Tsallis statistics generalization of nonequilibrium work relations

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Nonequilibrium work relations such as Jarzynski equality and Crooks fluctuation theorem relate the free energy differences between two equilibrium states and the work distribution of nonequilibrium processes. We use the third constraint formulation of Tsallis statistics and derive the q-statistics generalization of nonequilibrium work relations.

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I. INTRODUCTION

Recent advances in theory of nonequilibrium statistical mechanics have established the methods to calculate the free energy differences between the two equilibrium states of the driven system from the nonequilibrium work measurements [1–3]. These methods are generally called nonequilibrium work relations and, in particular, named as the Jarzynski equality [1] and the Crooks work fluctuation theorem [2]. Consider a system initially in equilibrium at temperature (inverse) $\beta = 1/kT$ (k is the Boltzmann constant), which is externally driven from its initial equilibrium state A to final equilibrium state B by nonquilibrium process. Let $P_F[\gamma^F]$ be the probability of the phase-space trajectory γ^F, for the system driven between the two states in forward direction. This satisfies the Crooks work fluctuation theorem [2,4],

$$\frac{P_F[\gamma^F]}{P_R[\gamma^R]} = e^{\beta(W-\Delta F)}, \tag{1}$$

where W is the work performed on the driven system, ΔF is the free energy difference between the two equilibrium states, and $P_R[\gamma^R]$ is the probability of the phase-space trajectory γ^R, for the system driven in the reversed direction. This is the direct relation between the work dissipation and the ratio of probabilities for the forward and the reversed trajectories and its integrated version is Jarzynski equality [1,5],

$$\langle \exp[-\beta W]\rangle = \exp[-\beta \Delta F]. \tag{2}$$

The average $\langle \cdots \rangle$ is over a statistical ensemble of realizations of a given thermodynamic process.

In Crooks work fluctuation theorem, the probabilities of nonequilibrium forward and reversed trajectories are related by taking the initial conditions from the Boltzmann-Gibb's (BG) equilibrium distribution. There are very few studies on work fluctuation theorem relating the nonequilibrium forward and reverse trajectories taken from other statistical distributions which are based mainly on q statistics [6–10]. Although the foundations of q statistics seem to face certain difficulties [11], considerable effort has been made to resolve them [12].

Based on Tsallis statistics [13], finite bath work fluctuation theorem was derived [7], which includes the microcanonical work fluctuation theorem and the Crooks work fluctuation theorem as the two limiting cases. This has been obtained by considering Tsallis statistics as a finite heat bath statistics [7]. However, this theorem generally contains two temperatures instead of one as observed usually in nonequilibrium work relations [Eqs. (1) and (2)]. There is no generalized connection established between Tsallis statistics and nonequilibrium work relations at a single temperature [9,10]. In this paper, we derive the q-statistics generalization of Jarzynski equality and the Crooks work fluctuation theorem for the classical system driven between two equilibrium states by a nonequilibrium process using Tsallis statistics. This generalized connection may exhibit interesting applications in complex systems [10,14,15].

The theory of Tsallis statistics based on a generalized form of entropy, S_q, characterized by the index $q \in R$, such that $q = 1$ recovers the standard theory of Boltzmann and Gibbs. This generalized (Tsallis) entropy is given by the expression [13]

$$S_q = k\frac{1-c_q}{(q-1)}, \tag{3}$$

where k is the positive (Boltzmann) constant and

$$c_q = \sum_{i=1}^{w} p_i^q. \tag{4}$$

Here, w is the total number of microstates of the system and p_i is the probability of the system at microstate i. In the limit $q \to 1$ one can recover BG entropy

$$S_{\rm BG} = -k\sum_{i=1}^{w} p_i \ln p_i. \tag{5}$$

Preserving the standard variational principle, Tsallis established the canonical generalized distributions and its refinements [14,16]. Using Tsallis statistics, Chame and Mello have derived the generalization of the fluctuation dissipation theorem [17]. Tsallis nonextensive statistical mechanics is also considered as an approach to nonequilibrium stationary states of small or complex systems [14]. However, its equilibrium formulation remains valid for obtaining thermodynamic properties of the equilibrium system [14,18]. There are four versions of Tsallis statistics [19]; in particular, we use the most widely accepted third constraint (escorted probability) [14] formulation of Tsallis statistics.

