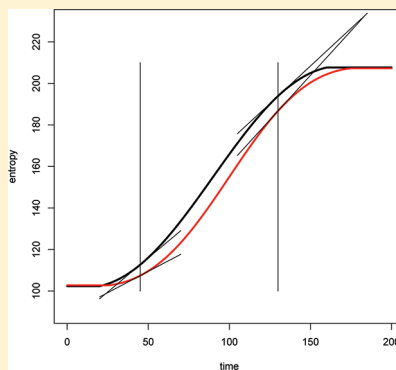# Proposed Principles of Maximum Local Entropy Production

John Ross,[*,†] Alexandru D. Corlan,[‡] and Stefan C. Müller[§]

[†]Chemistry Department, Stanford University, Stanford, California, United States
[‡]University Hospital of Bucharest, 169 Spl Independentei, 5 Bucharest, Romania
[§]Institut für Experimentelle Physik, Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany

ABSTRACT: Articles have appeared that rely on the application of some form of "maximum local entropy production principle" (MEPP). This is usually an optimization principle that is supposed to compensate for the lack of structural information and measurements about complex systems, even systems as complex and as little characterized as the whole biosphere or the atmosphere of the Earth or even of less known bodies in the solar system. We select a number of claims from a few well-known papers that advocate this principle and we show that they are in error with the help of simple examples of well-known chemical and physical systems. These erroneous interpretations can be attributed to ignoring well-established and verified theoretical results such as (1) entropy does not necessarily increase in nonisolated systems, such as "local" subsystems; (2) macroscopic systems, as described by classical physics, are in general intrinsically deterministic—there are no "choices" in their evolution to be selected by using supplementary principles; (3) macroscopic deterministic systems are predictable to the extent to which their state and structure is sufficiently well-known; usually they are not sufficiently known, and probabilistic methods need to be employed for their prediction; and (4) there is no causal relationship between the thermodynamic constraints and the kinetics of reaction systems. In conclusion, any predictions based on MEPP-like principles should not be considered scientifically founded.

INTRODUCTION

There have appeared in the literature many articles, with many claims, on the subject of "the principle of maximum (local) entropy production" (MEPP) (for example, refs 1 and 2 and references therein), mostly not in journals of physical chemistry or chemical physics.

Many of the applications are to very complex problems with imposing titles such as "Life, Hierarchy, and the Thermodynamic Machinery of Planet Earth".[1] Indeed, at least one paper[3] claims that the MEPP is only relevant in highly complex systems. We believe a critical analysis of some of the fundamentals of this subject is desirable, and we attempt it in this article. We do this by culling some statements from a few articles devoted to the fundamentals of this subject.[1,2,4,5] One of these, ref 2 claims "The present review is the first generalizing treatise on this topic." We restrict our critique to thermodynamics near and far from equilibrium, and chemical kinetics; we do not discuss statistical analyses of this principle (with which we have further difficulties). For easier reference, the statements that we discuss are numbered below with roman numerals in parentheses.

The lack of critiques of other statements in refs 1−5 or in other articles in the literature of this subject does not necessarily imply a lack of objections.

GENERAL ISSUES

This section deals with general statements and claims found in many MEPP papers that present the MEPP as supposedly consistent with a common sense interpretation of thermodynamic principles.

Jaynes[6] made the point that for deterministic kinetic systems there is no need, indeed no place, for any additional principle. We agree with this statement. Nonetheless, much of the discussions of MEPP are in reference to deterministic systems, as is the presentation of Ziegler's work[7] taken in ref 2 as a fundamental approach. For example, on page 10: (i) " ... if forces are prescribed, the entropy production is always maximized in a system with nonequilibrium processes described by linear nonequilibrium thermodynamics...."; then, the authors add on a cautionary tone: "It should be specially emphasized in conclusion that the rigorous substantiation of Ziegler's principle using relatively simple intuitive assumptions and just in terms of thermodynamic representations seems to us very difficult or impossible."

Second Law of Thermodynamics. (ii) Some MEPP papers[2,5] claim that common sense would dictate that entropy increases in systems far from equilibrium in all their localities because the second law would imply this, or it is valid because it is "a logical generalisation of the second law".[8] The second law is always valid for macroscopic systems in equilibrium and provides a Lyapunov function for nonequilibrium systems approaching equilibrium. Since MEPP is not always valid, it can hardly be a logical generalization of the second law of thermodynamics. Also,

the fact that a law is valid does not imply that any generalization of it is valid.

When only a nonisolated part of an isolated system is considered, even a decrease of the entropy in that part is not infringing the second law. Examples abound, for example, a freezing body of water evolves to lower thermodynamic entropy than its liquid form, although entropy is increased outside the body as heat is transferred from it. So is the process of a coalescing celestial body, followed by cooling though radiation: the thermodynamic entropy of the body itself decreases.

(iii) An example statement ignoring this fact is[9] "All processes follow the direction given by the second law ...". The second law only indicates that an isolated system would follow toward higher entropy, but not on what route. For nonisolated systems—such as local regions—not even the entropy increase is necessarily true. Rate processes are also always involved in determining the path and the direction of the system if the system approaches a nonequilibrium stationary state.

(iv) An example misunderstanding of the rates issue is[10] "Thus, apart from the direction of the evolution, which follows from the Clausius's formulation, we have information about the movement rate of a system." But this information is a consequence of the kinetic laws and of the details of the structure of the system.

