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THE FOURTH LAW OF THERMODYNAMICS OR THE LAW OF MAXIMUM ENTROPY PRODUCTION (LMEP)

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Abstract. In their recent paper entitled "A Fourth Law of Thermodynamics" Morel and Fleck propose what they say is a simply stated yet powerful new universal law that accounts for the ubiquitous production of order from disorder that characterizes the visible world and thereby, and in other ways, significantly expands the domain of thermodynamics. While we agree with their characterization of the law as the Fourth Law of Thermodynamics, and that it significantly expands thermodynamics, and that it is universal in scope applying near and far from equilibrium to all ranges and scales, and that it provides the basis for spontaneous transformations from disorder to order, the mistake they make is that the law is not a new law. It was proposed and demonstrated by my colleagues and me as "The Law of Maximum Entropy Production" (LMEP or previously MEP) more than two decades ago and subsequently in numerous articles since. This error in their paper, however, in no way diminishes what they say is the validity or significance of the law. The law with some additional background and context is further discussed.

Keywords: maximum entropy production, fourth law of thermodynamics, spontaneous order

1. Background

Recently, in their paper "A Fourth Law of Thermodynamics" [1] R.E. Morel and George Fleck, noting correctly that "the classical laws of thermodynamics....are silent about the means and pathways for achieving change", propose, in their words "a simply stated yet powerful Fourth Law of Thermodynamics that significantly extends the domain of thermodynamics," and they state the law as follows:

"Systems increase entropy at the maximum rate available to them"

The law, they say, is universal and "applies to every evolving system, whether far from equilibrium or near equilibrium," where the limiting case is a system at equilibrium where the maximum rate is zero, when the entropy is maximized so all flows stop. "Rather than being surprised," they say, the law "leads to the expectation" that dynamically ordered states ("dissipative structures") will emerge because they "facilitate entropy production."

We agree the law the authors propose, and rightfully call "The Fourth Law of Thermodynamics", is a universal law, and likewise that it makes spontaneous ordering expected rather than surprising and that it thereby, and in other ways, "significantly extends the domain of thermodynamics". But it is not a new law; It is the law my colleagues and I proposed and demonstrated more than twenty years ago and have elucidated in numerous articles, and with others in the time since, as the "Law of Maximum Entropy Production" (or "LMEP" and previously "MEP"). It states [2-12]:

"A system will select the path or assembly of paths out of available paths that minimizes the potential or maximizes the entropy at the fastest rate given the constraints."

In what follows, I provide some additional background and discussion of the law. Educators, I hope, will be particularly interested in this subject since it has broad application across the disciplines and is something about which students should know.

2. Discussion

In the 1980's when the Law of Maximum Entropy Production (LMEP) was formulated, the predominant view was of a world where physics and biology were seemingly at odds with each other. The second law, as the result of Boltzmann's [13] interpretation, was taken to be a 'law of disorder' believed to predict that the world according to physics should typically move from more ordered to less ordered states or remain in a state of disorder. Yet this was the opposite of what one saw in biology or planetary evolution writ large, as well as cultural evolution, and in fact most generally the visible world as we see it. Ilya Prigogine [14], following the developmental biologist, Ludwig von Bertalanffy [15], had under-scored that this general behavior was widespread in nonliving systems too. The classic Benard "cell" fluid dynamic experiment, being an example that is easy to replicate, demonstrated how Boltzmann's view of the second law readily broke down: the production of order occurs 'not infinitely improbably," as Boltzmann [13], p. 20, had asserted, but instead regularly and predictably, or as my colleague Michael Turvey and I put it in 1991 [6], "with a probability of one" in very ordinary circumstances.