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In Tsallis third constraint formulation, the generalized equilibrium canonical distribution at β is given by [16]

$$p_i = \frac{1}{Z_q}\left[1-(1-q)\frac{\beta[\epsilon_i - U_q]}{c_q}\right]^{1/(1-q)} \equiv \frac{\exp_q[-\beta(\epsilon_i - U_q)/c_q]}{Z_q}, \tag{6}$$

where ϵ_i is the energy of the ith microstate, U_q is the normalized constrained internal energy which is given by [16,20]

$$U_q = \frac{1}{c_q}\sum_i^w p_i^q \epsilon_i \tag{7}$$

and Z_q is the q-generalized partition function which is given by [14]

$$Z_q = \sum_i^w \left[1-(1-q)\frac{\beta[\epsilon_i - U_q]}{c_q}\right]^{1/(1-q)}. \tag{8}$$

The normalization condition of p_i leads to the relation [16]

$$c_q = Z_q^{1-q}. \tag{9}$$

This modified formalism also becomes ordinary canonical ensemble theory in the limit $q \to 1$ [14] with $c_{q=1} = 1$ and

$$Z_{q=1} = \exp[\beta U]\sum_i^w \exp[-\beta\epsilon_i] \equiv \exp[\beta(U-F)], \tag{10}$$

where the internal energy

$$U = \frac{\exp[\beta U]}{Z_{q=1}}\sum_i^w \epsilon_i \exp[-\beta\epsilon_i] = \frac{\sum_i^w \epsilon_i \exp[-\beta\epsilon_i]}{\sum_i^w \exp[-\beta\epsilon_i]} \tag{11}$$

and the free energy

$$F = -kT \ln \sum_i^w \exp[-\beta\epsilon_i]. \tag{12}$$

Consider a system in an initial macrostate A (for example, closed system of volume V_i) which is in equilibrium at β. The probability for the system in a microscopic phase space (microstate) Γ_A is given by [16,21]

$$P(\Gamma_A) = \frac{1}{Z_q(A)}\left[1-(1-q)\frac{\beta[H(\Gamma_A) - U_q(A)]}{c_q(A)}\right]^{1/(1-q)}, \tag{13}$$

where $H(\Gamma_A)$ is the Hamiltonian for the system in a microstate Γ_A, $U_q(A)$ is the internal energy which is the (escorted probability) weighted Hamiltonian eigenvalue [16] averaged over all microstates in an initial equilibrium state A [see, Eqs. (6)–(8)] and

$$Z_q(A) = \sum_{\Gamma_A}\left[1-(1-q)\frac{\beta[H(\Gamma_A) - U_q(A)]}{c_q(A)}\right]^{1/(1-q)} \tag{14}$$

with

$$c_q(A) = \sum_{\Gamma_A}[P(\Gamma_A)]^q. \tag{15}$$

Suppose the given system evolves in time under Hamiltonian dynamics and reaches a different macrostate B which is to be in equilibrium at same β. The probability distribution for the system in a microstate Γ_B is given by

$$P(\Gamma_B) = \frac{1}{Z_q(B)}\left[1-(1-q)\frac{\beta[H(\Gamma_B) - U_q(B)]}{c_q(B)}\right]^{1/(1-q)}, \tag{16}$$

where $H(\Gamma_B)$ is the Hamiltonian for the system in a microstate Γ_B, $U_q(B)$, $Z_q(B)$, and $c_q(B)$ have the same meaning as above but for the macrostate B. In order to derive the nonequilibrium work relations for a given β, we formulate the problem as follows.

II. SETUP

Consider a classical Hamiltonian system in a macrostate A which is initially in equilibrium with reservoir at inverse temperature β. Let λ_t be an external protocol applied in the arbitrary time interval τ to drive the system from its initial equilibrium state A to another state B at constant bath temperature β. It is assumed that the final state B is not necessarily to be in equilibrium. However, the system in the state B at the constant bath temperature relax towards the equilibrium state B for the same β without doing any work [5]. Let $H(\Gamma_t,\lambda_t)$ be the Hamiltonian with externally controlled time-dependent protocol λ_t and the phase-space coordinates of the system, Γ_t, at a particular time t. At $t=0$, the system Hamiltonian which is in any one of the microstates Γ_A is $H(\Gamma_0,\lambda_0) = H(\Gamma_A)$; and at time $t=\tau$, the system Hamiltonian is $H(\Gamma_\tau,\lambda_\tau)$. Let γ denote the entire trajectory of the driven system from $t=0$ to τ. One can obtain the statistical ensemble of possible realizations by performing the above process repeatedly. In following Refs. [4,5,7], the work performed on the system for a given trajectory can be defined as

