# "Reversed Reduction" in Gibbsian Statistical Mechanics

## An Investigation and Interpretation of Tolman's Approach

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Reduction and Emergence in the Sciences
November 15, 2013 CAS-LMU

# Overview

**Introduction:**

- The toy-structure of statistical mechanics
- Statistical mechanics as the paradigm case of reduction

**Investigation:**

- Tolman's approach to statistical mechanics
- Recovering the first law of thermodynamics

**Interpretation:**

- Reversing the reduction

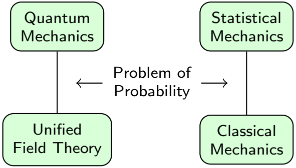
# A seemingly unrelated philosophical question

Does the quantum wave function provide a *complete* description for individual systems?

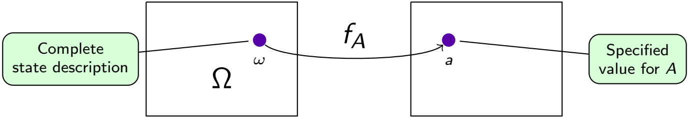
Einstein (1949):
"The attempt to conceive the quantum-theoretical description as the complete description of the individual systems leads to unnatural theoretical interpretations, which become immediately unnecessary if one accepts the interpretation that the description refers to ensembles of systems and not to individual systems."
"Assuming the success of efforts to accomplish a complete physical description, the statistical quantum theory would, within the framework of future physics, take an approximately analogous position to the statistical mechanics within the framework of classical mechanics."

# The paradigmatic view of complete descriptions

The parallel:




Paradigm structure adopted in no-go theorems for HVT's for QM:




$$Prob(A = a) = Prob(\{\omega \in \Omega\,;\; f_A(\omega) = a\}).$$

- A completed picture does not invoke an interpretation/explanation of probability.
- The structure is idealized compared to actual statistical mechanics.

# And what about the question of reduction?

Batterman (2006):

> *In this paper I want to consider the so-called reduction of thermodynamics to statistical mechanics [. . . ] As is well known, most philosophers not working in the foundations of statistical physics still take this reduction to be a paradigm instance of that type of intertheoretic relation. However, numerous careful investigations by many philosophers of physics and physicists with philosophical tendencies show this view is by and large mistaken. 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.*

Then why still study this reduction?

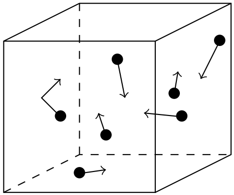
- Batterman: to obtain a better theory for intertheoretic relations.
- Today: to obtain a better understanding of statistical mechanics.

# A paradigm example

Clausius (1857): The reduction of the ideal gas law to the Kinetic theory of gases.

- $pV = CT$ ($p =$ pressure, $V =$ volume, $C =$ constant, $T =$ temperature).

**Three assumptions:**



1. Molecules only collide against the walls, and not against each other.
2. Collisions are fully elastic.
3. On the average, independent of the molecules speed, every direction is equally common.

- $pV = \frac{2}{3}N\langle E_k\rangle$ ($N =$ number of molecules, $\langle E_k\rangle =$ average kinetic energy).
- Bridge laws: $T \hat{=} \langle E_k\rangle$, $C \hat{=} \frac{2}{3}N$.

# Two issues with the paradigm example (1)

1. Thermodynamics is more than just the ideal gas law.
   The ideal gas is just a model within thermodynamics

**Laws of Thermodynamics:**

-1 Isolated systems will eventually reach a state of equilibrium.
(Establishes an arrow of time, and ensures applicability of (equilibrium) thermodynamics.)

0 Thermal equilibrium between systems is a transitive relation.
(Introduces experimental temperature.)

1 The change in internal energy $U$ of a system is the amount of heat $Q$ absorbed by the system minus the amount of work $W$ performed.
(Excludes perpetual motion of the first kind.)

$$dU = đQ - đW$$

2 The entropy of a thermally isolated system can never decrease.
(Excludes perpetual motion of the second kind.)

$$\Delta S \geq \int \frac{1}{T} đQ$$

# Two issues with the paradigm example (2)

2. Kinetic theory alone was recognized to be insufficient to recover the thermodynamic laws.

   Attempts to recover the thermodynamic arrow of time in particular suggested the necessity of *probabilistic explanations* rather than purely mechanical explanations.

But was Clausius' derivation free of probabilistic notion?

- Collisions are fully elastic.

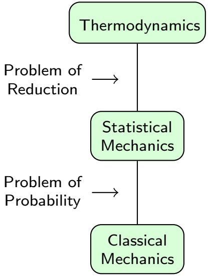
  Clausius invoked the rules of probability to argue that this holds on average.

