yes, provided that \star holds:

$$E_i(V(t)) = f(t).E_i(V(t_0))$$
 (8)

• At t_0 , $e^{-\frac{E_i(V(t_0))}{kT(t_0)}}$, which we can re-write in terms of \star

•
$$e^{-\frac{E_i(V(t))}{kT(t_0).f(t))}}$$
, so if $T(t) = f(t).T(t_0)$.

- Thus, if the change to the external parameter is slow (i.e. qs) and * holds, then the system will remain (close to) the canonical ensemble, with a varying temperature.
- The one hitch: there's no general proof of * (Baierlein, 1971, p. 380), but it does hold for a realistic gas (Katz, 1967, p. 84-90).

QUASI-STATIC CHANGE

- Provided that:
 - 1 the conditions of Ehrenfest's principle apply
 - $2 \star holds$

then the system will remain (approximately) canonical distributed, with a changing temperature.

- Furthermore, *S_G* will be constant: the dynamics are unitary.
- This is wholly unsurprising: the problem with S_G is working out to make it *increase*.

- If $t_1 t_0 \approx 0$, the system will not be in an energy eigenstate of $H(V_1)$, and so will not be at equilibrium.
- Instead: If we were to write $\rho(t)$ in the energy eigenbasis, we would see that the density matrix is not diagonal in this basis: $\rho(t) = \sum_{ij} \omega_{ij} |E_i(t)\rangle \langle E_j(t)|.$
- But we assume that the system will settle down to a new equilibrium.
- Of course, justifying this assumption is controversial (...H-theorem, coarse-graining, combinatoric argument?).

- My preferred approach: coarse-graining in the Zeh-Zwanzig-Wallace framework.
- In this framework, start with the unitary dynamics defined by $H(V_1)$, find a projector \hat{P} that kills off the off-diagonal terms, and build a master equation that quantitatively describes the approach to equilibrium.

• But in the absence of a concrete master equation, the pragmatic move is just to *adopt* a new canonical distribution with energy eigenstates appropriate for the new volume. In other words, we coarse-grain:

$$\rho = \sum_{ij} \omega_{ij} |E_i(t)\rangle \langle E_j(t)| \to \rho_{cg} = \sum_i \omega_{ii} |E_i(t)\rangle \langle E_i(t)|, \quad (9)$$

where we assume that the off-diagonal terms w_{ij} , $i \neq j$ are small so $\sum_{ij} \omega_{ij} |E_i(t)\rangle \langle E_j(t)| \approx \sum_i \omega_{ii} |E_i(t)\rangle \langle E_i(t)|$, where t is a long time after the external parameter has stopped changing.

• $S_G(\rho)$ increases as ρ is coarse-grained.

- But regardless of whether you endorse the ZZW framework, all schools of non-equilibrium SM agree that S_{SM} increases in the approach to equilibrium.
- Thus, we have achieved our goal: *S_G increases* in rapid, non-quasi-static adiabatic processes, but is *constant* in quasi-static processes.
- I conclude (in agreement with Maroney (2007)): S_G is the realiser of S_{TD} since it plays the right role and so the TDSL is reduced to SM.

THE GIBBS ENTROPY AND THE CONNECTION TO HEAT

• In thermodynamics, the relationship between heat Q and entropy S_{TD} is:

$$dS_{TD} = \frac{dQ}{T_{TD}} \tag{10}$$

• The First law of thermodynamics states that $dE_{TD} = dQ + dW$, and so

$$dS_{TD} = \frac{1}{T_{TD}} (dE_{TD} + p_{TD} dV)$$
(11)

THE GIBBS ENTROPY AND THE CONNECTION TO HEAT

• In SM, we find this relationship between heat and entropy as follows.

$$S_G(\rho_{can}) - k_B \Sigma_i p_i \ln p_i = -k_B(\beta \langle E \rangle + \ln Z) \qquad (12)$$

If the external parameter V is changed slowly enough that the system remains in the canonical distribution, then the differential form is:

$$dS_{G} = k(d\beta \langle E \rangle + \beta d \langle E \rangle + \frac{\partial \ln Z}{\partial \beta} \partial \beta + \frac{\partial \ln Z}{\partial V} dV)$$
(13)
$$= \frac{1}{T} (d \langle E \rangle + \langle p \rangle dV)$$
(14)

EXPECTATION VALUES, AND LIMITING THE TDSL

- A successor theory often limits the domain or scope of the older theory, and this is the case with TD.
- Since Maxwell (1891), all hands admit that the TDSL can be violated. The idea that the TDSL is not a strict law was suggested by Maxwell: "Hence the TDSL is continually being violated, and that to a considerable extent, in any sufficiently small group of molecules belonging to a real body." Maxwell (1891) as quoted by Cercignani (1998).