$$W = H(\Gamma_\tau,\lambda_\tau) - H(\Gamma_0,\lambda_0) \equiv H(\Gamma_\tau,\lambda_\tau) - H(\Gamma_A). \tag{17}$$

It should be noted that the work defined in Eq. (17) is different from the q-dependent work as given in Ref. [16] (see also Refs. [21,22]). A different definition of work and its physical meaning has been discussed in detail in Refs. [4,23,24].

During the time interval τ in which the system is driven, we assume that the reservoir should always be in equilibrium at a given β [25]. In such a case, the total heat transferred by the system can be written into two parts as

$$Q = Q_q^d + Q^r, \tag{18}$$

where Q_q^d is the q-dependent heat transferred between the system and the reservoir which should preserve the (q-dependent) equilibrium nature of the reservoir and Q^r is the heat transferred when the system relaxes towards the required equilibrium state from the final state B at a given β [26]. There is no work performed on the system during relaxation [5]. We can define the heat transfer due to relaxation as

$$Q^r = H(\Gamma_B) - H(\Gamma_\tau,\lambda_\tau). \tag{19}$$

Since the energy conservation is also valid for nonequilibrium process [25,27,28], the above driven system should obey the principle of energy conservation for any microscopic trajectory as

$$W + Q = \Delta U_q, \tag{20}$$

where $\Delta U_q = U_q(B) - U_q(A)$. The principle of energy conservation as given in Eq. (20) for the nonequilibrium process [28] is different from the q generalization of first law as proposed in Refs. [16,21,22] for an equilibrium system. Therefore, the q-dependent heat transferred by the driven system between the two equilibrium states is

$$\begin{aligned} Q_q^d &= \Delta U_q - W - Q^r \\ &= \Delta U_q - [H(\Gamma_B) - H(\Gamma_A)], \end{aligned} \tag{21}$$

which depends only on the initial and final system states. Since Q_q^d is independent of the nonequilibrium trajectories of the driven system, we impose the condition for the system relaxing towards the required (q-dependent) equilibrium state at a given β as

$$c_q(B) = c_q(A)\left[1 - (1-q)\frac{\beta Q_q^d}{c_q(A)}\right]. \tag{22}$$

Using Eq. (3), the above equation can be written as

$$\begin{aligned} -\beta Q_q^d &= \frac{1 - c_q(B)}{q-1} - \frac{1 - c_q(A)}{q-1} \\ &= \frac{1}{k}[S_q(B) - S_q(A)] \\ &= \frac{\sigma_q}{k}, \end{aligned} \tag{23}$$

where $\sigma_q = S_q(B) - S_q(A)$ is the q-dependent change in entropy of the equilibrium system [14]. From the above condition [Eq. (22)], the q-dependent change in (equilibrium) reservoir entropy for the driven nonequilibrium process is obtained as [28–30]

$$\frac{\Delta S_q^r}{k} = \beta Q_q^d. \tag{24}$$

The above equation provides the consistent usage of $\beta = 1/kT$ as the (inverse) reservoir temperature in Tsallis statistics [22].

The usage of thermodynamic laws is not mandatory for the proof of nonequilibrium work relations [4,5]. Since internal energy, applied work, and heat are formulated clearly for the above driven system [31], we use Eqs. (20) and (22) and obtain the q-generalized nonequilibrium work relations in which the initial probability distributions [Eqs. (13) and (16)] are taken from the Tsallis statistics.

