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Taking Thermodynamics Too Seriously

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This paper discusses the mistake of understanding the laws and concepts of thermodynamics too literally in the foundations of statistical mechanics. Arguing that this error is still made in subtle ways, the article explores its occurrence in three examples: the Second Law, the concept of equilibrium and the definition of phase transitions. © 2001 Elsevier Science Ltd. All rights reserved.

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> 'In this house, young lady, we OBEY the laws of thermodynamics.'
> (Homer punishing Lisa for making a perpetual motion machine;
> in the American television cartoon, *The Simpsons*)

1. Introduction

Classical phenomenological thermodynamics is a truly remarkable science. Using some relatively clear-cut concepts and straightforward relations among them, it is able to describe an impressive amount of physical behaviour in a surprisingly diverse range of systems. And it is able to do so accurately: there are no known exceptions to any of its principal laws. When one steps back and reflects on this fact, I think most will agree that it is simply amazing that the thermal phenomena in our world, be it of gases of chlorine or argon, solid plastics, iron bars or ice cubes, can be described and predicted using such general simply expressed laws.

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The great thinkers voice similar admiration for the theory. The following are a familiar sample:

> The law that entropy always increases,—the second law of thermodynamics—holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much the worse for Maxwell's equations. If it is found to be contradicted by observation—well, these experimentalists bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation (Eddington, 1935, p. 81).
>
> [Classical thermodynamics] is the only theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown (Einstein, 1970, p. 33).

One can find comparable endorsements from Maxwell, Pauli, Planck, Poincaré and others.

The great thinkers, and indeed, most who have studied thermodynamics, hold the field in high esteem. But some people, it seems to me, have *too much* respect for thermodynamics. They take the field, from a foundational perspective, *too seriously*. And this taking of the field too seriously is responsible for significant errors in the foundations of statistical mechanics. In particular, there are a cluster of beliefs shared by many working in the foundations of the field that are clearly mistakes (or as clearly mistakes as anything gets in philosophy), yet the people making these mistakes do so out of a professed desire to take thermodynamics seriously.

2. The Relationship between Thermodynamics and Statistical Mechanics

The problem for *foundations* of statistical mechanics arises from the fact that not only do we have a thermodynamic description of our (say) sample of gas and its behaviour, but we also have a mechanical theory describing the behaviour of the entities that constitute the gas. For our purposes, it will not hurt if we assume the mechanical theory in question is classical mechanics. The subject arises from a natural question: are the thermodynamic and mechanical descriptions compatible with one another? If thermodynamics implies a gas will later occupy a larger volume, does the classical mechanical evolution of that sample of gas also take it into a greater volume? Since we do not believe this physical behaviour falsifies either theory, the two theories' predictions had better be consistent when applied to the same phenomena. Supposing that classical mechanics is our more basic theory, the question is transformed into whether we can recover the essence of thermodynamics from classical mechanics. Kinetic theory and statistical mechanics are in part attempts to explain the success of thermodynamics in terms of the basic mechanics.

How do we go about 'recovering' one theory from another? This topic takes us into the thorny issue of theory reduction. Fortunately, for the points I wish to make we need not go into all the gory details of reduction. The main idea shared by many theories of reduction is that one theory reduces to another if we can in the reducing theory construct an *analogue* of the laws and concepts of the theory to be reduced. By specifying boundary conditions and other conditions we can logically deduce the analogue from the reducing theory, but we do not expect to be able to logically deduce from the reducing theory the theory to be reduced itself. The point of constructing an analogue of the theory to be reduced is to show that the reducing theory can account for the phenomena covered by the reduced theory; this would account for why the reduced theory manages to be so successful in its proper domain.

The thought underlying the above scheme stems from an obvious observation. Most people do not believe that the existence of the colours red and green refute classical mechanics, despite the fact that classical particles are neither red nor green. It would be a *big mistake* when reducing colour to physical terms to think particles must be literally red or green. Similarly, we do not expect to find the exact features of economic or psychological models reproduced literally at the lower level. In general, we do not expect laws of the reduced theory to be laws of the reducing theory; nor do we think the concepts used by the former to always be applicable at the level of the latter. We instead expect the laws and concepts to emerge as complicated, approximate statements true under certain conditions. Of course, it is logically possible that some of the laws and concepts of the theory to be reduced find themselves literally holding in the reducing theory too. But it is generally naïve to expect this to happen and plainly mistaken to view it as something that necessarily ought to happen.