EXPECTATION VALUES, AND LIMITING THE TDSL

- But nonetheless the TDSL seems to capture something true about our world; greater-than-Carnot efficiency engines are hardly a dime a dozen.
- Thus, the key issue is to establish under what circumstances the TDSL can be violated, and then restrict the scope of TDSL to exclude those circumstances. Here the orthodoxy is that the TDSL must be weaken to a probabilistic statement, at the very least...
- Fluctuation phenomena imply that heat can spontaneously flow from colder to hotter bodies (with no other effect), but *on average* there will be no net such flow. Thus, a weakening the TDSL to a probabilistic version, as reflected in the use of expectation values in SM, is appropriate.

EXPECTATION VALUES, AND LIMITING THE TDSL

- Thus, I conclude that the Gibbs entropy can play the right role, since it increases in non-quasi-static processes but is constant in quasi-static processes.
- Furthermore, S_G is connected to heat in the right way, and the presence of expectation values is a feature, not a bug.

Defending the Gibbs entropy

- S_G is less popular than S_B ...
- The main objection to S_G : it is an 'ensemble property' rather than a property of the individual system.
- Demystifying the 'infinite imaginary' ensemble:
 - Discussing the ensemble is just a vivid way to give SM probabilities a frequency interpretation.
 - Admittedly, there are many puzzles over understanding SM probabilities (e.g. Gibbs phase averaging)...
 - But ρ needn't be given a subjective interpretation following Jaynes (1957), instead SM probabilities can be considered to have an objective origin (cf. Myrvold (2012); Popescu et al. (2005))

- Why should the 'ensemble nature' of the Gibbs entropy worry us?
- As Callender (2001) emphasises, S_{TD} is a feature of the individual system, and so S_G does not match S_{TD} .
- In contrast, the Boltzmann entropy $S_B = k_B ln\Omega$ is a property of the individual system. Thus, Boltzmannians (cf. Callender (1999, 2001); Goldstein and Lebowitz (2004); Frigg (2010)) claim that S_B is superior, since it is a function of the microstate of the system.

- As such, there is a mismatch between S_G and S_{TD} .
- Yet this mismatch is a bad reason to worry about the ensemble nature of S_G . Mismatches are not problematic solely in virtue of revealing differences between the higher and lower-level quantities.
- According to functionalism, provided S_G plays the role of S_{TD} , then other differences are tolerated.
- S_G is not bad merely in virtue of not matching S_{TD} exactly. Such as, if 'being a property of the individual system' or 'being non-probabilistic' is not part of the essential role of S_{TD} , then the ensemble nature of the Gibbs entropy is not worrying.

QUANTUM OF SOLACE

- In CSM, even if the probability distribution is objective, the dichotomy between being 'an ensemble property' and a property of individual systems remains.
- But if we start from QSM this dichotomy never arises.

QUANTUM OF SOLACE

- Since the density matrix is a more general object than Ψ, it should be considered the fundamental represention of the state of the individual system.
- A probability distribution over these 'fundamental microstates' of QM, density matrices, just gives...another density matrix!
- As such, there is no difference in the mathematical object that represents the state of the individual system, and a probability distribution over it.
- Thus, in QSM, the dichotomy between 'being a property of a probability distribution' and 'being a property of the individual system' never arises.

QUANTUM OF SOLACE

- BUT...
- Insofar as this topic stemmed from the mystery mongering about probability in SM, there is bad news.
- Understanding, and giving an account of, probability in QSM involves tangling with the quantum measurement problem, and so in this way, we are out of the frying pan but into the fire.

- The functional role of *S*_{TD}: increasing in non-qs processes, but non-increasing in qs adiabatic processes.
- The traditional 'Holy Grail' doesn't capture the right role it is neither necessary nor sufficient for finding the realiser of S_{TD} in SM.
- Once we appreciate the true holy grail, we see that Gibbs entropy is the SM realiser.

Thank you!

Atkins, P. (2007). Four laws that drive the universe. Oxford University Press.

