Connections between efficient control and spontaneous transitions in an Ising model

Miranda D. Louwerse[1] and David A. Sivak[2,*]
[1]*Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A1S6*
[2]*Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A1S6*

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A system can be driven between metastable configurations by a time-dependent driving protocol, which uses external control parameters to change the potential energy of the system. Here we investigate the correspondence between driving protocols that are designed to minimize work and the spontaneous transition paths of the system in the absence of driving. We study the spin-inversion reaction in a 2D Ising model, quantifying the timing of each spin flip and heat flow to the system during both a minimum-work protocol and a spontaneous transition. The general order of spin flips during the transition mechanism is preserved between the processes, despite the coarseness of control parameters that are unable to reproduce more detailed features of the spontaneous mechanism. Additionally, external control parameters provide energy to each system component to compensate changes in internal energy, showing how control parameters are tuned during a minimum-work protocol to counteract underlying energetic features. This paper supports a correspondence between minimum-work protocols and spontaneous transition mechanisms.

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I. INTRODUCTION

Quantifying the dynamics and energetics of a system as it undergoes a spontaneous transition between metastable states is of interest to the natural sciences due to the ubiquity of such activated processes throughout chemistry and biology [1–3]. The system typically overcomes a free-energetic barrier separating metastable states in its high-dimensional configuration space, requiring collective motion of many degrees of freedom and heat flow from the environment to increase the system's internal energy (in reactions with an energy barrier). Characterizing the thermodynamics and kinetics of the collective variables involved in the motion is therefore of interest [4–7]. A system can also be driven through its configuration space through time-dependent variation of external control parameters that provide an energetic bias to (sets of) collective variables. Excess work (work above the equilibrium free-energy change) is done on the system during a protocol depending on how the system is driven, making it a target for optimization [8,9]. Here, we investigate the correspondence between driving protocols that minimize work in the long-duration limit and the spontaneous transition mechanism through configuration space, hypothesizing that minimum-work protocols effectively make use of spontaneous fluctuations by providing work to each degree of freedom in accordance with its required heat intake during a spontaneous transition.

Driving protocols can be implemented in experiment and simulation [10–15]; coupled with theoretical advances [16–18], driving protocols are a widely applicable tool for extracting equilibrium thermodynamic information about a variety of microscopic systems. The ability to estimate equilibrium properties is perhaps surprising since the system is out of equilibrium throughout the driving protocol, and therefore kinetic aspects of the system's response to control-parameter perturbations are highly relevant [8,18,19].

The excess work on the system during a driving protocol performed in long duration can be approximated by linear-response theory [9], yielding a geometry in control-parameter space with a generalized friction metric that quantifies the system's resistance to changes in control parameters. This approximation also yields an intuitive description of minimum-work protocols as geodesics (shortest paths) between endpoints in control-parameter space that minimize resistance to driving.

The generalized friction captures local features of the system's free energy and dynamic relaxation throughout collective-variable space; these features are also relevant to characterizing transient dynamics during a spontaneous transition path [20–23]. Intuitively, if the system must overcome a free-energy barrier during the reaction, the spontaneous transitions are likely to pass through a relatively low-free-energy region of collective-variable space to reduce heat absorption during the transient dynamics. It seems similarly intuitive that a minimum-work protocol would drive the system through the same low-free-energy region to reduce the work done that increases the system's energy. This leads us to hypothesize that protocols designed to minimize frictional resistance may also drive the system along the same configuration-space pathways favored by spontaneous transitions. This hypothesis is supported by Ref. [24], where a minimum-work protocol designed to invert the magnetization of a large 2D Ising model showed strong correspondence with the spontaneous transition pathways characterized by a minimum-free-energy path [25].

*dsivak@sfu.ca

recursion relation [37]

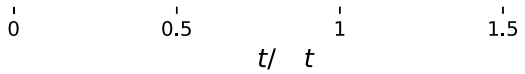
$$0 = \sum_{\boldsymbol{\sigma}'} T_{\boldsymbol{\sigma}'\boldsymbol{\sigma}} q(\boldsymbol{\sigma}'), \tag{4}$$

with boundary conditions $q(\boldsymbol{\sigma}_\mathrm{d}) = 0$ for $\boldsymbol{\sigma}_\mathrm{d}$ the all-down configuration and $q(\boldsymbol{\sigma}_\mathrm{u}) = 1$ for $\boldsymbol{\sigma}_\mathrm{u}$ the all-up configuration. The committor projects the state space onto the unit interval, $q(\boldsymbol{\sigma}) \in [0, 1]$, and serves as a reaction coordinate describing the transition, also allowing calculation of various reaction properties [37,38].

For the Ising system, the transition-state ensemble [set of configurations with $q(\boldsymbol{\sigma}) \approx 0.5$] poses an internal-energy barrier (compared to the configuration with $q(\boldsymbol{\sigma}) = 0$) of $8\,k_\mathrm{B}T$ and has entropy $\approx 3\,k_\mathrm{B}$, combining to yield a free-energy barrier of $\approx 5\,k_\mathrm{B}T$ [Fig. 1(b)]. Due to the system symmetry, there is no energy difference between reaction endpoints. The mean first-passage time for the reaction is ≈1890 attempted spin flips, and the mean transition-path duration is ≈89 attempted spin flips [38].

The system dynamics in the transition-path ensemble satisfy modified transition rates [38,39]. A trajectory is initialized in the all-down configuration $\boldsymbol{\sigma}_\mathrm{d}$, then transitions to $\boldsymbol{\sigma}$ with probability

$$p_\mathrm{R}^\mathrm{initial}(\boldsymbol{\sigma}) = \frac{T_{\boldsymbol{\sigma}\boldsymbol{\sigma}_\mathrm{d}} q(\boldsymbol{\sigma})}{\sum_{\boldsymbol{\sigma}''} T_{\boldsymbol{\sigma}''\boldsymbol{\sigma}_\mathrm{d}} q(\boldsymbol{\sigma}'')}, \tag{5}$$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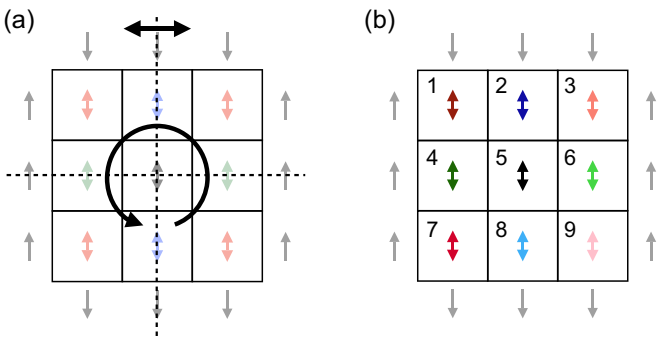
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V. DISCUSSION

We undertook the first systematic comparison of minimum-work protocols, determined by the generalized friction metric, and spontaneous transition paths in collective-variable space. We found intuitive ways to compare the two conceptually different processes that reveal qualitative similarities. We have investigated the transition mechanism for spin inversion in a 3×3 Ising model during the fully optimized 4D protocol and during a spontaneous transition path. During the minimum-work protocol, work is done on the system, which provides an energetic bias that drives the system over the energy barrier. In the transition-path