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It is not the entropy you produce, rather, how you produce it

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The principle of maximum entropy production (MEP) seeks to better understand a large variety of the Earth's environmental and ecological systems by postulating that processes far from thermodynamic equilibrium will 'adapt to steady states at which they dissipate energy and produce entropy at the maximum possible rate'. Our aim in this 'outside view', invited by Axel Kleidon, is to focus on what we think is an outstanding challenge for MEP and for irreversible thermodynamics in general: making specific predictions about the relative contribution of individual processes to entropy production. Using studies that compared entropy production in the atmosphere of a dry versus humid Earth, we show that two systems might have the same entropy production rate but very different internal dynamics of dissipation. Using the results of several of the papers in this special issue and a thought experiment, we show that components of life-containing systems can evolve to either lower or raise the entropy production rate. Our analysis makes explicit fundamental questions for MEP that should be brought into focus: can MEP predict not just the overall state of entropy production of a system but also the details of the sub-systems of dissipaters within the system? Which fluxes of the system are those that are most likely to be maximized? How is it possible for MEP theory to be so domain-neutral that it can claim to apply equally to both purely physical–chemical systems and also systems governed by the 'laws' of biological evolution? We conclude that the principle of MEP needs to take on the issue of exactly how entropy is produced.

Keywords: thermodynamics; entropy; Gaia; maximum entropy production; by-products; biosphere

1. INTRODUCTION

The second law of thermodynamics indicates that any physical process is associated with a positive entropy production if a wide enough environmental boundary is considered. Entropy production can be viewed as a measure of the irreversibility associated with a given transformation, and can be computed based on the fundamental principles of thermodynamics. Recently, there has been growing interest in extension of entropy theory by using a postulated principle of maximum entropy production (MEP). The special papers in the issue examine a variety of applications of this principle, which is defined in the Introduction by Kleidon, Malhi & Cox (Kleidon *et al.* 2010) when they state that processes far from thermodynamic equilibrium will 'adapt to steady states at which they dissipate energy and produce entropy at the maximum possible rate'.

Our paper is an 'outside view' solicited by Axel Kleidon to accompany the papers in this special issue. Neither author attended the 2008 conference on MEP in Jena, Germany, from which the papers in this issue were generated. One of us (Volk), however, did attend the May 2009 meeting of the MEP group and

both authors have published in the field (Volk 2007; Pauluis *et al.* 2000; see more references below). In general, we applaud the efforts of the MEP research community and look forward to more results that take the current papers to the next level. While MEP remains speculative, particularly for systems far from their thermodynamic equilibrium, it offers an intriguing conjecture that can provide a first approximation of the behaviour of a wide range of systems, as discussed through several articles here. Rather than a full review (if that is even possible) of the different applications of MEP, we would like to concentrate on a fundamental issue for both MEP and irreversible thermodynamics in the context of this special issue: Is it possible to determine the relative importance of specific processes for total entropy production?

In §2, we show that atmospheric convection offers an interesting example of our point. Pauluis & Held (2002*a,b*) compared the entropy production between dry and moist convection. In the case of dry convection, i.e. in the absence of water vapour, most of the entropy production is due to frictional dissipation of the convection eddies. In contrast, when water vapour is present, most of the entropy production is due to diffusion of water vapour and phase transition. As a result, a moist atmosphere produces much less kinetic energy than a dry atmosphere for the same total energy transport. These results raise challenges for MEP.

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One contribution of 17 to a Theme Issue 'Maximum entropy production in ecological and environmental systems: applications and implications'.

In §3, we turn to biological considerations. We use the modelling results of Meysman and Bruers in this issue (Meysman & Bruers 2010) to show that using MEP theory for organisms and ecosystems will require MEP theory to encompass the fact that some biological systems will produce less entropy than the maximum and yet still be stable. In other words, what exactly is the relationship between selection by the maximum entropy principle and selection by the principle of natural selection?

As currently applied, MEP theory puts competing processes within systems into black boxes. We will conclude that MEP theory should attempt to open these boxes and face questions not only about the amount of entropy produced but exactly how it is produced.

2. DISSIPATION BY ATMOSPHERIC CONVECTION DEPENDS UPON HUMIDITY

The studies of Pauluis & Held (2002*a,b*) offer a detailed analysis of how different processes end up competing with each other in terms of their entropy production. These papers analyse the entropy budget of an idealized atmosphere in radiative–convective equilibrium. The atmosphere is heated at the surface by the absorption of solar radiation and cooled through the troposphere. This radiative forcing destabilizes the air column, and convective motions develop. After some time, a statistical equilibrium is reached in which the destabilizing influence of radiation is balanced by an upward energy transport by convection. Radiative–convective equilibrium is an idealization that allows the study of the interactions between radiation and atmospheric flows, without the additional complexity that arises from rotation or the large-scale variations in insolation.