Yet this very mistake pervades an astonishing percentage of the work in foundations of statistical mechanics. No doubt many examples of this mistake easily come to mind. Boltzmann originally seeing the *H*-Theorem as a kind of deductive consequence of classical mechanics might be one example. Or one might think of the work of Prigogine and his co-workers, when they make statements expressly affirming the error:

> Irreversibility is either true on all levels or on none: it cannot emerge as if out of nothing, on going from one level to another (Prigogine and Stengers, 1984)

One might be forgiven for thinking those guilty of the mistakes I describe are either those who invented the theory and thus did not have the benefit of learning from previous mistakes like we do, or those like Prigogine, whose thoughts on the foundations of physics are very radical. However, my argument cuts a much wider swathe than this. My claim is that the *majority of mainstream* foundations of statistical mechanics, up to and including the present day, is also guilty of one or more of the above mistakes. A shocking and depressing amount of the research pursued in the field is possibly misdirected as a result. In what follows I will examine two examples where the mistake is particularly costly, and then a third example where the mistake can (and has) been made, but generally has not proved too costly. I will conclude by mentioning some other areas in which this mistake has been made.

3. Mistake One: The Second Law

Let us begin by briefly re-acquainting ourselves with the phenomena to be explained. Thermodynamics is essentially a system of relationships (i.e. equations of state) among the macroscopic parameters of a system at equilibrium. A system is in thermal equilibrium just in case these parameters are approximately constant.

Note that the thermodynamic definitions of most, if not all, thermodynamic properties are essentially tied to equilibrium. The entropy of a state A, $S(A)$, for instance, is defined as the integral

$$S(A) = \int_B^A \frac{dQ}{T} \tag{1}$$

over a reversible transformation, where B is some arbitrary fixed state. For A to have an entropy (for S to be a state function), the transformation between B and A must be quasi-static, i.e. a succession of equilibrium states. Continuity considerations then imply that the initial and final states B and A must also be equilibrium states.

For non-equilibrium states, therefore, the concepts of entropy, temperature, etc., simply do not apply. To talk of the entropy of the gas while it passes between equilibrium states in (say) Joule's free expansion experiment is, from the perspective of classical thermodynamics, a misuse of the concepts.[1] That is not to say it could not make sense. *Another* theory, for instance, non-equilibrium statistical mechanics, might well define a concept similar or interestingly related to the entropy of classical thermodynamics.

Using this concept of entropy, the Second Law of thermodynamics states the following:

> An extensive state function, $S(A)$, defined only for equilibrium states, is such that $\Delta S \geqslant \int \delta Q/T$.

Loosely put, for realistic systems, this implies that in the spontaneous evolution of a thermally closed system the entropy can never decrease and that it attains its maximum value for states at equilibrium. (For an interesting discussion of whether it says even this much, see Uffink (2001).)

In many statistical mechanics textbooks this is translated as

> The entropy of a thermally isolated system increases monotonically with time.

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[1] Of course, we can calculate ΔS even if the system does not actually follow a reversible path—we only need to be able in principle to connect two states by a quasi-static process.

Already we see that this seemingly innocent reading of the thermodynamic law is actually not so conservative, for the original law does not speak of monotonic increase with time.

The main problem with this approach, well known from a century's discussion of Boltzmann's notorious H-Theorem, is that a monotonically increasing entropy is plainly inconsistent with an underlying classical dynamics. The time-reversal invariance and quasi-periodicity of the dynamics place severe restrictions on any mechanical definition of entropy.

Assume the following:

A. Entropy is a function S of the dynamical variables $X(t)$ of an individual system;
B. $S(X(t)) = S(X^*(t))$, where '*' indicates a temporal reflection;
C. The system is closed (the phase space Γ is bounded).

If A, B, and C hold, then the time-reversal invariance of Hamilton's equations implies S cannot increase monotonically for all initial conditions; and if A and C hold then the quasi-periodicity of the solutions to these equations implies S cannot increase monotonically for all time. In short, if S is a function of the dynamical variables of an individual system, then S cannot exhibit monotonic behaviour.

