Shannon entropic temperature and its lower and upper bounds for non-Markovian stochastic dynamics

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In this article we have studied Shannon entropic nonequilibrium temperature (NET) extensively for a system which is coupled to a thermal bath that may be Markovian or non-Markovian in nature. Using the phase-space distribution function, i.e., the solution of the generalized Fokker Planck equation, we have calculated the entropy production, NET, and their bounds. Other thermodynamic properties like internal energy of the system, heat, and work, etc. are also measured to study their relations with NET. The present study reveals that the heat flux is proportional to the difference between the temperature of the thermal bath and the nonequilibrium temperature of the system. It also reveals that heat capacity at nonequilibrium state is independent of both NET and time. Furthermore, we have demonstrated the time variations of the above-mentioned and related quantities to differentiate between the equilibration processes for the coupling of the system with the Markovian and the non-Markovian thermal baths, respectively. It implies that in contrast to the Markovian case, a certain time is required to develop maximum interaction between the system and the non-Markovian thermal bath (NMTB). It also implies that longer relaxation time is needed for a NMTB compared to a Markovian one. Quasidynamical behavior of the NMTB introduces an oscillation in the variation of properties with time. Finally, we have demonstrated how the nonequilibrium state is affected by the memory time of the thermal bath.

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I. INTRODUCTION

The "H-theorem" of the Fokker-Planck equation [1] shows that the information entropy (S) [2,3] is analogous to the thermodynamic entropy, which implies that the entire theory of statistical mechanics can be elegantly reformulated by extremization of S, subject to the constraints imposed by the *a priori* information concerning the system of interest. The information entropy is thus the key state property of a Brownian system to understand the relaxation behavior of the same [4–9]. Hence the study of information entropy and related quantities is always an intriguing issue in the field of stochastic dynamics. In general, entropy measures the information content of a probability distribution and thus gives a criterion for decision: we have to choose the one which yields the most information concerning location and value of the global maximum sought from several possibilities. As a point of digression we may also note that in Ref. [10] it was shown that the Legendre-transformation structure of thermodynamics can be replaced without any change if one replaces the entropy S by Fisher's information measure (FIM), which obeys the important thermodynamic property of concavity. This method seems to be able to treat equilibrium and nonequilibrium situations in a manner entirely similar to the conventional one. Moreover, there exist interesting relationships invented by Kullback [11,12] that connect FIM and the relative Shannon information measure. These have been shown to have some bearing on the time evolution of arbitrary systems governed by the quite general continuity equation [4,13,14]. Using the definition of S in the Fokker-Planck equation one can easily get the information entropy balance equation [5,6]. From this equation it is possible to identify thermodynamically inspired quantities like entropy flux and production. Making use of the time-dependent solution of the Fokker-Planck equation in these quantities the relaxation mechanism may be understood in detail. Recently, a method has been developed in Ref. [5] based on the information entropy for the study of the relaxation processes in the mesoscopic system. The mesoscopic system has also been studied in recent papers [15–21] in terms of Gibbs entropy. An important application of information entropy in the context of Brownian motion is to solve the Fokker-Planck equation using the maximum entropy principle [22,23]. The von Newmann equation in quantum mechanics was also solved using this principle [24–27]. Based on information entropy a method for the global optimization of stochastic function has been developed very recently [28]. It is a useful tool to study the relaxation process in a stochastic system in detail. For example, heat conductivity in a medium has recently been studied when its constituents are stochastic [29].

In general, it is difficult to know the state properties of a system (like a thermodynamic system and similar to it) at a nonstationary state (NSS). Based on the dynamics of the system one can solve this problem. For example, in principle there is no problem to define the entropy of the system at NSS knowing the probability distribution function of the system. It implies that other properties can be defined at a nonstationary state by suitable connection of them with the entropy. Very recently, a nonequilibrium information entropic temperature has been defined in Ref. [30] based on information entropy to study the interaction of a system with its surroundings during the journey towards the equilibrium state [31–36]. In Ref. [30] it has been shown that the definition of the temperature deserves the name thermodynamical temperature for any distribution of a stochastic process. Using this definition, nonequilibrium temperature (NET) of a quantum system

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coupled to the Markovian bosonic or fermionic thermal bath was calculated in another recent paper [37]. The interaction of a system with its surroundings as well as the NET should depend on the characteristics of the thermal bath. Then there would be the following pertinent question: how does the nonequilibrium temperature of a Brownian system depend on the characteristics of the non-Markovian thermal bath (NMTB)?

The importance of studying non-Markovian dynamics was addressed around the early eighties of the past century. The experimental studies during the above-mentioned period [38–42] imply that the Markovian dynamics cannot accurately account for the effect of viscosity on the barrier crossing phenomenon in the solution phase. The theory developed based on the non-Markovian dynamics [42–46] shows a fair agreement between theoretical and experimental results. Thus the study of non-Markovian dynamics becomes a worthy issue [47–56] in the field of Brownian motion. Keeping that in mind one may become interested in exploring the answer of the above question and related topics. We have studied the dynamics of a Brownian particle (which is coupled to a NMTB) in three dimensions based on the Fokker-Planck description of the stochastic processes. Information entropy and its upper bound have been calculated in terms of nonequilibrium temperature. Using Schwartz inequality we have shown that at a nonstationary state the NET may have both lower and upper bounds. At the same time we have calculated thermodynamic quantities like internal energy, heat, and work. It is observed that the heat flux is proportional to the difference between the temperature of the thermal bath and the nonequilibrium temperature of the system. It is quite similar to Newton's law of cooling. Our other prediction is that heat capacity at a nonstationary state is independent of both NET and time. From the present study we realize that a certain time is required to develop maximum interaction between the system and the non-Markovian thermal bath (NMTB) and the relaxation time required for this case is relatively higher compared to the Markovian case. Quasi-dynamical behavior of the NMTB introduces an oscillation in the variation of properties with time. Finally, to study the effect of memory time on the nonequilibrium state we have demonstrated the variation of the above-mentioned and related quantities with the noise correlation time. It is observed that some quantities like time derivative of NET, energy, heat, and work show optimum behavior with noise correlation time.

The outlay of the paper is as follows. In Sec. II, we have calculated the nonequilibrium temperature in terms of time, characteristics of both systems, and thermal reservoir. Then we have connected it with the entropy production and the upper bound of the same. In this section we have also derived relations between NET and thermodynamic properties like internal energy, heat, and work, respectively. In the next section (Sec. III), we have presented two applications of the general theory of Sec. II. Section IV is devoted to a comparative study based on the relaxation behavior of the system for coupling with Markovian and non-Markovian thermal baths, respectively. The paper is concluded in Sec. V.

II. CALCULATION OF NONEQUILIBRIUM TEMPERATURE AND ITS BOUNDS FOR NON-MARKOVIAN STOCHASTIC DYNAMICS

A. Generalized Langevin equation: Evaluation of response function

We start with the following generalized Langevin equation of motion for a free Brownian particle having mass m:

$$m\frac{d\boldsymbol{u}(t)}{dt} = -m\int_0^t \gamma(t-\tau)\boldsymbol{u}(\tau)d\tau + \boldsymbol{f}(t), \tag{1}$$

where $\boldsymbol{f}(t)$ is the Gaussian colored thermal noise. The above integral is a frictional memory kernel. Time-dependent damping, $\gamma(t)$, in the kernel is related to the fluctuating force by the following standard fluctuation dissipation relation:

$$\langle \boldsymbol{f}(t)\cdot \boldsymbol{f_0}\rangle = 3k_BTm\gamma(t). \tag{2}$$

The above relation implies that the momentum distribution function of free Brownian particle relaxes to the Maxwellian form.

Using Laplace transformation, we have solved Eq. (1). The time-dependent velocity, $\boldsymbol{u}(t)$, of the particle (having initial velocity, $\boldsymbol{u}_0$) is given by

$$\begin{aligned}\boldsymbol{u}(t) &= \boldsymbol{u_0}\chi(t) + \frac{1}{m}\int_0^t \chi(t-\tau)\boldsymbol{f}(\tau)d\tau,\\ \chi(t) &= \mathcal{L}^{-1}[\tilde{\chi}(z)]\\ &= \mathcal{L}^{-1}\left[\frac{1}{z+\tilde{\gamma}(z)}\right].\end{aligned} \tag{3}$$

Here $\mathcal{L}^{-1}$ denotes Laplace inversion and $\tilde{\gamma}(z)$ is the Laplace transform of $\gamma(t)$:

$$\tilde{\gamma}(z) = \int_0^t e^{-zt}\gamma(t)dt. \tag{4}$$

$\chi(t)$ in Eq. (3) is known as the response function or the susceptibility. However, it can be verified from Eq. (3) and its time derivative and also Eq. (1) that

$$\chi(t=0) = 1, \quad \dot{\chi}(t=0) = 0. \tag{5}$$

Now from Eq. (3) it can be shown that the response function is related to the velocity autocorrelation function as

$$\chi(t) = \frac{m}{3k_BT}\langle \boldsymbol{u}(t)\cdot \boldsymbol{u_0}\rangle. \tag{6}$$

Using the above relations we shall present the Fokker-Planck description corresponding to Eq. (1) in the next subsection.