System Kinetics. Part of the MEPP is an attempt to deduce rates from thermodynamics. For example, in ref 11 the authors state: (v) "... the maximum entropy production principle suggests that a system tends to its state of maximum entropy at the largest rate". However, there is no connection between thermodynamic quantities, such as the Gibbs free energy difference, and kinetic quantities, such as the Gibbs free energy of activation, which governs rates of reactions. (In a few cases there are some empirical relations of limited value.) In yet another instance of this attempt,[12] there is a confusion of probabilities of fluctuations, transition probabilities, and rates. An attempt is made there to obtain transition probabilities from distribution functions, which cannot be done.

We show later on that the MEPP is not consistent with kinetics with calculations on simple examples from chemical kinetics; one example is taken from hydrodynamics. These calculations invalidate the descriptive statements of this principle.

On Degrees of Freedom in Macroscopical Physical Systems. MEPP is frequently expressed as a principle governing a "choice" that a complex system may "make", the choice being that evolution that corresponds to the maximum (local) entropy production rate.

(vi) The lack of meaning of such a maximum can be observed in Figure 1.1 from ref 2. Here, an imaginary but unspecified macroscopic system, for which thermodynamic entropy can supposedly be defined, is shown to be able to relax on two possible paths as far as entropy variation is concerned. The MEPP supposedly allows identification of the pathway that the system will actually follow, irrespective of any other features of the system, and that pathway would be the one characterized by the highest entropy production rate. But which one can that possibly be? If both pathways lead to the same entropy level (the equilibrium level), then if one is faster initially (path 2 in Figure 1.1 of ref 2) it is necessarily slower later. Figure 1 is a remake of the Figure 1.1 of ref 2 where the entropy production rates (the derivatives of the entropy function with time, tangent to the curves) are also shown and it can be seen that at one time one is higher and then the other is higher.
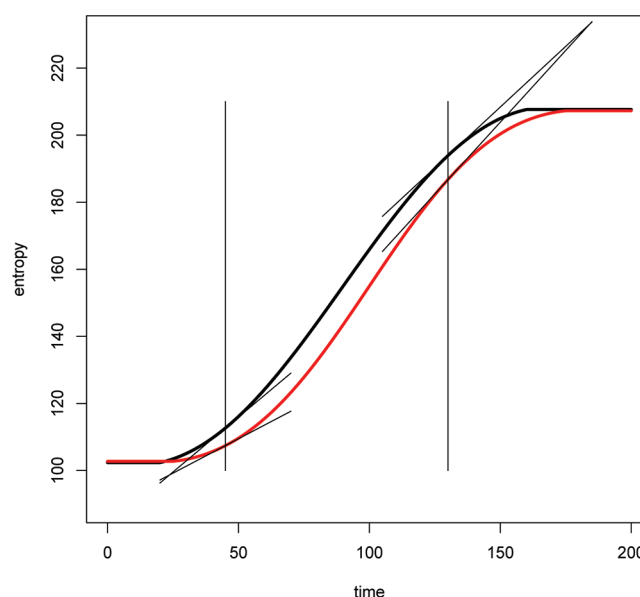

Figure 1. A remake of the Figure 1.1 from ref 2 with a representation of the entropy production rates at two instants (the tangents to the curves). If the rate for the black path is higher at one time, it is necessarily lower at another time to keep the integral of the rate the same. Thus, the statement that there could be a "faster" rate between two equilibrium states is fallacious.

In general, let us consider two equilibrium states, 0 and 1, at times t_0 and t_1, characterized by entropy S_0 and S_1. Let us assume there are k paths (continuous functions) that are in some way possible between the two states, $S^{(k)}(t)$, where the exponent denotes any of the paths. $S^{(k)}(t_0) = S_0$, $S^{(k)}(t_1) = S_1$ for all k. Let $\sigma^{(k)}(t) = (d/dt)S^{(k)}(t)$ be the entropy production rate, as a function of time, for path k.

For any two of the paths, k and j:

$$\int_{t_0}^{t_1} \sigma^{(k)}(t)\, dt = S_1 - S_0 = \int_{t_0}^{t_1} \sigma^{(j)}(t)\, dt \qquad (1)$$

For any time instant t_x, $t_0 \leq t_x \leq t_1$:

$$\underbrace{\int_{t_0}^{t_x} \sigma^{(k)}(t)dt}_{A_k} + \underbrace{\int_{t_x}^{t_1} \sigma^{(k)}(t)dt}_{B_k} = S_1 - S_0 = \underbrace{\int_{t_0}^{t_x} \sigma^{(j)}(t)dt}_{A_j} + \underbrace{\int_{t_x}^{t_1} \sigma^{(j)}(t)dt}_{B_j} \qquad (2)$$

Thus, $A_k + B_k = A_j + B_j$, where A represents entropy production before t_x and B represents entropy production after t_x. If $A_k < A_j$, then necessarily $B_k > B_j$ so unless the two paths are identical, either produces more entropy at some time.

The above is true even if the functions $S^{(k)}(t)$ are not monotonously increasing and even if the paths intersect each other any number of times. If t_x is chosen to coincide with an intersection (when $S^{(k)}(t_x) = S^{(j)}(t_x)$), the above deduction can be applied twice for the $[t_0 - t_x]$ and the $[t_x - t_1]$ intervals resulting in at least two intervals when one entropy changes faster on path k and two when it changes slower on path k.

Moreover, the choice discussed above is a philosophical statement that macroscopic systems would be intrinsically nondeterministic no matter how many measurements of them are considered and no matter how accurate they are. This statement plainly contradicts the results of statistical mechanics which state that, even if we use stochastic models at the molecular level, the macroscopic effect is deterministic.

The notion of intrinsically nondeterminstic "choice" is sometimes confusingly presented as "large number of degrees

of freedom".[4] Deterministic systems may have many degrees of freedom, but they still are entirely deterministic, that is they may only evolve in exactly one way if left isolated, thus they have no "choice" in the sense of the MEPP.