For an atmosphere in statistical equilibrium, the total energy is constant over time. This implies that the net energy input Q_{in} at the surface must balance the net radiative cooling of the troposphere Q_{out} :

$$Q_{\text{in}} + Q_{\text{out}} = 0. \quad (2.1)$$

Similarly, the total entropy of the atmosphere remains constant over time. This means that the sum of all entropy sources and sinks must cancel out. The surface heating and tropospheric cooling act, respectively, as an entropy source and an entropy sink, whose magnitude is given by the net energy flux divided by the average temperatures T_{in} and T_{out} at which the heating and cooling occur. In addition, there is an additional source of entropy associated with all the irreversible processes within the atmosphere ΔS_{irr} . The entropy budget of the atmosphere thus can be written as

$$\frac{Q_{\text{in}}}{T_{\text{in}}} + \frac{Q_{\text{out}}}{T_{\text{out}}} + \Delta S_{\text{irr}} = 0. \quad (2.2)$$

Equations (2.1) and (2.2) can be combined to derive an expression for the total internal entropy

production:

$$\Delta S_{\text{irr}} = Q_{\text{in}} \left(\frac{1}{T_{\text{out}}} - \frac{1}{T_{\text{in}}} \right). \quad (2.3)$$

This equation states that the net internal entropy production within the atmosphere is balanced by a net export of entropy resulting from the differential radiative heating.

A key issue in equation (2.3) is to identify the various processes that contribute to the internal entropy production ΔS_{irr} . In doing so, we should remember two things. First, as all physical processes produce entropy, any list of irreversible processes is likely to be incomplete. Our goal here is thus to identify the processes responsible for the bulk of the entropy production. Second, one should be careful to consider only processes that are *internal* to the system under considerations. In equation (2.2), radiative processes are treated implicitly as an external energy source or sink, which means that radiation is an external part of the system, and as such does not contribute to the internal production of entropy. Radiation could be treated as an internal process, but this significantly complicates the analytic treatment of the equation. For the interested reader, the paper by Wu & Liu (2010) offers an elegant analysis of the entropy flux and entropy production associated with radiative transfer in the Earth's atmosphere.

With this in mind, Pauluis & Held (2002*a,b*) identify four main processes as the main source of entropy in their idealized atmosphere: frictional dissipation, diffusion of heat, diffusion of water vapour, and irreversible phase transition. The entropy production by frictional dissipation is equal to the amount W of kinetic energy generated and dissipated by the flow divided by the temperature at which it occurs, T_{d} . Once this temperature is known, one can obtain an upper bound on the work produced by the atmosphere:

$$W_{\text{max}} = T_{\text{d}} \Delta S_{\text{irr}} = T_{\text{d}} \left(\frac{1}{T_{\text{out}}} - \frac{1}{T_{\text{in}}} \right) Q_{\text{in}}. \quad (2.4)$$

This expression is equal to the work done by a Carnot cycle when $T_{\text{d}} = T_{\text{out}}$, but is, however, slightly different. Note that W_{max} is the work produced and dissipated internally by atmospheric motions, not the work done on an ‘outside’ environment. As such, the efficiency of a dissipative heat engine defined as the ratio of the work produced and dissipated internally to the energy input can be larger than the Carnot efficiency, without violating Carnot's formulation of the second law of thermodynamics (which only puts an upper bound on the work done on an outside environment).

A central question here is whether the work done by the atmospheric circulation is anywhere close to this upper bound. In the presence of irreversible sources of entropy, the actual amount of work generated within the atmosphere is given by

$$W = W_{\text{max}} - T_{\text{d}} \Delta S_{\text{irr,nf}}, \quad (2.5)$$

where $\Delta S_{\text{irr,nf}}$ is the internal entropy production by processes other than friction dissipation. When other

irreversible processes do not contribute much to the overall entropy production, the work done will be close to the upper bound. Conversely, if other processes play a significant role, then the work that can be produced is significantly reduced. Pauluis & Held (2002a,b) use a high-resolution atmospheric model to address this issue, and to analyse the impacts of water vapour on entropy production. They find that in the absence of water vapour, frictional dissipation is indeed the primary source of entropy, or equivalently, that the maximum work W_{\max} (2.4) offers a good approximation for the mechanical output by atmospheric convection, i.e. $W \sim W_{\max}$. However, when water vapour is present, the situation changes dramatically, and the work done by atmospheric motions is only approximately one-third of the maximum possible: $W \sim 1/3 W_{\max}$.

