Fluctuation-Dissipation Theorem for Event-Dominated Processes

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(Received 17 April 2007; revised manuscript received 10 May 2007; published 6 July 2007)

We study a system whose dynamics are driven by non-Poisson, renewal, and nonergodic events. We show that external perturbations influencing the times at which these events occur violate the standard fluctuation-dissipation prescription due to renewal aging. The fluctuation-dissipation relation of this Letter is shown to be the linear response limit of an exact expression that has been recently proposed to account for the luminescence decay in a Gibbs ensemble of semiconductor nanocrystals, with intermittent fluorescence.

DOI: [10.1103/PhysRevLett.99.010603](https://doi.org/10.1103/PhysRevLett.99.010603)

PACS numbers: 05.20.-y, 05.40.Fb, 05.60.-k

The importance of the fluctuation-dissipation theorem (FDT) [1] in statistical physics has a long history, ranging from the 1905 Einstein paper on Brownian motion and Onsager's regression hypothesis [2] to the more recent work of Kubo [3], whose linear response theory (LRT) is in fact considered by Lee [4] to be the basic theoretical tool for the ergodic condition produced by Hamiltonian systems.

The main purpose of this Letter is to go beyond the ergodic condition and to propose a generalization of FDT compatible with the anomalous properties of intermittent fluorescence, denoted as blinking quantum dots (BQD) [5], including the important renewal property [6]. We note that Verberk *et al.* [7], using only the renewal and nonexponential distribution revealed by experimental observation, predicted an inverse power-law luminescence decay fitting the experiment results. They did not, however, make the connection between their prediction and the breakdown of FDT. To establish a connection between the theoretical prediction of Verberk *et al.* and the FDT breakdown, we write the most general form of the response of a physical system to a time-dependent perturbation:

$$\Pi(t) \equiv \langle A(t) \rangle = \epsilon \int_0^t \chi_{AB}(t, t') \xi_P(t') dt', \quad (1)$$

where A is a system variable, whose mean value in the absence of perturbation is assumed to vanish. Another system variable B is coupled to the time-dependent perturbation $\xi_P(t)$ of strength ϵ and $\chi_{AB}(t, t')$ is called the response function. In the recent condensed matter literature [1] the assumption is made that the external perturbation corresponds to adding to the unperturbed Hamiltonian the interaction term $H_{\text{pert}} = \epsilon B \xi_P(t)$, and the adoption of the Kubo approach [3] is shown to generate the response function

$$\chi_{AB}(t, t') = \frac{d}{dt'} \langle A(t) B(t') \rangle, \quad (2)$$

where the brackets denote an average on either the classical or the quantum equilibrium probability distribution. This simple formula does not imply that the correlation function depends on $t - t'$, and is consequently a generalization of the LRT of Kubo [3] obtained using Liouville or Liouville-like equations that determine the time evolution of the variable probability.

Herein we shift the focus from variables to events, an event being a collision that may produce an abrupt change in the value of a variable. We assume these events to be the renewal, non-Poisson, and nonergodic events studied by Barkai and co-workers [8], that $A = B = \xi_S$ and that the variable ξ_S has only two distinct values, $\xi_S = \pm 1$. Finally, we assume that the external perturbation changes the prescription that determines the times at which events occur, namely, the times at which the variable ξ_S may, or may not, change its sign. This final assumption reveals the lack of a Hamiltonian formalism, a condition shared by Refs. [5,7].

We define the nonstationary autocorrelation function

$$\Psi(t, t') \equiv \langle \xi_S(t) \xi_S(t') \rangle, \quad (3)$$

which is an average over a Gibbs ensemble derived from the non-Poisson renewal theories of Refs. [8,9] rather than from the distribution probability of a Hamiltonian generated equation of motion. Thus we express the central result of this Letter by the event-dominated fluctuation-dissipation theorem (EDFDT)

$$\chi(t, t') = -\frac{d}{dt} \Psi(t, t') = \psi(t, t'), \quad (4)$$

where $\psi(t, t')$ is the waiting-time distribution density of age t' [8,9].

