Kramers-type effective Reactive Flow in Structured-noise Environments

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Abstract

The non-Markovian features of three typical anomalous diffusing systems are studied by analytically solving the generalized Langevin equation directly driven by three kind of internal structured-noises: harmonic noise, harmonic velocity noise and harmonic acceleration noise, respectively. The time-dependent reaction rate and the transmission coefficient are calculated by using of the reactive flux method. A startling behavior of Kramers-type effective reactive flow is witnessed in the harmonic noise and harmonic acceleration noise systems.

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I. INTRODUCTION

Substantial progresses have been witnessed during the last few years in understanding the phenomenon of anomalous diffusion in disordered media and the statistical thermodynamic cases that dose not obey the law of large number [1–3]. For example, the ergodicity breaking behavior accompanied by a nonunique stationary probability density for the corresponding embedded Markovian dynamics is of great interest both theoretically and experimentally [4–7]. This very feature is believed to originate from a vanishing effective friction of the system [8]. However, noticing that the friction is in general consanguineously related to the stochastic force (or noise) via the fluctuation-dissipation theorem (FDT) [9], thus it is reasonable to argue that whether there exists some relationship between nonergodicity and the noise? Or in other words, is there a kind of noise environment that is relatively more favorable to the diffusing of a reactive particle? Such open problems are of great value to be considered.

Recently, three types of thermal colored noises are proposed which provide three new typical structured-noise environments namely harmonic noise (HN), harmonic velocity noise (HVN) and harmonic acceleration noise (HAN) respectively [10, 11]. Obtaining from solving a second-order stochastic differential equation driven by a Gaussian white noise and so on, these noises are found to have very different types of power spectrums. The long time behavior of them have been carefully investigated showing some newfangled properties but how these noises affect the instantaneous dynamical process of a diffusing particle has not yet been intrinsically elucidated. The primary purpose of this paper is then to report our recent study on these problems focusing in particular on the instantaneous diffusing process of a particle in the structured-noise environments where a Kramer’s-type effective reactive flow is witnessed.

The paper is organized as follows. In Sec. II, the probability of passing over the barrier for a particle diffusing in the structured-noise environments is obtained by analytically solving the generalized Langevin equation (GLE). In Sec. III, the time-dependent reaction rate is calculated by using of the reactive flux method and compared with the classical Kramers rate which is obtained in the case of Gaussian white noise. Sec. IV serves as a summary of our conclusion in which some implicit applications of this work are also discussed.
II. BARRIER PASSING PROBABILITY

Structured-noise environments are generally believed to originate from relevant kind of velocity-dependent system-reservoir couplings [10–13]. Among the three types of structured noises, the simplest one is the harmonic noise (HN) which is a zero-mean Gaussian quasi-monochromatic noise having a power spectrum with a narrow Lorentzian peak centered at a finite frequency instead of zero. It is the solution of a second-order stochastic differential equation driven by a Gaussian white noise and has widely been used in many field of studies [14–16]. The harmonic velocity noise (HVN), which can also be regarded as the time derivative of HN variable [11], can be obtained as a vortex transport of GLE in the presence of a magnetic field or a particle interacting via dipole coupling with a black-body radiation field [17] as well as in the presence of the velocity-coordinate coupling between the system and reservoir [12, 13]. The harmonic acceleration noise (HAN) due to the velocity-velocity coupling in physical situations [11, 13] cannot be procured exactly. However it can be taken as the second-order derivative of HN variable and the GLE driven by this noise can be solved numerically.

For the physical systems which might exhibit an internal structured noise, the GLE describing the motion of a particle can be derived by using of the Zwanzig-Mori projection method [18, 19] or the system-plus-reservoir method [20–22] as

\[ m \ddot{x}(t) + \int_0^\infty dt' \beta(t - t') \dot{x}(t') + \partial_x U(x) = \xi(t), \]

where \( m \) is the mass of the particle, \( U(x) \) the potential energy, \( \beta(t) \) the friction kernel due to the structured noise relating via Kubo’s second kind of fluctuation-dissipation theorem (FDT II) \[ \langle \xi(t)\xi(t') \rangle = mk_B T \beta(t - t') \]

to the correlation function of each noise

\[ \langle \xi(t)\xi(t') \rangle_{\text{HN}} = \frac{\eta}{\mu_1^2 - \mu_2^2} \left( \frac{1}{\mu_1} e^{\mu_1|t-t'|} - \frac{1}{\mu_2} e^{\mu_2|t-t'|} \right); \]

\[ \langle \xi(t)\xi(t') \rangle_{\text{HVN}} = \frac{\eta}{\mu_1^2 - \mu_2^2} \left( -\mu_1 e^{\mu_1|t-t'|} + \mu_2 e^{\mu_2|t-t'|} \right); \]

