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The problem of equilibrium processes in thermodynamics

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ABSTRACT

It is well-known that the invocation of 'equilibrium processes' in thermodynamics is oxymoronic. However, their prevalence and utility, particularly in elementary accounts, presents a problem. We consider a way in which their role can be played by sets of sequences of processes demarcated by curves carrying the property of accessibility. We also examine the vexed question of whether equilibrium processes are necessarily reversible and the revision of this property in relation to sets of sequences of such processes.

1. Introduction

The systems of classical thermodynamics – that is to say equilibrium thermodynamics, as distinct from various possible extensions to non-equilibrium situations – have no spontaneous behaviour. The states of the system are ***equilibrium states*** and the space Ξ of these states is a ***thermodynamic system***. All transitions between states, called ***processes***, are a result of an outside intervention using a set of ***control variables***. As Wallace (2014) points out the name for the study of systems with this character is ***control theory*** and the question to be asked is: Given the system is in a particular state, can the control variables be manipulated to bring the system into another specified state?

It is convenient to use the symbol Ξ to denote both the thermodynamic system and its space of states. In the latter sense Ξ is an open convex set in $\mathbb{R}^{n+1}$ for some integer $n > 0$. The elements of the state-vector $\boldsymbol{x} \in \Xi$ are extensive variables. Those of mechanical type are referred to as ***deformation variables***, with each being associated with an intensive control variable. Examples are the volume of a fluid with associated control variable being the pressure exerted by the force on a piston and the magnetic moment of a magnet controlled by an applied magnetic field.[1]

The characteristic feature of a thermodynamic as distinct from a mechanical system is the presence of at least one ***thermal variable***. A system with exactly one thermal variable is called ***simple***[2] and that one thermal variable can be identified with the internal energy U.[3] We shall, henceforth, suppose that the system in question is simple; so to be specific $\boldsymbol{x} := (x^{\mathrm{T}}, \boldsymbol{x}^{\mathrm{D}})$, where $x^{\mathrm{T}} := U$ and $\boldsymbol{x}^{\mathrm{D}}$ is an n-dimensional vector of deformation variables. A ***thermodynamic process*** $\boldsymbol{x} \to \boldsymbol{x}\prime$ is a manipulation of the control variables to change the state of the system from $\boldsymbol{x}$ to $\boldsymbol{x}\prime$. For this statement to make sense we must assume:

> **The Hypothesis of Controllability**: that *all* interactions between the system and its environment are controllable. This includes not just manipulations of the control variables associated with the deformation variables but also all other means by which the internal energy can be changed.
>
> **The Hypothesis of Achievability**: that a possible process is achievable, *exactly in a finite amount of time* (which will normally include a final 'leave-it-alone' stage, Wallace, 2014) by a purposeful manipulation of the control variables.

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[1] And it is, of course, the case that, once the equations of state relating the extensive and intensive variables are known, the state of the system can be specified in a state space coordinated by a mixture of extensive and intensive variables.

[2] In the account of thermodynamics by Lieb and Yngvason (1999) a simple system has this property together with a number of additional properties (op. cit. Section 3), which do not concern us at this stage.

[3] The thermal variable could be identified as the entropy S, but in most accounts that is a derived quantity appearing later in the analysis.

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A number of points are of note:

(i) These hypotheses encompass the ***minus first law*** of thermodynamics of Brown and Uffink (2001).[4]

(ii) Although, as we shall see, the work of this paper has similarities with that of Norton (2016), a significant difference between us is his (implicit) rejection of the hypothesis of achievability.[5]

(iii) The existence of a process $\boldsymbol{x} \to \boldsymbol{x}'$ does not imply the passage along a sequence of (equilibrium) states in Ξ from $\boldsymbol{x}$ to $\boldsymbol{x}'$. With some exceptions (e.g. Giles, 1964) accounts of classical thermodynamics restrict, as we have indicated, the states of the system to equilibrium states, meaning that the only defined states of a process are its end points.

(iv) As a consequence of (iii), a process is specified in terms of its end points together with a description of the manipulations of the control variables used to bring it about.

(v) As a consequence of (iv), there will in general be many different processes denoted by $\boldsymbol{x} \to \boldsymbol{x}'$. Thus a useful concept is that of accessibility (Buchdahl, 1966; Lieb & Yngvason, 1999). The state $\boldsymbol{x}'$ is ***accessible*** from $\boldsymbol{x}$, written $\boldsymbol{x} \prec \boldsymbol{x}'$ if there is at least one process $\boldsymbol{x} \to \boldsymbol{x}'$.

Accessibility $\boldsymbol{x} \prec \boldsymbol{x}'$ can be unqualified, meaning that there exists at least one among all the possible manipulations of the control variables which can be employed to produce a process $\boldsymbol{x} \to \boldsymbol{x}'$, or qualified, meaning that only certain manipulations are allowed. The case of importance in the latter category is the implementation of an adiabatic process as described in Section 2.1.1. Buchdahl and Lieb and Yngvason consider only adiabatic accessibility, for which they use the symbol '$\prec$'. We shall begin by considering unqualified accessibility using '$\prec$'. If $\boldsymbol{x} \prec \boldsymbol{x}'$ and $\boldsymbol{x}' \prec \boldsymbol{x}$ then $\boldsymbol{x}$ is said to be ***recoverable*** from $\boldsymbol{x}'$ (and vice-versa),[6] denoted as $\boldsymbol{x} \succ\prec \boldsymbol{x}'$, with $\boldsymbol{x} \ll \boldsymbol{x}'$ asserting that $\boldsymbol{x}$ is ***irrecoverable*** from $\boldsymbol{x}'$; that is $\boldsymbol{x} \prec \boldsymbol{x}'$ but not $\boldsymbol{x}' \prec \boldsymbol{x}$. When we need to discuss adiabatic accessibility, recoverability and irrecoverability we use '$\overset{A}{\prec}$', '$\overset{A}{\succ\prec}$' and '$\overset{A}{\ll}$', respectively.