III. q-GENERALIZED JARZYNSKI EQUALITY

In order to obtain the q-generalized version of Jarzynski equality for the above driven process, one can take the following q-exponential average over an ensemble of realizations in which the initial distribution is taken from Tsallis statistics.

$$\left\langle e_q^{-\beta(W+Q^r-\Delta U_q)/c_q(B)}\right\rangle = \int e_q^{-\beta(W+Q^r-\Delta U_q)/c_q(B)} P(\Gamma_A) d\Gamma_A. \tag{25}$$

Using the q-exponential identity $e_q^x e_q^y = e_q^{[x+y+(1-q)xy]}$ [14] and Eq. (13), the integral of the above equation can be rewritten as

$$\left\langle e_q^{-\beta(W+Q^r-\Delta U_q)/c_q(B)}\right\rangle = \frac{1}{Z_q(A)} \int e_q^{M_q+N_q} d\Gamma_A, \tag{26}$$

where

$$M_q = -\frac{\beta[W + Q^r - \Delta U_q]}{c_q(B)} \tag{27}$$

and

$$N_q = -\frac{\beta[H(\Gamma_A) - U_q(A)]}{c_q(A)}[1 + (1-q)M_q]. \tag{28}$$

Using Eqs. (20) and (22), one can rewrite

$$\begin{aligned} 1 + (1-q)M_q &= 1 + (1-q)\frac{\beta Q_q^d}{c_q(B)} \\ &= 1 + \frac{c_q(A) - c_q(B)}{c_q(B)} \\ &= \frac{c_q(A)}{c_q(B)}. \end{aligned} \tag{29}$$

Using Eqs. (17) and (19), one can obtain

$$M_q + N_q = \frac{-\beta}{c_q(B)}[H(\Gamma_B) - U_q(B)]. \tag{30}$$

Therefore, Eq. (26) becomes

$$\left\langle e_q^{-\beta(W+Q^r-\Delta U_q)/c_q(B)}\right\rangle = \frac{1}{Z_q(A)} \int e_q^{-\beta[H(\Gamma_B)-U_q(B)]/c_q(B)} d\Gamma_A.$$

Since Hamiltonian dynamics preserve the phase-space volume, $d\Gamma_A = d\Gamma_B$ [4,5], and using Eq. (16) we can rewrite the above equation as

$$\begin{aligned} \left\langle e_q^{-\beta(W+Q^r-\Delta U_q)/c_q(B)}\right\rangle &= \frac{Z_q(B)}{Z_q(A)} \int P(\Gamma_B)\, d\Gamma_B \\ &= \frac{Z_q(B)}{Z_q(A)}. \end{aligned} \tag{31}$$

We have obtained a q-generalized version of one of the nonequilibrium work relations. It should be noted that β appeared in the q-exponential average to ensure that the temperature of the reservoir remains the same, however, one does not know anything about system temperature during the driven process. Further, Q^r and $c_q(B)$ in the above relation also takes care of the heat exchange due to relaxation of the system towards the final equilibrium state [26]. This may provide a possible physical meaning of the above average for the driven nonequilibrium process instead of thinking of it as an *ad hoc* method [5,26].

The interesting aspect of Jarzynski equality is to obtain the free energy difference between two equilibrium states from the nonequilibrium process. In this nonequilibrium process, initially the system should be in equilibrium at the given temperature, however, it is not necessary that the final state also be in equilibrium. This raises the criticism that the heat due to relaxation is not taken properly in the original Jarzynski equality [26]. Our general formulation may solve this issue as follows.

In the limit $q \to 1$, $\exp_q(x) = \exp(x)$ and $c_q = 1$ [14], then using Eqs. (10)–(12), Eq. (31) becomes

$$\langle \exp[-\beta(W + Q^r - \Delta U)]\rangle = \exp[\beta(\Delta U - \Delta F)],$$
$$\langle \exp[-\beta(W + Q^r)]\rangle = \exp[-\beta \Delta F], \tag{32}$$

where $\Delta U = U(B) - U(A)$ is the change in internal energy and $\Delta F = F(B) - F(A)$ is the change in equilibrium free energy of the BG canonical system. Thus, we can obtain a more general form of Jarzynski equality which includes heat due to system relaxation [26] for the BG canonical system in the limit $q \to 1$.