\[ \langle \xi(t)\xi(t') \rangle_{\text{HAN}} = \eta \delta(t - t') - \langle \xi(t)\xi(t') \rangle_{\text{HN}} - \left( 1 - \frac{2\Omega^2}{\Gamma^2} \right) \langle \xi(t)\xi(t') \rangle_{\text{HVN}}, \]

where \( \eta \) denotes the intensity of a Gaussian white noise, \( \Gamma \) and \( \Omega \) are the damping and frequency parameters in a RLC electric circuit respectively. \( \mu_1 \) and \( \mu_2 \) are the roots of the characteristic equation \( \mu^2 + \Gamma \mu + \Omega^2 = 0 \). \( k_B \) is the Boltzmann constant, \( T \) the temperature of the reservoir.
Due to the initially decoupling property between the system and reservoir, the structured noises are also of vanishing mean and not correlated with the initial velocity. The reduced distribution function of the particle can still be written as the classical Gaussian form

\[ W(x, t; x_0, v_0) = \frac{1}{\sqrt{2\pi\sigma_x(t)}} \exp\left[ -\frac{(x - \langle x(t) \rangle)^2}{2\sigma_x^2(t)} \right]. \]  

(3)

in which the average position \( \langle x(t) \rangle \) and variance \( \sigma_x^2(t) \) can be obtained by Laplace solving the GLE. In the case of an inverse harmonic potential \( U(x) = -\frac{1}{2}m\omega_b^2x^2 \), they are

\[
\langle x(t) \rangle = \left[ 1 + \omega_b^2 \int_0^t H(t')dt' \right] x_0 + H(t)v_0 \
\sigma_x^2(t) = \int_0^t dt_1H(t-t_1)\int_0^{t_1} dt_2\langle \xi(t_1)\xi(t_2) \rangle H(t-t_2)
\]

(4)

(5)

where \( H(t) \) namely the response function can be yielded from inverse Laplace transforming \( \hat{H}(s) = \left[ s^2 + s\beta(s) - \omega_b^2 \right]^{-1} \) with residue theorem \([24]\) by inserting in the Laplace transformation of the friction kernel function

\[
\hat{\beta}(s) = \begin{cases}
\frac{\eta\Omega^2(s+\Gamma)}{\Gamma(s^2+s\Gamma+\Omega^2)}, & \text{HN;} \\
\frac{\eta\Gamma}{s^2+s\Gamma+\Omega^2}, & \text{HVN;} \\
\frac{\eta s\Gamma}{\Gamma(s^2+s\Gamma+\Omega^2)}, & \text{HAN;}
\end{cases}
\]

(6)

approaching from Eq.(2).

Under the influence of thermal fluctuations, the probability density function (PDF) that is originally at one side of the barrier spreads with time, its center moves as well driven by its initial velocity. The probability of passing over the saddle point (namely also the characteristic function) can then be determined mathematically by integrating Eq. (3) over \( x \) from zero to infinity

\[
\chi(x_0, v_0; t) = \int_0^\infty W(x, t; x_0, v_0)dx,
\]

\[
= \frac{1}{2}\text{erfc}\left( -\frac{\langle x(t) \rangle}{\sqrt{2\sigma_x(t)}} \right).
\]

(7)

Generally this will in the long time limit result in a finite real number range from 0 to 1 depending on the initial position and velocity of the particle with 1 for reactive trajectories and 0 for nonreactive ones. However, a fantastic \( \chi(x_0, v_0; t) \) is found in the case of structured-noise environments.

As is shown in FIG. 1, where dimensionless parameters such as \( k_B T = 1.0 \) are used in the calculation, the time-dependent barrier passing probability oscillates almost periodically.
FIG. 1: Time-dependent barrier passing probability $\chi(x_0, v_0; t)$ for various kind of structured-noise environments: HN (solid), HVN (dash) and HAN (dot) plotted in the case of dimensionless parameters: $m = k_B T = \Gamma = \eta = \omega_0 = 1.0$ and $\Omega^2 = 2.0$ as well as $x_0 = 0.0$ and $v_0 = 2.0$.

with time and that the “oscillating frequency” of which in the HAN case is about five times that of the HN or HVN case. This is a very fantastic phenomenon for the structured-noise environments that has never been witnessed before. The origin of this phenomenon may be retrospected to the implicit periodicity of the friction kernel function shown in Eq. (2). On this point one may argue: what a dynamical process on earth is the particle just experiencing; has a diffusing particle really passed the saddle point at $t = t_1$ time? Many of such questions are now becoming wide open to dispute.

