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The quantitative content of statistical mechanics



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ABSTRACT

I give a brief account of the way in which thermodynamics and statistical mechanics actually work as contemporary scientific theories, and in particular of what statistical mechanics contributes to thermodynamics over and above any supposed underpinning of the latter's general principles. In doing so, I attempt to illustrate that statistical mechanics should not be thought of wholly or even primarily as itself a foundational project for thermodynamics, and that conceiving of it this way potentially distorts the foundational study of statistical mechanics itself.

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1. Introduction

Classical equilibrium thermodynamics is characterised by laws of great generality and scope, but which have no justification within thermodynamics itself. Historically, much of the original impetus of statistical mechanics was to provide a microphysical justification: almost from its outset, the subject had to grapple with the apparent inconsistency between the apparent time-irreversibility of thermodynamics and the apparent time-reversibility of microphysics.

If a 19th-century physicist were transported to the present day and perused the philosophical literature on statistical mechanics, they would be forgiven for thinking that little has changed. Overwhelmingly, the focus of discussion is on the use of statistical-mechanical methods to underpin thermodynamics. For instance, Roman Frigg's recent review states that

Thermodynamics (TD) correctly describes a large class of phenomena we observe in macroscopic systems. The aim of statistical mechanics is to account for this behaviour in terms of the dynamical laws governing the microscopic constituents of macroscopic systems and probabilistic assumptions. ... The fact that many processes in the world are irreversible is enshrined in the so-called Second Law of Thermodynamics ... It is the aim

of non-equilibrium [statistical mechanics] to give a precise characterization of irreversibility and to provide a microphysical explanation of why processes in the world are in fact irreversible. (Frigg, 2007, pp. 99–100)

Callender (2001), slightly more cautiously, observes that “Kinetic theory and statistical mechanics are *in part* attempts to explain the success of thermodynamics in terms of the basic mechanics.” (p. 540; emphasis mine.) In similar vein, Ridderbos (2002) notes that “One of the cardinal aims of the theory of statistical mechanics is to underpin thermodynamic regularities by a theory formulated in terms of the dynamical laws governing the motion of the microscopic constituents of a thermodynamic system.” (p. 66). Examples could easily be multiplied.

Notwithstanding Callender's and Ridderbos' caveats, this essentially *foundational* construal of statistical mechanics is dominant in philosophical discussion. The field is presented as concerned primarily with providing a microscopic underpinning of already-known macroscopic generalities; the point of philosophical concern is whether it does so adequately.

Part of the point of this paper is to suggest that this focus on the foundational role of statistical mechanics is in danger of distorting the discussion. Statistical mechanics is both a huge field in its own right in contemporary physics and a hugely important tool across many (most?) other areas of physics, and only a very small part of the work done under the label of statistical mechanics has anything much to do with the foundations of thermodynamics. Insofar as there are important questions to ask about the

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conceptual underpinnings of statistical mechanics, it may be misleading to regard statistical mechanics itself as itself wholly or primarily a conceptual underpinning for thermodynamics. I mostly use the neo-Boltzmann approach (advocated recently by, inter alia, Albert, 2000; Callender, 2001; Goldstein, 2001; Lebowitz, 2007; North, 2002; Penrose, 1989, 1994) to illustrate where this can be significant.

But the main point of the paper is just to give an overview of what statistical mechanics, as used in contemporary physics, actually does, over and above its supposed foundational role—something that seems to be rather little understood in foundational circles. I make no pretense at conceptual or mathematical rigor: I attempt simply to lay out what the actual methods and (broad-level) techniques of thermodynamics, and of equilibrium and then non-equilibrium statistical mechanics, actually are. I take it that any satisfactory conceptual account of statistical mechanics must succeed not simply at underpinning the general predictions of thermodynamics, but the predictive and explanatory successes of statistical mechanics itself.