For example, in protein unfolding experiments or simulations, one end of the biomolecule is fixed and the other end can be driven either by constant force or constant velocity. In our earlier work for a fixed unfolding distance, we find that the folded protein which is initially in equilibrium with the reservoir undergoes different unfolding pathways which depends on the nature of the unfolding pulling protocols [32,33]. For fast pulling protocols the final state of the unfolded protein need not to be in equilibrium with the reservoir [33]. The system relaxes to final equilibrium state by exchanging heat with the surroundings without doing any work. Since heat due to relaxation is not taken properly in the original Jarzynski equality, our general formulation of Jarzynski equality which includes heat due to system relaxation can be useful for free energy calculation of such complex systems. If Q_r is within the measurements or numerical error for work calculation in experiments or simulations, the original Jarzynski equality (without the heat term due to relaxation [5,26]) can provide reliable estimates of the free energy differences.

IV. q-GENERALIZED CROOKS WORK FLUCTUATION THEOREM

In order to derive the q-generalized version of the Crooks work fluctuation theorem, we proceed with the problem analogous to Ref. [4] as follows. Since $H(\Gamma_0,\lambda_0) = H(\Gamma_A)$, the probability of the phase-space trajectory γ^F, for the system driven between the two equilibrium states obtained from the initial equilibrium distribution in the forward direction (A to B) is given as [4]

$$P_F[\gamma^F] = P_A^{\rm eq}(\Gamma_0^F) = \frac{1}{Z_q(A)}\left[1 - (1-q)\frac{\beta[H(\Gamma_A) - U_q(A)]}{c_q(A)}\right]^{1/(1-q)}. \tag{33}$$

Suppose the system is driven from equilibrium state B to state A using the time reversed protocol, $\lambda_t^R = \lambda_{\tau-t}^F$, $H(\Gamma_t^R,\lambda_t^R)$ is the Hamiltonian for the externally controlled time-dependent protocol λ_t^R, and Γ_t^R is the phase-space coordinate of the system at a particular time t. At $t = 0$, the system Hamiltonian which is in any one of the microstates Γ_B is $H(\Gamma_0^R,\lambda_0^R) = H(\Gamma_B)$; and at time $t = \tau$, the system Hamiltonian is $H(\Gamma_\tau^R,\lambda_\tau^R)$. The probability of the phase-space trajectory γ^R, for the system driven in reverse direction obtained from the initial equilibrium distribution is given as [4]

$$P_R[\gamma^R] = P_B^{\rm eq}(\Gamma_0^R) = \frac{1}{Z_q(B)}\left[1 - (1-q)\frac{\beta[H(\Gamma_B) - U_q(B)]}{c_q(B)}\right]^{1/(1-q)} \tag{34}$$

Using Eq. (17), Eq (19), and Eq. (20), Eq. (33) can be rewritten as

$$P_F[\gamma^F] = \frac{1}{Z_q(A)}\left[1 - (1-q)\frac{\beta[H(\Gamma_B) - U_q(B) + Q_q^d]}{c_q(A)}\right]^{1/(1-q)}.$$
$$P_F[\gamma^F] = \frac{1}{Z_q(A)}\left[1 - (1-q)\frac{\beta Q_q^d}{c_q(A)}\right]^{1/(1-q)} \times\left[1 - (1-q)\frac{\beta[H(\Gamma_B) - U_q(B)]}{c_q(A)\left[1-(1-q)\frac{\beta Q_q^d}{c_q(A)}\right]}\right]^{1/(1-q)}. \tag{35}$$

Using Eq. (22) and Eq. (34), Eq. (35) becomes

$$P_F[\gamma^F] = \frac{Z_q(B)}{Z_q(A)}\left[1 - (1-q)\frac{\beta Q_q^d}{c_q(A)}\right]^{1/(1-q)} P_R[\gamma^R]. \tag{36}$$

We can get from Eq. (20) that

$$\frac{P_F[\gamma^F]}{P_R[\gamma^R]} = \frac{Z_q(B)}{Z_q(A)}\left[1 + (1-q)\frac{\beta[W + Q^r - \Delta U_q]}{c_q(A)}\right]^{1/(1-q)}.$$
$$\equiv \frac{Z_q(B)}{Z_q(A)}\exp_q\left[\frac{\beta(W + Q^r - \Delta U_q)}{c_q(A)}\right]. \tag{37}$$

We have obtained the q-generalized version of another nonequilibrium work relation. In the limit $q \to 1$, $\exp_q(x) = \exp(x)$ and $c_q = 1$ [14], then using Eqs. (10)–(12), Eq. (37) becomes

$$\frac{P_F[\gamma^F]}{P_R[\gamma^R]} = \exp[\beta(W + Q^r - \Delta F)]. \tag{38}$$

Thus, we can obtain a more general form of Crooks work fluctuation relation which includes heat due to system relaxation [26] for the BG canonical system in the limit $q \to 1$.