■ CHEMICAL KINETICS EXAMPLES

In order to illustrate the inconsistency between current theories on deterministic, macroscopic systems and the supposed principle of maximum entropy production, interpreted literally as stated in much of the recent literature, we performed a numerical simulation of a simple chemical system. We consider the reactions taking place in a well-stirred reactor, in isothermal conditions. Initial concentrations and reaction rates are listed in Table 1.

Table 1

init species	concn (mol/L)[a]	reaction	rates (s^{-1})[a]
A	10	A′ → A	0.04
B	2	A′ → A	0.03
C	2	A → B	5.00
A′	1000	A → B	4.90
		A → C	3.00
		A → C	2.90

[a]Initial concentrations and reaction rates for the system simulated in Figure 2.

A straightforward implementation using the Euler method was used. In this system, species A is transformed into B and C through reversible reactions. A large amount of A′ is also present that is transformed slowly into A. This reaction provides a steady supply of A that is relatively quickly transformed into B and C. Thus, rates in the system stabilize to relatively steady values in about 0.2 s, and the system remains far from equilibrium during the simulation. The reactions involving A, B, and C (without A′) model an open system far from equilibrium. All reactions have first-order kinetics.

$$A' \Leftrightarrow A \Leftrightarrow C$$

$$\Updownarrow \qquad\qquad\qquad (3)$$

$$B$$

The rates of local entropy production for each of the A ⇔ B and A ⇔ C reactions were computed at every step using eq 12.23 from ref 13

$$\sigma(a, x) = k_B \sum_{w=1}^{R} \left[r_w^+(a, x) - r_w^-(a, x) \right] \ln\left[\frac{r_w^+(a, x)}{r_w^-(a, x)} \right]$$

$$(4)$$

where σ is the entropy production rate, k_B is Bolzmann's constant, w are reactions in the system, a is the vector of concentrations of stable species, x is the vector of concentrations of intermediate species, and r_w^+ and r_w^- are backward and forward rates of reaction w.

The variations of concentration and entropy production rate in time are shown in Figure 2. Also, at every simulation step, entropy production rates were computed for all possible combinations of fluctuations of 5% of the concentrations of A, B, and C. These rates are also shown in Figure 2, as the dotted lines accompanying each of the thick lines. For each reaction there are four possible combinations of fluctuations consisting of either increasing or decreasing the instantaneous concentration

of each reactant by 5%. For the sum there are eight possible combinations.

We see from Figure 2 that the local entropy production rates for the concentrations and reaction rates that occur in the system are never maximal, nor minimal, in the sense that small fluctuations of the concentrations of the species may result in either higher or lower entropy production rates. This is illustrated by the fact that dotted lines, corresponding to fluctuations, are present both above and below thick lines at any time during the simulation.

On the statement that (v) "A system tends to its state with maximum entropy at the largest rate":[2,14]

After a second, we find the concentrations [A] = 19.92 mol, [B] = 17.64 mol, and [C] = 16.02 mol. The concentrations of B and C grow over the next second at the relatively constant rates of 12.9 mol/s and 13.2 mol/s.

Let us assume that the standard entropy is 130 J/(K mol) for A, 250 J/(K mol) for B, and 145 J/(K mol) for C. Then the entropy change will be (250 − 130) × 12.9 = 1548 J/K per second for the reaction producing B and (145 − 130) × 13.2 = 198 J/K per second for the reaction producing C.

Thus, the faster reaction produces less entropy, contrary to statement (v).

If the system would "rearrange" itself so as to proceed at the largest rate, only the A ↔ C reaction would take place; if it would "rearrange" itself so as to produce the most possible entropy, only the A ↔ B reaction would take place. However, none of these occur.

We also simulated the following system (Figure 3):

$$A' \Leftrightarrow A \Leftrightarrow C \Leftrightarrow C_1 \Leftrightarrow \cdots \Leftrightarrow C_{20}$$

$$\Updownarrow \qquad\qquad\qquad (5)$$

$$B$$
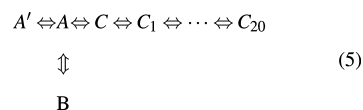
On the statement that (vii) "A system develops so as to maximize its entropy production",[2] panels b, c, and d show the production of entropy in time for the A ⇔ B and the A ⇔ C reaction as the thick lines. (computed according to eq 12.23 from ref 13). In the first 0.15 s the entropy production per second is higher for the A ⇔ B reaction, then it becomes higher for the A ⇔ C reaction.

The rates of the reaction (the slopes of the graphics of concentrations of B and C in the top panel) are generally equal.

If the system would develop so as to maximize entropy production, then the rate of the A ⇔ C reaction would increase and the A ⇔ B reaction would stop. However, this does not happen as different chemical pathways proceed independently, governed only by the nature and concentration of the reactants.

Also, changing the number of C_k reactants from 1 to 20 will not qualitatively change the above results, and thus the same conclusions apply for more complex systems as well.

Schlögl Model. The statement (viii) "The proposed thermodynamic principle of maximum entropy production[4] which states that thermodynamic processes in nonequilibrium systems assume steady states at which their rates of entropy production are maximized" does not hold, for example, for systems with hysteresis. Consider the Schlögl model, a two-variable system

$$A + 2X \underset{k_2}{\overset{k_1}{\Leftrightarrow}} 3X \qquad\qquad (6)$$

$$X \underset{k_4}{\overset{k_3}{\Leftrightarrow}} B \qquad\qquad (7)$$

with the rate coefficients k_1 and k_2 for the first direct and reverse reaction and k_3 and k_4 for the second. There exists the possibility of

multiple stationary states for given constraints on the pressures of A and B. The kinetic equation for the concentration of X, in terms of partial pressure, is

$$\frac{dX}{dt} = k_1 A X^2 + k_4 B - k_2 X^3 - k_3 X \qquad (8)$$

which is cubic in X and hence may have three stationary states (three solutions for the rate of change of X to be 0).