2. The content of thermodynamics

What does classical thermodynamics actually tell us about the systems to which it applies? Roughly speaking (that is, with no pretensions to completeness, historical accuracy, conceptual independence or mathematical precision), something like the following:

- That each system, if isolated, relaxes in some reasonable time towards an *equilibrium state* whose “thermodynamic parameters” (roughly speaking, its macroscopically accessible features) are time-invariant and are determined only by its internal energy U and by whatever external parameters (paradigmatically, its volume V) constrain it. (This equilibration principle is called the ‘minus first law of thermodynamics’ by Brown & Uffink (2001).)
- That any two such systems can be placed in ‘thermal contact’, whereby they may be treated as parts of a single system that will reach a joint state of equilibrium.
- That the relation of ‘being in equilibrium with’, that holds between any two systems at equilibrium which remain unchanged when placed in thermal contact, is an equivalence relation, and that the relation of ‘being hotter than’, which holds between two systems when energy is transferred from the first to the second when they are placed in thermal contact, is an ordering relation. (The Zeroth Law.)
- That, in part as a consequence of the above, we can define ‘empirical temperatures’, real-valued functions of an equilibrium system’s internal energy and external constraints, so that system 1 has a higher temperature than system 2 iff it is hotter.
- That the energy transferred to a system as a result of its transition between two equilibrium states can be consistently divided into ‘work’, which is energy transferred via variation of the external parameters, and ‘heat’, which is energy transferred via thermal contact, and that energy is conserved, so that the change in internal energy of a system equals the net work done on the system by varying its parameters plus the net heat flowing into the system from other systems in which it is in thermal contact. (The First Law.)
- That it is possible to speak consistently of arbitrarily small and slow transitions of a system between equilibrium states, so that the infinitesimal change of energy of the system dU in such a transition can be decomposed as

$$dU = \delta Q + \delta W, \quad (1)$$

where δQ and δW are the infinitesimal work done, and heat transferred, in the transition.

- That the work δW can be decomposed as

$$\delta W = \sum_i -P_i dV^i,$$

where the V^i are the external constraints on the system and the P_i are functions of an equilibrium system’s internal energy and external constraints, which can be defined as the rate of change of U with respect to V^i while the system is thermally isolated.

- That there exist functions S (‘thermodynamic entropy’) and T (‘thermodynamic temperature’) of an equilibrium system’s internal energy and external constraints, such that

$$\delta Q = T dS,$$

such that T is an empirical temperature, and such that no transition of a thermally isolated system between two equilibrium states can induce a decrease in S . (The Second Law.)

Famously, the above principles (collectively speaking) are *primitives* of thermodynamics: although there are various logical interconnections between them, the system as a whole is merely postulated, and thermodynamics in itself offers no justification for them. But never mind: let us accept them, and take for granted that all of the above is known to hold of, say, a box of gas of known total volume and external energy, and ask: what can be deduced about the behaviour of the box?

The answer, so far as I can see, is virtually nothing. The box will have *some* equilibrium state, to which it will relax on some unspecified timescale. Increasing or decreasing its volume may (or may not) lead to changes in its internal energy. It will not be possible to use the box to play certain roles in various heat engines: it will not, for instance, be possible to operate on it in a cycle to turn heat into work. It will have some thermodynamical temperature, and if placed in thermal contact with a lower-temperature system, will transfer heat to that system. It will have some entropy, which cannot be induced to decrease in an adiabatic process. But on what the temperature is, or the entropy, for a given volume; on how much work must be done (or will be generated) in contracting the box; on even whether the box is of uniform density... on all these questions, thermodynamics in the abstract is silent. The Second Law, or the First, or the Zeroth, or the Minus First, or all of them together, do not so much as predict that a box of gas initially confined to one half of a box will expand to occupy the whole box.

Nor can it be expected to: the very neutrality of thermodynamics forbids it. Thermodynamics is intended to apply to gases, to liquids and to solids: to boxes filled with plasma, treacle or stone as surely as boxes filled with gas. And it is not a law of nature that a chunk of rock, initially ‘confined’ to the lower half of a box by a partition, will expand to fill the whole box.

Thermodynamics only begins to get its bite when its *abstract* principles are supplemented by physical details that pick out the particular system under study. This is normally done via the *equations of state* of the system: the concrete mathematical expressions for the functions P_i and T in terms of the energy U and the constraints V^i . In the case of a gas, for instance, the only salient constraint is the total volume V (note that this already tells us a lot about the gas, for instance that its macrophysics depends on the size of its container but not on the shape) and, in the idealisation of a sufficiently dilute gas, the equation of state for the parameter $P_1 = P$ is

$$P = \frac{1}{\alpha} \frac{U}{V}, \quad (2)$$

where α is a dimensionless parameter dependent upon the species

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