- On the average, *independent* of the molecules speed, every direction is equally common.

  Independence as a form of the Principle of Insufficient Reason? (Without a reason to think otherwise, quantities should assumed to be uncorrelated.)

# Then what is Statistical Mechanics?

- In the light of reduction, Statistical Mechanics is the bridge between Thermodynamics and Classical Mechanics.
- A possible reduction cannot be understood independent of this bridging role.




**Laws of Statistical Mechanics:**

1. The laws of Classical Mechanics?
2. The laws of Probability?

- There is no agreed upon axiomatization of Statistical Mechanics.
- Then look at what Statistical Mechanics does. Be selective: look at tradition that follows Gibbs.

# Gibbsian Statistical Mechanics

- Gibbs (1902) was very cautious about the explanatory power of his methods.
- Tolman (1938) was more optimistic:

  *The explanation of the complete science of thermodynamics in terms of the more abstract science of statistical mechanics is one of the greatest achievements of physics.*

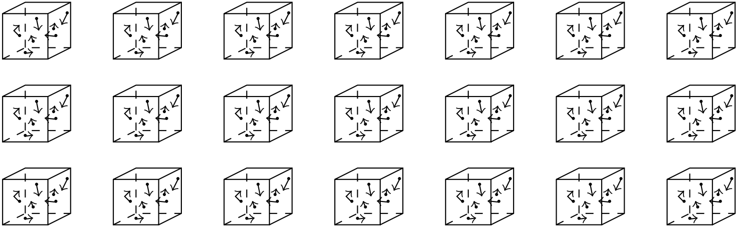
**Ingredients:**

1. Hamiltonian mechanics
2. Tolman's fundamental idea:

   *we take the procedure of correlating any actual mechanical system of interest, in an incompletely specified state, with an appropriately chosen representative ensemble of such systems [. . . ] followed by the procedure of then using average values for the members of this ensemble as furnishing good estimates as to what we can expect for the actual system.*

# The notion of an ensemble (1)

- In the ensemble approach the single (actual) system is described with the use of an ensemble $E$ of $N$ *similar* systems.



- The average is determined by Tolman's hypothesis of *equal a priori probabilities for different regions in the state space*.
- A (macro) property $A$ of the actual system $s$ is estimated by taking the average of $A$ over the ensemble.

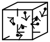
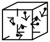
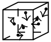
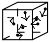
$$A(s) \simeq \frac{1}{N} \sum_{s' \in E} A(s')$$

# The notion of an ensemble (2)

- The number of systems in an ensemble $N$ is assumed to be large enough such that it can be approximated by a distribution $\rho$.
- Then the estimate for $A$ becomes

$$A(s) \simeq \frac{1}{N} \sum_{s' \in E} A(s') \simeq \langle A \rangle_\rho \equiv \int A(s')\rho(s')ds'.$$

- The distribution $\rho$ reflects the notion of *similarity* adopted in constructing the ensemble: Two states $s_1$ and $s_2$ are similar (w.r.t $E$) when they are equally probable (w.r.t. $\rho$).

 $\simeq_E$  iff $Prob_\rho($$) = Prob_\rho($$)$

Two sides of the same coin:

1. The ensemble $E$ provides the conceptual side.
2. The probability distribution $\rho$ provides the technical side.

# Putting ensembles to work: First derivation of the first law

$$S_h \xrightarrow{Q} S_s \xrightarrow{W} S_e \qquad \Delta U = \Delta_\gamma Q - \Delta_\gamma W$$

Tolman: for an appropriate ensemble assume total system is isolated on average to get

$$\Delta \langle H_s \rangle = -\Delta \langle H_h \rangle - \Delta \langle H_e \rangle \, .$$

And bridge laws $\langle \Delta Q \rangle \hat{=} - \Delta \langle H_h \rangle$, $\langle \Delta W \rangle \hat{=} - \Delta \langle H_e \rangle$.

1. Khinchin's methodological paradox: (on average) there is no interaction between the systems.
2. No mechanical explanation of what heat and work are is given.

   This is done in a separate story that doesn't connect to the derivation.
3. The path-dependence of changes in heat/work are left unexplained.
4. Why should the individually chosen ensembles line-up to give the correct relation? What makes an ensemble appropriate?

# Selecting a specific ensemble

- An ensemble may be considered appropriate if it gives good estimates for the macroscopic variables.
- For a system in equilibrium, the estimate of a (macro) property $A$ should be time-independent.

