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COMMENTS

Objections to a proposal on the rate of entropy production in systems far from equilibrium

Bjarne Andresen,^{a)} E. C. Zimmermann, and John Ross

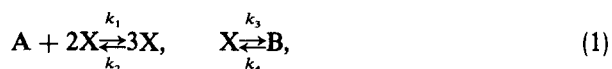
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In a recent paper¹ Sawada postulates as a general thermodynamic principle that an isolated system consisting of a set of reservoirs connected through a small nonlinear mechanism evolves spontaneously in time in such a way that the rate of entropy production of the whole system is at all times maximized over the allowed paths. The rate of entropy production is a product of fluxes and forces as calculated from deterministic equations. In a subsequent paper² Shimizu and Sawada present a numerical calculation of spontaneously appearing spatial structures in a one-dimensional Brusselator³ and claim that, among the several possible spatial structures, the system tends to prefer the one producing entropy at the largest rate. In other words, the most stable stationary state is said to be associated with the largest \dot{S} .

In this article we show that this thermodynamic postulate is not general by providing several theoretical counter examples and an experimental counter example. We conclude with a brief remark on the inapplicability of the calculations in Ref. 2 to the issue of relative stability.

Consider the Schlögl reaction⁴



with fixed reactant concentrations A, B, in contact with a thermal reservoir at temperature T_b . For a certain range of concentrations A, more than one stationary state ($\dot{X} = 0$) is possible, as illustrated in Fig. 1(a). The rate of entropy production of the whole system, including the reservoirs of fixed concentrations of A and B and the thermal reservoir, in a stationary state is proportional to the rate of the overall reaction $A \rightleftharpoons B$, $\dot{S} = (-\Delta G/T_b)\dot{B}$, where ΔG is the change in free energy for the overall reaction, and \dot{B} is the rate of production of B. Since \dot{B} is a linear function of X, then according to Sawada's postulate the upper branch γ should always be the more stable from its beginning at the marginal stability point F_1 . This is not in agreement with the calculations below.

If instead of fixing the concentrations A and B, the Schlögl reaction is contained in a continuously stirred tank

reactor (CSTR) with constant input flow j of A and corresponding withdrawal of reaction mixture to keep the volume constant, then a picture of stationary states [Fig. 1(b)] similar to Fig. 1(a) emerges.⁵ As \dot{S} is again linear in X, the Sawada postulate would again predict the upper branch of steady states to be most stable throughout the region of bistability, in contradiction to stochastic analyses.

As a last example, consider the endothermic isomerization reaction⁶



carried out in a constant pressure cell in contact with a heat bath at temperature T_b and irradiated with light of power Φ_0 . The light is absorbed only by X and instantaneously converted into thermal energy of the reaction mixture. The appropriate material, energy, and pressure balance equations⁶ have stationary solutions very similar to Fig. 1(a) with the abscissa relabeled incident light power Φ_0 and the ordinate relabeled absorption A . If we make the adequate, but not necessary, assumption that the incoming light (e.g., from a laser) carries no entropy, then the overall rate of entropy production, in steady state, is simply $\dot{S} = A\Phi_0/T_b$ which clearly is largest on the upper branch γ . Both theoretical and experimental analyses indicate, however, that the lower branch α is more stable to the left of some point F_2 .

Several attempts have been made to assess the relative stability of stationary states, as, e.g., α and γ in the interval F_1 to F_3 of Fig. 1(a) (β is unstable). All stochastic descriptions, independent of the assumption of fluctuation (noise) functions, yield a bimodal probability distribution for a range of pump parameter values for which there exist two stable stationary states.⁷ Somewhere within the bistability region the probability distribution changes rapidly at a given value F_2 of the pump parameter. Below that value the probability of branch α is much higher than that of branch γ , and above that value the reverse holds. If noise is assumed constant, the stochastic description predicts the same equestabi-