Perhaps the most common response in the physics literature is to take this implication as effectively a *reductio* of assumption A. (Assumption B is never challenged; 'interventionists' challenge C.) The thermodynamic entropy is understood as displaying monotonically increasing behaviour; therefore, many argue, the statistical mechanical analogue of the entropy cannot be a function of the dynamical variables of an individual system. We should instead conceive of entropy in terms of some function of a collection of systems. Clearly, the fact that $S(X(t))$ cannot monotonically increase is compatible with some *other function* defined on an *ensemble* of systems monotonically increasing. The move to ensembles is sometimes advertised as a 'way around' the reversibility and recurrence properties of the classical dynamics (in the quantum case one must additionally take the thermodynamic limit in order to avoid recurrence). Denying A is seen as the 'answer' to the reversibility and recurrence paradoxes, and it is the first step in seeking a mechanical entropy that monotonically increases so that the Second Law can remain exceptionless. The reader of Sklar (1993), for instance, will recall the denial of A as a refrain repeated with the introduction of nearly every approach to the subject. One of the principal reasons given for this common response is that it 'respects thermodynamics'. Thermodynamics allegedly says that entropy increases monotonically; therefore, so should statistical mechanics.

But there is a great cost to this manoeuvrer that somehow escapes attention (described at length in Callender (1999)). The cost is that the behaviour of this ensemble function, should one be able to find it, is completely severed from and indifferent to the dynamics of the classical particles constituting the system. If a gas really is composed of classical particles, then it really can and will (if left to itself) recur to a microstate arbitrarily close to the one it is in (say) now. Since the difference (if there is one) between the state to which it recurs and the one it is in now is arbitrarily small, it will not make a difference to the macrostate of the system. So if the thermodynamic entropy has anything to do with this gas, it had better turn around and decrease as the sample of gas returns (arbitrarily close) to the microstate it is in now. But that is precisely what will not happen to the statistical mechanically defined entropy if it is guaranteed to increase monotonically. Therefore, since this function will not track the thermodynamic entropy, it cannot possibly be what the thermodynamic entropy reduces to, nor can it possibly play a role in the explanation of why the thermodynamic entropy behaves as it does. No function of an individual system's classical dynamical variables can display monotonic behaviour. The massive drive to keep the Second Law exceptionless runs directly contrary to the very goals of the field.[2]

The problem is not the use of ensembles. One can make true, informative statements using ensembles, e.g. the Ehrenfest's 'concentration curve' version of the *H*-theorem (Ehrenfest and Ehrenfest, 1912). And of course, when actually doing statistical physics almost everything we learn is derived using ensembles. The problem is instead thinking that one is *explaining* the thermal behaviour of *individual real systems* by appealing to the monotonic feature of some function, be it of ensembles or not, that is not a function of the dynamical variables of real individual systems.

It is impossible to calculate the intellectual cost this mistake has had on the foundations of statistical mechanics. The vast majority of projects in the field in the past century have sought to explain why my coffee (at room temperature) tends to equilibrium by proving that an ensemble has a property evincing monotonic behaviour. It is worth pointing out, furthermore, that these projects invariably invoke re-randomisation processes that are inconsistent with the underlying dynamics, or commit some other 'sin'. The reader can consult Sklar (1993, Chs 6 and 7) for examples.

It is clear that a 'too-literal' mechanical translation of the Second Law of thermodynamics is harmful to statistical mechanics. A weakened alternative reading of the Second Law, mindful of our mistake, would not try to 'save' the literal truth of the law. For instance, it might say:

> For equilibrium states, entropy does not decrease for very long observational time scales.

As is well known, we can secure the truth of this posit using an individual system's (Boltzmann) entropy if we stipulate that in the very distant past the

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[2] Compare with Maudlin:

> If something is guaranteed to increase then that something cannot be a function of the physical state before me. Since phenomenological thermodynamics originally was about such individual boxes [of gas], about their pressures and volumes and temperatures, 'saving' it by making it be about probability distributions over ensembles seems a Pyrrhic victory (Maudlin, 1995, p. 147).