Note that Eq. (4), as well as Eq. (2), is a generalization of the Kubo FDT [3]. When $\Psi(t, t') \neq \Psi(t - t')$, $(d/dt)\Psi(t, t')$

can be significantly different from $(d/dt')\Psi(t, t')$. In this Letter we show that when the nonstationary condition is produced by the nonergodic non-Poisson events discussed by Barkai and co-workers [8], the correct generalization of the FDT is given by Eq. (4).

To derive the EDFDT we use the stochastic Liouville equation of Kubo [10,11], which, in a discrete time representation, yields the matrix equation

$$\mathbf{f}(t+1) - \mathbf{f}(t) = -\frac{1}{2} \begin{bmatrix} r_+(t) & -r_-(t) \\ -r_+(t) & r_-(t) \end{bmatrix} \mathbf{f}(t), \quad (5)$$

where $\mathbf{f}(t) \equiv (f_1(t), f_2(t))$ denotes a two-dimensional vector, whose components $f_1(t)$ and $f_2(t)$ are the probabilities that the system is in the state $|1\rangle$ and $|2\rangle$, respectively, at time t . We refer to $\mathbf{f}(t)$ as a *stochastic trajectory*. To explain the meaning of Eq. (5), let us consider the unperturbed case, where $r_+(t) = r_-(t) = r_0(t)$. The unperturbed function $r_0(t)$ is a fluctuating quantity that is zero except when an event occurs, at which time it takes on the value of 1. Thus, Eq. (5) yields the transition $(f_1(t), f_2(t)) \rightarrow (1/2, 1/2)$, as can be easily checked using the property $f_1(t) + f_2(t) = 1$. Consequently, when $r_0(t) = 1$ at all times, Eq. (5) becomes equivalent to an ordinary Markov master equation forcing the system to reach equilibrium in one time step. If the time distance between two consecutive times at which $r_0(t) = 1$ is not fixed and is given by the nonexponential waiting-time distribution $\psi(\tau)$, averaging over the fluctuations of $\mathbf{f}(t)$ yields a non-Markovian master equation [9]. In conclusion, Eq. (5) is a way to realize a physical condition equivalent to that prescribed by the continuous time random walk (CTRW) approach [11,12] without building up a generalized master equation (GME). The direct use of the GME would make it difficult, if not impossible, to deal with a perturbation changing the event-occurrence time. The adoption of Eq. (5), on the contrary, simplifies the formalism to take into account the influence of a perturbation on the event-occurrence time. To realize this condition we limit ourselves to assuming that in a single stochastic trajectory events cannot occur at the same time in $|1\rangle$ and $|2\rangle$, except at time $t = 0$, where we set the initial condition $r_+(0) = r_-(0) = 1$, which allows us to keep aging under control, according to the prescriptions of Refs. [8,9].

The solving of (5) is facilitated using

$$\Sigma(t) = f_1(t) - f_2(t) \quad (6)$$

to obtain the difference equation

$$\Sigma(t) = [1 - S(t-1)]\Sigma(t-1) - D(t-1), \quad (7)$$

where the difference variable is given by

$$D(t) \equiv [r_+(t) - r_-(t)]/2 \quad (8)$$

and the sum variable is given by

$$S(t) \equiv [r_+(t) + r_-(t)]/2. \quad (9)$$

Equation (7) is solved subject to the initial condition $\Sigma(0) = 0$, to yield

$$\Sigma(t) = - \sum_{t'=0}^{t-1} D(t') Q(t, t'), \quad (10)$$

where

$$Q(t' + 1, t') \equiv 1, \quad (11)$$

and, for $t > t' + 1$,

$$Q(t, t') \equiv \prod_{j=1}^{t-t'-1} [1 - S(t-j)]. \quad (12)$$

The function $Q(t, t')$ is always equal to 1 if no event occurs in between times t' and $t > t'$. Note that the preparation condition $r_+(0) = r_-(0) = 1$ yields $\Sigma(1) = 0$, which extends to $t = 1$ the initial condition $\Sigma(0) = 0$.