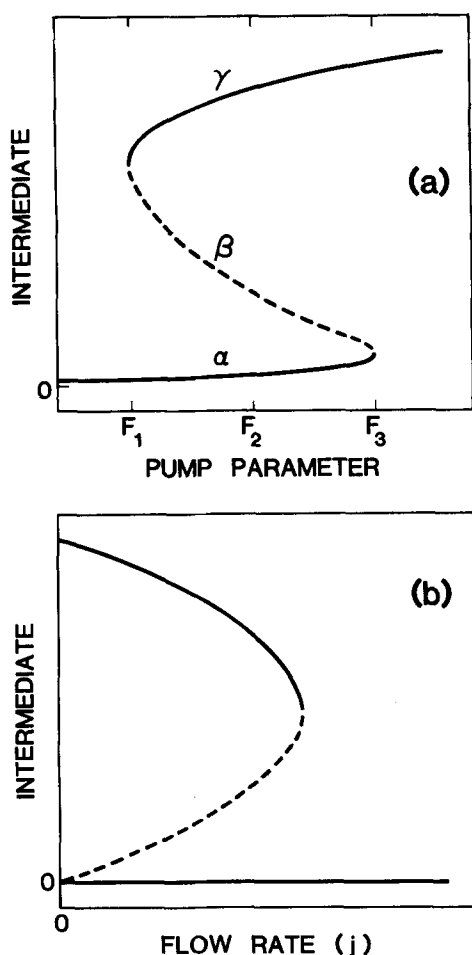


FIG. 1. Stationary states of the Schlögl reaction, Eq. (1): (a) with fixed reactant concentrations; (b) with fixed input flow j of reactant A. F is a pump parameter, e.g., the reactant concentration A.

lity point F_2 , as a potential function based on the deterministic rate equations.⁸ A comparison of the mean first passage times for going from branch α to branch γ and vice versa leads to essentially the same result,⁹ that there is a switch in the preferred state somewhere within the bistability region. However, even if the ratio of mean first passage times shows the α state to the left of F_2 to be more stable, both times may become exceedingly long away from the marginal stability point,¹⁰ and the system may therefore effectively be locked in the less stable state if initially prepared in that state. Monte Carlo calculations¹¹ on the Schlögl model are in agreement with the analytical stochastic predictions.

To summarize, all theoretical analyses of bistable systems, like those depicted in Fig. 1, predict that the lower branch α is more stable to the left of a point F_2 , and the upper branch γ is more stable to the right of this point, even though they do not agree on the precise location of this equistability point. This prediction is irreconcilable with Sawada's postulate of maximum rate of entropy production which implies that γ is more stable everywhere it exists.

We have recently conducted experiments on a system similar to that of Eq. (2): The gas phase dimerization $S_2O_6F_2 \rightleftharpoons 2SO_3F$, subject to irradiation at a wavelength absorbed only by the monomer.¹² As predicted, two stationary states of distinct absorption A are experimentally accessible at the

same value of the incident light power Φ_0 in a certain range of that power.

Subsequent investigations¹³ have demonstrated metastability of the high absorption branch γ in the vicinity of the marginal stability point F_1 [Fig. 1(a)]: If the system is prepared in a steady state of high absorption at a value of Φ_0 very near the marginal stability value F_1 , a spontaneous transition occurs to the steady state of low absorption (on α) in a matter of minutes. Once this transition has occurred, the system remains in the low absorption state for as long as experiments have been carried out (several hours). Such results are to be expected, from a mean first passage time analysis. The rate of entropy production in steady state is again given by $A\Phi_0/T_b$, and hence the Sawada postulate is in contradiction with experiment.

In Ref. 2 a computer study was made of the stable stationary states of a multistable system. By applying a constant perturbation to all the stationary states, that study probed the relative sizes of the deterministic domains of attraction. We know of no relation of the sizes of these domains to the issue of relative stability of stationary states. That issue also depends on the strength of attraction of the fixed points and the fluctuations, which are concentration dependent.

Sawada now proposes that his hypothesis applies only to newly named, but not well-defined ideal nonequilibrium systems. By what criteria is the example treated in Ref. 2 to be classified as an ideal nonequilibrium system? We believe that in that reference Sawada used invalid tests of relative stability.

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