Pauluis & Held (2002a,b) showed that the difference between the actual work W and the maximum theoretical work W_{\max} can be explained by the fact that in their moist experiment, diffusion of water vapour and irreversible phase transition account for approximately two-thirds of the entropy production. (Diffusion of heat is, on the other hand, negligible.) Pauluis & Held (2002a,b) argue that, in addition to acting as a heat engine, moist convection also acts as a dehumidifier, which continuously removes water vapour from the atmosphere by lifting moist air, condensing water vapour and letting it fall. In effect, deep convection takes parcels of moist air from the boundary layer and turns them into very dry air parcels in the upper troposphere and falling precipitation. In statistical equilibrium, the dry air must be re-humidified. This occurs as the air subsides and is re-injected into the planetary boundary layer. This re-humidification involves either diffusion of water vapour from moister air or, eventually, irreversible evaporation of water vapour into unsaturated air. Both processes are irreversible and produce entropy, which implies a reduction in the mechanical work generated by convection.

A second effect of the hydrological cycle on atmospheric convection lies in how frictional dissipation takes place. It is usually assumed that frictional dissipation in the atmosphere occurs as the end result of a turbulent energy cascade from the scale of motions to the smaller scales at which viscosity can act. However, in a precipitating atmosphere, each falling hydrometeor (water droplet) generates a microscopic flow around it, which can be either laminar, i.e. a Stokes flow, or turbulent. This flow acts to slow down the falling hydrometeors. A typical raindrop reaches a terminal velocity of the order of 5 m s^{-1} . In contrast, if that droplet had undergone a free fall from 2000 m (a typical condensation level in the atmosphere), it would reach a velocity of 200 m s^{-1} . In addition to preventing drizzle from being a deadly atmospheric hazard, these microscopic shear flows also dissipate a large amount of kinetic energy. Pauluis *et al.* (2000) estimated that dissipation rate of kinetic energy in falling precipitation should account for $2\text{--}4 \text{ W m}^{-2}$ when averaged through the tropics, an estimate that is comparable to kinetic energy dissipation in larger scale atmospheric motions. In

the simulations described in Pauluis and Held, precipitation-induced dissipation accounts for about three-quarters of all frictional dissipation.

So, it turns out that entropy production differs dramatically depending on whether water vapour is present in the atmosphere or not. A dry atmosphere acts primarily as a heat engine, and generates strong sustained winds. In contrast, a moist atmosphere with an active hydrological cycle acts also as a dehumidifier. Diffusion of water vapour and irreversible phase transition accounts for a large entropy production, and greatly reduces the amount of work that can be produced. On Earth, the subtropical regions are characterized by a large entropy production associated with the evaporation of water vapour over the warm ocean, but very little frictional dissipation. This illustrates the fact that even though two systems—here a dry and a moist atmosphere—might have the same entropy production, there might be fundamental differences in how the entropy is generated, and hence in the overall behaviour of the systems.

A last question is whether one can determine *a priori* the relative importance of different irreversible processes for the total entropy production. There might be some hope of doing so. Indeed, close enough to thermodynamic equilibrium, the same conditions that lead to the derivation of the MEP also make it possible to determine the internal entropy production by individual processes. Unfortunately, the situation is more complicated for complex systems—such as the atmosphere or biological systems—for which MEP may not hold. The atmosphere can be used to illustrate this issue. Indeed, the amount of water vapour in the air depends strongly on the absolute temperature. It is thus very probable that in a cold climate such as during the last ice age, frictional dissipation would have accounted for a much larger fraction of the total entropy production. Conversely, one would expect that in warmer, moister climates, diffusion of water vapour and irreversible phase transition would play a bigger role. However, to determine quantitatively the entropy production by moist processes amounts to obtaining effectively a theory for the atmospheric relative humidity—a problem whose solution that still eludes us.

