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

Haixia Gao, Ting Li, Changming Xiao**

Department of Physics, Hunan Normal University, 410081, Changsha, China

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.

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** Corresponding author, Email: cmxiao@hunnu.edu.cn

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 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 θ , then the most probable probability distribution of ensembles $P(\theta)$ that maximizes the entropy $H(P(\theta))$ of the hyperensemble

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

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

$$d\theta = \delta\left(\sum_{i=1}^K \theta_i - 1\right) d\theta_1 d\theta_2 \dots d\theta_K \quad (2)$$

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

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

$$\int P(\theta) d\theta = 1 \quad (3)$$

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

$$\langle S \rangle = \int P(\theta) \left[-\sum_i \theta_i \ln \theta_i \right] d\theta \quad (5)$$

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

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

where λ and β are the Lagrange multiples, and β 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,

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

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

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

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 λ and β and the reference conical distribution $\{\rho_i\}$: the dispersion of the hyperensemble about the mode is controlled by the inverse scale parameter λ . It is evident that the hyperensemble has the functional form of entropic distribution, a probability of probabilities that occasionally occurs in Bayesian statistics. And the entropic distribution over a binary state space with a Gaussian reference was discussed by Gavin E. Crooks in Ref. [5]. In this paper, another important case with the Poisson reference will be discussed.

It is well known that there are two types of transition when a system shifts from its nonequilibrium state to the equilibrium one: they are the two cases of with or without metastable state (or states), and the system of the later can be called as a simple

system. In fact, no matter the system is simple or not, until now the information about the nonequilibrium states is very little. We only qualitatively know that the probability of a simple system in its equilibrium state is much larger than that of the nonequilibrium one. If these equilibrium and nonequilibrium states are selected as the basic elements or the bases of a binary state space, in which only the equilibrium state and non equilibrium state are possible, the metaprobability of the corresponding hyperensemble will play a very important role. By the way, the nonequilibrium state should be described in more details with a series of nonequilibrium states, so one of nonequilibrium states can be denoted by a distance to demonstrate how far it is away from the equilibrium state. For a simple system, there is no metastable state, and the far away from its equilibrium state, the smaller probability of this state will be. In this binary state space, the probabilities of the equilibrium and the initial nonequilibrium states are selected as the reference conical distribution $\{\rho_1, \rho_2\}$, obviously, $\rho_1 \rightarrow 1$ and $\rho_2 \rightarrow 0$. In this way, the following two cases with $\lambda=1$, $\rho_1=0.01, 0.001, 0.0001$ and $\lambda=2$, $\rho_1=0.01, 0.001, 0.0001$ are studied by Eq. (8) respectively, and the results are shown in Figs. 1-2, respectively.

Fig. 1 The black, green and red lines denote the probability distribution of the equilibrium state and nonequilibrium states of the simple systems with $\lambda=1$, $\rho_1=0.01, 0.001$, and 0.0001 , respectively.

Fig. 2 The black, green and red lines denote the probability distribution of the equilibrium state and nonequilibrium states of the simple systems with $\lambda=2$, $\rho_1=0.01, 0.001$, and 0.0001 , respectively.

In both Figs. 1 and 2, the red, green and black lines denote the distributions with the

reference distributions $\rho_1=0.01, 0.001, 0.0001$, respectively. From Figs.1 and 2, it is easy to get that, corresponding to above two sets of parameters, the metaprobabilities $P(\theta)$ are the Poisson type: the largest of $P(\theta)$ is at $\theta=0$, then it decreases quickly with the increase of θ , and finally gets to the smallest value 0 when $\theta \rightarrow 1$; the smaller the value ρ_1 is, the larger the $P(\theta)$ at $\theta=0$ will be. In fact, when $\rho_1 \rightarrow 0$ or $\rho_2 \rightarrow 1$, it means the reference distribution is a Poisson type, so, through a Poisson type of reference distribution, we get the Poisson type of distribution for the hyperensemble of a simple system. Furthermore, if the value of parameter θ is selected to specify the distance of the corresponding nonequilibrium state away from the equilibrium, then $\theta=0$ denotes the equilibrium state, and $\theta=1$ stands for the furthest distance of the nonequilibrium state away from the equilibrium. Now Figs. 1-2 also remind us that, the larger the value of θ is, the far Nonequilibrium state will be, and the smaller the probability $P(\theta)$ is. On the other hand, from Figs. 1-2, it is easy to get that the probability distribution is also affected by the parameter λ : near to the equilibrium, for the same ρ_1 and ρ_2 , the larger the parameter λ is, the larger value of $P(\theta)$ at the peak will be; however, when the system is far away from the equilibrium, the probability is just the opposite case.

