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How Many Aims Are We Aiming At?

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Abstract

I highlight that the aim of using statistical mechanics to underpin irreversible processes is, strictly speaking, ambiguous. Traditionally, however, the task of underpinning irreversible processes has been thought to be synonymous with underpinning the Second Law of thermodynamics. I claim that contributors to the foundational discussion are best interpreted as aiming to provide a microphysical justification of the Minus First Law, despite the ways their aims are often stated. I suggest that contributors should aim at accounting for both the Minus First Law and Second Law.

1 Introduction

Many authors claim that an aim of statistical mechanics is to provide a suitable foundation for thermodynamics.¹ Some even claim that it is the aim of statistical mechanics.² A great deal of philosophical literature has been devoted to this project. However, despite its size, much of this work has focused on underpinning irreversible processes.³ This is likely because many regard this as one of the most important parts, if not the most important part, of the foundational project.

For a long time the Second Law of thermodynamics was thought to be the only thermodynamic law that dealt with irreversible processes. Naturally then, many of those contributing to the foundational project, both past and present, have seen the task of underpinning irreversible processes as synonymous with underpinning the Second Law. In 2001, Jos Uffink and Harvey Brown revealed that the spontaneous approach to equilibrium, an irreversible process previously thought to be part and parcel of the Second Law, is actually captured by an independent and more basic law of thermodynamics: the Minus First Law.

The separation of these laws forces us to consider two questions. First, how should we interpret those who state that their aim is to account for irreversible processes? Should we interpret them as aiming to account for the Second Law? The Minus First Law? Or both laws? And second, what should those contributing to the foundational project be aiming for?

As I intend to make clear in this paper, the aim of underpinning irreversible processes is, strictly speaking, ambiguous. It depends on what is meant by "irreversible". However, I will suggest, by reviewing relevant ways of interpreting "irreversible", the content of the Minus First and Second Laws of thermodynamics, and by noting the most prominent projects in current foundational discussions of irreversible processes, that contributors to the discussion are best interpreted as aiming to provide a microphysical justification of the Minus First Law, despite the ways their aims are often stated. I will also suggest that contributors to the foundational project should aim at accounting for both the Minus First Law and Second Law of thermodynamics.

This paper will proceed as follows. I begin, in the next section, with a discussion of several notions of irreversibility. I then discuss the content of both the Minus First Law and Second Law of thermodynamics. Since much of the foundational literature on thermodynamics is concerned with recovering *classical thermodynamics*, I follow suit and focus on classical thermodynamic

¹Callender (2001: p.540) and Ridderbos (2002: p.66) are but two examples.

 2 For example, in a recent review article, Roman Frigg (2008: p.99) writes:

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.

³See, for example, Bricmont (1995), Frigg (2008, 2009, 2011, 2012), Frigg and Werndl (2011, 2012a, 2012b), Goldstein (2001), Lebowitz (1993a, 1993b, 1994, 1999), Penrose (2005), Ridderbos (2002), Sklar (1995), and Uhlenbeck and Ford (1963).

laws and concepts—though often in their modern guise.⁴ The results of my discussion prompt the conclusion that the goal of underpinning irreversible processes is, strictly speaking, ambiguous. In the third section I note the most prominent approaches to current foundational discussions of irreversible processes, along with their goals. I use this as the basis for my claim that contributors to the discussion are best interpreted as aiming to provide a microphysical justification of the Minus First Law. I then end this section and paper by suggesting and motivating why those contributing to the project of providing a foundation for thermodynamics should aim at accounting for both the Minus First Law and Second Law.

2 Classical Thermodynamics

Classical thermodynamics was developed around 1850. It is usually associated with authors such as Rudolf Clausius, Lord Kelvin, and Max Planck—though some trace its origins back to Sadi Carnot's work on heat engines.⁵ Thermodynamics characterises macroscopic systems in terms of macroscopically measurable quantities, e.g. temperature, pressure, volume, etc. It also describes changes in them in terms of heat or work exchanges with an environment. The theory rests on a set of fundamental laws. These laws are intended to be independent of any particular hypothesis concerning the microscopic constitution of macroscopic systems. They have traditionally been understood as generalised statements of experimental facts. This section discusses two thermodynamic laws, the Minus First Law and the Second Law of thermodynamics. But before turning to a discussion of these laws it is important to first disentangle some important and closely related concepts.

2.1 Time-Reversal Invariance and "Reversibility"

The state of a system is typically represented by a point in some state space Ω . For example, the *thermodynamic state* of a system is represented by a point in a state space characterised by a small number of macroscopically measurable parameters (e.g. temperature, pressure, and volume).