The stationary solutions for some range of A and B are shown in Figure 4 in which we label the lower branch α, the upper branch γ, and the transition branch β. Stable stationary states are denoted by solid lines; unstable stationary states by the dotted line. The upper branch exists only after F_1, and the lower branch exists only before F_3. The entropy production, however, is everywhere higher on the upper branch than it is on the lower branch.[15] Hence in the region of multiple stationary states, say between F_1 and F_2, a system at a given value of F is more stable on the lower branch, but has a lower entropy production than at that value of F on the upper branch. This a clear example of violation of the above statement.

The inapplicability of MEPP to systems with hysteresis has been cited in several articles.[15,16]

Heat Transfer Example. We examine here the Rayleigh–Benard problem (adopted from ref 13) in view of the claim (vii) that "the system develops as to maximise its entropy production".[2] See also Figure 5.

An interesting experiment has been carried out by Zamora and Rey de Luna[17] on the Rayleigh–Benard problem in an apparatus that could be inverted 180° in the gravitational field. In their experimental arrangement, the bottom and top sides of the fluid are connected to heat reservoirs at different temperatures. Suppose a stationary state is homogeneous and conductive, achieved by setting the low-temperature reservoir below the one at high temperature in the gravitational field. Next, the entire apparatus is turned in the gravitational field; then the conductive state becomes unstable and a stable convective state appears. Throughout the experiment the reservoir temperatures are held fixed and the average temperature of the fluid is nearly constant. They measured the heat fluxes into and out from the reservoirs during all transients, that is the relaxations from a conductive to a convective state, and the reverse. For example, say the fluid is in a convective state; invert the apparatus; the convective state is unstable and a transient change to a conductive state takes place. Measure the heat fluxes in and out of the reservoirs. The integration of the differences of the heat fluxes in and out during this transient process is the total energy change accompanying the destruction of the convective rolls. Similarly, they measured the total energy change accompanying the formation of the convective rolls. The results show that the heat releases for both the destruction and formation of convective structures are positive, which means that the system always releases energy in the form of heat when it approaches a stable stationary state, either the convective state or the motionless conductive state. In an auxiliary experiment, they found that the change in average temperature of the system is very small; the change in internal energy due to this small temperature is less than 10% of the heat release during the relaxation processes, so this cannot be the reason for the experimental observations. Moreover, the change in internal energy cannot explain the observed heat release in both the destruction and the formation of a convective structure.

The rate of entropy production increases with the rate of heat transfer through the above device. It is smaller in the conductive state and larger in the convective state. It has intermediate values in each of the states that occur when the device is rotated. It is generally determined by the position of the device and by the recent history of the positions, and is not the maximum possible rate except in stable convection.

Since the change from the convective to the conductive state is spontaneous, and so is the reverse, there is a rate of entropy production associated with each change, which leads to the production of heat. Furthermore, the entropy production in the convective stationary state is always higher than in the conductive stationary state, so in the approach of the system to the conductive state the system goes to a state of lower entropy production, contrary to the claims stated above.

Martyushev and Seleznev[18] also mention a theoretical and experimental proof that some of the states in a Rayleigh–Benard system amount to lower than maximum heat-transfer rates, and thus entropy production, but dismisses them because of the difficulties of calculation and measurement. We hope the above, simpler example, is more illustrative.

(Non)scientific Nature of the MEPP. In another article[19] we find (ix) "Note first that a principle like (MEPP) cannot be proved. Examples of its successful application ... just support this principle, while experimental results (if they appear) contradicting this principle will just point to the region of its actual applicability". It is a generally accepted definition, first formulated by K. Popper, that a scientific hypothesis must satisfy a falsifiability possibility, otherwise it fails as a scientific hypothesis. Thus, the authors remove MEPP from being a scientific hypothesis. Dyke and Kleidon admit that[20] (x) " ... if one requires falsification to be a necessary condition of any scientific theory, the MEP principle is not a scientific theory." These authors, however, are not discouraged by this conclusion. They continue (xi) " ... any empirical evidence that does not agree with a MEP principle prediction does not represent any falsification of the theory, rather the identification of the "fact" that the system is not a MEPP system. What appears to be required is the formulation of the rules of engagement for the MEPP; under what conditions will the MEPP apply to certain systems. In the absence of a set of rules or guidelines that allow us to identify MEPP systems, the MEPP itself cannot be a scientific theory because it will always be possible to explain erroneous predictions as instances where the MEP principle was applied incorrectly. The natural law interpretation solution to this problem is to argue that the MEPP is a developing theory and that at some point in the future a derivation may be produced that details exactly under what circumstances systems will and will not produce maximum rates of entropy." The requirements for denoting a statement like that as a principle should be set higher. "Principles should be made of sterner stuff" (with apologies to Wm. Shakespeare, from Julius Ceasar, the eulogy of Anthony at Ceasar's death, "Ambition should be made of sterner stuff".)