Using the form of the difference variable, we rewrite the formal solution (10) for a single stochastic trajectory as

$$\Sigma(t) = -\frac{1}{2} \sum_{t'=0}^{t-1} r_+(t') Q(t, t') + \frac{1}{2} \sum_{t'=0}^{t-1} r_-(t') Q(t, t'). \quad (13)$$

The statistical average over a Gibbs ensemble of stochastic trajectories yields

$$\begin{aligned} \Pi(t) &\equiv \langle \Sigma(t) \rangle \\ &= -\frac{1}{2} \sum_{t'=0}^{t-1} \langle r_+(t') Q(t, t') \rangle + \frac{1}{2} \sum_{t'=0}^{t-1} \langle r_-(t') Q(t, t') \rangle. \end{aligned} \quad (14)$$

Let us consider, for instance, a trajectory where $r_-(t) = 1$. This is a trajectory corresponding to the first term on the right-hand side of Eq. (13), where an earlier event occurred in the state $|1\rangle$, thereby making this trajectory waiting for the delayed event that is expected to occur in the state $|2\rangle$. To evaluate the statistical average $\langle r_+(t') Q(t, t') \rangle$, we must take into account that no event occurs in either $|1\rangle$ or $|2\rangle$ in between t' and t , thereby setting $Q(t, t') = 1$. Thus,

$$\langle r_+(t') Q(t, t') \rangle = \langle r_-(t) r_+(t') Q(t, t') \rangle = \langle r_-(t) r_+(t') \rangle \quad (15)$$

and

$$\langle r_+(t') Q(t, t') \rangle = \psi^{(-)}(t, t') \pi^{(+)}(t'), \quad (16)$$

where $\pi^{(+)}(t')$ is the probability that an event occurs in $|1\rangle$ at time t' and $\psi^{(-)}(t, t')$ is the probability that an event occurs at time t in $|2\rangle$, given that the stochastic trajectory begins waiting for the occurrence of this event at time t' . In the continuous time limit $\psi^{(-)}(t, t')$ becomes a probability density. Using the same arguments for the second term on the right-hand side of Eq. (14) and adopting the continuous time representation, we obtain

$$\Pi(t) = -\frac{1}{2} \int_0^t dt' [\psi^{(-)}(t, t') \pi^{(+)}(t') - \psi^{(+)}(t, t') \pi^{(-)}(t')], \quad (17)$$

where, of course, $\pi^{(-)}(t')$ [$\pi^{(+)}(t')$] is the probability that an event occurs in $|2\rangle$ [$|1\rangle$] at time t and $\psi^{(+)}(t, t')$ is the probability density that an event occurs at t in $|1\rangle$ given that we begin waiting for the occurrence of this event at time t' .

Note that Eq. (17) is exact, but it does not necessarily fit the requirement of being a linear response to perturbation. To establish the condition for a linear response let us consider the case where the events are generated at each time step with the probability

$$g_{\pm}(t) = \frac{r_0[1 \mp \epsilon \xi_P(t)]}{1 + r_1[1 \mp \epsilon \xi_P(t)]\Delta t}, \quad (18)$$

where $\Delta t \equiv t - t_i$, with t_i denoting the time of occurrence of the last event prior to time t . In the absence of perturbation $\epsilon = 0$ and this resetting time is consistent with the renewal nature of BQD. We note that for very short time intervals $\Delta t \ll 1/r_1$ the probability of generating an event is

$$g_{\pm}(t) = r_0[1 \mp \epsilon \xi_P(t)] \quad (19)$$

and for very long time intervals $\Delta t \gg 1/r_1$ the probability becomes

$$g_{\pm}(t) = \frac{r_0}{1 + r_1\Delta t}. \quad (20)$$

The latter probability is independent of the perturbation because at large time intervals the external perturbation does not produce first-order effects on the distribution of sojourn times between consecutive events. It is straightforward to establish that the unperturbed generator of events is the survival probability