B. Generalized Fokker-Planck equation and its solution

To calculate properties like nonequilibrium temperature for a non-Markovian stochastic process, first we need to know the relevant distribution function, the solution of the Fokker-Planck equation (FPE). Following Ref. [57] one can write the generalized Fokker-Planck equation which is equivalent to Eq. (1). Here the Langevin equation [Eq. (1)] is a linear one with Gaussian noise and it implies that using variance of the velocity vector the velocity distribution function can be written as

$$P(\boldsymbol{u},\boldsymbol{u_0};t) = \left[\frac{3}{2\pi A(t)}\right]^{\frac{3}{2}} \exp\left[-\frac{3}{2}\,[\boldsymbol{g}(t)\cdot\boldsymbol{g}(t)]\,A^{-1}(t)\right], \tag{7}$$

where $\boldsymbol{g}(t)$ is the fluctuation in velocity and is given by

$$\begin{aligned}\boldsymbol{g}(t) &= \boldsymbol{u} - \chi(t)\boldsymbol{u}_0\\ &= \frac{1}{m}\int_0^t \chi(t-\tau)\boldsymbol{f}(\tau)d\tau.\end{aligned} \tag{8}$$

$A(t)$ in Eq. (7) is the variance of the velocity and it can be written in compact notation as

$$A(t) = \langle \boldsymbol{g}(t)\cdot\boldsymbol{g}(t)\rangle. \tag{9}$$

The above form of the distribution function $P(\boldsymbol{u},\boldsymbol{u_0};t)$ ensures that initially it is a Dirac δ function like quantity and with time it spreads to the equilibrium Maxwellian form. However, after some variable transformation and back transformation technique [57], the following differential equation can be generated whose solution satisfies the above-mentioned velocity distribution function:

$$\begin{aligned}\frac{\partial P}{\partial t}(\boldsymbol{u},\boldsymbol{u_0};t) = &-\left[\frac{\dot{\chi}(t)}{\chi(t)}\right]\nabla\cdot[\boldsymbol{u}P(\boldsymbol{u},\boldsymbol{u_0};t)]\\ &+\frac{1}{6}\nabla^2 P(\boldsymbol{u},\boldsymbol{u_0};t)\left[\chi^2(t)\frac{d}{dt}[\chi^{-2}(t)A(t)]\right].\end{aligned} \tag{10}$$

Using Eqs. (2), (3), and (9), one can simplify the above equation. Based on these equations $A(t)$ and its time derivative can be written in terms of $\chi(t)$ as

$$\begin{aligned}A(t) &= \left(\frac{3k_BT}{m}\right)[1-\chi^2(t)],\\ \dot{A}(t) &= -\left(\frac{6k_BT}{m}\right)\dot{\chi}(t)\chi(t).\end{aligned} \tag{11}$$

Equation (5) suggests that, at long time, $A(\infty) = \frac{3k_BT}{m}$. Thus the velocity distribution function [Eq. (7)] reduces to the Maxwellian form at equilibrium. It is an important check of our calculation. Now incorporating Eq. (11) into Eq. (10), we get the following generalized FPE:

$$\begin{aligned}\frac{\partial P}{\partial t}(\boldsymbol{u},\boldsymbol{u_0};t) = &\ \beta\nabla\cdot[\boldsymbol{u}P(\boldsymbol{u},\boldsymbol{u_0};t)]\\ &+\frac{k_BT}{m}\beta(t)\nabla^2 P(\boldsymbol{u},\boldsymbol{u_0};t),\end{aligned} \tag{12}$$

where

$$\beta(t) = \left|-\frac{\dot{\chi}(t)}{\chi(t)}\right|. \tag{13}$$

Using the above generalized Fokker-Planck equation we calculate nonequilibrium temperature and related quantities in the next subsection.

C. Calculation of nonequilibrium temperature and its bounds

The distribution function [Eq. (7)] gives the measure of Shannon information. For the present problem it is given by

$$S = -k_B\int P(\boldsymbol{u},\boldsymbol{u_0};t)\ln P(\boldsymbol{u},\boldsymbol{u_0};t)du. \tag{14}$$

We now calculate the Shannon entropy based nonequilibrium temperature (θ) of the system following Refs. [30,37]. In Ref. [30], the authors used the relationship $dS = dQ_{\rm rev}/T$ as a mean for defining temperature. Here S is the Shannon or Gibbs entropy of a distribution. The entropic or thermodynamic temperature for any system (irrespective of whether it is in equilibrium or not) has been defined by developing a statistical notion of "infinitesimal heating" of the system as a particular form of perturbation of the microstate of the same in such a way that it increases the Shannon entropy by an amount δS and the energy associated with the distribution by an amount δQ. The final form of the definition has been obtained in Ref. [30] calculating the ratio of the change in energy to that in the Shannon entropy, and by using the de Bruijn identity of information theory [58]. Thus the notion of thermodynamical temperature can be extended to nonequilibrium distributions in a relatively straightforward way as the ratio between the average curvature of the Hamiltonian and k_B times of the trace of the Fisher information matrix associated with the probability distribution. It can be mathematically represented for the present system as

$$\frac{1}{\theta} = \frac{k_B}{3m}\int_{-\infty}^{+\infty}\frac{1}{P}(\nabla P\cdot\nabla P)\,du. \tag{15}$$

$3m$ in the above equation corresponds to the average curvature of the Hamiltonian. Thus, for the free Brownian particle, the entropic temperature is inversely proportional to the trace of the Fisher information matrix which is a measure of the broadening of the probability distribution function. If the distribution function becomes wider then the trace of the Fisher information matrix (TFIM) decreases and the temperature increases. This is consistent with our expectation. In other words, the connection between the temperature and the TFIM matches with our imagination.

Now using the distribution function [Eq. (7)] in Eq. (15) we get the explicit expression of θ in terms of $\chi(t)$ as

$$\theta = T[1-\chi^2(t)]. \tag{16}$$

Using Eq. (5) in the above equation one can immediately check that, at equilibrium, $\theta = T$. This is consistent with our natural demand. The above equation and Eq. (9) give some impression about the nonequilibrium temperature. These equations imply that the nonequilibrium temperature is proportional to the width of the distribution function. In other words, the NET is proportional to the variance of the velocity. Thus it carries the signature of randomness in the system at nonequilibrium state. Then it is expected that the properties of the system at nonequilibrium state can be understood in terms of nonequilibrium temperature. Keeping this in mind, to proceed further we rearrange the Fokker-Planck Eq. (12) as

$$\frac{\partial P}{\partial t}(\boldsymbol{u},\boldsymbol{u_0};t) = -\nabla\cdot\boldsymbol{j},$$
$$\boldsymbol{j} = -\beta(t)\boldsymbol{u}P - \beta(t)\frac{k_B T}{m}\nabla P. \tag{17}$$

Using the above equation, the time evolution of information entropy can be written in terms of $\boldsymbol{j}$ after performing a partial integration and setting the appropriate boundary condition [37] as

$$\dot{S} = -k_B\int du\frac{1}{P}\boldsymbol{j}\cdot\nabla P. \tag{18}$$

Applying Schwartz inequality $|\int dq\, AB|^2 \leqslant \int dq|A|^2\int dq|B|^2$ to Eq. (18) with properly identified A and B, an upper bound U for the rate of information entropy change may be found as

$$\dot{S} \leqslant U,$$
$$U = k_B\left[\int du\frac{\boldsymbol{j}\cdot\boldsymbol{j}}{P}\right]^{\frac{1}{2}}\left[\int du\frac{1}{P}(\nabla P)\cdot(\nabla P)\right]^{\frac{1}{2}}. \tag{19}$$

It may be noted here that the second integral is same as the trace of the Fisher information matrix. For a one-dimensional system the integral becomes the Fisher information [59,60]. Thus the maximum rate of increase of S for an isolated system is limited by the Fisher information level. Since the information entropy is the average missing information, the rate of change of entropy can be interpreted as the rate of the average missing information transmission. So the upper bound (19) is interesting in the sense that the amount of the average missing information transmitted per unit time cannot exceed this quantity. For the present system, using Eq. (7) and Eq. (18), we get the explicit rate of information entropy change and its upper bound as

$$\dot{S} = 3k_B\beta(t)\left[\frac{\chi^2(t)}{1-\chi^2(t)}\right] \tag{20}$$

and

$$U = 3k_B\beta(t)\left[\left[\frac{\chi^2(t)}{1-\chi^2(t)}\right]^2 + \frac{mu_0^2}{3k_BT}\left[\frac{\chi^2(t)}{1-\chi^2(t)}\right]\right]^{\frac{1}{2}}. \tag{21}$$