This happens if $\rho(s) = \rho(s(t))$ is time-independent. This is the case if it is a function of the Hamiltonian $H$:

$$\rho = f(H).$$

- Gibbs: $\rho$ should be normalizable and no state $s$ should be excluded as a possible state.

Simplest distribution satisfying these criteria is the *Canonical ensemble*:

$$\rho_{\text{Can}} := \exp(\alpha - \beta H).$$

# Validating the Canonical ensemble

Gibbs' motivation for $\rho_{\mathsf{Can}}$ is very short and pragmatic. Tolman has a very elaborate and technical derivation of $\rho_{\mathsf{Can}}$ from some postulates. However

> *"These postulates will be chosen in ways which are familiar or plausible, but their ultimate validity will be regarded as resting on the correspondence between deduced results and empirical findings."*

In other words: The proof of the pudding is in the eating

The First law in Thermodynamics:

$$\begin{aligned} dU &= đQ - đW \\ &= TdS - pdV \end{aligned}$$

And in Statistical mechanics:

$$d\langle H\rangle_{\mathsf{Can}} = \frac{1}{\beta}dh - \langle p\rangle_{\mathsf{Can}}dV$$

# Meanwhile on the conceptual side…

…there are some conceptual problems:

1. Mechanical explanation of thermodynamic variables?
   - The bridge laws

$$T \hat{=} \frac{1}{\beta},\ S \hat{=} -h = -\int \rho(s) \log \rho(s) ds$$

   do not conform to Tolman's fundamental idea that $A(s) \simeq \langle A \rangle_{\mathrm{Can}}$.

2. Subjective notion of probability?
   - The special role played by $\rho_{\mathrm{Can}}$ in recovering thermodynamics does not fare well with the interpretation of an ensemble which is

     *appropriately chosen so as to correspond to the partial knowledge that we do have as to the initial state of the system of interest.*

- The temperature of the system appears to depend on our knowledge of the state.

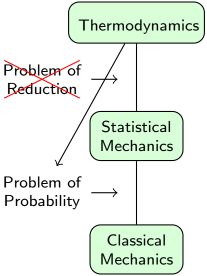
# Subjective probability in statistical mechanics

Albert (2000):
"Can anybody seriously think that our merely being *ignorant* of the exact microconditions of thermodynamic systems plays some part in *bringing it about*, in *making it the case*, that (say) *milk dissolves in coffee*?"

Uffink (2010):
"our beliefs or lack of knowledge do not explain or cause what happens in the real world. Instead, if we use subjective probability in statistical physics, it will represent our beliefs about what is the case, or expectations about what will be the case. And the results of such considerations may very well be that we ought to expect gases to disperse, ice cubes to melt, or coffee and milk to mix."
"The theory is applied to physical systems, to be sure, but the probabilities specified do not represent or influence the physical situation: they only represent our state of mind."

# Reversing the reduction

- If a reduction of Thermodynamics is to be accompanied by an explanation of thermodynamic laws, then adopting subjective probabilities in Statistical Mechanics is a departure from the reduction program.
- Then what explains our knowledge? Where does it come from? From Thermodynamics!




A reversal of reduction: Thermodynamics informs Statistical Mechanics rather than that it reduces to Statistical Mechanics. As a peculiar slogan:

> *thermodynamics is the science where probabilities can be measured with thermometers and calorimeters. - Martin-Löf 1979 p.70*

# Reversing the reduction: some possible worries

Can thermodynamics be reconciled with classical mechanics?

- Classical mechanics is (in a sense) incomplete. Sure, Hamilton's equations allow one the calculate all possible paths for a particle in a certain potential. But just like how logic doesn't tell us which propositions are true, Classical mechanics doesn't tell us which path is the case.
- Thermodynamic phenomena may in part reflect regularities in initial conditions. If so, it is not surprising that these regularities cannot be derived from classical mechanics.

If statistical mechanics doesn't explain thermodynamics, isn't statistical mechanics obsolete?

- Statistical mechanics above all advances thermodynamics, providing methods to e.g. compute equations of state instead of having to derive them from empirical observations.

# Summary

- The reduction from Thermodynamics to Statistical Mechanics is not a clear-cut case.
- Further, sharp formulations of Thermodynamics and (particularly) Statistical Mechanics are sparse.
- Tolman's formulation explicitly adopts a subjective approach towards probabilities (ensembles).
- This view is problematic when interpreting established relations between Thermodynamics and Statistical Mechanics as reduction relations.
- Give up the reduction and reverse it: take Thermodynamics to inform probabilities in Statistical Mechanics.

**Thank You!**