$$\Psi(t) = \left[\frac{T}{t + T} \right]^{\mu-1}, \quad (21)$$

with the power-law index given by $\mu - 1 = r_0/r_1$ and the time $T = 1/r_1$. It is evident that the perturbed generator of events Eq. (18) is a proper representation of a perturbation sufficiently weak as to leave the inverse power-law (complexity) index μ unchanged, leaving only the effect of changing T : $T \rightarrow T[1 \pm \epsilon \xi_P(t)]$. We see that this weak perturbation results in

$$\pi^{(\pm)}(t') \rightarrow \frac{1}{2}[1 \mp \epsilon \xi_P(t')], \quad (22)$$

$$\psi^{(\pm)}(t, t') \rightarrow \psi(t, t'), \quad (23)$$

namely, in the long-time limit the waiting-time distributions of age t' are state independent. By inserting these two conditions into Eq. (17) we get Eq. (1) with the response function defined by the EDFDT of Eq. (4). In fact, according to Ref. [9], $\psi(t, t') = -\frac{d}{dt}\Psi(t, t')$.

To fully appreciate the difference between the FDT given by Eq. (2) and the EDFDT of Eq. (4), we follow Onsager's prescription [1,2] of adopting a steplike perturbation, of intensity ϵ , so that the system moves from the equilibrium condition in the absence of perturbation to the equilibrium condition corresponding to $\epsilon \neq 0$. Inserting the Heaviside unit step function into (1) for the time-dependent perturbation and using for the response function, according to Eq. (2), $\chi(t, t') = \frac{d}{dt'}\Psi(t, t')$, yield by direct integration

$$\Pi(t) = \epsilon[1 - \Psi(t)], \quad (24)$$

with $\Psi(t) \equiv \Psi(t, t' = 0)$, a correlation function proportional to $1/t^{\mu-1}$, which from (24) confirms the close connection between the FDT of Eq. (2) and the correlation function perspective. Adopting the EDFDT from Eq. (4) tells a quite different story, however. In fact, the aged waiting-time distribution is determined by [9] to be

$$\psi(t, t') = \psi(t) + \int_0^{t'} P(t - \tau)\psi(\tau)d\tau, \quad (25)$$

where $P(t) = \sum_1^\infty \psi_n(t)$ is the density of event production of the unperturbed generator and $\psi_n(t)$ is the probability density that the last event of a sequence of n uncorrelated events driven by $\psi(t)$ occurs at time t . Using the Laplace transform technique described in detail in [13], we find in this case that Eq. (1) yields

$$\Pi(t) = \epsilon(\mu - 1) \left[1 - \frac{T}{\mu - 1} P(t) \right]. \quad (26)$$

We see that moving from the variable-based to the event-based FDT produces visible effects. In fact the response for $t \rightarrow \infty$ is proportional to $(\mu - 1)\epsilon$ rather than ϵ , as in Eq. (24). Furthermore the slow process of equilibration is now determined by $P(t)$, which is proportional to $1/t^{2-\mu}$, rather than by $\Psi(t)$, which is proportional to $1/t^{\mu-1}$.

In the case of a harmonic perturbation $\xi_P(t) = \cos(\omega t)$, adopting Eq. (2) generates a strong dependence on the initial condition, called the Freudian effect [14]. This effect is vitiated [15] using the EDFDT of Eq. (4), although also in this latter case as well as in [14] the decay of the system response is proportional to $1/t^{2-\mu}$ [16], which is demonstrably a consequence of renewal aging.