Using Eq. (16) in Eqs. (20) and (21) one can realize how entropy production and its bound depend on the temperature of the system at nonequilibrium state. In terms of NET the above equations can be written as

$$\dot{S} = 3k_B\beta(t)\left(\frac{T-\theta}{\theta}\right) \tag{22}$$

and

$$U = 3k_B\beta(t)\left[\left(\frac{T-\theta}{\theta}\right)^2 + \frac{mu_0^2}{3k_BT}\left(\frac{T-\theta}{\theta}\right)\right]^{\frac{1}{2}}. \tag{23}$$

It is clear from the above two equations that, at equilibrium, $\dot{S} = U = 0$. This is consistent with our expectation as well as Eq. (19). From the above two relations one can measure the deviation of entropy production from its upper bound as

$$\Delta U = 3k_B\beta(t)\left[\left[\left(\frac{T-\theta}{\theta}\right)^2 + \frac{mu_0^2}{3k_BT}\left(\frac{T-\theta}{\theta}\right)\right]^{\frac{1}{2}} - \frac{T-\theta}{\theta}\right]. \tag{24}$$

Now using Eq. (22) in Eq. (19) one can easily show that there is a lower bound of nonequilibrium temperature as

$$\theta \leqslant L_\theta,$$
$$L_\theta = \frac{3k_B\beta(t)T}{3k_B\beta(t)+U}. \tag{25}$$

Equation (23) suggests that, at long time, $L_\theta = T$. It satisfies the equality condition of Eq. (19). However, deviation of nonequilibrium temperature from its lower bound can be calculated from Eq. (16) and Eq. (25) as

$$\Delta L_\theta = T[1-\chi^2(t)] - \frac{3k_B\beta(t)T}{3k_B\beta(t)+U}. \tag{26}$$

The existence of the bound and its importance are discussed in Ref. [37]. We now explore another bound of the NET from the inequality relation [Eq. (19)]. The second integral in Eq. (19) is directly connected to the nonequilibrium temperature, θ. It is clear from Eq. (19) that, as there exists an upper bound of $\dot{S}$, there must exist an upper bound (U_θ) of θ also. We may now derive that bound. Combining Eq. (16) and Eq. (19) we get

$$U^2 = \frac{3mk_B}{\theta}\int du\frac{\boldsymbol{j}\cdot\boldsymbol{j}}{P}$$
$$= \frac{3k_B\beta^2(t)}{\theta}\left[\frac{3k_BT\chi^4(t)}{1-\chi^2(t)} + mu_0^2\chi^2(t)\right]. \tag{27}$$

In Eq. (19), $\dot{S} \leqslant U$ implies $\dot{S}^2 \leqslant U^2$ as both $\dot{S}$ and U are real and positive quantities. Thus, from Eq. (27),

$$\dot{S}^2 \leqslant \frac{3k_B\beta^2(t)}{\theta}\left[\frac{3k_BT\chi^4(t)}{1-\chi^2(t)} + mu_0^2\chi^2(t)\right]. \tag{28}$$

Rearranging the above equation, the upper bound of θ is given by

$$\theta \leqslant U_\theta,$$
$$U_\theta = \frac{3k_B\beta^2(t)}{\dot{S}^2}\left[\frac{3k_BT\chi^4(t)}{1-\chi^2(t)} + mu_0^2\chi^2(t)\right]. \tag{29}$$

Near equilibrium, $\dot{S}$ is very close to its upper bound (U) and hence Eq. (29) reduces to

$$U_\theta \simeq \frac{3k_B\beta^2(t)}{U^2}\left[\frac{3k_BT\chi^4(t)}{1-\chi^2(t)} + mu_0^2\chi^2(t)\right]. \tag{30}$$

From Eq. (21) and the above, for the near equilibrium situation we get

$$U_\theta \simeq \frac{3k_B\beta^2(t)\left[\frac{3k_BT\chi^4(t)}{1-\chi^2(t)} + mu_0^2\chi^2(t)\right]}{9k_B^2\beta^2(t)\left[\left[\frac{\chi^2(t)}{1-\chi^2(t)}\right]^2 + \frac{mu_0^2}{3k_BT}\left[\frac{\chi^2(t)}{1-\chi^2(t)}\right]\right]}$$
$$= T[1-\chi^2(t)]. \tag{31}$$

It is clear from Eq. (16) and the above equation that, for a near equilibrium situation, the Shannon entropic temperature θ is essentially the same to its upper bound U_θ, as the equality sign in Eq. (29) holds for the equilibrium situation. However, using Eq. (20) the expression for the upper bound of the NET at the short-time limit can be written in simple form as

$$\theta < U_\theta,$$
$$U_\theta = T[1-\chi^2(t)] + \frac{mu_0^2}{3k_B}\left[\chi(t) - \frac{1}{\chi(t)}\right]^2. \tag{32}$$

One can calculate the deviation of θ from its upper bound at the short-time regime from Eq. (16) and Eq. (32) as

$$\Delta U_\theta = \frac{mu_0^2}{3k_B}\left[\chi(t) - \frac{1}{\chi(t)}\right]^2. \tag{33}$$

Before leaving this part we would like to mention that the upper bound of the NET has the significance and importance similar to that of L_θ. We now calculate another important property of the system, the internal energy (ϵ), using the following relation:

$$\epsilon = \frac{m}{2}\int_{-\infty}^{+\infty} u^2 P\, du. \tag{34}$$

Making use of Eq. (7) in the above equation we have

$$\epsilon = \frac{3}{2}k_B T[1-\chi^2(t)] + \frac{mu_0^2}{2}\chi^2(t)$$
$$= \theta\left(\frac{3}{2}k_B - \frac{mu_0^2}{2T}\right) + \frac{mu_0^2}{2}. \tag{35}$$

Using Eq. (5) in the above equation one can easily show that the equation satisfies the equilibrium result. The time derivative of the energy can be obtained from the above Eq. (35) as

$$\dot{\epsilon} = -\dot{\chi}(t)\chi(t)\big[3k_B T - mu_0^2\big]$$
$$= \beta(t)\left(1-\frac{\theta}{T}\right)\big[3k_B T - mu_0^2\big]. \tag{36}$$

We now connect thermodynamic quantities based on the laws of thermodynamics. One can relate the rate of change of heat ($\dot{Q}$) with the rate of change of information entropy as

$$dS = \frac{dQ}{\theta},$$
$$\text{or}\quad d\dot{S} = \frac{d\dot{Q}}{\theta}, \tag{37}$$

that finally gives

$$\dot{Q} = \theta\dot{S}. \tag{38}$$

Now making use of Eqs. (20) and (16) in the above equation we have

$$\dot{Q} = 3k_B T\beta(t)\chi^2(t)$$
$$= 3k_B T\beta(t)(T-\theta). \tag{39}$$

This is an interesting result. It shows that heat flux is proportional to temperature difference between the thermal bath and the system. This is quite similar to Newton's law of cooling. But from the perspective of system-thermal bath interaction one can comment that the above relation is a law of heating. An integrated form of the above equation can be read as

$$Q = \tfrac{3}{2}k_B T[1-\chi^2(t)]$$
$$= \tfrac{3}{2}k_B\theta. \tag{40}$$

Now one can define the heat capacity at nonequilibrium state as

$$\frac{dQ}{d\theta} = \frac{3}{2}k_B. \tag{41}$$

Thus the heat capacity of the system is independent of both temperature and time. We now invoke the first law of thermodynamics. Based on this one can write the following relation among heat, work (W), and internal energy as

$$\dot{W} = \dot{\epsilon} - \dot{Q}. \tag{42}$$

An immediate check of the above calculation is that at equilibrium $\dot{\epsilon} = \dot{Q} = \dot{W} = 0$ as $\chi(t) = 0$ then. This is consistent with our natural demand. Using Eqs. (36) and (39) in the above equation one can write that

$$\dot{W} = -mu_0^2\beta(t)\chi^2(t)$$
$$= -mu_0^2\beta(t)\left(1-\frac{\theta}{T}\right). \tag{43}$$

An integrated form of the above equation can be written in terms of nonequilibrium temperature as

$$W = \frac{mu_0^2}{2}\chi^2(t)$$
$$= \frac{mu_0^2}{2}\left(1-\frac{\theta}{T}\right). \tag{44}$$

It is apparent in the above equation that total work done on the particle is maximum at initial time through the introduction of velocity, u_0. The above equation also suggests that W decreases with time as a function of the square of the response function. This decrease is a signature of frictional loss. It is justified as the total work is proportional to the square of the response function. However, in Sec. III, we utilize the general calculations performed in the present section for calculating the properties of some specific stochastic systems.

III. APPLICATION

A. Markovian dynamics

We consider the first application to the Markovian stochastic process. For this case $\gamma(t)$ takes the following form:

$$\gamma(t-t') = 2\gamma_0\delta(t-t'). \tag{45}$$

The response function $\chi(t)$ for such a system happens to be

$$\chi(t) = \mathcal{L}^{-1}\left[\frac{1}{z+\gamma_0}\right] = e^{-\gamma_0 t}. \tag{46}$$

It is clear from Eq. (46) that at $t=0$, $\chi(t=\infty)=0$ and it vanishes at equilibrium. The above equation suggests that $\beta(t) = \gamma_0$ for the Markovian dynamics and the FPE Eq. (12) reduces to the standard form. Using the above equation in the previous section one can calculate all the quantities for the Markovian stochastic dynamics.

