About some common slipups in applying Prigogine's minimum entropy production principle to living systems.

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Prigogine's theory for thermodynamic nonequilibrium stable steady states: the Minimum Entropy Production rule

To begin consider a system which exchanges mass and energy with its environment. "Let dS_i be the entropy production in the system due to irreversible processes and dS_e be the entropy flux due to exchanges between the system and environment[1]. The total entropy change in the system is given by

$$dS = dS_e + dS_i \tag{1}$$

The second law states that $dS_i \geq 0$. However if sufficient low entropy flux enters the system then $dS_e \leq 0$ and it is possible that $|dS_e| > |dS_i|$ which implies that $dS < 0$. If this is the case then the system will be driven away from equilibrium. It is also possible for the system to eventually reach a steady state ($dS = 0$). It is the process which leads to this steady state and the accompanying coherent behavior which Prigogine, for special cases, has developed a theory for.

Central to this theory is the Minimum Entropy Production rule. Let P = entropy production due to irreversible processes in the system and σ = local entropy production.

Then

$$P = \frac{dS_i}{dt} = \int \sigma \, dV \geq 0 \tag{2}$$

where the integral is over the spatial volume of the system.

Using Onsager's Reciprocity Relations it is possible to write

$$\sigma = L_{kl} X_k X_l \tag{3}$$

where X_k is the thermodynamic force acting on the system and the summation convention over repeated indices is in effect[2]. Substituting for σ, making several assumptions about the forces, and differentiating with respect to time, leads to[3]:

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[1] The notation used in this section is the same as used in the book: Nicolis, G. and Prigogine, I. Self-Organization in Non-equilibrium Systems. New York: J. Wiley & Sons; 1977.

[2] Summation convention in effect for repeated indices. That is $\sigma = L_{kl} X_k X_l$ is taken to mean:

$$\frac{dP}{dt} = \frac{2}{T}\int \frac{\partial\mu_i}{\partial\rho_j}\frac{\partial\rho_i}{\partial t}\frac{\partial\rho_j}{\partial t}\, dV \qquad (4)$$

The quadratic form in the integral can be shown to be positive semi-definite. It is zero at a steady state. Hence

$dP/dt < 0$ away from steady-state

$dP/dt = 0$ at a steady state.

This is the famous Minimum Entropy Production rule[4] which governs the behavior of dissipative structures in the steady-state. It can be easily shown that this rule guarantees the stability of steady non-equilibrium states.

However the derivation of this rule depends on seven assumptions which I can identify.

1) Local Equilibrium Thermodynamics applies. The system must be well enough behaved that locally (spatially) equilibrium thermodynamics apply.

2) The fluxes can be expressed as a linear combination of the flows using Onsager's Reciprocity Relationship.

3) The L_{ij} used in the expansion of the fluxes are time independant.

4) The medium is isotropic.

5) The boundary conditions imposed on the system are time independant.

6) The system is isothermal.

7) The system is in mechanical and thermal equilibrium with its environment. Only mass flow occurs across the boundary.

This set of constraints means that the minimum entropy production rule and most of Prigogine's results apply to a very restrictive set of systems. A general far from equilibrium thermodynamics and theory of self-organization does not exist. Any attempt

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$$\sigma = \sum_{k=1}^{n} \sum_{l=1}^{n} L_{kl}\, x_k\, x_l$$

[3] It takes Prigogine 12 pages of text to develop the assumptions which lead to this result (eq 3.42, p. 43 of Self-Organization in Nonequilibrium Systems" (1977)). Going from (2) to (4), given all the assumptions are previously worked out, took me 7 pages of algebra and integration. It seemed merciful to spare the reader.