However we noticed that although there lives some time-dependent uncertainties the periodical average of the barrier passing probability is near 0.5 for all the cases. This implies there would be on average about one-half amount of all the particles or a fifty-fifty chance for a particle to pass over the saddle point. Therefore the occurrence of an effective barrier escaping behavior is still expected for the particles diffusing in a structured-noise controlled metastable state potential.
III. RATE OF REACTIVE FLOW

Now let us consider the time-dependent barrier passage of a particle diffusing in the structured-noise environments. Instead of solving the related Fokker-Planck equation [20] we derive the rate constant by using the method of reactive flux [25–27]. In the spirit of its calculations, the escape rate of a particle is defined by assuming the initial conditions to be at the top of the barrier, by investigating the ensemble of trajectories which start with identical initial conditions but experience different stochastic histories to determine whether a particle has successfully escaped or not. Mathematically it can be yielded from

\[ k(t) = \frac{m}{Qh} \int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} v_0 W_{st}(x_0, v_0) \delta(x_0 - x_b) \chi(x_0, v_0; t) dv_0 \]

\[ = k_{TST} \frac{m}{k_B T} \int_{-\infty}^{\infty} v_0 \exp \left( -\frac{mv_0^2}{2k_B T} \right) \chi(x_0 = x_b, v_0; t) dv_0, \]

where \( Q \) is the partition function for reactions integrating over the distribution of the ground state; \( W_{st}(x_0, v_0) = H(x_0, v_0)/k_B T \) is an initial Boltzmann form stationary probability distribution with \( H(x_0, v_0) = \frac{1}{2} mv_0^2 + \frac{1}{2} m\omega_b^2 x_0^2 \) representing the system Hamiltonian.

\[ k_{TST} = \frac{k_B T}{Qh} e^{-V_B/k_B T} \]

is the classical rate resulted from the transition state theory (TST) [28–30] in which \( V_B > 0 \) denotes the height of the reactive barrier of the potential energy surface (PES).

In order to make an isolated inspection on the dynamical corrections of \( k(t) \) to the TST rate, it is convenient to define the time-dependent transmission coefficient \( \kappa(t) \) which describes the probability for a particle already escaped from the metastable well to recross the barrier point. By substituting Eqs.(4), (5) and (7) into Eq.(8) we obtain

\[ \kappa(t) = \left( 1 + \frac{m \sigma_x^2(t)}{k_B T H^2(t)} \right)^{-1/2}, \]

which leads immediately to the Kramers formula for the rate constant derived from using a “flux over population” algorithm [31, 32]. However, a even funny behavior of \( \kappa(t) \) is found in the case of structured-noise environments.

As is shown in FIG. 2 where the instantaneous variation of \( \kappa(t) \) for various kind of structured-noise environments is plotted, we meet again in the long time with a periodical or more accurately semi-periodical oscillating \( \kappa(t) \) in the HN and HAN case while a decaying to zero behavior in the HVN case. The stationary average of \( \kappa(t) \) is about 0.43 in the HN case and 0.85 in the HAN case. This is also a startling phenomenon that has never been
FIG. 2: Instantaneous variation of $\kappa(t)$ for various kind of structured-noise environments: HN (solid), HVN (dash) and HAN (dot). Identical dimensionless parameters are used as those shown in FIG.1.

witnessed before. This reveals that there exists on average an effective reactive flow in both HN and HAN noise environments. However, by comparing with those shown in Fig. 1, we can find that although the average barrier escaping probability may exist there is actually no effective reactive flow for a particle diffusing in the HVN noise environment. In other words, all the particles are absorbed in a finite range near the PES saddle point keeping on crossing and recrossing the barrier without contributing to an effective reactive flow. Therefore one may raise from these results that although some very features are believed to originate from the fluctuation and dissipation of the system, actually not all kinds of noise environments are beneficial to the diffusing particle, pessimistically some noise environments are even harmful.

IV. SUMMARY AND DISCUSSION

In summary we have studied in this paper the instantaneous dynamical process of a particle diffusing in various structured-noise environments. The time-dependent barrier passing
probability, reactive rate and transmission coefficient are calculated in the framework of statistical Langevin reactive dynamics. A periodically oscillating barrier passing probability is witnessed in all the cases while an effective reactive flow only in the HN and HAN case. These meaningful results bring us with many totally brand-new understandings about the structured-noise environments.

In further, due to their particular origins, this study will in no doubt renew our knowledge on some crucial problems in many field of studies such as the origin of nonergodicity in anomalous dissipation systems, reaction thermodynamics in chemical events, black-body radiation field studies and even those relevant to nanoscience experiments where the small systems are velocity-dependently coupled to a structured heat bath.

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