3. LIMITATIONS TO APPLYING MEP TO LIVING SYSTEMS

We next turn to considerations of entropy production and biology. A number of papers in this special issue deal with organisms and ecosystems (Dewar 2010; Holdaway *et al.* 2010; Meysman & Bruers 2010; Schymanski *et al.* 2010; Vallino 2010; Županović *et al.* 2010). There are substantial differences in the scales of systems in these papers and in the components that possess entropy fluxes that are being measured or modelled; it is beyond the scope of this essay to compare and contrast all these papers. But our main point in this biological section of our paper—it is not the entropy you produce but rather how you produce it—can be made by discussing the results from the modelling work of Meysman and

Bruers, followed by related shorter comments on several of the other papers.

Meysman and Bruers set up three modelling experiments, using standard ecosystem formulations. All modelled ecosystems have a flux of organic resource that enters the 'system.' Within the system is the abiotic degradation of the resource and biological components that feed and die. In addition, the first experiment includes within the system a consumer population that feeds on the resource. The second adds a predator population that feeds on the consumer. Finally, in the third experiment, the predator becomes an omnivore that is able to feed on both the consumer and the resource.

Meysman and Bruers establish equations for sources and sinks for the various system components (resource, consumer, predator) and for entropy generation for the total system. They find that in all cases, entropy generation in the biotic condition exceeds entropy generation in the abiotic state in which there is abiotic resource degradation alone and no biology. But, crucially, they then find that experiments 2 and 3 violate key principles that from their interpretation of MEP theory they conclude should hold true.

In the system with the predator (experiment 2), compared with the system with just the consumer alone as the biological component, the system's entropy production goes down. This is because the predator decreases the mass of the consumer population in the steady state, a canonical result from what is termed top-down control in ecosystem populations. So, if the ecosystem can be thought of as a system with degrees of freedom presented by biodiversity (a point made by Kleidon 2004), then that ecosystem, according to MEP theory, should find the steady-state with the largest entropy production. In this case the predator should not exist. But predators do exist in nature. This fact contradicts the prediction that MEP theory would make, at least according to the deductions of Meysman and Bruers before they ran their models.

Meysman and Bruers also deduce from MEP theory that if an externally applied gradient increases, the system should respond by generating more entropy. But as they emphasize, their experiment 3 contradicts even this. In a system in which the predator (now modelled as an omnivore) can also feed on the resource as well as on the consumer, the entropy generation decreases with an increasing external gradient, modelled by an increased resource supply flux.

What we see here supports our main point and poses a challenge to MEP theory: the details of the internal dynamics make a tremendous amount of difference to the entropy generated. Meysman and Bruers did not create the varying systems through evolutionary algorithms. However, they showed reasonable systems that could be stable, in which biology trumped MEP. Thus natural selection can dominate selection by maximum entropy. In the real world a predator certainly can evolve and participate within the network of a system, even if that system is in a state of lower total entropy production as a result. The existence of an omnivore, or any creature that draws from multiple trophic levels is also well known. MEP theory, to advance, will have to face

issues raised by studies such as those of Meysman and Bruers.

We also suggest the following Gedanken (thought) experiment to show that even the consistent finding by Meysman and Bruers (that all models produced a higher entropy flux in the biotic condition) can be contradicted. Their result stems from the fact that the abiotic rate of resource degradation is less than the rate of consumption by the consumer. So the consumption rate of the resource, or entropy generation, always increases when there is a consumer. But in our Gedanken experiment, what if the consumer has a lower rate of feeding than the abiotic degradation? Then the entropy generation would decrease in the presence of the consumer, compared with the abiotic entropy production. There is nothing in the concept of the evolutionary stable state to prevent this from being the case. Indeed, this case, in which the system entropy would be lower with the consumer, is a perfectly reasonable biological possibility, even if one not found very often in the real world.

But are we sure the entropy is being calculated in the way demanded by MEP theory? Entropy was relatively simple to calculate in the model systems of Meysman and Bruers. But even they raise the question. In their introduction they say that there are 'many ways in which 'maximization' can be interpreted, and there are different ways in which the 'entropy production rate' is defined (depending on which processes one accounts for).' Dewar (2010), in his fascinating paper that examines entropy production across three scales of plant systems, focuses on chemical entropy production, but ignores radiative exchange, water transport, liquid water evaporation, and other 'potential contributions' to entropy production. He does not justify this choice. He might not need to, if MEP theory itself can meet the challenge of becoming more explicit about where to draw system boundaries and what fluxes from which components would be expected to become maximized as the system adapts to the predicted steady state, according to what Dewar, following the phrase from Whitfield (2007), calls 'survival of the likeliest'.