B. Non-Markovian dynamics

To capture essential features of the non-Markovian dynamics, we consider an exponentially decaying frictional memory kernel [45,51–56,61–65] which is generally used in the field of non-Markovian dynamics. Then $\gamma(t-t')$ in the present model can be represented as

$$\gamma(t-t') = \frac{\gamma_0}{\tau}\exp\left(\frac{-|t-t'|}{\tau}\right), \tag{47}$$

where τ is the memory time of the non-Markovian dynamics. We shall now discuss the feasibility of finite memory time. The Brownian particle is coupled to the bath modes of vibration and their collective effect on the particle is the Langevin equation of motion. The Fourier transform of the two-time correlation function of the random force depends upon the frequency distribution of the bath modes [1]. It is obvious that if the medium is incompressible like water, the frequency distribution must have a cutoff and the corresponding noise process is then called colored noise. For such a system, the dissipation in the Langevin equation should be present as a memory kernel [Eq. (3)] and the memory time should depend on the collective dynamics of the constituents of the medium. Therefore, for water as a thermal bath the memory time should be of same order of magnitude as that of the vibration time for the water system, $\tau_v^w = 2\pi\sqrt{m_w/K_r^w}$ (m_w being the mass of the water molecule and K_r^w being the spring constant of the spring which connects two water molecules by hydrogen bonds).

We now consider the spectral density [$\rho(\omega)$] of the noise corresponding to the above form of time-dependent friction. According to the WienerKhintchine theorem [1] it is the Fourier transformation of the two-time correlation function shown in Eq. (2) and is given by

$$\rho(\omega) = \frac{6k_BT\eta_0}{(1+\tau^2\omega^2)}. \tag{48}$$

Dependence of the above distribution function on the memory time of the thermal bath is demonstrated in Fig. 1. It shows that bath modes of higher frequency become less probable as the noise correlation time grows. Using this observation one can describe the behavior of the response function. The response function corresponding to the exponentially decaying memory kernel (47) is given by

$$\chi(t) = e^{-at}\left(\cos bt + \frac{a}{b}\sin bt\right),$$
$$a = \frac{1}{2\tau}, \tag{49}$$
$$b = \left(\frac{\gamma_0}{\tau} - \frac{1}{4\tau^2}\right)^{\frac{1}{2}}.$$

The above equation [Eq. (49)] implies that at $t=0$, $\chi(t=\infty)=0$ and it vanishes at long time. Using this response function one can easily show that

$$\beta(t) = \left|\frac{b\left(1+\frac{a^2}{b^2}\right)\sin bt}{\left(\cos bt + \frac{a}{b}\sin bt\right)}\right|. \tag{50}$$

In the next section, we shall compare the effects of Markovian and non-Markovian baths on the Brownian system based on the results of the present and the previous sections. Before leaving this section we include a discussion here on the response function (RF) which is the key quantity to understand all the results. There is an important difference between Markovian and non-Markovian baths. The response function depends on the damping strength in the former case and it decays exponentially with time. But for the latter case the RF depends on both noise correlation time and damping strength and during the relaxation process $\chi(t)$ decreases as a damped oscillation. The effect of noise correlation time on the RF and the oscillation behavior can be interpreted in the following way. For the Markovian case ($\tau=0$), bath modes of all frequency are equally probable [1]. But in the case of non-Markovian thermal bath, with increase in noise correlation time the frequency distribution of the bath modes becomes narrower (as shown in Fig. 1) with the elimination of higher frequencies. As a result, the equilibration time increases as the thermal bath deviates more from the Markovian nature. We now consider damped oscillating behavior of the response function for the non-Markovian bath. The above explanation based on frequency distribution suggests that the thermal bath would have a signature as an oscillating dynamical system and it would be prominent as the noise correlation time grows. Using this discussion we shall explain the analytical results in the next section.

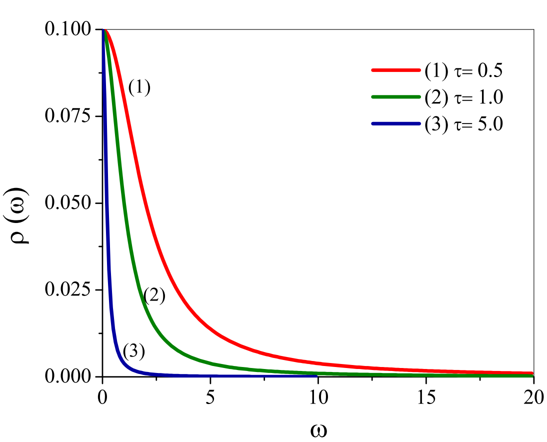

FIG. 1. (Color online) Plot of the spectral density [$\rho(\omega)$] vs frequency (ω) of the bath mode for the parameter set $m=1$, $3k_BT = 0.1$, and $\gamma_0 = 0.5$. (Units are arbitrary.)

IV. COMPARATIVE STUDY ON THE EFFECTS OF MARKOVIAN AND NON-MARKOVIAN THERMAL BATHS ON THE NONEQUILIBRIUM ENTROPIC TEMPERATURE AND ITS LOWER AND UPPER BOUNDS

The time dependence of the entropy production (EP), its upper bound (UB), and the deviation of EP from UB are explored by calculating those quantities as functions of time and plotting the same in Fig. 2. It is clear from Fig. 2 that EP and UB decrease monotonically with time to their equilibrium values for a Markovian thermal bath. Such decrease in the case of quantum stochastic processes has been explained in Ref. [37]. Here we give a brief explanation for our present system following the same line of argument. The effect of noise in expanding the phase-space volume against damping is more prominent initially (when phase-space

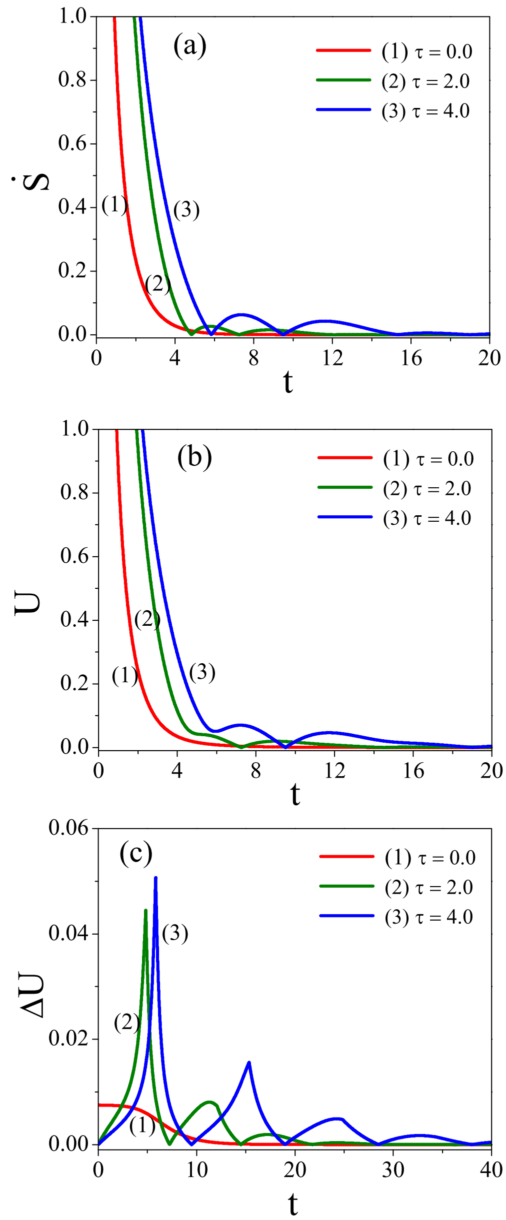

FIG. 2. (Color online) Variation of (a) entropy production ($\dot{S}$), (b) its upper bound (U), and (c) the deviation of entropy production from its upper bound (ΔU) as a function of time for the parameter set $m = 1$, $k_B = 1$, $u_0^2 = 0.03$, $\gamma_0 = 0.5$, and $T = 1.0$. (Units are arbitrary.)