Looking for universal principles that could describe nonequilibrium systems, Prigogine had noted that near equilibrium (where the flows are linearly related to the "forces" or gradients of potentials, and the entropy production is given as the sum of the product of the flows and the forces) as the forces are progressively reduced or dissipated as mandated by the Second Law the entropy production will steadily go down until (a) in the limit it goes to zero as the ("balance equation", discussed below, or the) Second Law requires and the system reaches equilibrium (where the potential is thus fully minimized or equivalently the entropy maximized and all flows stop), or (b) if the system cannot get to equilibrium because some thermodynamic force is externally maintained then, again as expected by the second law, it will get as close as it can where, if conditions are maintained, it will remain in a nonequilibrium near equilibrium steady state. Given that the flows in this region are linearly related to the forces, which have now been minimized or dissipated to the greatest extent possible under the particular circumstances, the entropy production is likewise at a low point or minimum relative to the whole process where it remains. Prigogine called this the "theorem of minimum entropy production", and it is not much more than the fully expected consequences of the second law and the fact that in this range the flows and forces are linearly related.

Despite the very limited range of this theorem, a number of people have unfortunately attempted to apply it universally, for example, to far from equilibrium or spontaneously ordered systems where it clearly does not apply. With respect to these systems, like Benard cell, for example, Prigogine [14], p. 88, repeatedly wrote that "It came as a great surprise when it was shown that for systems far from equilibrium the thermodynamic behavior could be quite different...even directly opposite that predicted by the theorem of minimum entropy production" because the rate of the entropy production increased instead of going down. In hindsight, it is now easy to see why this increase in the rate of entropy production during the transition from disorder to order should be no surprise at all. What is more, the assertion "could be quite different" implies that sometimes it does increase at such points and sometimes it does not. Yet the increase in the rate of entropy production with the transition from disorder to dynamic order always happens. It must. And the reason had actually given indirectly many years before by Bertalanffy [15] and Schroedinger [16] when they argued that living things do not violate the the second law as clas-sically stated because they produce enough entropy (minimized enough potential or gradient or sufficiently 'feed on negentropy" as Schroedinger put it) to compensate or "pay for" their own internal entropy reduction, or ordering. In other words, whenever spontaneous ordering occurs and there is a transition from disorder to order the rate of the entropy production must increase, and always does, in order to satisfy the balance equation of the second law (that in all natural processes the net entropy always increases or remains the same at equilibrium when all processes or flows have ceased).

But now it was thought there was no general or universal law or principal that could explain the selfevident drive to order production seen in the world but instead somehow two opposite or competing principles to entropy production in natural systems (monotonically going down near equilibrium and dramatically increasing with the production of order), The problem was that it was the wrong question that was being asked. As Morel and Fleck correctly point out in their paper, and as my colleagues and I have pointed out during the last two decades, classical thermodynamics tells us the entropy is maximized at thermodynamic equilibrium but tells us nothing about which means or paths out of otherwise available paths the system will take to get there, e.g., [3-5] and also Prigogine's theorem of minimum entropy production. All it points out is that the entropy production goes down in near equilibrium systems as they act to minimize potentials and move towards or as close as they can get to equilibrium. It does not ask or answer the question about which paths out of available paths the systems will take to get there. The important thing to me at the time, following from what Bertalanffy and Schroedinger had indirectly noted, was that every time a system opted or "chose" the production of order from disorder it was concomitantly 'choosing' to increase the rate of entropy production. And we could see from simple experiment that every time certain minimal conditions were met such that it could produce order from disorder it would. The answer to the whole conundrum was now for me starting to suggest itself. If it were the case that a system will select the path that minimizes the potential or maximizes the entropy at the fastest rate given the constraints then the answer to the question of "why the world is in the order production business" contra Boltzmann would be solved.