For a simple example of a Gibbs entropy that monotonically increases see Klein (1955).

universe was wildly out of equilibrium. This statement is fully compatible with Poincaré recurrence, time-reversal invariance and all thermodynamic phenomena; for more discussion see Albert (2001), Callender (1999), Lebowitz (1999).

4. Mistake Two: Equilibrium

Equilibrium holds when the macroscopic parameters of a system are approximately constant. The concept of equilibrium state is intimately connected with that of observation time. To use Ma's (1985, p. 3) example, pour some boiling water from a thermos into a teacup. Within the span of a few seconds, the measured volume and temperature will not change significantly, and we can regard the system as being in equilibrium. After a little while, the temperature will decrease until, after an hour, the temperature of the water is equal to room temperature. Again, we have equilibrium if the observation time is considered a few hours. In two to three days, though, enough water will have evaporated so that the measured volume will vary, and we can no longer regard the cup of water as in equilibrium. Eventually it will empty and the cup will be in equilibrium again, but since even the molecules of the cup can evaporate, on the scale of a few years it will again be out of equilibrium.

The existence of equilibrium states in thermodynamics is either a basic or near basic assumption. Thermodynamics assumes something like the following:

> Under a given set of environmental conditions (determined externally by temperature, pressure, etc.), a system will have approximately constant macroscopic properties. A system is in equilibrium just in case it is in such a state.[3]

Statistical mechanics 'translates' the last claim as:

> Thermal equilibrium is a stationary probability distribution.

Within the dominant Gibbsian approach, states of systems are described with probability distributions on hypothetical ensembles (for instance, the microcanonical ensemble). Equilibrium is viewed as a stationary distribution. The idea arises naturally. Thermal equilibrium, unlike mechanical equilibrium, does not demand strict temporal invariance since fluctuations are expected. Thermodynamic variables are consequently associated with the mean values of dynamical quantities, and thermal equilibrium is defined by the condition that $d\bar{Q}/dt = 0$. This straightforwardly implies that the probability density on the ensemble with which the average is defined should also have no explicit time

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[3] This is of course a loose statement, standing in for one specifying exactly the factors relevant and the precise meaning of constancy. In mathematical physics, one can find postulates that are more precise, especially as regards clarifying that equilibrium is a relation between systems (cf. Thompson, 1972, p. 33).

dependence. This definition causes difficulties—e.g. the fine-grained entropy is temporally invariant—but it also causes more local worries. I will describe three.

First, though this is perhaps not too serious, the claim is quite unrealistic. As we saw, phenomenological equilibrium is intimately tied to an observation time scale. Despite this, statistical mechanics generally starts with a stationary probability distribution—what Ma calls 'absolute equilibrium', an idealisation referring to an isolated system over an infinitely long observation time. This idealisation is potentially unproblematic, yet it may contribute to a mistaken view of what the explanandum of equilibrium statistical mechanics is. As Leeds (1989) emphasises, the explanandum is not so much 'why does Gibbs phase averaging work?', but instead 'why does it work, for one observable quickly, for another slowly, and for another not at all?' This is of course the point of Ma's example.

Second, and much more serious, there is the 'flip side' of the earlier complaint about monotonic entropy increase.[4] The recurrence theorem essentially implies, not only that there cannot be any monotonic tendencies, but also that no individual microstate can correspond to any macrostate that is unchanging. Again, in assuming otherwise by adopting the above statistical definition of equilibrium, one ends up proving results about systems that could not possibly be the systems we talk about in thermodynamics. Even if left to itself, the microstate underlying the cup of coffee at room temperature next to my computer cannot remain in this macrostate forever, and so cannot be strictly stationary. This is because (a) it was not always in this macrostate and (b) it will recur to the macrostate in which it was. Premise (b) is justified by the recurrence theorem; premise (a) is justified by experience. Those using a strict reading of the concept of thermal equilibrium must again shift the target. They do not try to demonstrate why individual systems tend to settle into states that *seem* stationary for 5 or 6 thermodynamic observables over the time scales we usually deal with; rather they try to demonstrate that fictional ensembles have probability distributions on them that are *strictly* stationary. As with the Second Law, things have been turned back to front: the explanandum has been abandoned in favour of a strict reading of the thermodynamic claims. In large measure this is no doubt due to the relative mathematical tractability of the above 'translation' in comparison with any more accurate translation suitable for real microstates.