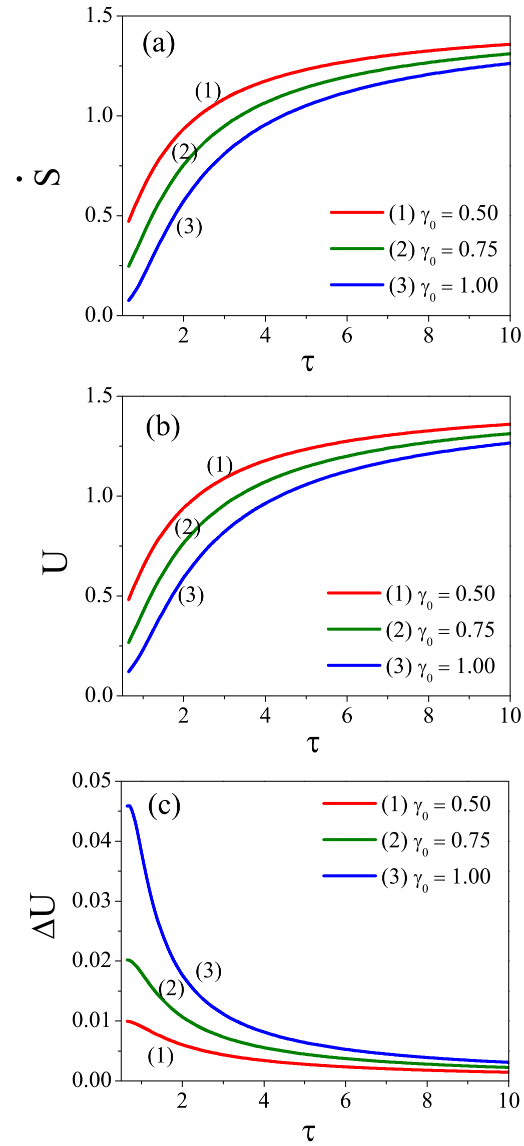

FIG. 3. (Color online) Variation of (a) entropy production ($\dot{S}$), (b) its upper bound (U), and (c) the deviation of entropy production from its upper bound (ΔU) as a function of relaxation time (τ) for the parameter set $m = 1$, $k_B = 1$, $u_0^2 = 0.03$, $t = 2.0$, and $T = 1.0$. (Units are arbitrary.)

volume is small) compared to later times. At equilibrium, the phase-space volume becomes maximum. Hence EP and UB, which are directly associated with phase-space expansion rate, are maximum initially and, with progression of time, they monotonically decrease to their equilibrium value (zero). Such an explanation is consistent with Eqs. (20), (21), and (46). We now consider the case of non-Markovian thermal bath. In this case both entropy production and its upper bound decay nonmonotonically just like a damped oscillation. This is a reflection of coupling of the Brownian particle with the non-Markovian thermal bath which behaves as a quasidynamical system. Now we should consider the memory effect of the thermal bath on the relaxation time. Figure 2 shows that, with increase in τ, the time required to attain equilibrium becomes longer. This is due to the gradual elimination of the bath modes of higher frequencies with increase in noise correlation time that we have mentioned earlier, while explaining the behavior of the response function. We now consider the remaining part of Fig. 2. It shows that the deviation of the upper bound from the entropy production decreases monotonically for the Markovian thermal bath. From the above discussion we realize that at the early stage of the dynamics the entropy production is very high. The fluctuations in entropy production would be maximum during this time. Thus monotonic decrease of entropy production with time suggests a regular decay of the deviation for the Markovian bath. But there are multiple maxima in the variation of the deviation as a function of time for NMTB. The optimum values before equilibrium state are the signature of oscillating behavior of the response function.

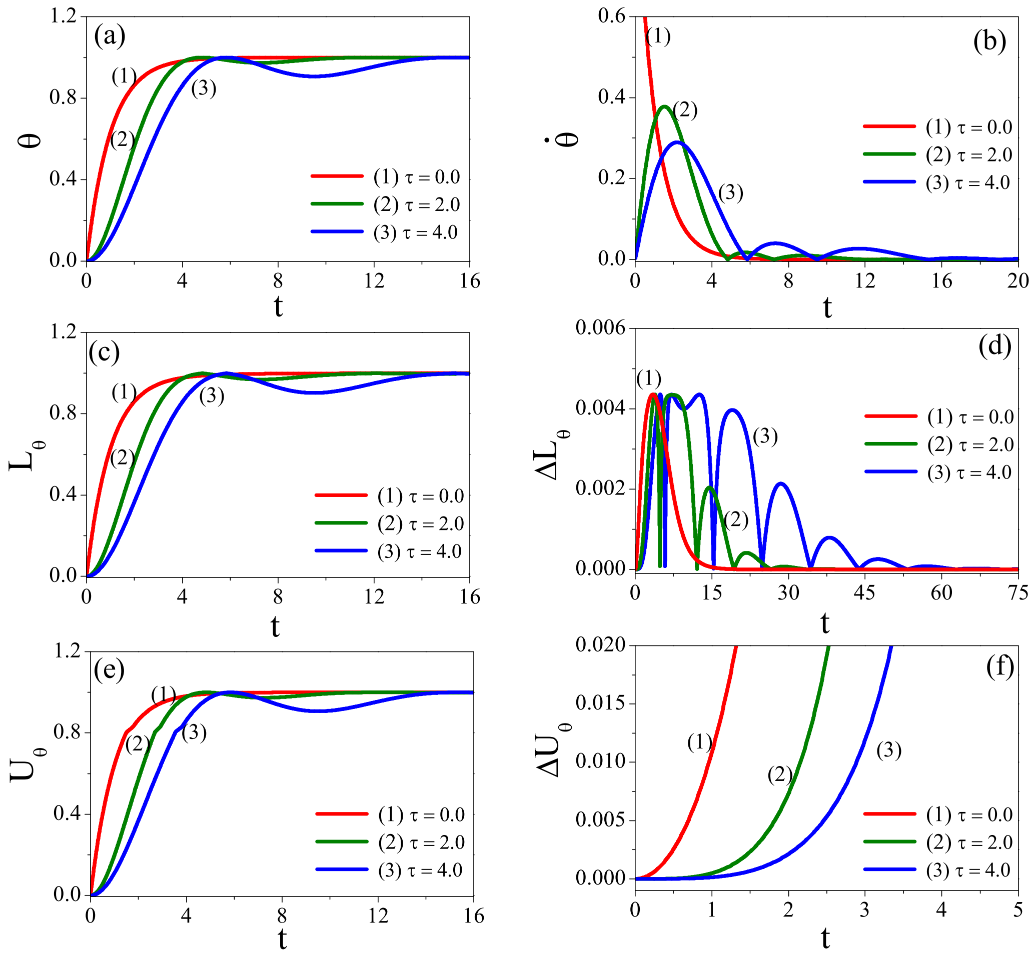

FIG. 4. (Color online) Variation of (a) NET (θ), (b) rate of change ($\dot{\theta}$) of NET, (c) the lower bound (L_θ) of NET, (d) the deviation of NET from its lower bound, (e) the upper bound (U_θ) of NET, and (f) the deviation of NET from its upper bound (ΔU_θ) as function of time (t) for the parameter set $m = 1$, $k_B = 1$, $u_0^2 = 0.03$, $\gamma_0 = 0.5$, and $T = 1.0$. (Units are arbitrary.)

In the next step, we have investigated how the nonequilibrium state of the system is affected by noise correlation time and damping strength. We have calculated entropy production, upper bound of entropy production, and their difference as a function of noise correlation time for different damping strength and plotted in Fig. 3. It depicts that EP and UB increase rapidly at the regime of small correlation and, for an appreciably large value of τ, these quantities slowly rise. One can explain this observation in the following manner. With increase in noise correlation time the system moves away from the equilibrium state where entropy production and its upper bound are higher. Here one should consider another effect of noise correlation time. Strength of fluctuating force reduces with increase in noise correlation time as a result of the elimination of bath modes of higher frequencies. This is implied through the decrease in noise variance [Eq. (2)] as a function of memory time of the bath. It suggests that entropy production and its bound are reduced with increase in noise correlation time. Interplay of these two aspects is the cause of the change of the rate of increase of EP and UB as the noise correlation time grows. One can account for the decrease in the deviation of the bound from the entropy production as a function of noise correlation time (as demonstrated in Fig. 3) considering that reduction in the strength of the fluctuating force. Another feature of Fig. 3 is that, for a given time and τ, both EP and UB get lowered as the damping strength grows since the system gets closer to the equilibrium state then.

In Fig. 4, we have demonstrated the time dependence of nonequilibrium temperature and related quantities. It shows that at an early stage of the dynamics NET rapidly increases as a consequence of the enhancement of the phase-space volume with time. As the time grows, the system attains a larger phase-space volume and accordingly the temperature changes slowly towards the equilibrium value. As discussed earlier, the expected oscillating behavior of the NET for the non-Markovian case appears in Fig. 4.

According to Fig. 4(b) an interesting point is to be noted here. The rate of increase of nonequilibrium temperature during the relaxation process decreases regularly for the coupling of the system with the Markovian thermal bath. But there are multiple maxima in the variation of the rate as a function of time for the case of non-Markovian thermal bath. The first maximum is an interesting one. It implies that an appreciable amount of time is required for the system reservoir interaction to start significantly. During this period $\dot{\theta}$ increases until the maximum extent of interaction occurs. After that it decreases as a result of the relaxation process.

