reaction coordinate [4,8–11]. The committor allows calculation of the reaction rate from a one-dimensional description [12] and identifies the transition-state ensemble as states making up the $q_\phi = 0.5$ isocommittor surface [13].

In this Letter, we derive a novel information-theoretic justification of the committor as the reaction coordinate.

selected based on the trajectory outcome S_+ [the next mesostate (A or B) visited by the system] and origin S_- (the mesostate most recently visited by the system). This partitions the supertrajectory into four trajectory subensembles, each with particular $\boldsymbol{s} \equiv (\mathsf{s}_-$

where $\mathsf{p}(\boldsymbol{s}) = \sum_{\boldsymbol{\phi}} \mathsf{p}(\boldsymbol{\phi}; \boldsymbol{s})$ is the marginal probability

Combining Eqs. (1), (8a), and (9b) gives the full TPE entropy production as a function of the forward committor,

$p_R\Sigma$

for which one has physical intuition can provide a low-dimensional model that allows increased insight into the reaction mechanism.

More concretely, this connection we have established between transition-path theory and stochastic thermodynamics suggests a novel method for rigorously grounded inference of reaction coordinates: generate an ensemble of transition paths using transition-path sampling [6,31] or related algorithms [32–34]; estimate entropy production along chosen coordinates [35–37] or identify linear combinations of coordinates producing the most entropy using dissipative components analysis [38]; use these most dissipative coordinates to enhance sampling of transition paths, and through further iteration identify system coordinates producing the most entropy in the transition-path ensemble and hence of most relevance to the reaction.

Machine-learning approaches to solve for high-dimensional committor coordinates