Third, even from the perspective of probability distributions we have problems. This is pointed out by Leeds (1989). As I understand him, Leeds (especially pp. 328–331) is saying the following. What we are trying to explain is the phenomenological fact that if we prepare or are presented with a non-equilibrium system, after a certain period of time it will relax to a state where its usual thermodynamic observables will be stable and predictable by phase averaging. But equilibrium statistical mechanics proceeds as if divorced from

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[4] It should not be surprising that the problem with the Second Law should affect equilibrium, given the intimate ties between the two: e.g. equilibrium is often defined as the absence of entropy production.

this phenomenon. Temporarily ignoring non-equilibrium may be okay, but still, the theory should not make claims that *contradict* the fact that equilibrium states evolved from non-equilibrium states.[5] But that is precisely what is going on. Statistical mechanics says equilibrium is given by a stationary probability distribution f, the microcanonical distribution. But *physical* probabilities do not just pop in and out of existence. If it makes sense to attribute f to the system after it is relaxed in say t seconds, it must also make sense to attribute a probability distribution to the system earlier, in particular, $f_0 = U_t^{-1}(f)$, where U_t is the Hamiltonian motion of the distribution t seconds forward. However, f_0 cannot be the microcanonical distribution. f_0 gives large weight to gases being in one corner of a box, cream in clumps separated from coffee, etc. The microcanonical distribution does not do this. Since $f_0 \neq f$, and f is stationary, f_0 cannot evolve into f.

It is true that we can bring in mixing and other dynamical hypotheses to rescue the idea that one measure approaches another. Even if this answers the above, there are two objections: (a) it is controversial since mixing is a very strong property, stronger than ergodicity which is itself unlikely to hold in general of systems, and (b) it is an odd place to bring in mixing—as a justification for thinking of equilibrium as stationary (there would be little point in then going on to justify the measure being unique, for instance).

Once again, it is not hard to think of a possible weakening of the statistical mechanical 'translation' that avoids these troubles. Here is one:

> Thermal equilibrium corresponds to a special set of microscopic trajectories that leave the macroscopic properties of a system, for a certain observational time scale, approximately constant (and the time scales need not be the same for all macroscopic observables).

A more precise definition awaits specification of the system, the microstates' properties, the relevant observables, a technical definition of approximate constancy, etc. The key point for us, however, is the relativisation to particular observational time scales.

5. Mistake Three: Phase Transitions

The final example of taking thermodynamics too seriously has caused by far the least amount of damage. People simply have not worked on the philosophical foundations of phase transitions in the same way that they have worked on (say) the foundations of the Second Law. But it too is an area wherein strange conclusions can arise if one takes a too literal mechanical counterpart of the claims of thermodynamics.

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[5] Compare with Ma (1985, p. 4): 'to understand equilibrium, we must also consider nonequilibrium problems'.

The most familiar examples of phase transitions are those involving H_2O. Water at room temperature and atmospheric pressure is liquid, but if cooled below 273.15 K it solidifies and if heated above 373.15 K it vaporises. Similar behaviour occurs for most substances; at certain temperatures the substance undergoes a sharp change of properties—a phase transition. The types of phase transition that occur are wonderfully diverse, since there are many different types of phase and very different kinds of transitions: e.g. ferromagnetism and critical opalescence.

Consider a so-called first-order phase transition. These are characterised in thermodynamics by a finite discontinuity in a thermodynamic potential such as the free energy $F(V,T)$. For fluid phase transitions, the discontinuity in F implies a discontinuity in the entropy (and volume):

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{2}$$

and causes the specific heat to diverge at a critical temperature.

Classical thermodynamics describes these transitions as (loosely):

> Phase transitions occur when there is singular behaviour in the relevant thermodynamic potentials.

Statistical mechanics defines the free energy F as

$$F = -kT \ln Z, \tag{3}$$

with

$$Z(T,V) = \sum_r e^{-\beta Er}, \tag{4}$$

where the sum is over all states r with energy E_r and $\beta = 1/kT$.

Statistical mechanics then states (in terms of the free energy)

> Phase transitions occur just in case, in the thermodynamic limit (particle number N and volume V go to infinity with V/N fixed), the free energy has a non-analytic point, i.e. not expandable in a Taylor series. (Z above is sensitive to particle number through $k = R/N$.)