[4] In English the principle is: The rate at which a stable, steady state, non-equilibrium system produces entropy, internally, is a minimum.

to apply Prigogine's theory must be viewed with skepticism because of its lack of generality." (Kay 1984[5], p. 348-349)

The derivation of the entropy production minimization principle by Prigogine, and Onsanger's relationships, require the assumption of local equilibrium thermodynamics (LET), which is made in order to limit the discussion to a domain in which a linear expansion of the entropy terms can be made. This validity of the LET assumption is quite debatable for living systems. Furthermore, except in the immediate neighbourhood of equilibrium, the criteria is sufficient for a stable steady state but NOT necessary. So steady states can exist which do NOT meet this criteria. And living systems are not near thermodynamic EQUILIBRIUM although they may be in a steady state. It is not at all clear that there is any justification for assuming the minimum entropy production principle is THE criteria (i.e. necessary condition) for the existence of steady state non-equilibrium thermodynamic systems, and in particular living systems. To make matters even more confusing, earlier Prigogine[6] derived a more general but still restricted criteria, the minimum SPECIFIC entropy production[7] criteria for stable steady states. Therefore any use of either Minimum Entropy Production principle must be treated with much skepticism and be very well justified and the limits of its use in the specific situation clearly stated.

Sloppiness in terminology: The need for a thermodynamic system description

In what follows I will use *irreversibilities* throughout to mean processes which contribute to entropy production[8]. In Prigoginean terms, this would correspond to dissipation. However dissipation is often used as a synonym for waste energy that is dumped out the back end of a system or heat released by a system. Thus a second law notion (amount of irreversibility) gets confused with a first law notion, energy flux of some sort. The differentiation is important because in some situations irreversibilities in the system can cause changes in the quality (i.e. the exergy content) of the energy flow out of the system and this can be quite independent from the amount (quantity) of energy flow out of the system. So one can increase the dissipation (irreversibilities) by a system without increasing the energy flux. For example dissipation can be increased by increasing the exergy destruction per unit energy flow out of the system. So for example, if we compare a lawn with a forest in the same circumstances (and both in a steady state) the total energy input will balance the total energy output. The energy output of both systems will be the same. However the exergy output of the forest will be less than that of the lawn. The forest is thermodynamically more active, it produces more entropy. A

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[5] Kay, J. Self-Organization in Living Systems [Ph.D. Thesis]. Waterloo, Ontario, Canada: Systems Design Engineering, University of Waterloo; 1984

[6] I. Prigogine, J.M. Wiame Biologie et Thermodynamique des phenomenes irreversibles. Experientia II (1946) 451-453.

[7] That is the entropy production per unit mass!

[8] It is implicit that irreversibilities refers to those which occur in the system and not its environment, as the irreversibilities are associated with (internal) entropy production as defined in equation 2.

common mistake, made in many discussions of Prigogine's work, is the assumption that increases in dissipation (and I take it to mean irreversibilities, that is increases in ΔS_i) are necessarily coupled to an increase in energy flux. This is simply not so. The quantity of energy flux and the quality of energy flux are different characteristics of energy, each of which can, in its own way, reflect the overall dissipation in the system.

Also dissipation and degradation are often used in sloppy ways, including by this author. It is never quite clear if one is talking about entropy change, entropy generation, exergy change, gradient change, or heat transfer and if it is for the system, or system plus environment. For this reason, any discussion of thermodynamics of a situation must begin with a thermodynamic system description. Thermodynamics is contingent on a system description of that which is being investigated. Such a description identifies the elements which make up the system and its environment, all the modes of energy transfer between the system and environment, and internal thermodynamic processes. Without such a statement of context, the meaning of a thermodynamic discussion is mute. Only with such a description can a discussion begin with everyone on the same page. A thermodynamic system description, including an explicit system diagram, is absolutely necessary to anchor thermodynamic discussion about a situation.

Entropy production, dissipation, energy flux, heat transfer and irreversibilities.

The relationship between entropy production, dissipation and energy flux or heat transfer is often assumed and not clearly established or stated for the situation under investigation. They are not necessarily the same thing. Often in the literature, erroneously, entropy production, dissipation and heat transfer by a system are treated as the same quantity. This because of the relationship $dS = dQ/T$. ($S \equiv$ entropy and $Q \equiv$ heat). Many people misuse this relationship to say $\Delta S = \Delta Q/T$ and thus conclude that

$\Delta S \propto \Delta Q$.