We submit that the modelling work of Meysman and Bruers, as well as the examples in Volk (2007) demonstrate that survival of the fittest in the biological sense can dominate in at least some cases over survival of the likeliest in the thermodynamic sense. Does that invalidate MEP theory? That depends on how MEP theory is formulated. Currently, MEP theory admits that constraints can prevent systems from reaching the MEP state (Kleidon 2010). When the nature of these constraints becomes part of the theory itself, we suggest that some basic difference in the 'rules' for applying MEP will emerge between physical-chemical systems and those containing biology. Some fundamental difference was postulated by Vallino (2010), who states that the 'difference between abiotic and biotic processes is that the former always follows a pathway of steepest descent (of entropy production), while the latter follows a pathway dictated by information that leads to greater entropy production when averaged over time'. (Parenthetical material added.)

Vallino postulates these dynamics after considering the fact that a forest does not just immediately burn up, which would be the largest possible entropy generation. In that case the forest would die and be unable to produce entropy in the future. How exactly this postulated process of integrating the future works is still to be elucidated, but obviously if true, it holds the potential of yoking natural selection to entropy selection, and is along the lines of our challenge for MEP theory to deal with the ‘how’ of entropy production.

Holdaway *et al.* (2010) also see the challenge, as they suggest ‘three different MEP selection pressures at work during ecosystem development,’ and discuss constraints, such as nutrient limitations during later periods in ecosystem succession. Obviously MEP theory is not going to be able to postulate a single holistic calculation that can simply be applied across the boards of physical-chemical and biological systems.

4. CONCLUSION: CHALLENGES FOR MEP

On the white board created by public discussion led by one of us (Volk) at the Jena, Germany, 2009 MEP meeting, Roderick Dewar, Filip Meysman, Stanislaus Schymanski, and Joseph Vallino all noted that an outstanding question for MEP theory is ‘Which flux to maximize?’ The details of the substrates must be important. As Filip Meysman said at that meeting (notes by T. Volk), it must surely matter to Earth’s meridional transport were the ocean to be made of vinegar, yet not to MEP theory as currently formulated.

The modelling reviewed above in §2 (Pauluis *et al.* 2000; Pauluis & Held 2002a,b) demonstrates that the entropy production by atmospheric convection depends on the presence or absence of water and water vapour; the substrate is of crucial importance. The modelling described in §3, primarily by Meysman & Bruers (2010) shows that the presence or absence of various biological components in an ecosystem affects the overall production of entropy, and our Gedanken experiment suggested that it is not even a certainty that a biotic system will have a higher entropy production rate than an abiotic system, a conclusion also discussed by Volk (2007).

Our analysis reinforces the core argument previously made by one of us (Volk 2007; in response to Kleidon 2004), with additional biological discussion, namely that MEP theory has substantial problems when one attempts to apply it to biology. The problems come about because evolution will produce biological adaptations that might either increase or decrease the entropy production rate, so long as the entropy production rate is positive. Phillips (2008), in his quest for the goal functions of ecosystems and the biosphere, focuses on the importance of biological adaptations to acquire and process resources (broadly defined). Arguments that emphasize adaptations and resources seem essential in analyses of systems that incorporate living things, because such arguments home in directly on the concept of fitness, which entropy theory by itself will have difficulty in doing.

Kleidon (2007) claimed Volk’s examples and therefore conclusions did not take into account the full complexity of the dissipative processes and focused only on a single flux of entropy within more complex systems. However, as we noted in §2, there are dominant forms of entropy production in systems, and one should not let inherent incompleteness and the impossibility of counting every minor hair prevent the possibility of forming robust conclusions through careful analysis. Otherwise, the same criticism could be leveled at MEP theory itself. The discussion of Caldeira (2007), who calls for definite statements from the MEP theorists of what would constitute falsification, is relevant.

In this paper, we have extended the analysis of the problems of MEP to biology and to the Earth’s geophysical systems as well, assuming that our modelling-based findings about the atmosphere will generalize to other physical-chemical systems. We have not performed that generalization and so leave this as an open question. However, the facts seem indisputable: there are multiple processes that produce entropy in the Earth’s system and those processes are only going to be understood by delving into the details of the components and substrates of the system.

Until MEP theory can make predictions about the details of the internal states of the dissipating systems, it will remain a heuristic. It might be able to set limits on the entropy production rates and then point to questions when systems fail to reach that state (and this is of course very useful), but it will not be able to say anything more about the details of the states. In that case science will then continue to rely on the standard means of searching for reductionist answers into components of systems. We hope that the theory of MEP, in its next incarnation, will take on these challenges.

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