


Free-energy transduction within autonomous systems

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and molecular machines. For instance, it is conceptually straightforward to view the chemical hydrolysis of ATP as driving the processive motion of the molecular motor kinesin [20], or the F_o component of ATP synthase as mechanically driving the rotation of a central crankshaft, inducing the F_1 component to catalyze the production of ATP [16]. Thus there is a natural appeal to quantifying the work (and the excess work) done by one component of an autonomous biomolecular machine on another. Indeed, such internal energy flows have been used to aid in the identification of reaction coordinates in biomolecular dynamics [21].

Given the biophysical importance of entropy production, and the mathematical constraints imposed on it by fluctuation theorems and second-law-like inequalities, it is tempting to use the correspondence between excess work and entropy production in systems driven by an external control parameter to aid in the conceptual and quantitative understanding of biomolecular machines [22–24]. However, while it is still possible to define excess work internal to such systems as an energy flow, it has no direct relationship to the entropy production.

In this article, we investigate excess work and entropy production in strongly coupled autonomous systems and present an alternative measure of dissipation—the *transduced additional free-energy rate*—which plays the same thermodynamic role in autonomous systems as excess power does in externally driven systems. Specifically, the steady-state transduced additional free energy rate (differing from the excess power by an information rate that captures the effects of intersystem coupling) equals an entropy production rate. We then illustrate our results in a simple model of a cyclic mechanochemical motor, where a mechanical system is driven via its strong coupling to a stochastic nonequilibrium chemical reaction.

II. STRONGLY COUPLED MULTICOMPONENT SYSTEMS

Throughout this article, we consider a bipartite system described by two coordinates X

implies that, on average, dynamics of X increase (decrease) the mutual information between the two subsystems.

At steady state, the joint-system entropy is unchanging ($d_t S_{XY} = 0$), as are the entropies of each subsystem ($d_t S_X = d_t S_Y = 0$). Thus, the combined effect of X and Y dynamics leaves the mutual information unchanged, so the information rates are opposite ($\dot{I}^X = -\dot{I}^Y$) and cancel when summing the entropy production rates $\dot{\Sigma}^X$ and $\dot{\Sigma}^Y$ of each subsystem [Eq. (6)] [14]. Therefore, the total steady-state entropy production is the sum of each subsystem's heat flows:

$$\dot{\Sigma} = -\beta\dot{Q}^Y - \beta\dot{Q}^X. \quad (8)$$

However, unlike the entropy productions of each subsystem in Eq. (6), neither RHS term is lower bounded by zero.

B. Excess work

B. Thermodynamically complete system

In autonomous systems (such as molecular machines consisting of multiple strongly interacting components) not subject to temporal variation of an external control parameter, thermodynamic consistency requires that the entries of the transition rate matrix R_{yy}^{xx} satisfy local detailed balance [3,4,34],

$$\ln \frac{R_{yy}^{xx}}{R_{yy}^{xx}} = -\beta(\Delta\epsilon_{yy}^{xx} + \Delta\mu_{yy}), \quad (18)$$

where $\Delta\epsilon_{yy}^{xx} + \Delta\mu_{yy}$ is the change in thermodynamic potential during the transition $(x, y) \rightarrow (x, y)$, involving the change $\Delta\epsilon_{yy}^{xx} = \epsilon_{xy} - \epsilon_{yx}$ in system energy during transitions in X and Y and the change $\Delta\mu_{yy}$ in chemical potential during transitions of subsystem Y (satisfying $\Delta\mu_{yy} = -\Delta\mu_{yy}$ and hence $\Delta\mu_{yy} = 0$). Despite the particular form of thermodynamic potential implied by the RHS, the theoretical framework we present is more broadly applicable so long as the dynamics of subsystem X are detailed balanced.

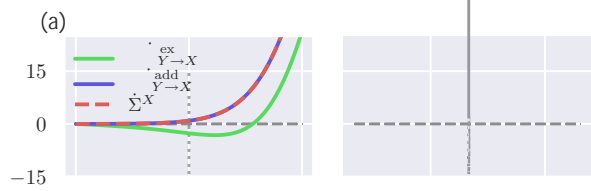
We call systems *thermodynamically complete* when all rates satisfy local detailed balance [Eq. (18)]. Conversely, we call systems (such as the independent Y dynamics in Sec. III A) *thermodynamically incomplete* when the transition rates violate Eq. (18), as some external influences are required to ensure thermodynamic consistency. Thus, thermodynamically complete systems are those which in the absence of driving relax to equilibrium, though with driving present (our case here) they need not.

In detailed-balanced dynamics—or any dynamics where subsystem Y receives feedback from X —the excess work [Eq. (15)] associated with a particular Y transition is not lower bounded by zero and can be negative.

We present the *transduced additional free energy rate* or TAFER (the name will become clear),

$$\beta\dot{F}_Y^{\text{add}} - \beta\dot{W}_Y^{\text{ex}} + \dot{I}_o$$

where Γ_{chem} and Γ_{mech} are kinetic prefactors for the chemical and mechanical rates, quantifying the *bare rates* of each process in the absence of any differences $\Delta\epsilon_{yy}^{xx} = \epsilon_{xy} - \epsilon_{xy}$ in state energies ϵ_{xy}



- collects information about an external and independent stochastic variable Y . Rearranging the second law with the information rate on the RHS of Eq. (6) yields a refined lower bound on the steady-state dissipation for the system in terms of the *nostalgia* [42,43] or *learning rate* [44,45].
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