We note that the steplike perturbation is equivalent to observing the time evolution of a two-state process with two different waiting-time distributions, $\psi_+(t)$ and $\psi_-(t)$, moving from an initial condition with half the systems in state $|1\rangle$ and the other half in state $|2\rangle$. Thus we use the same approach as that adopted by the authors of [7] who have successfully studied the BQD fluorescence decay. Notice that $\Pi(t) = p_1(t) - p_2(t)$, where $p_1(t)$ ($p_2(t)$) is the probability of being in the “on” (“off”) state. It is a simple matter to express the corresponding Laplace transforms, $\hat{p}_1(u)$ and $\hat{p}_2(u)$, as

$$\begin{aligned}\hat{p}_1(u) &= \frac{1 - \hat{p}(u)}{u[1 - \hat{p}(u)\hat{q}(u)]}; \\ \hat{p}_2(u) &= \frac{1 - \hat{q}(u)}{u[1 - \hat{p}(u)\hat{q}(u)]},\end{aligned}\quad (27)$$

where $\hat{p}(u)$ and $\hat{q}(u)$ are the Laplace transforms of the probability densities of the on and off experimental times, denoted by $p(t)$ and $q(t)$, respectively. Using the asymptotic inverse power-law probabilities, the probability of being in the fluorescing state can be determined from $\hat{p}(u) = 1 - \kappa_p u^{\mu_1-1}$ and $\hat{q}(u) = 1 - \kappa_q u^{\mu_2-1}$ to be $\hat{p}_1(u) \approx \frac{\kappa_q}{\kappa_p} u^{\mu_1-\mu_2-1}$. The application of a Tauberian theorem to this probability implies that the BQD luminescence intensity can be written

$$I(t) \propto \frac{1}{t^{\mu_1-\mu_2}}, \quad (28)$$

since $I(t) \propto p_1(t)$, in exact agreement with the theoretical predictions of Verberk *et al.* [7] which, in turn, agree with experiment. We interpret (28) as the effect of an abrupt perturbation making $\mu_1 > \mu_2$, thereby producing the luminescence decay.

Using the same approach we get for the Laplace transform of $\Pi(t)$,

$$\hat{\Pi}(u) = \frac{1}{1 - \hat{p}(u)\hat{q}(u)} \frac{\hat{q}(u) - \hat{p}(u)}{u}. \quad (29)$$

The perturbation of μ implies that only the coefficient r_0 depends upon the external perturbation, thereby replacing the event generator of Eq. (18) with

$$g_{\pm}(t) = \frac{r_0[1 \mp \epsilon \xi_P(t)]}{1 + r_1 \Delta t}. \quad (30)$$

This choice would make $\psi^{(\pm)}(t, t')$ state dependent, thus preventing the exact prescription of Eq. (17) from being compatible with a LRT. Therefore to compare the exact result of Eq. (29) with the prediction of the LRT of this Letter, we have to adopt the time perturbation: $T \rightarrow T^{(\pm)} \equiv T(1 \pm \epsilon)$. Thus, we express $p(t)$ and $q(t)$ in terms of $\psi_+(t)$ and $\psi_-(t)$ [9], through the Laplace transform quantities

$$\hat{p}(u) = \frac{\hat{\psi}_+(u)}{2 - \hat{\psi}_+(u)}; \quad \hat{q}(u) = \frac{\hat{\psi}_-(u)}{2 - \hat{\psi}_-(u)}. \quad (31)$$

Then, we use [13]

$$\psi^{(\pm)}(u) = 1 - \Gamma(2 - \mu)(T^{(\pm)}u)^{\mu-1} + (T^{(\pm)}u)/(\mu - 2). \quad (32)$$

Substituting all this into the exact expression (29), after some lengthy but straightforward algebra, in the limiting condition $\epsilon \rightarrow 0$ yields Eq. (26), thereby confirming the EDFDT of this Letter.

In conclusion, herein we establish the linear response prescription

$$\Pi(t) = \epsilon \int_0^t \psi(t, t') \xi_P(t') dt'. \quad (33)$$

The physical meaning of (33) is evident from the event perspective. At time t' the external perturbation $\xi_P(t')$, does not generate an event, but it sets the beginning of the waiting process for the occurrence of an event at the later time t . The aging waiting-time distribution $\psi(t, t')$ acting as a linear response function shows that it is the phenomenon of renewal aging that leads to the EDFDT.

P.G. acknowledges financial support from ARO and Welch through Grants No. W911NF-05-1-0205 and No. B-1577, respectively.

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