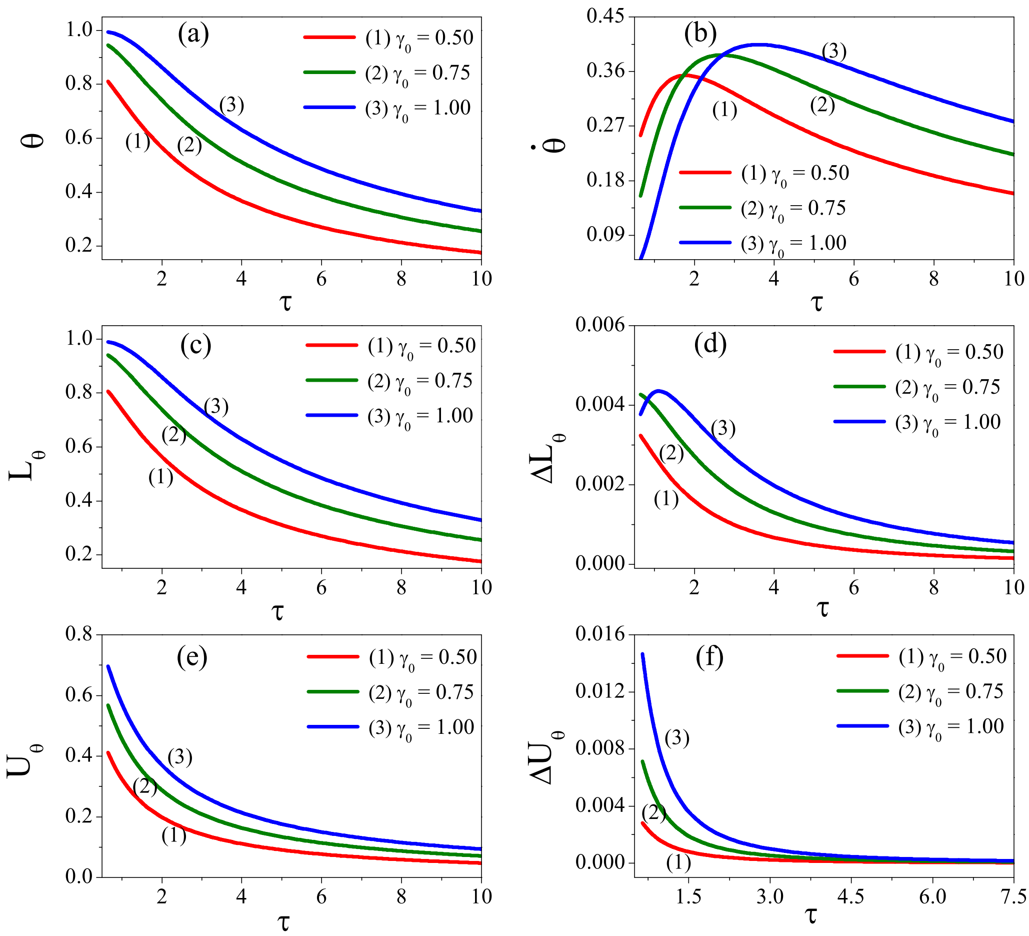

FIG. 5. (Color online) Variation of (a) NET (θ), (b) rate of change ($\dot{\theta}$) of NET, (c) the lower bound (L_θ) of NET, (d) the deviation of NET from its lower bound, (e) the upper bound (U_θ) of NET, and (f) the deviation of NET from its upper bound (ΔU_θ) as a function of relaxation time (τ) for the parameter set $m = 1$, $k_B = 1$, $u_0^2 = 0.03$, and $t = 2.0$ [for (a), (b), (c), and (d)] or $t = 1.0$ [for (c), (d)], and $T = 1.0$. (Units are arbitrary.)

The other optimum values of the rate are the signature of the dynamical behavior of the non-Markovian bath. We now consider the time dependence of lower and upper bounds of the nonequilibrium temperature. It is apparent in Fig. 4 that the bounds as the functions of time behave quite similarly to the NET as we expect. We have plotted the subfigure [Fig. 4(e)] for the upper bound by smooth joining of results of short- and long-time limits. However, the deviation of lower bound from θ varies nonmonotonically with time as shown in Fig. 4(d). For the Markovian bath there is only one optimum value. It implies that, during the rapid growth of phase-space volume, fluctuations of the temperature enhance until the phase-space volume is appreciably large. As the system approaches the equilibrium state with large phase-space volume, the fluctuations gradually diminish. Thus the deviation passes through a maximum. The expected additional optimum values of the deviation appear for a non-Markovian thermal bath due to the oscillating behavior of both NET and its lower bound. We now consider the deviation of the upper bound from the NET. Because of the entropy production term in the denominator of Eq. (29), U_θ has a diverging nature. Near equilibrium, the upper bound should converge to the equilibrium value of NET, i.e., T, as the fluctuation of temperature near the equilibrium state is negligibly small. Therefore, we cannot calculate its exact value near equilibrium by the present method. Keeping that in mind, we have presented the behavior of the deviation at early time in Fig. 4(f). It and Fig. 4(d) imply that the nature of fluctuations of the NET is such that the deviation of the upper bound from the NET is significant if the system is a little bit aged. Another observation is that at a given time the deviation is smaller as the non-Markovian character of the bath grows. This is a result of lowering of the strength of fluctuating force with increase in noise correlation time.

We now explore how the NET and the related quantities depend on the noise correlation time. Variation of these quantities with noise correlation at a given time is demonstrated in Fig. 5. Monotonic decay of nonequilibrium temperature and its bounds as shown in Figs. 5(a), 5(c), and 5(e) is a measure of the deviation of the nonequilibrium state from the equilibrium situation (ES). With increase in noise correlation the system moves away from the equilibrium state as the relaxation time grows. As a signature of that the nonequilibrium temperature and its bounds decrease regularly with increase in noise correlation time. These quantities become larger at a given time as the damping strength grows because the system becomes closer to the equilibrium state then. We now consider the variation of the time derivative of nonequilibrium temperature as a function of noise correlation time. Figure 5 shows that $\dot{\theta}$

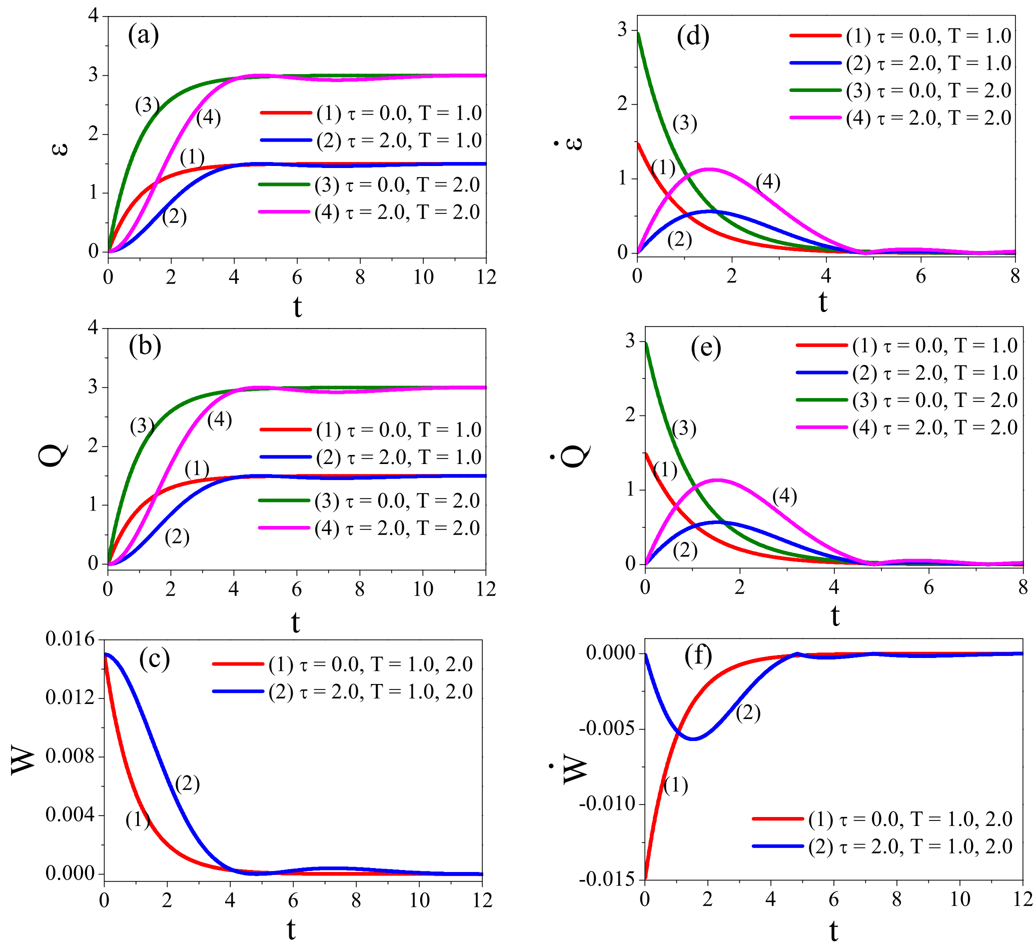

FIG. 6. (Color online) Variation of (a) energy (ϵ) of the system, (b) heat absorbed (Q), (c) work done (W) by the system, (d) rate of change of energy ($\dot{\epsilon}$), (e) rate of change of heat absorption ($\dot{Q}$), and (f) rate of change in work done ($\dot{W}$) as a function of time (t) for the parameter set $m = 1$, $k_B = 1$, $u_0^2 = 0.03$, and $\gamma_0 = 0.5$. (Units are arbitrary.)

passes through a maximum with increase in noise correlation time. At small τ, the system is near the equilibrium state and so $\dot{\theta}$ of the nonequilibrium state (NES) is small. It enhances with further increase in τ due to more deviation of the NES from the ES. This happens up to a critical value of the noise correlation time. After that the strength of the fluctuating force becomes so small that the time derivative of nonequilibrium temperature decreases with increase of τ. Both critical noise correlation time and optimum value of the derivative increase as the damping strength grows. This is a result of enhancement of the strength of the fluctuating force by the strong coupling between system and thermal bath. Based on the above explanation one can account for nonmonotonic and regular variation of the deviation of the NET from its bound as shown in Figs. 5(d) and 5(f).