In order to obtain the q-generalized version of Jarzynski equality from the q-generalized work fluctuation relation, one can take the following q-exponential average over ensemble of realization in forward direction as

$$\left\langle e_q^{-\beta(W+Q^r-\Delta U_q)/c_q(B)}\right\rangle = \int e_q^{-\beta(W+Q^r-\Delta U_q)/c_q(B)} P_F[\gamma^F]\, d\gamma_F. \tag{39}$$

Using Eq. (37), the above equation can be rewritten as

$$\left\langle e_q^{-\beta(W+Q^r-\Delta U_q)/c_q(B)}\right\rangle = \frac{Z_q(B)}{Z_q(A)} I_q, \tag{40}$$

where

$$I_q = \int e_q^{-\beta(W+Q^r-\Delta U_q)/c_q(B)} e_q^{\beta(W+Q^r-\Delta U_q)/c_q(A)} P_R[\gamma^R] d\gamma_R. \tag{41}$$

Since Hamiltonian dynamics preserve the phase-space volume, $d\gamma_F = d\gamma_R$ [4,5]. Using the q-exponential identity

$e_q^x e_q^y = e_q^{[x+y+(1-q)xy]}$ [14], we rewrite the integral of the above equation as

$$I_q = \int e_q^{\beta(W+Q^r-\Delta U_q)D_q} P_R[\gamma^R]d\gamma_R. \tag{42}$$

where

$$D_q = \left[\frac{1}{c_q(A)} - \frac{1}{c_q(B)} - (1-q)\frac{\beta(W+Q^r-\Delta U_q)}{c_q(A)c_q(B)}\right]. \tag{43}$$

Using Eq. (20) and Eq. (22), the above equation becomes

$$D_q = \left[\frac{1}{c_q(A)} - \frac{1}{c_q(B)} - \frac{[c_q(B)-c_q(A)]}{c_q(A)c_q(B)}\right] = 0. \tag{44}$$

Since $e_q^0 = 1$, $I_q = \int P_R[\gamma^R]d\gamma_R = 1$ and Eq. (40) becomes

$$\left\langle \exp_q\left[\frac{-\beta(W+Q^r-\Delta U_q)}{c_q(B)}\right]\right\rangle = \frac{Z_q(B)}{Z_q(A)}. \tag{45}$$

We have obtained the q-generalized version of Jarzynski equality.

V. CONCLUSION

We have derived the more general form of Jarzynski equality and Crooks work fluctuation theorem which include the heat due to system relaxation in the framework of Tsallis statistics. Our general result may resolve the criticism raised earlier that heat due to relaxation is not taken properly in the original Jarzynski equality [5,26]. In the Tsallis third constraint formulation, one cannot directly obtain the canonical probability distribution because the distribution [Eq. (6)] is self-referential [14,19]. Since p_i depends upon c_q, one should iterate Eqs. (6), (8), and (9) repeatedly until numerical consistency is achieved. We have utilized the self-referential nature of the Tsallis distribution and have obtained the q-generalized version of nonequilibrium work relations. This generalized relation may also find interesting applications in complex systems [10,33].

In our Tsallis statistics formulation the initial and the final states of the system are in equilibrium. So we have taken the escorted averages only in the initial and the final equilibrium states as given in Eq. (7). Since we have taken the work as defined by Jarzynski (but not q-dependent work) and also the averages of Eqs. (25) and (39), taken from the nonequilibrium trajectories whose distribution does not necessarily follow the Tsallis statistics, we have not taken escorted averages for Eqs. (25) and (39). This type of average can be useful for protein unfolding experiments since proteins exhibit refolding behavior during unfolding only for slow pulling rate protocols [32,33]. This behavior can not be observed for fast pulling rate protocols even though the system has long range interactions.

There is a general impression among a few of us that Tsallis's formalism has nothing to do with equilibrium statistical mechanics. If the system relaxes towards the equilibrium, one may not rule out the equilibrium formulation of the Tsallis statistics. Although we have taken the initial distribution as the equilibrium, our formulation may also be applicable for nonequilibrium stationary state conditions [9].

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