Loosely put, a phase transition occurs when the partition function (in the thermodynamic limit) has a singular point. The reasoning behind this is that all thermodynamic observables are partial derivatives of the partition function, so you need a singularity in the partition function in order to obtain a singularity in the thermodynamic function.[6]

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[6] For instance, when melting ice to liquid water you get a discontinuity in the entropy. Since $S = -(dF/dT)v$ and $F = -kT \ln Z, Z$ needs to vanish to obtain a discontinuity in S. That is, as T goes to its critical point, $Z \to 0$, and this implies that $\ln Z \to \infty$, which in turn implies that $F \to \infty$. This will imply that S at the critical temperature is not continuous. But since Z is not 0, the only way to get the desired result is for Z to have a singularity.

The immediate problem is that the partition function is analytic and so can only have singularities when it vanishes. (For details and references see Liu (1999); Thompson (1972).) Mathematical physics avoids this result by taking the thermodynamic limit, for it is possible for systems with infinite N to display singular behaviour for non-vanishing partition functions. This was ingeniously shown for a $d = 2$ Ising model by Onsager in 1944, an event which precipitated a great revolution in the study of phase transitions; for a history see Domb (1996) and for a recent review see Lebowitz (1999).

The problem is that phase transitions—as understood by statistical mechanics—can only occur in infinite systems, yet the phenomena that we are trying to explain clearly occur in finite systems. Liu (1999) writes, based on this consideration, that the property of being a phase transition is 'not reducible to properties in statistical mechanics'; phase transitions are 'truly emergent properties' (p. S92).[7] Prigogine (1997, p. 45) writes: 'The existence of phase transitions shows that we have to be careful when we adopt a reductionist approach. Phase transitions correspond to emerging properties'. Later he claims that the need for the thermodynamic limit in describing phase transitions implies that only a statistical (non-trajectory) description applies, and that this is a deviation from Newtonian physics (p. 126). His suggestion is that phase transitions are emergent in the sense that they cannot be explained solely within Newtonian physics.

Now consider the following propositions:

1. real systems have finite N;
2. real systems display phase transitions;
3. phase transitions occur when the partition function has a singularity;
4. phase transitions are governed/described by classical or quantum statistical mechanics (through Z).

The conclusion that phase transitions are emergent follows (more or less) by affirming 1–3 and concluding the denial of 4. Statistical mechanics for finite N is incomplete, unable to describe phase transitions; therefore, they are in some sense emergent. Can this be right?

Most physicists, I suspect, would say it is not right; and that the error lay in not thinking of the infinite N system in the thermodynamic limit as a good approximation to the finite N system. It is no doubt true that in some pragmatic sense, it is a good approximation. After all, virtually all of the novel

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[7] Liu (2001) discusses some difficulties with the view expressed in his (1999). In fact, in his (1999) he arrives at one possible conclusion with which the present study is in sympathy; see footnote 8 below. In Liu (2001) the worry seems to be that phase transitions ruin some types of reduction because there are no types in (finite) statistical mechanics that can be identified with singularity types in thermodynamics; and that if one then reacts by saying that thermodynamic singularities are 'fictions' this will imply that we must retire them from usage in practical physics. Contrary to Liu, however, I do not think a failure of type-type identification means the higher level predicate no longer applies, nor do I think this would mean we cannot use it successfully in practical physics (any more than a failure of type-type reduction for chairs means that we must retire chairs from furniture talk).

predictions in the post-Onsager revolution are derived from infinite N models, so there has to be something accurate about them. Furthermore, we can see from a variety of considerations that the thermodynamic limit will approximate features of systems in which we are interested: (a) thermal features are often largely independent of the size and shape of a system's boundaries, (b) systems we deal with have large N, so fluctuations are small, (c) the thermodynamic limit is often equivalent to the continuum limit, which is sometimes said to be the limit of thermodynamics; see Compagner (1989).

On the other hand, the thermodynamic limit may not be a good approximation in a more foundational, philosophical sense. Liu (1999) details many ways in which the current case diverges significantly from standard cases of theory approximation.