In Fig. 6, we have presented the variation of the energy of the system (ϵ), the heat absorbed (Q), the work done (W), and related quantities during the journey of the system towards the equilibrium state. It shows that the trend for the change of energy and the total heat flow to the system is quite similar to the change of nonequilibrium temperature with time as we expect. But the total work decreases with time monotonically for the Markovian bath due to the frictional loss and it becomes zero at equilibrium as a signature of the nullifying of average velocity. The variation of W with time is a damped oscillation for the non-Markovian thermal bath as shown in Fig. 6(e). However, the rate of change of the above-mentioned quantities with time shows optimum behavior for the non-Markovian bath. One can explain this aspect using an earlier discussion in the context of Fig. 4(b). We now demonstrate the variation of energy, heat, and work and their time derivatives with memory time of the thermal bath in Fig. 7. It is to be mentioned here that one can explain this figure based on the similar argument given while discussing Fig. 5.

V. CONCLUSION

In this article, we have studied the equilibration process *in detail* for the non-Markovian thermal bath driven Brownian motion in terms of information entropy and nonequilibrium entropic temperature. We have calculated these and related quantities based on the generalized Fokker-Planck description corresponding to the generalized Langevin equations of motion. We have also calculated some thermodynamic quantities like the internal energy change, heat, and work associated with the process and their time derivatives. Our study may be summarized through the following major points.

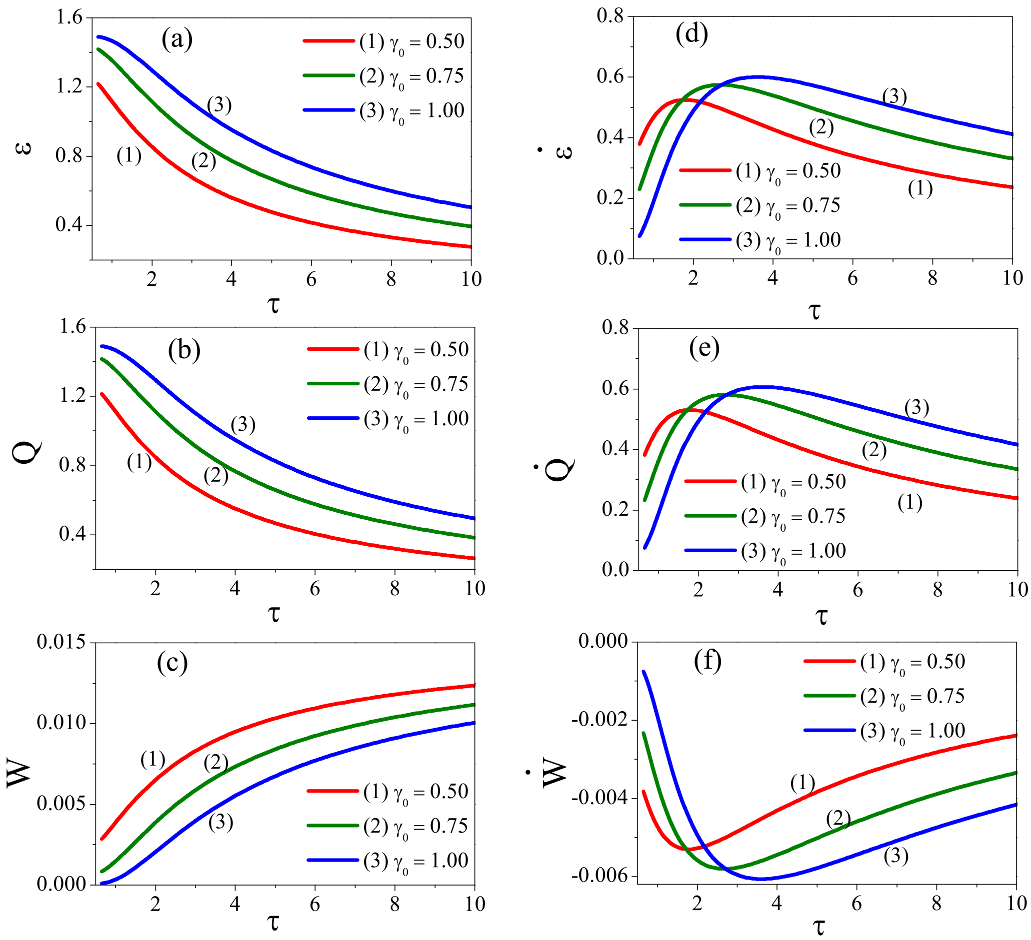

FIG. 7. (Color online) Variation of (a) energy (ϵ) of the system, (b) heat absorbed (Q), and (c) work done (W) by the system, (d) rate of change of energy ($\dot{\epsilon}$), (e) rate of change of heat absorption ($\dot{Q}$), and (f) rate of change in work done ($\dot{W}$) as a function of relaxation time (τ) for the parameter set $m = 1$, $k_B = 1$, $u_0^2 = 0.03$, $t = 2.0$, and $T = 1.0$. (Units are arbitrary.)

(i) We have calculated properties of the system at a nonstationary state in terms of the nonequilibrium temperature.

(ii) Near equilibrium, the rate of heat flow to the system is proportional to the difference between temperature of the thermal bath and the nonequilibrium temperature of the system. This is quite similar to Newton's law of cooling. But from the perspective of system reservoir interaction one can comment that the above-mentioned relation is a law of heating.

(iii) We have defined heat capacity at a nonequilibrium state. It is independent of both time and NET.

(iv) Entropy production, its upper bound, and their difference decrease monotonically during the relaxation process when the system is coupled with the Markovian thermal bath. But for the non-Markovian thermal bath the decay pattern is quite similar to damped oscillation, which may be considered as a signature of the quasidynamical behavior of the bath. The relaxation time increases as the non-Markovian character of the bath grows.

(v) The enhancement of the memory time or the strength of fluctuating force results in the suppression of the increase in entropy production and its bound. The rate of decrease of the deviation of the entropy production from the upper bound also gets suppressed with increase in memory time.

(vi) There exists a lower as well as an upper bound to the Shannon entropic temperature. Nonequilibrium temperature and its bounds increase regularly to the equilibrium value for the case of the Markovian thermal bath (MTB). But in the case of the non-Markovian thermal bath (NMTB), these quantities grow with an oscillation. The rate of change of the temperature gets suppressed monotonically with the progression of time for MTB. Multiple maximum appear for the NMTB, out of which the first maximum is an interesting one. It suggests that a certain time is required for the strengthening of the system-bath interaction for the NMTB. The time dependence of the deviation of the nonequilibrium temperature from its lower bounds is also interesting. It rises up to a critical time and then decreases monotonically to the equilibrium value for the Markovian thermal bath. But, in the other case, multiple optimum values appear. The deviation of the NET from its upper bound also increases at the early stage of dynamics. Because of the limitation of the present method we could not predict its long-time behavior. But intuitively one can say that both the deviations as a function of time may behave similarly.

(vii) Nonequilibrium temperature and its bounds decrease regularly with increase in noise correlation time. But there is an optimum value in the variation of the time derivative of NET as a function of memory time of the non-Markovian thermal bath. The optimum behavior also occurs in the change of deviation (of the nonequilibrium temperature from its lower bounds) with increase in noise correlation time at the large damping limit.

(viii) The time variation of the internal energy and the total heat flow to the system are quite similar to the variation of the nonequilibrium temperature as a function of time. But the same for the total work done on the system is completely opposite. It may be noted here that their rate of change with time again implies that an appreciable time is required to develop maximum interaction between the system and the non-Markovian thermal bath.

(ix) Finally, the variation of the internal energy and the total heat flow to the system with noise correlation time is the same as in the case of nonequilibrium temperature. But the change of total work as a function of noise correlation time follows the opposite pattern.