Thus, incorrectly, they conclude that the entropy change in the system is proportional to the heat transfer, which (both the entropy change and heat transfer) is often referred to as dissipation. It is fair to say this, if and only if, there is only one mode of energy transfer from the system, heat transfer to a single environment (reservoir) which is at a fixed temperature. Entropy production and energy dissipation (i.e. the energy coming out the back end) are only equivalent when you have a SINGLE thermal dissipation route. Otherwise they are not equivalent (but obviously related).

For example in the Bénard cell (Prigogine's favorite example):

In a steady-state, the magnitude of $Q_{in} = Q_{out}$ and $\Delta S_i = Q / T_{out} - Q/T_{in}$ so $\Delta S_i = Q(1/T_{out} - 1/T_{in})$. For fixed temperatures, an increase in the flux of Q increases the rate of ΔS and hence the irreversibility and the dissipation. When Bénard cells form, they increase the flux of Q and hence the irreversibility and the dissipation. This example is the source of confusion about the relationship between increasing energy dissipation (Q flux) and entropy production (ΔS_i which Prigogine refers to as dissipation and which I am calling irreversibility for the sake of clarity).

If there is more than one thermal transfer route then we have an equation that doesn't not allow the total Q_{out} to be extracted and the rest to become a constant. Heat transfer can occur at different temperatures (T_1, T_2, …… T_n) depending on the processes. So the relationship dS=dQ/T cannot be used to linearly relate dQ with dS. (Since($dS = \sum_{i=1}^{i=n} dQ_i/T_i$) i.e. dS is not proportional to dQ!)

If other forms of irreversibilities (Prigoginean dissipation), besides heat transfer, are taken into account, things gets worse. For example if there is mass flow across the boundaries of the system, then, even if the system is in steady state (no change in the chemical species composition or total mass of the system), one must add terms to the ΔS equation which correspond to the entropy production due to the change in chemical species composition between the input and output mass flows, even though total mass in = total mass out for a steady state. (See Bejan[9], p. 67.) There may also be terms related to diffusion across membranes. Furthermore if there is a phase change as in evaporation or, in forests, evapotranspiration (ET), then another term must be added. In the case of forests, the ET term tends to swamp the other terms. For systems that move spatially, there must be an irreversibility term for locomotion.

Zotin, in his well known work, failed to recognize this and this error was corrected by:

Briedis, D. and Seagrave, R. C. Energy Transformation and Entropy Production in Living Systems I. Applications to Embryonic Growth. J. Theor. Biol. 1984; 110: 173-193.

My colleague, R. Fraser, looked at the Breidis and Seagrave equations and he pointed out that while it works for an egg because it is usually sat on, there also, in general, needs to be a radiation dissipation term. He noted that if anyone didn't believe this that they should try sitting near an open window on a cold winters night. You get a chill and this due to your radiating energy out the open window. (He has been involved in the experiments and noted that even though the air temperature near the subject was room temperature, the subject felt a chill. This is why a well insulated house feels warmer than a poorly insulated house, even though the air temperature is the same. You are experiencing net radiation loss with the colder walls.) So radiation loss is important for us warm blooded beings and can be a major source of irreversibility/dissipation.

Failure to keep these issues in mind has lead many researchers to flounder. The total irreversibility in an organism is not just the sum of the irreversibilities of its cells, i.e. the organism's metabolic activity.

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[9] Bejan, A. Advanced Engineering Thermodynamics. New York: John Wiley and sons; 1997.

Confusion between steady-state, thermodynamic equilibrium, and local equilibrium

There is confusion in the literature about the difference between steady-state, thermodynamic equilibrium, and local equilibrium as used by Prigogine. There is a fundamental difference between a system which is in a thermodynamic steady state and one which is in thermodynamic equilibrium. This point is commonly missed in the literature. (Recall that Prigogine got the Nobel prize for demonstrating that thermodynamic systems can be in a steady state while being NOT in equilibrium!)

