

# Irreversible processes at nonequilibrium steady states and Lyapounov functions

(stability theory/nonequilibrium thermodynamics/fluctuation theory)

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**ABSTRACT** Nonequilibrium stability theory is reviewed. In answer to recent comments by Fox [Fox, R. F. (1979) *Proc. Natl. Acad. Sci. USA* 76, 2114-2117], it is pointed out that various choices of Lyapounov functions are possible in the nonlinear range of irreversible phenomena.

In 1974, Keizer and Fox (1) published a paper entitled "Qualms regarding the range of validity of the Glansdorff-Prigogine criterion for stability of nonequilibrium states" in which they attributed to us claims that actually were not made. Glansdorff and the present authors replied to this paper (2) and gave at the same time a brief review of the stability theory of nonequilibrium states. The central quantity in this theory is  $(\delta^2 S)_{ss}$ , the second-order excess entropy around the steady state, which is used as Lyapounov function to derive linear stability criteria.

A similar situation has again arisen with the recent paper by Fox (3), entitled "Irreversible processes at nonequilibrium steady states," in which it is stated: "However, Keizer's work suggests, as has been demonstrated in this paper, that the 'excess entropy' does *not* provide a Liapounov criterion near steady states, and that, instead, the covariance of the fluctuating thermodynamic variables *does* provide such a criterion."

In what follows, we briefly summarize the current status of stability and fluctuation theory and show that Fox's claim arises from a misunderstanding of our work.

## The status of $(\delta^2 S)_{ss}$

In the vicinity of equilibrium  $(\delta^2 S)_{eq}$  plays a double role (4, 5): it may be used as a Lyapounov function and at the same time it generates the probability of fluctuations around equilibrium. On the other hand, away from equilibrium,  $(\delta^2 S)_{ss}$  does *not* generate the probability of fluctuations. We proved this statement for reaction-diffusion systems in 1971 (ref. 6; see also ref. 5 for a recent survey of the subject).

Now, this fact about  $(\delta^2 S)_{ss}$  has nothing to do with the requirements one sets traditionally for a Lyapounov function. Indeed, as we emphasized in our answer (2) to Keizer and Fox,

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the stability criterion

$$\begin{aligned}(\delta^2 S)_{ss} &\leq 0 \\ \frac{d}{dt} (\delta^2 S)_{ss} &\geq 0\end{aligned}\quad [1]$$

need *not* be an identity, because it has to be fulfilled only *along a solution of the conservation equations* for given constraints. In the light of these definitions of stability and of Lyapounov functions (7),  $(\delta^2 S)_{ss}$  keeps its significance entirely. As we pointed out (4, 5), its usefulness is 2-fold: first, it has a macroscopic meaning below, at, and across bifurcation points, independently of the fine—and often complex—details of the behavior of the fluctuations; and second, it enjoys universality, as it can be applied to a wide class of systems including those subject to spatially inhomogeneous disturbances, surface effects, and so forth.

## Nonuniqueness of Lyapounov functions

Naturally, the above summarized properties of  $(\delta^2 S)_{ss}$  do not imply that there is an argument against the use of other Lyapounov functions. This nonuniqueness is widely recognized in the mathematical literature. To quote Hirsch and Smale (7): "... There is no cut-and-dried method of finding Lyapounov functions; it is a matter of ingenuity and trial and error in each case. Sometimes there are natural functions to try."

The covariance of the fluctuating thermodynamic variables advocated by Fox (3) provides an example of just such another Lyapounov function applicable to certain classes of systems. Actually, as far back as 1967, Schlögl (8) introduced an analogous quantity in his analysis of the statistical foundations of the Glansdorff-Prigogine criterion. Fox did not mention this reference or the work of Lax (9) and Mazo (10), in which an explicit formulation of the fluctuation-dissipation relationship for steady states was given.

In short, in so far as we can see, there is nothing in Fox's proposal (3) that has not already appeared in the literature. Moreover, certain drawbacks of his approach should be pointed out. For instance, in the presence of bifurcations and of spatially inhomogeneous fluctuations, not only is the covariance matrix ill-behaved but also the Gaussian approximation itself may break down (11, 12).

### Conclusion

Stability theory remains a challenging subject. Fluctuation theory is a useful complement to macroscopic stability and bifurcation analyses. We therefore appreciate the attempts of Keizer and Fox to study the statistical foundations of stability theory. However, on view of the nonuniqueness of Lyapounov functions, various choices are possible, depending on the context in which the problem is stated.

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