Keeping in mind the role of temperature on the natural phenomena, one may comment that the nonequilibrium temperature would get strong attention in various fields of basic science from the following perspectives: (a) its effect on the natural phenomena at the nonstationary state and (b) understanding of the path of the journey from a given nonequilibrium state to an equilibrium state. The present study has been completed under these guidelines. It corresponds to the Brownian motion in the condensed phase which covers a large area in the field of nonequilibrium statistical mechanics. Thus the present calculation may find application in different contexts and give support to the formation of a new branch based on the newly born quantity [30], nonequilibrium temperature. Following the present method, study of NET of a Brownian particle in the presence of Lorentz force or force derived from the potential energy may appear elsewhere. One may also extend the present study for the quantum non-Markovian thermal bath.

ACKNOWLEDGMENT

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[1] H. Risken, *The Fokker-Planck Equation: Methods of Solution and Applications* (Springer-Verlag, Berlin, 1984).

[2] E. T. Jaynes, in *Statistical Physics*, edited by W. K. Ford (Benjamin, New York, 1963).

[3] A. Katz, *Statistical Mechanics* (Freeman, San Francisco, 1967).

[4] B. R. Frieden, *Physics from Fisher Information* (Cambridge University Press, Cambridge, England, 1998).

[5] D. Daems and G. Nicolis, Phys. Rev. E **59**, 4000 (1999).

[6] B. C. Bag and D. S. Ray, J. Stat. Phys. **96**, 271 (1999).

[7] B. C. Bag, S. K. Banik, and D. S. Ray, Phys. Rev. E **64**, 026110 (2001); B. C. Bag, *ibid.* **66**, 026122 (2002).

[8] B. C. Bag, Phys. Rev. E **65**, 046118 (2002); B. Q. Ai, X. J. Wang, G. T. Liu, and L. G. Liu, *ibid.* **67**, 022903 (2003); A. Baura, M. K. Sen, and B. C. Bag, Eur. Phys. J. B **75**, 267 (2010); Phys. Rev. E **82**, 041102 (2010).

[9] J. I. Jiménez-Aquino, Phys. Rev. E **82**, 051118 (2010); H. Jiang, T. Xiao, and Z. Hou, *ibid.* **83**, 061144 (2011); T. Koide and T. Kodama, *ibid.* **83**, 061111 (2011).

[10] B. R. Frieden, A. Plastino, A. R. Plastino, and B. H. Soffer, Phys. Rev. E **60**, 48 (1999).

[11] S. Kullback, *Information Theory and Statistics* (Wiley, New York, 1959).

[12] M. Raviculé, M. Cassas, and A. Plastino, Phys. Rev. A **55**, 1695 (1997).

[13] A. R. Plastino, H. G. Miller, and A. Plastino, Phys. Rev. E **56**, 3927 (1997).

[14] A. Plastino, A. R. Plastino, and H. G. Miller, Phys. Lett. A **235**, 129 (1997).

[15] H. Qian, Phys. Rev. E **65**, 016102 (2001).

[16] D. V. Gonzaler, M. Mayorga, J. Orozco, and L. R. Salazar, J. Chem. Phys. **118**, 6989 (2003).

[17] U. Seifert, Phys. Rev. Lett. **95**, 040602 (2005).

[18] M. Esposito, U. Harbola, and S. Mukamel, Phys. Rev. E **76**, 031132 (2007).

[19] U. Seifert, Eur. Phys. J. B **64**, 423 (2008).

[20] M. Hoyuelos, Phys. Rev. E **79**, 051123 (2009).

[21] A. Saha, S. Lahiri, and A. M. Jayannavar, Phys. Rev. E **80**, 011117 (2009).

[22] P. Hick and G. Stevens, Astron. Astrophys. **172**, 350 (1987).

[23] J. B.-Jarvis, M. Racine, and J. Alameddine, J. Math. Phys. (NY) **30**, 1459 (1989).

[24] Y. Alhassid and R. D. Levine, J. Chem. Phys. **67**, 4321 (1977).

[25] Y. Alhassid and R. D. Levine, Phys. Rev. A **18**, 89 (1978).

[26] D. Otero, A. Plastino, A. N. Proto, and G. Zannoli, Phys. Rev. A **26**, 1209 (1982).

[27] D. Otero, A. Plastino, A. N. Proto, and G. Zannoli, Z. Phys. A **316**, 323 (1984).

[28] T. C. Schmidt, H. Ries, and W. Spirkl, Phys. Rev. E **75**, 021108 (2007).

[29] D. Alonso, R. Artuso, G. Cassati, and I. Guarneri, Phys. Rev. Lett. **82**, 1859 (1999); D. Alonso, A. Ruiz, and I. de Vega, Phys. Rev. E **66**, 066131 (2002); B. Li and J. Wang, Phys. Rev. Lett. **91**, 044301 (2003); S. Denisov, J. Klafter, and M. Urbakh, *ibid.* **91**, 194301 (2003); S. Lepri, R. Livi, and A. Politi, Phys. Rep. **377**, 1 (2003); X.-P. Zhang and J.-D. Bao, Phys. Rev. E **73**, 061103 (2006).

[30] K. R. Narayanan and A. R. Srinivasa, Phys. Rev. E **85**, 031151 (2012).

[31] J. Casas-Vazquez and D. Jou, Rep. Prog. Phys. **66**, 1937 (2003).

[32] T. Hatano and D. Jou, Phys. Rev. E **67**, 026121 (2003).

[33] E. Bertin, K. Martens, O. Dauchot, and M. Droz, Phys. Rev. E **75**, 031120 (2007).

[34] J. L. Garden, J. Richard, and H. Guillou, J. Chem. Phys. **129**, 044508 (2008).

[35] W. G. Hoover and C. G. Hoover, Phys. Rev. E **77**, 041104 (2008).

[36] A. Criado-Sancho, D. Jou, and J. Casas-Vazquez, Phys. Lett. A **372**, 2172 (2008).

[37] S. Ray, A. Baura, and B. C. Bag, Phys. Rev. E **89**, 032148 (2014).

[38] D. L. Hasha, T. Eguchi, and J. Jonas, J. Chem. Phys. **75**, 1571 (1981).

[39] S. P. Velsko and G. R. Fleming, J. Chem. Phys. **76**, 3553 (1982).

[40] S. P. Velsko, D. H. Waldeek, and G. R. Fleming, J. Chem. Phys. **78**, 249 (1983).
[41] K. M. Kerry and G. R. Fleming, Chem. Phys. Lett. **93**, 322 (1982).
[42] P. Hänggi, H. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[43] R. F. Gorte and J. T. Hynes, J. Chem. Phys. **73**, 2715 (1980).
[44] P. Hänggi and F. Mojtabai, Phys. Rev. A **26**, 1168 (1982).
[45] B. Bagchi and D. W. Oxtoby, J. Chem. Phys. **78**, 2735 (1983).
[46] F. Marchesoni and P. Grigolini, Physica A **121**, 269 (1983); E. Guàrdia, F. Marchesoni, and M. San Miguel, Phys. Lett. A **100**, 15 (1984).
[47] G. R. Haynes, G. A. Voth, and E. Pollak, J. Chem. Phys. **101**, 7811 (1994).
[48] D. Banerjee, B. C. Bag, S. K. Banik, and D. S. Ray, Phys. Rev. E **65**, 021109 (2002).
[49] D. Banerjee, S. K. Banik, B. C. Bag, and D. S. Ray, Phys. Rev. E **66**, 051105 (2002).
[50] D. Banerjee, B. C. Bag, S. K. Barik, and D. S. Ray, J. Chem. Phys. **120**, 8960 (2004).
[51] B. C. Bag, C. K. Hu, and M. S. Li, Phys. Chem. Chem. Phys. **12**, 11753 (2010).
[52] P. K. Ghosh, M. S. Li, and B. C. Bag, J. Chem. Phys. **135**, 114101 (2011).
[53] A. Baura, M. K. Sen, G. Goswami, and B. C. Bag, J. Chem. Phys. **134**, 044126 (2011).
[54] A. Baura, M. K. Sen, and B. C. Bag, Chem. Phys. **417**, 30 (2013).
[55] A. Baura, S. Ray, M. K. Sen, and B. C. Bag, J. Appl. Phys. **113**, 124905 (2013).
[56] S. Ray, D. Mondal, and B. C. Bag, J. Chem. Phys. **140**, 204105 (2014).
[57] S. A. Adelman, J. Chem. Phys. **64**, 124 (1976).
[58] T. Cover and J. Thomas, *Elements of Information Theory*, 2nd ed. (Wiley, New York, 2006).
[59] B. R. Frieden, Opt. Lett. **14**, 199 (1989).
[60] B. R. Frieden, J. Mod. Opt. **35**, 1297 (1988).
[61] B. C. Bag, J. Chem. Phys. **119**, 4988 (2003).
[62] G. Goswami, B. Mukherjee, and B. C. Bag, Chem. Phys. **312**, 47 (2005).
[63] P. Majee, G. Goswami, and B. C. Bag, J. Stat. Mech.: Theory Exp. (2008) P11015..
[64] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976).
[65] S. Okuyama and D. W. Oxtoby, J. Chem. Phys. **84**, 5830 (1986).