Kleidon also refers to Popper and his theories of falsification of scientific hypotheses. But then, similar to Martyushev and Seleznev, Dyke and Kleidon state[21] (xii) "If MEPP is subjected to these two constraints (constraints which yield the classical thermodynamic variables as Lagrange multipliers) does not yield predictions consistent with observations, it should not be seen as a failure of MEPP per se, but rather as the lack of further relevant information, for instance, in terms of additional constraints".
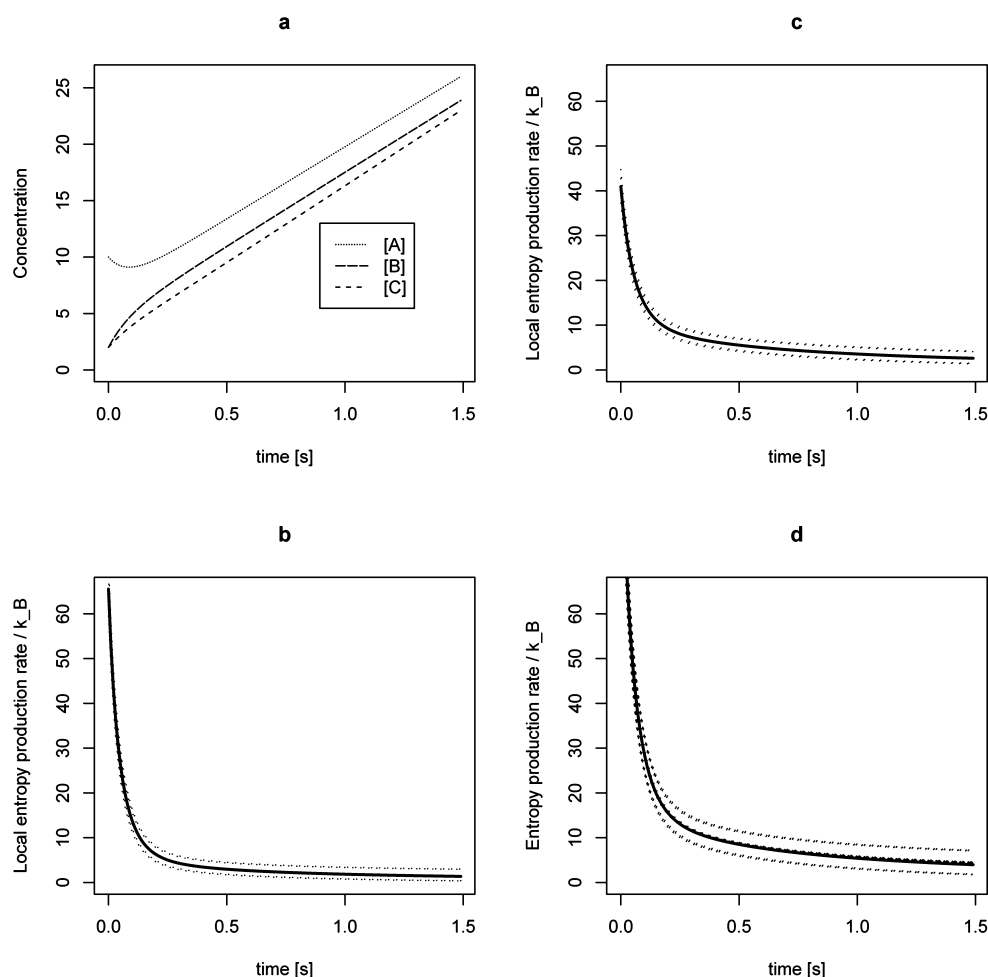
Figure 2. Panel a represents the concentration of species A, B, and C in time for the system in eq 3 with the reaction rates and initial conditions specified in Table 1. Panel b represents the local entropy production rate (scaled with k_B and volume) in time for the A $\leftrightarrow$ B reaction. The thick, continuous line corresponds to the actual entropy production rate at each step during simulation. The thinner, dotted lines, represent the local entropy production rate that would result if the reactants would have, at every instant, a concentration 5% higher, or lower, than that actually reached during simulation; for each combination of fluctuations there is a dotted line. Panel c is for the A $\leftrightarrow$ C, and panel d is for both reactions, with the same conventions as in panel b. The fact that the dotted lines in panels b, c, and d are always found both above and below the continuous line (the actual simulation result) means that the entropy production rate, as the reactions develop, is never maximum or minimum with respect to fluctuations of concentration.

In that case one cannot falsify a hypothesis and hence it ceases to be a scientific hypothesis.

In the same article, Dyke and Kleidon propose a scheme for a thermodynamics far from equilibrium. We believe the scheme to be untenable; a comparison of his suggestions with our theory (see Appendix) shows that in detail.

Stochastic versus Deterministic Systems. Stochastic models of macroscopical physical systems are used to represent a variety of unknown elements about such systems. Some of the unknown elements can be fluctuations of undetectable origin. Some may be macroscopic effects of intrinsically random phenomena at the mesoscopic or microscopic level. Some may be unknown features about the structure of a system—such as slower, small-scale reactions that are usually ignored in a chemical system.

When the entropy resulting from calculations on such a model is considered, depending on how the system is formulated, the proposed entropy may occur either (1) as combining thermodynamic entropy with information entropy due to lack of knowledge of some of the structure of the system or (2) as a probability distribution of thermodynamic entropy. Purely thermodynamic principles are inadequate to deal with the first

case. In the second case, the actual entropy reached would depend on the unknown components, not on any maximization or minimization principle.

An example of the second case: an isolated chemical system is at equilibrium. An unknown amount of a substance, x, is added. Reactions are taking place and equilibrium is reached again. The entropy of the system changes by an amount that obviously is determined by the actual value of x.

However, if we model x as a random variable and the evolution of the system as a random function, with possible paths and their probabilities, then entropy change is a random variable. If we only look at equations, it may seem like it is a system with "choices" as in the MEPP papers. However, the actual value of the entropy change in a realization of the system depends on the realization of x, not on any other principle.