At that point, in 1989, it was reasonably simple to come up with a model based on a simple physical experiment in the spirit of the most elementary experiments or demonstrations in thermodynamics (e.g., such as Joule's weight on a pulley and paddle wheel) to test or demonstrate what by then we already intuited if not knew was true. Borrowing some basic tools from classical thermodynamics, in this case a gas in a box closed to heat flow with its environment and divided into two chambers, A and B, by an adiabatic wall (so that there is initially no heat flow between the two), and where A is heated to some temperature greater than B, so as to produce a force or gradient between the two, and where the magnitude of the force is kept within the linear range, and then dividing the adiabatic wall into four regions, 1-4, each made of a material with a different coefficient of thermal conductivity where the adiabatic seal can be removed from each individually as one chooses, the result was easy to show. In each case, if the experiment is run by removing one and one only of the seals from any one of the four regions, the system will immediately produce a flow that will minimize the potential, or maximize the entropy to bring the system to equilibrium with the rate determined by the coefficient of conductivity of the respective material of the respective region. For four different runs with a different seal pulled off for each run, the system will thus achieve the same end state (the maximization of entropy) by four different rates. If the seals are instead pulled off of regions 1 and 2 at the same time, however, where 2 has a faster rate than 1, it becomes more interesting. The system does not give half the potential to 1 and half to 2. It gives as much as it can to 2, the faster path, and then since 2 cannot dissipate it all at once the remainder to 1. One can now do further combinations with 1-4 and the results will be the same. The system will select the path or assembly of paths out of available paths that minimizes the potential or maximizes the entropy at the fastest rate given the constraints. And this of course is the statement I have given above of the Law of Maximum Entropy Production. The first time this was published in this form was in the research journal of the Center for the Ecological Study of Perception and Action (CESPA) at the University of Connecticut in 1989 [3] and not long after, in a variety of publications across the disciplines, e.g, [4-6].

To further elucidate the law for a broader audience in our paper 'Thermodynamic Reasons for Perception-Action Cycles" in 1991 [6], Michael Turvey and I provided the example of a warm mountain cabin (say where there had been a burning fire in the fireplace that has now gone out) in a snowcovered woods, an example that makes the Law of Maximum Entropy Production simple and intuitive to grasp for the transdisciplinary scientist, the philosopher, or even, I think, for the nonscientist. Here again, we are confronted with a thermodynamic field with a thermodynamic force or gradient that the system, according to the Second Law, spontaneously works to reduce, dissipate or minimize. The opportunities, or pathways in this case include heat flux through the walls, through the cracks around the windows, or elsewhere in the cabin, under the door, and in addition through the door or windows if they are opened. Almost everyone will understand that if the goal of the inhabitants is to keep the heat in the cabin it is important to close the door after entering because as soon as the door is opened the system will begin allocating otherwise allocated potential to the open door. In short, the system will immediately begin to reallocate potential or gradient to seize the opportunity to minimize the potential at the now faster available rate. And the same is true if a window is partially opened, fully opened or several are opened. The Law of Maximum Entropy Production, of course, is not only universal for heat flows or temperature gradients, it is universal for all energy flows and gradients the equivalence of which was shown by Mayer and Joule in their formulation of the First

Law of Thermodynamics in the nineteenth century with the demonstration of the equivalence of mechanical energy and heat. And, as has been discussed above, and as Morel and Fleck correctly point out in their paper, it makes the production of order from disorder no longer surprising or unexpected, or "infinitely improbable" as Boltzmann asserted, but instead the expected consequence of universal law. In conclusion, then, in their interesting, albeit brief, paper "A Fourth Law of Thermodynamics"[1] , Morel and Fleck correctly point to an important universal law, which they rightly call "The Fourth Law of Thermodynamics". The main problem with their paper, however, is that they were apparently unaware that contrary to their assertion that this is a "new" law, it is a law that was instead advanced, demonstrated, and elaborated more than two decades ago and in numerous publications since. This does nothing of course to detract from their general statements about the importance of the law or the problems previously existing that it resolves.

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ЧЕТВЪРТИ ЗАКОН НА ТЕРМОДИНАМИКАТА ИЛИ ЗАКОН ЗА МАКСИМАЛНО ПРОИЗВОДСТВО НА ЕНТРОПИЯТА

Резюме. Четвъртият закон на термодинамиката бе предложен от Morel & Fleck (Chemistry 15, 305-310 (2006)). По-рано, под името “закон за максимално производство на ентропията” този закон бе коментиран от Swenson. Обстоятелствата, които налагат това уточнение на термодинамиката, са разгледани подробно в настоящата работа.

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