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# A probable probability distribution of a series nonequilibrium states in a simple system out of equilibrium ☆

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## HIGHLIGHTS

- The probable probability distribution of all the nonequilibrium states was determined by maximizing the hyperensemble entropy in binary state space.
- The velocity of nonequilibrium state returning back to its equilibrium is the reciprocal of the derivative of this probability.
- The same conclusion was also obtained in the multi-state space.
- It reminds that the multi-state space can be decomposed into two or several binary spaces.

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## ABSTRACT

When a simple system is in its nonequilibrium state, it will shift to its equilibrium state. Obviously, in this process, there are a series of nonequilibrium states. With the assistance of Bayesian statistics and hyperensemble, a probable probability distribution of these nonequilibrium states can be determined by maximizing the hyperensemble entropy. It is known that the largest probability is the equilibrium state, and the far a nonequilibrium state is away from the equilibrium one, the smaller the probability will be, and the same conclusion can also be obtained in the multi-state space. Furthermore, if the probability stands for the relative time the corresponding nonequilibrium state can stay, then the velocity of a nonequilibrium state returning back to its equilibrium can also be determined through the reciprocal of the derivative of this probability. It tells us that the far away the state from the equilibrium is, the faster the returning velocity will be; if the system is near to its equilibrium state, the velocity will tend to be smaller and smaller, and finally tends to 0 when it gets the equilibrium state.



It is well known that many systems of great experimental interest in the molecular sciences consume and dissipate energy through separate channels and are thus far from equilibrium. However, compared with the equilibrium states, the non-equilibrium ones are much more complex. Recently, there has been renewal and dramatic expansion of the study of such systems owing to advances in both the theory and experiment [1–3]: in theory, the development of a statistical mechanics of trajectories, and, in experiment, the development of improved methods for detecting stochastic fluctuations in single molecules.

On the other hand, the nonequilibrium state can also be dealt in the same idea of equilibrium statistical mechanics. It is known that, in classical mechanics, we typically assume that we know the exact microstate of the system. However, in statistical mechanics, we recognize that such a detailed description is frequently neither possible nor desirable. When a

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macro system gets to its equilibrium state, all the past history of it is forgotten, and all the macroscopic quantities cease to change in time. Though the system contains many degrees of freedom, their thermodynamic state can be specified completely in terms of a few state variables, such as the temperature, pressure, volume, etc. [4]. That the equilibrium entropy is maximized is a strong condition that uniquely determines the probability distribution, so there is only one ensemble that can describe a given system in its thermal equilibrium. However, when a system is out of equilibrium, it changes with time. Obviously we essentially face the same problem: we cannot obtain enough information from a few measurements to determine the microscopic state of the system. Therefore, the correct approach is not to try to determine what the probability distribution of the system is, but instead attempt to determine what the probabilities could be. So instead of thinking about an ensemble of system, Gavin E. Crooks [5] envisaged an ensemble of ensembles, a hyperensemble, to describe the average behavior of the hyperensemble with a few given parameters or measurements. Each member of the hyperensemble has the same instantaneous Hamiltonian, but is described by a different probability. Obviously, each ensemble denotes a different non equilibrium state of the system. This basic idea of estimating the probability of a probability density (a "metaprobability") is often used in Bayesian statistics [6], especially when the available data is too sparse to reliably estimate the probability directly.

When a system shifts from its initial nonequilibrium state to its final equilibrium one there are a lot of nonequilibrium states. According to the idea of Gavin E. Crooks [5], we also suppose that each nonequilibrium state of the system is characterized by an energy $E_i$ and a corresponding ensemble, then a hyperensemble is obtained. If each ensemble is denoted by a probability $\theta$, then the most probable probability distribution of ensembles $P(\theta)$ that maximizes the entropy $H(P(\theta))$ of the hyperensemble

$$H(P(\theta)) = -\int P(\theta) \ln \frac{P(\theta)}{m(\theta)} \mathrm{d}\theta \tag{1}$$

will be found while maintaining certain appropriate constraints. Here $\theta$ is the positive vector $\{\theta_1, \theta_2, \ldots, \theta_K\}$, and the integration is performed over normalized probabilities:

$$\mathrm{d}\theta = \delta\left(\sum_{i=1}^{K} \theta_i - 1\right) \mathrm{d}\theta_1\, \mathrm{d}\theta_2 \cdots \mathrm{d}\theta_K \tag{2}$$

and $m(\theta)$ is a prior distribution of $\theta$, and it is usually selected as $m(\theta) = constant$.

Usually the normalization, the mean energy of the hyperensemble and the entropy itself can be used as the appropriate constraints, i.e.

$$\int P(\theta)\, \mathrm{d}\theta = 1 \tag{3}$$

$$\langle\langle E\rangle\rangle = \int P(\theta) \left[\sum_i \theta_i E_i\right] \mathrm{d}\theta \tag{4}$$

$$\langle S\rangle = \int P(\theta) \left[-\sum_i \theta_i \ln \theta_i\right] \mathrm{d}\theta. \tag{5}$$

So subjected to these three constraints mentioned above, the probability distribution of the hyperensemble can be obtained by maximizing the entropy of the hyperensemble as follows

$$P(\theta) \propto \exp\left(-\beta\lambda \sum_i \theta_i E_i + \lambda \sum_i \theta_i \ln \theta_i\right) \tag{6}$$

where $\lambda$ and $\beta$ are the Lagrange multiples, and $\beta$ has units of entropy per unit of energy and is effectively an inverse temperature. By the way, a canonical ensemble with the same effective temperature is introduced as follows,

$$\rho_i = \frac{1}{Q(\beta)} \exp(-\beta E_i) \tag{7}$$

and then the distribution of distributions $P(\theta)$ is rewritten as

$$P(\theta) = \frac{1}{L(\beta, \lambda)} \exp\left(-\lambda \sum_i \theta_i \ln \frac{\theta_i}{\rho_i}\right) \tag{8}$$

where $L(\lambda, \beta)$ is the normalization constant. From Eq. (8), it is known that the distribution $P(\theta)$ is completely determined by the parameters $\lambda$ and $\beta$ and the reference conical distribution $\{\rho_i\}$: the dispersion of the hyperensemble about the mode is controlled by the inverse scale parameter $\lambda$. It is evident that the hyperensemple has the functional form of entropic distribution, a probability of probabilities that occasionally occurs in Bayesian statistics. And the entropic distribution over