A state history (or process) is a trajectory through state space. That is, a mapping $\sigma : I \subseteq$ $\mathbb{R} \to \Omega$, for some time interval I. A theory's laws delimit a definite class of state histories, D. For any time t_0 , we can define a reflection of the time axis around t_0 by

⁴This is distinguished from the less orthodox, more formal, axiomatic treatments of thermodynamics that have appeared since the early 1900's, and which are associated with Constantin Carathéodory (1909), and Elliott Lieb and Jakob Yngvason. Other axiomatic approaches have been offered by Robin Giles (1964), John Boyling (1972), and Josef-Maria Jauch (1972, 1975), among others.

⁵See Mendoza and Carnot (1960). Most authors consider classical thermodynamics to have emerged around 1850, in works that attempted to recast Carnot's theorem—which was originally expressed using terms familiar to the caloric theory of heat—in what we now call classical thermodynamic terms. Other early, important, but lesser known contributors to classical thermodynamics are Emile Clapeyron, William Rankine, and Ferdnand Reech. ´ See Uffink (2001, 2007) for more on the interesting history of thermodynamics.

$$
t \to t^T = t_0 - (t - (t_0)). \tag{1}
$$

Standardly, we take $t_0 = 0$, so that $t^T = -t$.

We can talk about a state's time-reversal. This is determined by a state reversal operation, whose general form we write as

$$
\omega \to \omega^T. \tag{2}
$$

In classical mechanics, for example, the state reversal operation reverses the sign of all momenta and magnetic fields. In classical thermodynamics, however, whose states do not contain velocity-like parameters, the state reversal operation is simply the identity operation.

We can also talk about the time-reversal invariance of laws and theories. Given a time reflection (i.e. (1)) and a state reversal operation, we can define an operation that reverses state histories. Define the history-reversal operation

$$
\sigma \to \sigma^T \tag{3}
$$

by

$$
\sigma^T(t) = \sigma(t^T)^T.
$$
\n(4)

So then, if σ includes a sequence of states $\ldots \sigma(t_1), \sigma(t_2), \sigma(t_3), \sigma(t_4), \ldots$, then the timereversed history includes a sequence of states $\ldots \sigma(t_4^T)^T, \sigma(t_3^T)^T, \sigma(t_2^T)^T, \sigma(t_1^T)^T, \ldots$

A theory is said to be time-reversal invariant (or symmetric under time-reversal) iff, whenever a state history σ is permitted by its laws, the time-reversed state history σ^T is also permitted. Another way of putting this is to say that the theory is time-reversal invariant iff $\mathcal{D}^T \subseteq \mathcal{D}$.

Notice that it is the form of a theory's laws, given a state reversal operation, that determine whether or not the *theory* is time-reversal invariant. This is why authors often speak of the time-reversal invariance of laws rather than the time-reversal invariance of theories, and why they sometimes use the expression "time-reversal invariant theory" interchangeably with "timereversal invariant laws".

"Reversible" is a term that has several meanings. Sometimes it is used to refer to timereversal invariant processes. That is, to state histories whose time-reverse state histories are also permitted by the theory's laws. In these contexts, "irreversible" is used to refer to timereversal non-invariant processes. That is, to state histories whose time-reverse state histories are not, according to the laws of the theory, possible.

In other situations, "reversible" is used to mean, what Jos Uffink (2001: p.316) has called, recoverable. Ordinary experience suggests that the move from an initial thermodynamic state s_i to a final thermodynamic state s_f , cannot be fully undone, once such a process has taken place. Here, the expression "fully undone" is meant to indicate not just a return of the system to its initial state but also its environment. The free expansion of an adiabatically isolated ideal gas that does no work on its surroundings is an obvious example of an irreversible process, in this sense. In situations such as these, there is no available process that takes us from the final state s_f and restores the initial state s_i , completely. As Uffink (2001: pp.316-317) notes, this concept of reversibility differs from reversibility understood as time-reversal invariance in the following three ways. First, the only thing that matters for reversibility understood as recovery is a return of the initial state. We do not need to specify a history-reversal operation that ensures that the system and environment pass through their reversed sequence of states. A second difference is the concept's reference to and emphasis on the system's environment. For a process to be recoverable, it must be the case that the system and its environment return to their initial state. Reversibility understood as time-reversal invariance is simply concerned with states of the system. It is not also concerned with states of the environment. A third difference concerns the concept of possibility that is implicitly invoked in talk of undoing the process. This concept of reversibility differs from reversibility understood as time-reversal invariance in that recoverability is concerned with state histories that can be actualised, not merely ones that are compatible with a theory's laws. For a process to be reversible in this sense it needs to be the case that it is possible for beings like us, with our epistemic and physical limitations, to recover the initial state.

