Stochastic Processes and Statistical Mechanics

Themis Matsoukas
Pennsylvania State University, University Park, United States

Statistical thermodynamics delivers the probability distribution of the equilibrium state of matter through the constrained maximization of a special functional, entropy. Its elegance and enormous success have led to numerous attempts to decipher its language and make it available to problems outside physics, but a formal generalization has remained elusive. Here we show how the formalism of thermodynamics can be applied to any stochastic process. At its most elementary level a stochastic process is a random walk in the event space of stochastic variable. This walk is defined by the current state of the walker and a set of rules that determine the set of feasible states in the next step. A stochastic path is a specific sequence of transitions from initial state to current state. The idea then is to count the number of paths that arrive to a particular state, then send a set of N walker to perform a walk by following any feasible path with equal probability. The state of this N-dimensional walk represents a sample of the stochastic process and the distribution of states in the sample a feasible probability distribution, and the probability of a feasible distribution is given by the number of distinct paths that can produce it. We construct the master equation that governs the flow pf probability –the Liouville equation of the stochastic process–and show that the ensemble of feasible distributions in the asymptotic limit obeys statistical thermodynamics: (i) the most probable distribution is overwhelmingly more probable than all others; (ii) it maximizes a homogeneous functional analogous to entropy (microcanonical functional); (iii) it is expressed in terms of parameters (canonical partition function, microcanonical partition function, generalized temperature) that obey the familiar network of Legendre relationships. Thus the formalism of thermodynamics is shown to be a stochastic calculus of stochastic processes. We present examples of simple stochastic processes and how to construct the corresponding thermodynamic functional. We are particularly interested in systems that lead to phase transitions and show how the emergence of multiple phases is governed by the same principles as vapor-liquid equilibrium in molecular systems.