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Near-equilibrium measurements of non-equilibrium free energy
DAVID SIVAK, GAVIN CROOKS, Physical Biosciences Division, Lawrence Berkeley National Laboratory — Researchers can, with increasing ease, engineer artificial microscopic machines, structures for the deliberate and efficient manipulation of energy, matter and information on the nanometer scale. Although free energy is of primary importance to thermodynamics, typically we have no good way of measuring this quantity out of thermodynamic equilibrium, impeding our ability to predict the behavior of these microscopic molecular machines, which typically operate far from equilibrium. We herein develop an experimentally tractable approach to measure free energy away from equilibrium. We derive a formally exact expression for the probability distribution of a driven system, involving path ensemble averages of work over trajectories of the time-reversed system. From this we find a simple near-equilibrium approximation in terms of a time-reversed excess mean work, which can be experimentally measured in real systems. With analysis and computer simulation, we demonstrate that for several simple models, our approximation is accurate a substantial distance from equilibrium.

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