Other Specific Issues. The defining statement of the second law of thermodynamics[22] is incorrect (xiii) in both refs 1 and 2. The equation connecting a small change of the entropy to a small change in heat, dQ and the temperature holds only for reversible processes. Small changes in dQ may be irreversible and then the equation does not hold.
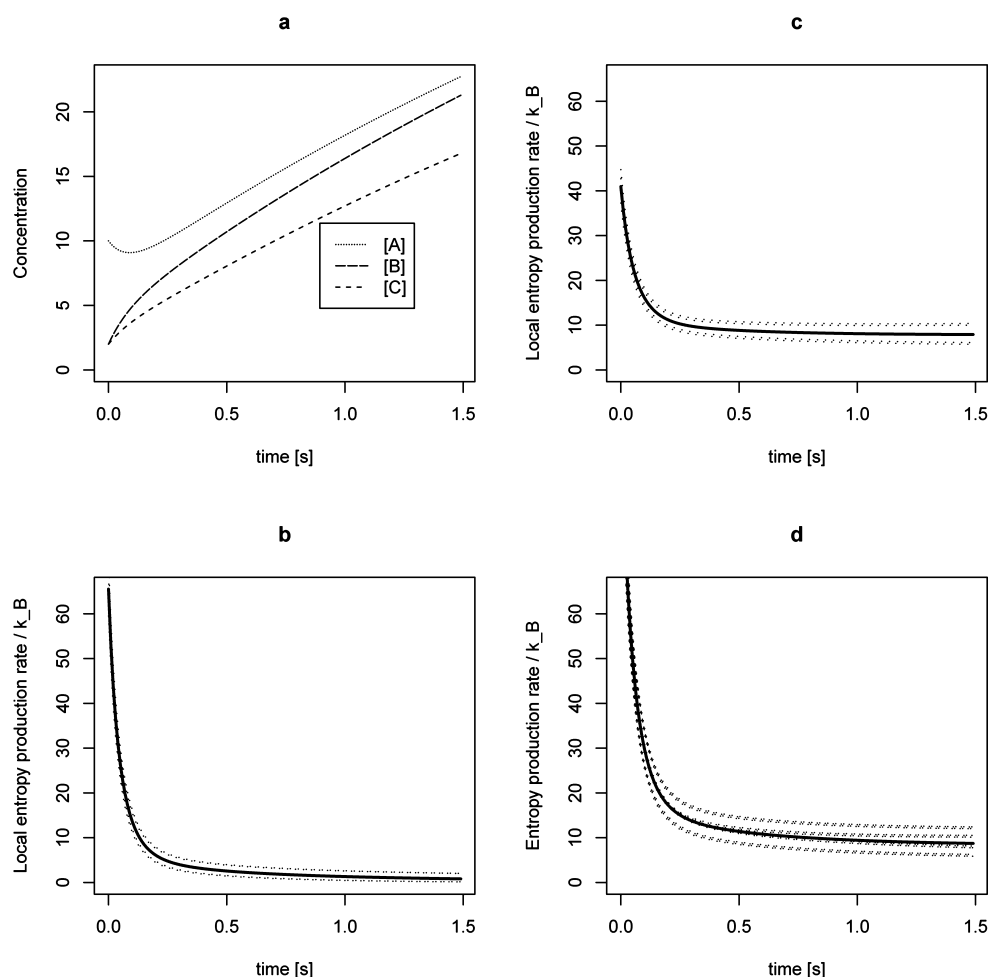
Figure 3. With the same conventions as in Figure 2, the concentration and local entropy production in time for the same reactions when species C is farther entering a chain of 20 more reactions (eq 5). Despite the increase in complexity, the conclusions are the same as in Figure 2.

In both refs 1 and 2, there is seldom made a distinction between a process going to a nonequilibrium state and a process going to equilibrium. There is a distinct difference in the thermodynamics of these two possibilities, and it is an error to gloss over this difference (see ref 15 for an extensive treatment of this subject, and a brief summary at the end of this section).

The authors state on linear nonequilibrium thermodynamics (xiv):[23] "in this case, a nearly linear relationship may be assumed between thermodynamic fluxes and forces. However, the spectrum of problems which can be solved in terms of this simple formalism, is sufficiently wide." We need to disagree: linear laws are insufficient for nearly all of chemistry, biochemistry, biotechnology, and genetics.[13]

Another issue[3] (xv) concerns the supposed applicability of this principle only to sufficiently large systems, but no concise criterion of "large" is given. We suspect "large" actually means "not characterisable sufficiently through measurements", which links the MEPP to partial knowledge rather than thermodynamic entropy.

A. Kleidon published an article in *Physics of Life Reviews*[1] with the title "Life, Hierarchy and the Thermodynamic Machinery of Planet Earth". We regret to point out several fundamental errors in the thermodynamics presented in this article, in the discussion of the issue of maximum entropy production, and in the norms of acceptance, or rejection, of a scientific hypothesis.

The author states:[24] (xvi) "the overall effect of this hierarchy is to enhance the overall entropy production, resulting in the fastest approach to thermodynamic equilibrium that is possible...". The entropy production is a product of a rate of reaction and a thermodynamic force. The rate of a reaction depends on Gibbs free energies of activation; the thermodynamic force on Gibbs free energies. There is in general no relation between the thermodynamic quantities and the kinetic quantities, and hence the quoted statement is generally not correct.

In ref 25 there is a statement: (xvii) "If we assume that dissipation is proportional to the amount of free energy in the system ...." which is a state function. If that proportionality were indeed the case, then dissipation would be a state function, which is clearly wrong. Dissipation depends on the irreversible process associated with the generation of power and is not a state function. This comment is made in an attempt to describe thermodynamic systems neither at nor close to equilibrium. The attempt is not successful for the reason given in the previous paragraph and other reasons as well.