On the basis of the differences between these two senses of "reversible", it is the case that recoverability does not imply, and is not implied by, time-reversal invariance, and irrecoverability does not imply, and is not implied by, time-reversal non-invariance. The two concepts are logically distinct.

Let's remind ourselves of the foundational project that prompted this discussion: underpinning irreversible processes. We can already see from this discussion of time-reversal invariance and interpretations of "reversible" that the task of underpinning irreversible processes is, as it stands, ambiguous. It can be interpreted in at least one of two ways. The task could be understood as one that involves using statistical mechanics to account for processes described by laws that are time-reversal non-invariant or it could be understood to involve accounting for processes that render initial states irrecoverable.

2.2 The Minus First Law

In 2001, Harvey Brown and Jos Uffink coined the expression "Minus First Law".⁶ Earlier authors, however, both appreciated its content and considered it, like Brown and Uffink, to be more fundamental than the other laws of thermodynamics.⁷ Commonly, however, the law is

⁶See their article, "The Origins of Time-Asymmetry in Thermodynamics: The Minus First Law".

⁷See, for instance, Uhlenbeck and Ford (1963: p.5), Kestin (1979: p.72), and Lebowitz (1994: p.135).

invoked without being flagged as a law.⁸ It states:

Minus First Law: An isolated system in an arbitrary initial state within a finite fixed volume will spontaneously attain a unique state of equilibrium.

Like the other laws of thermodynamics, the Minus First Law intends to capture a phenomenological fact. It can be thought to consist of three independent claims: an existence claim, a uniqueness claim, and a claim about the spontaneity of the approach to equilibrium. The Minus First Law claims that for any isolated system in an arbitrary initial state within a finite fixed volume there exists a state of equilibrium that the system will approach. The Law also claims that this equilibrium state is *unique*, and that, beginning from an arbitrary initial state, the approach to it happens *spontaneously*. What is important for our purposes, however, is the characterisation of equilibrium that underlies the existence claim. As Brown and Uffink (2001: p.528) note, the defining property of an equilibrium state is that once it has been reached, it remains thereafter constant in time. Spelled out like this, it is clear to see that the Minus First Law is time-reversal non-invariant. The Law is time-reversal non-invariant because of how equilibrium states are understood. Once the system's equilibrium state has been reached, no spontaneous departure from it is possible without some kind of intervention from the environment.

The Minus First Law says that isolated systems will either be in a unique state of equilibrium or else be spontaneously approaching equilibrium. If we take the goal of underpinning irreversible processes to be understood as synonymous with the goal of accounting for the spontaneous approach to equilibrium of an isolated system in an arbitrary initial state, then the goal is aimed at underpinning processes captured by the time-reversal non-invariant Minus First Law.

2.3 The Second Law

There are several statements of the Second Law of thermodynamics.⁹ Classical thermodynamics standardly identifies three. These are: the Kelvin statement, the Clausius statement, and the Entropy statement.

Kelvin Statement: No process is possible whose sole result is the complete conversion of heat into work.¹⁰ (Kardar 2007: p.9)

 8 See, for instance, Pauli (1973: p.1) and Sklar (1995: p.20).

⁹See Uffink (2001) for an interesting and detailed discussion of the many versions of the Second Law of thermodynamics.

 10 This is a common, modern, presentation of the Kelvin statement of the Second Law. As Uffink (2001: p.327-328) notes, this statement of the Law was inspired by what Kelvin considered to be an axiom of thermodynamics:

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects. (Kelvin 1851: p.265)

Clausius Statement: Heat can never pass from a colder body to a warmer body without some other change, connected therewith, occurring at the same time. (Clausius 1856: p.86)

Entropy Statement: The thermodynamic entropy of an adiabatically isolated system cannot decrease. That is, $dS \geq 0$.

These three statements are equivalent.¹¹ This, presumably, is the reason why many have expressed the goal of underpinning irreversible processes as one that aims at accounting for the Second Law, rather than to any particular statement of the law.

Importantly, the Second Law only applies to systems at equilibrium. In fact, thermodynamics is, with the exception of the Minus First Law, a theory about equilibrium states. That thermodynamics is a theory about equilibrium states is readily seen in familiar pressure-volume (P-V) and temperature-entropy diagrams, which are representations of the theory's state space. These spaces solely consist of equilibrium states. As such, processes described by the Minus First Law cannot be properly represented in them.

Figure 1: The P-V diagram of two different expansions of an ideal gas.

Figure 1 contains two different expansions of an ideal gas. The solid line represents a reversible (i.e. recoverable), quasi-static isothermal expansion of a gas by a path of equilibrium states. The dashed line represents the adiabatic free expansion of an isolated ideal gas that does no work on its environment. Both systems begin and end at the same temperature, pressure, and volume, but only one of these paths is described completely. Properly speaking, the free expansion of the gas is represented only by points at 1 and 2—when it is in equilibrium.