Steady-state means that certain state variables do not change in time. Most of the time this corresponds to the inputs = the outputs of the system. However one is cautioned that the while the total mass flow must be balanced at the mass and elemental level, the specific chemical constituents need not be. The same is true for the energy as the quality and form of the inputs may differ from the outputs (food in, heat out.)

A state of equilibrium is not related to the inputs and outputs of a system. It is about the spatial variation in intensive variables (temperature, pressure etc.) If there is a spatial difference in intensive variables then a gradient exists and the system is not in equilibrium. (This is the concept of internal equilibrium of a system. There is also the issue of equilibrium between the system and its environment. A house can have a constant temperature inside, be in internal equilibrium, but be at a different temperature than the outdoors, so not be in equilibrium with its environment.)

A system can be in a steady state, but not equilibrium and vice versa.

Is the steady state assumption reasonable?

There is a more fundamental problem. Given an understanding of ecosystems as dynamic complex systems (i.e. Holling four box or shifting steady state mosaic or benthic-pelagic dual attractor) how important is a stable steady state in ecology anyway? Do ecosystems tend to a stable (thermodynamic) steady state? Lots of examples suggest otherwise. So is it useful to think of departure from steady-state as stress, i.e. a negative unhealthy situation? Is the well-being of ecosystems or communities tied to a stable steady state?

(Think about a tree over the course of a day. It is not in a steady state. To use a mechanical analogy it is more like the engine in a car. The state of an engine changes throughout the day as the throttle setting is changed (stepping on the gas). It is not in a steady state except momentarily. Trees are the same depending on the air temperature, moisture content and insolation throughout the day. The same can be said for me as I go about my business during a day. My R/B ratio is much higher when I am cycling to the university than when I am sleeping.)

This assumption of the importance of a stable steady state, as a criteria for biological well-being, is a core assumption of many researchers. There is reason to doubt it. I have discussed this point at some length in my papers, particularly the ones on ecosystem integrity. (For the best discussion of this issue that I have read, see Holling 1986[10].)

Discussions of human impacts on ecosystems started as the effect of single actions on an ecosystem. Then the notion of stress-response emerged, both one to one and many to many. With this came the notion of buffering and generalized stress response. This lead to the idea of evaluating ecosystem health. However this assumed that the ecosystem was homeostatic in its nature and that the climax community was the end goal of ecosystem development, a stable steady state. However the notion of a climax community and a stable steady state are now clearly problematic. The situation is much more complex. The target is moving. And it is this realization which has lead to the notion of ecological integrity. (Notwithstanding the legislative imperative.)

Furthermore it is one of the axioms of middle number systems that extremum principle do not apply, the game is optimization and tradeoffs. (Too much biodiversity is as big a problem as not enough.) So the direction of change in any measures of ecosystem state cannot be used to infer the positive or negativeness of the change, except in the context of the history and circumstances of the particular ecosystem. Also such measures cannot be used to compare ecosystems that are in different circumstances. They are just different.

So I think that the entire agenda of measuring departure from steady state is missing the point. Instead we need to understand the dynamics of self-organization. What we need is to develop measures of ecosystem organizational state and understand how changes in these reflect different changes in circumstances and organization. We need to understand what the propensities for change with self-organization are. Certainly thermodynamic irreversibilities are useful measures of biological organization. And I am convinced that there are patterns in the change in these that are helpful to our understanding. But this is very different from saying that an increase in specific irreversibility in a biological system necessarily has negative implications for the system.

So if steady state is going to be used as a criteria for biological well-being then it needs to carefully justified. In particular a rational for steady-state as the norm for a biological system needs to be justified for each and every scale it is being used. (i.e. If one justifies using steady state as a criteria for well being of an organism, this does not mean that it is a criteria for populations, communities or ecosystems.) If there is no justification for assuming a steady-state, then the whole discussion of application of Prigogine's ideas and principles is moot.

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[10] Holling, C. S. The Resilience of Terrestrial Ecosystems: Local Surprise and Global Change. Clark, W. M. and Munn, R. E., Eds. Sustainable Development in the Biosphere. Cambridge: Cambridge University Press; 1986; pp. 292-320.