GENERALIZED FREE ENERGY AND EXCESS ENTROPY PRODUCTION FOR ACTIVE SYSTEMS

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ABSTRACT

In thermodynamics, the free energy potential is typically defined as the relative entropy between the system's actual state and the equilibrium state. This potential governs many important thermodynamic and statistical properties, but by definition it is restricted to detailed-balanced systems that relax toward equilibrium.

Recently, however, nonequilibrium thermodynamics has focused on active systems that undergo continuous driving. Such "genuine nonequilibrium" systems violate detailed balance and relax toward nonequilibrium steady states, oscillations and/or chaos. Because such system lack equilibrium states, they do not possess a free energy potential as usually defined.

In our recent work [1], we propose a *generalized free energy potential* appropriate for active systems, including both stochastic master equations and deterministic nonlinear chemical reaction networks (possibly without steady states). Our potential is defined variationally as the "most irreversible" state observable. This variational principle is motivated from several perspectives, including large deviations theory, thermodynamic uncertainty relations, and optimal transport. Our approach leads to a universal definition of the excess entropy production, the nonstationary contribution to dissipation that vanishes in steady-state. The remaining "housekeeping" term quantifies the magnitude of cyclic fluxes and nonconservative forces. We derive thermodynamic speed limits for excess entropy production for both linear and nonlinear systems.

We also show that our approach overcomes several limitations of the steady-state potential and the Hatano-Sasa (adiabatic/nonadiabatic) decomposition.

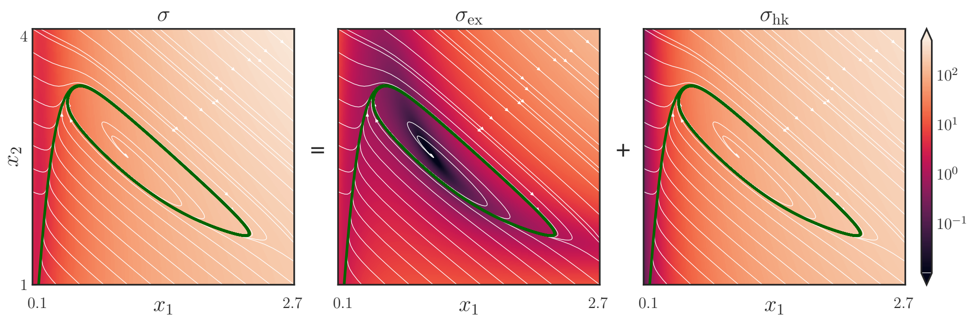

Figure 1: Using our potential, entropy production rate σ is decomposed into excess σ_{ex} and housekeeping σ_{hk} for the Brusselator (a nonlinear chemical oscillator). Colors indicate entropy production rate as a function of concentration of the two species. The green line indicates an example trajectory that approaches the limit cycle.

REFERENCES

[1] A. Kolchinsky, A. Dechant, K. Yoshimura, S. Ito, Generalized free energy and excess entropy production for active systems, *arXiv preprint*, 2412.08432, 2024.