(xviii) "Thermodynamics, basically the first and second law, set the rules for operating these power transfer processes ...."[26] This is incomplete and basically wrong. Power cannot be generated in a reversible process, which takes an infinite time. Power generation requires processes to occur in finite time and hence these processes are irreversible. This is beyond the first two laws
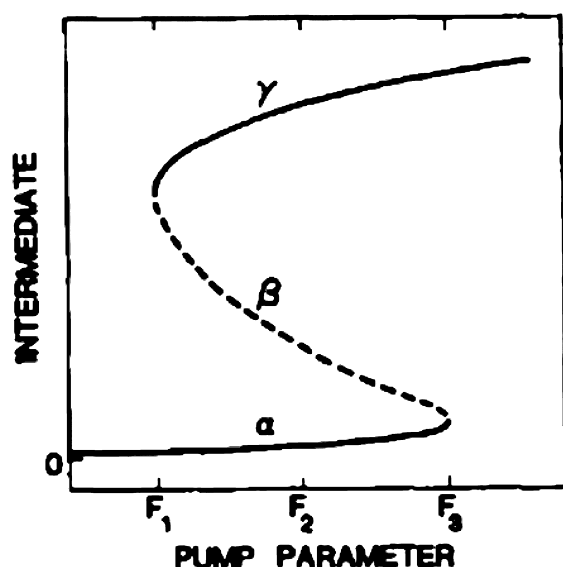
Figure 4. Stationary states of the Schlögl model with fixed reactant and products pressures. Plot of the pressure of the intermediate p_X vs the pump parameter (p_A/p_B). The branches of stable stationary states are labeled α and γ and the branch of unstable stationary states is labeled β. The marginal stability points are at F_1 and F_3, and the system has two stable stationary states between these limits. The equistability point of the two stable stationary states is at F_2. Reproduced with permission from ref 13.
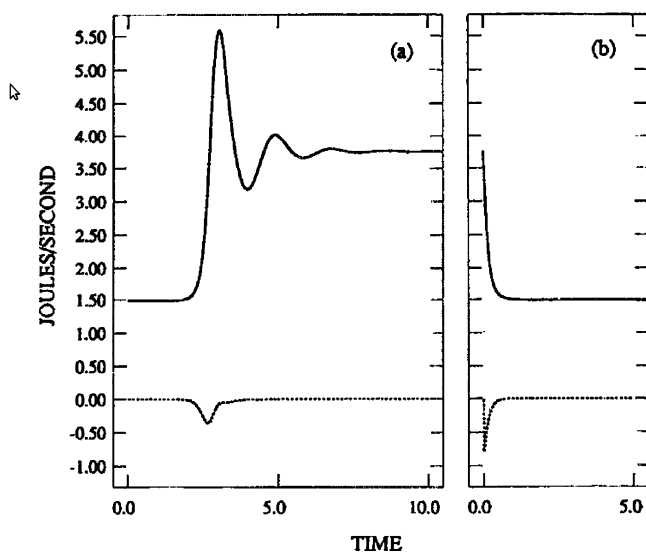

Figure 5. Panel a is for the transition from a conductive to a convective state and panel b for the reverse transition. The solid line is the derivative of excess work in time. The dashed line is the excess work in time. In each case the integral of the derivative over time is negative; that is, excess work is dissipated and heat is generated. Further, we note that the entropy production in the convective state is always larger than that in the conductive state, and no explanation of heat release in the transition from one state to the other, and its reverse, can thereby be derived. Reproduced with permission from ref 13.

of thermodynamics, as the specification of the irreversible process is necessary.

CONCLUSION

While we only examined some of the papers on the maximum entropy production principle, we found many of the statements

mentioned here, as formulated, to be obviously inconsistent with the current laws[27,28] and assumptions of most physics and chemistry. The current laws provide a very effective scheme to predict quantatively the behavior of a wide variety of systems. Some supporters of the MEPP-like theories do not even consider experimental falsifiability of a hypothesis to be a requirement for a theory, although some[3] do admit, simultaneously, that the lack of this quality puts a hypothesis outside the field of science.

Thus, predictions based on MEPP-like principles should not be considered scientifically founded.

APPENDIX

A Brief Summary of the Essentials of Nonequilibrium Thermodynamics and Fluctuations Near and Far from Equilibrium

The following treatment is modified from Chapter 8.1 of ref 13

For illustration, we use the Schlögl model as an example

$$A + 2X \overset{k_1}{\underset{k_2}{\Leftrightarrow}} 3X \tag{9}$$

$$X \overset{k_3}{\underset{k_4}{\Leftrightarrow}} B \tag{10}$$

and define a species-specific affinity in terms of chemical potentials:

$$\Phi(X) = \int^X (\mu_X - \mu_{X*}) \, dX \tag{11}$$

which is an excess work relative to a starred reference state defined by the kinetics of the system. The relation of eq 11 to the chemical kinetics comes from the rate equation for the intermediate X:

$$\frac{dX}{dt} = r_X^+ - r_X^- \tag{12}$$

where

$$r_X^+ = k_1 A X^2 + k_4 B \tag{13}$$

$$r_X^- = k_2 X^3 + k_3 X \tag{14}$$

for the model. The relation is

$$\mu_X - \mu_{X*} = -kT \ln\left(\frac{r_X^+}{r_X^-}\right) \tag{15}$$

and the quantity μ_X* approaches its value in each of the stationary states μ_X^S as each of the stationary states in the reaction model is approached. The theory reviewed here can be generalized to multivariable systems and to other choices of reference states (see chapter III of ref 13).