However, even if the thermodynamic limit can be given a full philosophical justification, that justification cannot turn an infinity into a finite quantity. We can grant that it is often fine to substitute finite N with infinite N for the purposes of practical physics. But if the system is really finite N, what we have until we say more is a mathematical proof that it cannot undergo a phase transition. So we ought to grant that, practically speaking, it is often a good approximation, but point out that this just does not touch this particular problem. We need to deny propositions 1, 2, or 3.

Clearly the weakest link in the chain is 3; consequently, we ought to affirm $1, 2, 4$ and conclude the denial of 3. That is, we should say that real finite systems give rise to the sort of behaviour associated with phase transitions in thermodynamics even when the partition function is not singular. After all, the fact that thermodynamics treats phase transitions as singularities does not imply that statistical mechanics must too. To assume that would be to take thermodynamics too seriously. It will now come as no surprise that I believe the source of this 'emergence' is again the result of a too-literal translation from thermodynamics to statistical mechanics. Thermodynamics represents (for pretty good reasons) phase transitions as singularities, and statistical mechanics (for pretty good pragmatic reasons) takes this to mean a non-analyticity in the partition function. But from a foundational perspective we cannot endorse this knee-jerk identification of mathematical definitions across levels.

Presumably, there are non-singular solutions of the partition function describing real systems that give rise to the macroscopic transitions called phase transitions. There cannot really be singularities in the partition function whenever there are such transitions. Perfect singularities occur only in the thermodynamic limit where there are no fluctuations. But in the real world there are fluctuations; consequently, there cannot be genuine singularities in the partition function. Analytic partition functions must govern the phase transition and in some sense approximate a singularity. (And because of the fluctuations we do not actually measure perfect singularities either.)[8]

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[8] I thus agree with Liu (1999, p. S102) when he writes: 'Actual systems are finite and phase transitions in them are never real singularities'.

Now, to some this may seem an article of faith because we cannot actually show this. The equations for actual systems are too difficult to solve. Indeed, this is the very reason why statistical mechanics uses singularities in the partition function as a way of studying phase transitions: singularities can be found using all sorts of general topological and geometric techniques that do not require exact solutions. Fortunately nature is kind to us and allows us to make do with singularities in infinite systems rather than exact solutions to finite systems. Furthermore, physics is hardly impotent in the face of phase transitions in finite N systems. We have mean field theory, which is very accurate except near some critical points. And we have the finite scaling done in computer modelling of phase transitions. There—as in real systems and real experiments—the characteristic discontinuities and singularities accompanying phase transitions appear as rounded and smeared; accordingly there are different criteria for phase transitions here (see Mouritsen, 1984). Justification for our 'article of faith' therefore arises from all of these sources in addition to our conviction that phase transitions can be described by mechanics.

6. Conclusion

The areas that I have concentrated upon in this article are by no means all that special. Though I believe the first two errors have caused by far the most damage, the error itself is all too common. An article with the same moral, but different examples, could easily be written. Consider, for instance, a hypothetical article with the following two examples.

1. The huge industry of exorcising Maxwell's demon is motivated by the desire to 'save' the strict Second Law from the demon. But the main reason to conceive the creature as a dark threat is that one takes the laws of thermodynamics too seriously, as universally true and somehow independent of the statistics of the micro-constituents of thermal bodies. See Earman and Norton (1999); Albert (2001).
2. There exists a long and very confused debate about the correct way in which thermodynamic quantities behave under Lorentz transformations. Perhaps the principal reason for the confusion is the fact that investigators simply assumed that relativistic counterparts of some laws of thermodynamics would look just like the phenomenological laws—they took (some) thermodynamics too seriously. Earman, diagnosing the trouble, writes: 'the pioneers of 'relativistic thermodynamics' were led astray [...] they acted as if thermodynamics were a self-contained subject, existing independently of any statistical mechanical interpretation. Within this setting, many different 'transformation laws' for the thermodynamic quantities are possible' (Earman, 1981, p. 178).

Wherever foundational issues in statistical mechanics are discussed our mistake of taking thermodynamics too seriously rears its head. It is time we identify this problem for what it is and take appropriate action; namely, we should start taking thermodynamics *really* seriously, seeing what it actually says and appreciating its limits. The phenomenological laws of thermodynamics lose none of their luster after we understand where and why they hold.

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