Obviously, the Poisson type distribution correctly describes the probability distribution of the series of nonequilibrium states when a simple system is out of its equilibrium states. Based on this fact, we are going to study another interesting problem about the velocity of a simple system returning back from its nonequilibrium state to the equilibrium one. Obviously, the derivative $\frac{\partial P(\theta)}{\partial \theta}$ is a parameter describing the probability variation. According to the definition of differential coefficient, it can be written as,

$$\frac{\partial P(\theta)}{\partial \theta} = \frac{-\lambda}{L(\beta, \lambda)} \exp \left(-\lambda \left(\theta_1 \ln \frac{\theta}{\rho_1} + (1-\theta) \ln \frac{1-\theta}{1-\rho_1} \right) \right) \left(\ln \frac{\theta}{\rho_1} - \ln \frac{1-\theta}{1-\rho_1} \right) \quad (9)$$

However, as $P(\theta)$ denotes the probability of the state corresponding to θ , so $P(\theta)$ also denotes the relative time the corresponding state stays at θ in a way. Compared with the parameter θ , $P(\theta)$ can be taken as the parameter corresponding to the time t .

If this idea is correct, then the parameter

$$\frac{\partial \theta}{\partial P(\theta)} = \frac{1}{\frac{\partial P(\theta)}{\partial \theta}} \quad (10)$$

can be taken as the velocity of the system to go from the nonequilibrium state to its equilibrium one, or go from the far away nonequilibrium state to the near nonequilibrium state, and the relation between $\frac{\partial \theta}{\partial P(\theta)}$ and θ can be determined through Eqs. (9) and (10). Taking the same parameters of above two cases, the corresponding velocities of a simple system returning back when it is out of equilibrium are obtained and the results are shown in Figs. 3-4, respectively, and the black, green and red lines denote the velocities of $\rho_1=0.01$, 0.001 and 0.0001, respectively.

Fig. 3 The black, green and red lines denote the velocities of the nonequilibrium state returning back to the equilibrium one with $\lambda=1$, $\rho_1=0.01$, 0.001 and 0.0001, respectively.

Fig. 4 The black, green and red lines denote the velocities of the nonequilibrium state returning back to the equilibrium one with $\lambda=1$, $\rho_1=0.01$, 0.001 and 0.0001, respectively.

Both Figs. 3 and 4 remind us that, when a simple system is out of its equilibrium state, it will return back quickly to the equilibrium state; the larger the θ is, or the far away from the equilibrium the state is, the faster the returning velocity will be; when 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. Obviously our results are also in accordance with the daily experiences.

It is clear that lots of useful information have been obtained from above discussions in the binary states space. Yet, it is still very useful to extend our discussions to the multi-state space. For simplicity, only the tristate space will be taken into our considerations. It should be noted that, in this tristate space, the third state is not a metastable state, it is just a transition one. Firstly, in the tristate space, Eq. (8) can be rewritten as

$$P(\theta_1, \theta_2) = \frac{1}{\mathcal{Z}(\beta, \lambda)} \exp \left(-\lambda \left(\theta_1 \ln \frac{\theta_1}{\rho_1} + \theta_2 \ln \frac{\theta_2}{\rho_2} + (1 - \theta_1 - \theta_2) \ln \frac{1 - \theta_1 - \theta_2}{1 - \rho_1 - \rho_2} \right) \right) \quad (11)$$

Obviously, in this tristate space, besides the probabilities of the final equilibrium and the initial nonequilibrium states, a transition state is also selected as the reference conical distribution, i.e., $\{\rho_1, \rho_2, \rho_3\}$. Supposing ρ_1 denotes the probability of the initial nonequilibrium state, so $\rho_1 \rightarrow 0$; ρ_2 denotes a transition state, and its value is given by a measurement; then the probability of the final equilibrium state ρ_3 should satisfy the relation $\rho_3 = 1 - \rho_1 - \rho_2$. In this paper the case of $\lambda=1$, $\rho_1=0.0001$ and $\rho_2=0.1$ is studied by Eq. (11), and the results are shown in Fig. 5. From Fig. 5, it is clear that both the relations of $P(\theta_1, \theta_2) - \theta_1$ and $P(\theta_1, \theta_2) - \theta_2$ are the Poisson type. Obviously, this result is reasonable, because all the states in the system transited from the initial nonequilibrium state via the transition state to the final equilibrium state abide by the Poisson type, and this physical nature of the system cannot be changed

by the transition state introduced in our discussions. It is reasonable to believe that, even in the multi-state space, the probabilities of all the transition states should also abide by the same rule, so, for a simple system, the information of it can be completely described in the binary state space, and the multi-state space can be decomposed into two or several binary spaces.

Fig. 5, The probability distribution of a simple system in its tristate space with $\lambda = 1, \rho_1 = 0.0001, \rho_2 = 0.1$.

In conclusion, with a special reference distribution, a probable probability distribution for the series of nonequilibrium states is obtained through the maximum of the hyperensemble's entropy, and the same conclusion can also be obtained in the multi-state space. In addition, if the probability is further taken as the time the corresponding state lasted, then the velocity of a nonequilibrium state shifting to its neighbor is determined through the reciprocal of the differential coefficient of the probability, and it tells us that, when a simple system is out of its equilibrium, it will return back to the equilibrium one automatically, and the far away to the equilibrium one, the faster the velocity of the system returning back will be.

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