- Baierlein, R. (1971). Atoms and information theory: An introduction to statistical mechanics. WH Freeman San Francisco.
- Batterman, R. (2010). Reduction and renormalization. Time, Chance, and Reduction: Philosophical Aspects of Statistical Mechanics, pages 159–179.
- Brown, H. R. and Uffink, J. (2001). The origins of time-asymmetry in thermodynamics: The minus first law. Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics, 32(4):525–538.
- Butterfield, J. (2011a). Emergence, reduction and supervenience: a varied landscape. Foundations of Physics, 41(6):920–959.
- Butterfield, J. (2011b). Less is different: emergence and reduction reconciled. Foundations of Physics, 41(6):1065–1135.
- Callender, C. (1999). Reducing thermodynamics to statistical mechanics: the case of entropy. *The Journal of Philosophy*, 97(7):348–373.
- Callender, C. (2001). Taking thermodynamics too seriously. Studies In History and Philosophy of Science Part B: Studies In History and Philosophy of Modern Physics, 32(4):539–553.
- Cercignani, C. (1998). Ludwig Boltzmann: the man who trusted atoms. Oxford University Press.
- Clausius, R. (1864). Abhanglungen über die mechanische Wärmetheorie, volume 1. F. Vieweg und Sohn, Braunschweig.

Dennett, D. (2001). Are we explaining consciousness yet? Cognition, 79:221-237.

Frigg, R. (2010). A field guide to recent work on the foundations of statistical mechanics. In Rickles, D., editor, The Ashgate companion to contemporary Philosophy of Physics. Ashgate, Aldershot.

- Goldstein, S. and Lebowitz, J. L. (2004). On the (boltzmann) entropy of non-equilibrium systems. *Physica D*, pages 53–66.
- Jaynes, E. T. (1957). Information theory and statistical mechanics. Physical review, 106(4):620.
- Katz, A. (1967). Principles of statistical mechanics: the information theory approach. WH Freeman.
- Kelvin, W. T. B., Larmor, J., and Joule, J. P. (1882). Mathematical and Physical Papers: By Sir William Thomson... At the University Press.
- Kirchhoff, G. (1894). Vorlesungen über die theorie der waerme. Teubner, Leipzig.
- Knox, E. (2016). Abstraction and its limits: Finding space for novel explanation. Noûs, 50(1):41-60.
- Lavis, D. A. (2017). The problem of equilibrium processes in thermodynamics. http://philsci-archive.pitt.edu/12748/.
- Luczak, J. (2018). How many aims are we aiming at? Analysis, 78(2):244-254.
- Maroney, O. (2007). The physical basis of the gibbs-von neumann entropy. arXiv preprint quant-ph/0701127.
- Maroney, O. (2009). Information processing and thermodynamic entropy. The Stanford Encyclopedia of Philosophy.
- Maxwell, J. C. (1878). Diffusion. In Encyclopedia Britannica (Nineth Ed.), volume 7, pages 214–221. Cambridge University Press.
- Maxwell, J. C. (1891). Theory of heat. Longmans, Green.
- Myrvold, W. C. (2011). Statistical mechanics and thermodynamics: A maxwellian view. Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics, 42(4):237–243.
- Myrvold, W. C. (2012). Deterministic laws and epistemic chances. In Yemima Ben-Menahem, M. H., editor, Probability in Physics, pages 73–85. Springer, New York.

- Niven, W., editor (1965). The Scientific Papers of James Clerk Maxwell, volume 2. Dover Publications, New York, reprint of CUP edition of 1890 edition.
- Norton, J. D. (2016). The impossible process: thermodynamic reversibility. Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics, 55:43–61.
- Palacios, P. (2018). Had we but world enough, and time... but we don't!: Justifying the thermodynamic and infinite-time limits in statistical mechanics. *Foundations of Physics*.
- Popescu, S., Short, A., and Winter, A. (2005). The foundations of statistical mechanics from entanglement: Individual states vs. averages. eprint. arXiv preprint quant-ph/0511225.
- Popper, K. R. (1957). Irreversibility; or, entropy since 1905. The British Journal for the Philosophy of Science, 8(30):151–155.
- Prunkl, C. (2018). The road to quantum thermodynamics. In C. Timpson, D. B., editor, Quantum Foundations of Statistical Mechanics. OUP, Oxford.
- Rosaler, J. (2017). Reduction as an a posteriori relation. The British Journal for the Philosophy of Science.
- Rueger, A. (2006). Functional reduction and emergence in the physical sciences. Synthese, 151(3):335-346.
- Tong, D. (2012). Statistical physics. Cambridge Lecture Notes, available at http://www.damtp.cam.ac.uk/user/tong/statphys.html.
- Uffink, J. (2006). Compendium of the foundations of classical statistical physics, handbook for philosophy of physics, eds. Butterfield, J. and Earman, J.
- Uffink, J. (2013). Three concepts of irreversibility and three versions of the second law. From ontos verlag: Publications of the Austrian Ludwig Wittgenstein Society-New Series (Volumes 1-18), 1.

Valente, G. (2018). On the paradox of reversible processes in thermodynamics. Synthese.

Wallace, D. (2014). Thermodynamics as control theory. Entropy, 16(2):699-725.

Wallace, D. (2015). The quantitative content of statistical mechanics. Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics, 52:285–293.

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