¹¹Actually, these statements are equivalent, modulo a few basic qualifications. See Kardar (2007: Ch.1) for a proof of their equivalence. And see Uffink (2001: pp.328-329) for a discussion of the necessary qualifications.

The Minus First Law predicts that the freely expanding gas will spontaneously attain a unique state of equilibrium. The Second Law makes no such prediction. It says nothing about transitions from nonequilibrium states. It is concerned only with transitions between systems initially and finally at equilibrium. It says that some of these transitions are reversible. That is, that the system-environment initial state can be fully recovered. In the context of our example, it maintains that the quasi-static isothermal expansion of the gas is reversible and that the free expansion is not.

3 What Are The Aims? What Should They Be?

As the previous section hopes to have made evident, if the goal of underpinning irreversible processes is understood to be synonymous with the aim of using statistical mechanics to provide a justification of the Second Law, then the aim is to justify why certain transitions between equilibrium states render initial states irrecoverable. On the other hand, if the goal of underpinning irreversible processes is understood to be synonymous with the aim of accounting for the spontaneous approach to equilibrium from some nonequilibrium state, then the aim is to underpin the Minus First Law. Since these laws are distinct and logically independent, claims that underpinning irreversible processes involve justifying the Minus First Law can not be understood to be synonymous with claims that maintain that such an underpinning involves accounting for the Second Law.

So what then do contributors to the foundational project mean when they claim that it is an aim of statistical mechanics to account for irreversible processes?

Unlike many other successful physical theories, statistical mechanics does not possess a generally accepted formalism. Rather, it consists of a collection of different approaches and schools each with their own agenda, tool-box of techniques, and mathematical apparatus. Within foundational debates on irreversible processes however, the most prominent approaches that are drawn from include various strands of neo-Boltzmannianism, Gibbesians who rely on mixing, and Interventionism.¹² While these approaches are quite different, they are united in the sense that when we look beyond their stated aims they are all primarily concerned with accounting for the fact that systems initially prepared in some arbitrary nonequilibrium state spontaneously approach a state of equilibrium. That is, these approaches are united in their pursuit of underpinning the irreversible processes captured by the time-reversal non-invariant Minus First Law.

 12 For comprehensive and contained discussions of the various approaches, schools, and mathematical frameworks that appear in foundational discussions of statistical mechanics see Frigg (2008) and Uffink (2007). Neo-Boltzmannian approaches are discussed in, for example, Bricmont (1995), Frigg (2008, 2009, 2011, 2012), Frigg and Werndl (2011, 2012a, 2012b), Goldstein (2001), and Lebowitz (1993a, 1993b, 1994, 1999). Gibbesian approaches (with mixing) are discussed in, for example, Frigg (2008), Gibbs (1902), Lavis (2005), Penrose (1970), Ridderbos (2002), Ridderbos and Redhead (1998), Sklar (1995), Uffink (2007), and van Lith (1999). Interventionist approaches are discussed in, for example, Bergmann and Lebowitz (1955), Blatt (1959), Frigg (2008), Ridderbos and Redhead (1998), Sklar (1995), and Uffink (2007).

So, on the basis of this, it appears that despite the ways those working on these programs often state their aims, it is best to interpret them as aiming to provide a microphysical justification of the Minus First Law.

One final question, however, remains. What should those attempting to underpin irreversible processes be aiming at? As I have indicated in this paper, one way of interpreting this aim is to view it as the goal of justifying why certain transitions between equilibrium states render initial states irrecoverable. That is, to see it as an aim that is synonymous with the aim of using statistical mechanics to provide a justification of the Second Law. So, in contrast to work that has historically and that is currently being done on trying to account for the Minus First Law, should contributors also aim at underpinning the Second Law? Since the larger foundational project is concerned with underpinning all that thermodynamics tells us about the world, the answer is yes. Foundational programs should aim at accounting for both the Minus First Law and Second Law. The rationale for this wider aim is this: since the Minus First Law and Second Law are logically independent (with the caveat that arguably the Second Law only makes sense given a notion of equilibrium, and, to some extent, the Minus First Law makes that notion coherent), it can not be that a derivation of one is ipso facto a derivation of the other. So, even if foundational programs succeed in accounting for the Minus First Law, we will still be left with the task of accounting for the Second Law. Naturally, the same would also be true if, instead, we first set our sights on accounting for the Second Law. It is worth noting, however, that how large and difficult the remaining task will be will depend on the details of whichever law is accounted for first, since it might be that results used in some particular justification of one of these laws (e.g. a result that Boltzmann entropy, with high probability, is nondecreasing) in fact also contributes, perhaps significantly, to the justification of the other.

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