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Thermodynamic efficiency out of equilibrium DAVID SIVAK, GAVIN CROOKS, Lawrence Berkeley National Laboratory — Molecular-scale machines typically operate far from thermodynamic equilibrium, limiting the applicability of equilibrium statistical mechanics to understand their efficiency. Thermodynamic length analysis relates a non-equilibrium property (dissipation) to equilibrium properties (equilibrium fluctuations and their relaxation time). Herein we demonstrate that the thermodynamic length framework follows directly from the assumptions of linear response theory. Uniting these two frameworks provides thermodynamic length analysis a firmer statistical mechanical grounding, and equips linear response theory with a metric structure to facilitate the prediction and discovery of optimal (minimum dissipation) paths in complicated free energy landscapes. To explore the applicability of this theoretical framework, we examine its accuracy for simple bistable systems, parametrized to model single-molecule force-extension experiments. Through analytic derivation of the equilibrium fluctuations and numerical calculation of the dissipation and relaxation time, we verify that thermodynamic length analysis (though derived in a near-equilibrium limit) provides a strikingly good approximation even far from equilibrium, and thus provides a useful framework for understanding molecular motor efficiency.

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