From eq 11 we can draw several important consequences:

1. The function Φ provides necessary and sufficient conditions of global stability; it has an extremum at each stationary state

$$\frac{\partial \Phi}{\partial X} = 0 \tag{16}$$

and its second derivative shows whether a given stationary state is stable or unstable

$$\frac{\partial^2 \Phi}{\partial X^2} \begin{cases} > 0 & \text{for stable stationary states} \\ < 0 & \text{for unstable stationary states} \end{cases} \tag{17}$$

2. The function Φ is the driving force (frequently so-called, but in fact a potential) toward stable stationary states. Φ is lower bounded and is a Lyapunov function (a function which gives the direction of motion of the system), with the derivative of Φ with respect to time given by

$$\frac{d\Phi}{dt} = -kT \ln(r_X^+/r_X^-)[r_X^+ - r_X^-] \leq 0 \tag{18}$$

in the form of Boltzmann's H theorem, where T is the temperature.

3. Φ is a component of the total dissipation and is zero at stationary states.

4. $d\Phi$ is a measurable excess work: for a linear system it is the negative of the work, other than pressure–volume work, obtained from the spontaneous relaxation dX at X along the deterministic trajectory, minus the work of displacing the system the same extent dX at X_S. For a nonlinear system we substitute in the prior sentence X^* for X_S. For each X of a nonlinear system there is an X^* and an instantaneous linear equivalent system at each instant, which makes this substitution possible.

5. If a system approaches the stationary state of equilibrium then Φ approaches correctly the thermodynamic Gibbs free energy change.

6. The function Φ provides a criterion of relative stability of two stable stationary states, labeled 1 and 3, separated by an unstable stationary state labeled 2; at equistability of the two stationary states the condition holds

$$\int_1^3 (m_X - m_{X^*}) \, dX = 0 \tag{19}$$

7. The function Φ yields the stationary probability distribution of a stochastic, birth–death master equation for single-variable systems

$$P_{st}(X) = P_0 e^{-\Phi(X)/kT} \tag{20}$$

where P_0 is a normalization constant. The combination of eqs 11 and 20 is a generalization of the fluctuation equation of Einstein[29] to stationary nonequilibrium states and conditions far from equilibrium. For one-variable systems the excess work Φ is a state function. In general, the excess work is not a state function for the reference state as defined in this section (see also Chapter IV of ref 13). The excess work is a state function for the reference state as defined in Chapter III of ref 13.

In ref 13 this work has been presented for multivariable chemical systems, for nonideal systems, for systems with multiple stationary states, for transport processes, for hydrodynamics, for electrochemical systems, and for fluctuations far from equilibrium. The theory has been applied to dissipation in irreversible processes, and to the issue of efficiency in irreversible processes, including biochemical reactions, proton pumps, and forced oscillatory reactions. Comparison with experiments is made throughout the presentation. We believe that the theory provides a firm foundation for the thermodynamics and fluctuations for irreversible processes far from equilibrium.

The hope and expectation has been expressed of the "possibility that all non-equilibrium thermodynamics and statistical physics can be constructed on the basis of entropy production ... maximization ...".[19] In the brief outline of the theory of ref 13 given above, neither the entropy production nor its maximum plays any fundamental or direct role, nor does it

seem that that quantity can provide answers to the issues cited in points 1–7.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: john.ross@stanford.edu.

Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Kleidon, A. *Phys. Life Rev.* **2010**, *7*, 424−460.
(2) Martyushev, L. M.; Seleznev, V. D. *Phys. Rep.* **2006**, *426*, 1−45.
(3) Dyke, J.; Kleidon, A. *Entropy* **2010**, *12*, 613−630.
(4) Kleidon, A. *Philos. Trans. R. Soc. B* **2010**, *365*, 1303−1315.
(5) Niven, R. K. *Philos. Trans. R. Soc. B* **2010**, *365*, 1323−1331.
(6) Jaynes, E. T. *Annu. Rev. Phys. Chem.* **1980**, *31*, 579−601.
(7) Ziegler, H. In *Progress in Solid Mechanics*; Sneddon, I. N., Hill, R., Eds.; North Holland: Amsterdam, 1963; Vol. *4*.
(8) Reference 2, page 41.
(9) Reference 4, page 1309, top paragraph.
(10) Reference 2, page 3.
(11) Reference 1, page 435.
(12) Reference 1, page 440.
(13) Ross, J. *Thermodynamics and Fluctuations Far from Equilibrium*; Springer: New York, 2008.
(14) Reference 1, page 435.
(15) Andresen, B.; Zimmermann, E. C.; Ross, J. *J. Chem. Phys.* **1984**, *81*, 4676−4677.
(16) Sawada, J. *J. Stat. Phys.* **1984**, *34*, 1039−1045.
(17) Zamora, N.; de Luna, R. *J Fluid Mech.* **1986**, *167*, 427−437.
(18) Reference 2, page 27, second paragraph.
(19) Martyushev, L. M. *Philos. Trans. R. Soc. B* **2010**, *365*, 1333−1334.
(20) Reference 3, page 620.
(21) Reference 3, page 624.
(22) Reference 2, eq 1.2.
(23) Reference 2, page 5.
(24) Reference 1, page 429.
(25) Reference 1, page 438.
(26) Reference 1, page 427.
(27) Tolman, R. C. *The Principles of Statistical Mechanics*; Clarendon Press: Oxford, UK, 1938.
(28) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular theory of gases and liquids*; Wiley: New York, 1954.
(29) Reif, P. *Fundamentals of Statistical and Thermal Physics*; McGraw-Hill: New York, 1965; Chapters 1 and 15.

■ NOTE ADDED IN PROOF

After this paper was accepted, we learned of the existence of another paper supporting conclusions similar to ours (Nicolis, G.; Nicolis, J. *Q. J. R. Meteorol. Soc.* **2010**, *136*, 1161-1169).