In Section 2 we discuss the weaknesses of the standard definition of an equilibrium process along a curve in Ξ, emphasising the distinction between this and the question as to whether the process is reversible, and in Section 2.1 we propose replacement definitions for both of these based on accessibility. Sections 2.1.1 and 2.1.2 apply these new definitions to adiabatic and isothermal processes, respectively and Sections 3.1 and 3.2 discuss the cases of a perfect fluid and a cycle of processes. We compare and contrast our account with that of Norton (2016) in Section 4 and our conclusions are contained in Section 5.

2. Equilibrium processes

At the outset there is a problem of terminology in the intimate and often confusing relationships between:

(a) a quasi-static process,
(b) an equilibrium process,
(c) a reversible process.

This is compounded by the profusion of overlapping and sometimes contradictory definitions of what is meant by a 'quasi-static process',[7] containing as they do both a reference to what such a process *is* and *how it is implemented*. Thus we read that quasi-static processes are "those that may be considered as a sequence of neighbouring equilibrium states" (Lebon, Jou, & Casas-Vázquez, 2008, p. 4) and that "a quasi-static process is a change in the state of the system that is conducted infinitesimally slowly such that, at each instant, the system is in thermodynamic equilibrium with its environment, and its thermodynamic properties [⋯] remain well-defined throughout the process" (Samiullah, 2007, p. 608). Taken together we may infer from these quotes that a quasi-static process is just an equilibrium process together with some gloss as to how this process may be carried out. So, for the sake of discussion, let us agree to take 'equilibrium process' and 'quasi-static process' as synonyms and pass to the more interesting relationship between (b) an equilibrium process, and (c) a reversible process. Norton (2016, p. 43) refers to "thermodynamically reversible or quasi-static processes" at the outset of his paper and tends throughout to treat them as synonyms.[8] While, as we shall argue, reversibility (as distinct from recoverability) is a useful description only for equilibrium processes (and our replacement thereof) the converse is by no means obvious. Thus, for example, Buchdahl (1966, pp. 52–54) gives a proof of the reversibility of quasi-static processes and MacDonald (1995, p. 1122) gives an example of a quasi-static irreversible process. In the interests of clarity it seems important to keep separate the question of the replacement for equilibrium processes and the second question as to whether, and in what sense, they can be regarded as reversible.

Let $\mathcal{L}(\boldsymbol{x}_0, \boldsymbol{x}_1)$ be a simple, directed and continuous curve in Ξ parameterized by $\boldsymbol{x} = \boldsymbol{x}(\lambda)$, for $\lambda \in [0,1]$, with $\boldsymbol{x}(0) := \boldsymbol{x}_0$ and $\boldsymbol{x}(1) := \boldsymbol{x}_1$. The curve parameterized in the reverse direction is denoted by $\mathcal{L}(\boldsymbol{x}_1, \boldsymbol{x}_0)$.

Definition 1. $\mathcal{L}(\boldsymbol{x}_0, \boldsymbol{x}_1)$ is an ***accessible curve*** if $\boldsymbol{x}(\lambda) \prec \boldsymbol{x}(\lambda')$, $\forall\ 0 \le \lambda < \lambda' \le 1$.

It should be emphasised that just as *accessibility* can be unqualified or qualified, an *accessible curve* (that is to say the property of having accessibility between all directed pairs on the curve) can also be unqualified or qualified. And it is, of course, the case that a particular curve may be piecewise divisible into parts having different types of accessibility. In particular we shall be concerned with the case where $\mathcal{L}(\boldsymbol{x}_0, \boldsymbol{x}_1)$ is an ***adiabatically accessible curve*** and situations where the curve may be accessible but not adiabatically accessible.

Consider now the:

Definitions 2.

2–1: *An* ***equilibrium process*** *along the curve* $\mathcal{L}(\boldsymbol{x}_0, \boldsymbol{x}_1)$

[4] They argue that none of the laws of thermodynamics actually asserts that a system not in equilibrium attains an equilibrium state and that it does so must constitute an addition law.

[5] This is discussed in Section 5.

[6] The minefield associated with the various uses of the term 'reversible' in thermodynamics is carefully negotiated by Uffink (2001). He points out that some confusion is generated in the English translations of the writings of Planck and Clausius where the terms *umkehrbarheit* and *reversibel* are conflated to the single word 'reversible'. He recommends the use of the term *recoverable* when "the only thing that counts is the retrieval of the initial state" (ibid, p. 316). Following this advice we restrict the use of the term 'reversible' to situations where, within the development of a picture of an equilibrium process, the path of the process is reversed.

[7] The literature for this is extensively documented and analysed by Norton (2016). In consequence our comments are rather brief.

[8] Although, in Sect. 7.9, he does discuss both reversible and irreversible equilibrium processes, giving as an example the case of a perfect fluid where, along a curve in the thermodynamic space, there can be both a reversible and a "fully irreversible" process.