Distributional behaviors of time-averaged observables in the Langevin equation with fluctuating diffusivity: Normal diffusion but anomalous fluctuations

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We consider the Langevin equation with dichotomously fluctuating diffusivity, where the diffusion coefficient changes dichotomously over time, in order to study fluctuations of time-averaged observables in temporally heterogeneous diffusion processes. We find that the time-averaged mean-square displacement (TMSD) can be represented by the occupation time of a state in the asymptotic limit of the measurement time and hence occupation time statistics is a powerful tool for calculating the TMSD in the model. We show that the TMSD increases linearly with time (normal diffusion) but the time-averaged diffusion coefficients are intrinsically random when the mean sojourn time for one of the states diverges, i.e., intrinsic nonequilibrium processes. Thus, we find that temporally heterogeneous environments provide anomalous fluctuations of time-averaged diffusivity, which have relevance to large fluctuations of the diffusion coefficients obtained by single-particle-tracking trajectories in experiments.

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I. INTRODUCTION

The law of large numbers plays an important role in statistical physics. In stationary stochastic processes $\boldsymbol{X}_t$, the law of large numbers or the central limit theorem tells us that time-averaged observables such as diffusivity and the ratio of occupation time converge to a constant when the measurement time goes to infinity:

$$\frac{1}{t}\int_0^t O(\boldsymbol{X}_{t'})dt' \to \langle O(\boldsymbol{X})\rangle \quad \text{as } t \to \infty, \tag{1}$$

where t is the measurement time, the observable $O(\cdot)$ is a function of the stochastic process $\boldsymbol{X}_t$, and the ensemble average $\langle O(\boldsymbol{X})\rangle$ must be finite. This property, i.e., the time average equals the ensemble average, is called ergodicity in dynamical systems.

In experiments, time-averaged observables are not constant and thus their fluctuations are inevitable because of the finite measurement times. However, in some stochastic processes describing nonequilibrium phenomena, time-averaged observables are intrinsically random even in the long-time limit because of the breakdown of the law of large numbers or the central limit theorem [1–4]. In other words, they do not converge to a constant even when the measurement time goes to infinity and the fluctuations never disappear. Such anomalous behavior has been studied by infinite ergodic theory in dynamical systems [5]. Infinite ergodic theory is closely related to the above stochastic processes and states that time-averaged observables converge in distribution and the distribution function depends on the invariant measure as well as a class of the observation function [6–9].

The continuous-time random walk (CTRW) is a model of anomalous diffusion, where the mean-square displacement (MSD) increases sublinearly with time, and has been extensively studied to understand anomalous diffusion in disordered materials [10,11] as well as biological environments [12,13]. In the CTRW model, a random walker waits for the next jump and the waiting time is a random variable whose probability density function (PDF) $\rho(\tau)$ follows a power-law distribution

$$\rho(\tau) \sim \frac{c_0}{|\Gamma(-\alpha)|}\tau^{-1-\alpha} \quad (\tau \to \infty), \tag{2}$$

where c_0 is a scale factor. In the CTRW model it was shown that the time-averaged MSD (TMSD), defined as

$$\overline{\delta^2(\Delta;t)} \equiv \frac{1}{t-\Delta}\int_0^{t-\Delta} dt'[\boldsymbol{r}(t'+\Delta)-\boldsymbol{r}(t')]^2, \tag{3}$$

increases linearly with the lag time Δ for $\Delta \ll t$ [14], where $\boldsymbol{r}(t)$ is the position of a particle and t is the measurement time. When $\alpha \leqslant 1$, the mean waiting time diverges, leading to anomalous diffusion [15]. In particular, the TMSD with a fixed lag time Δ does not converge to a constant. Instead, it converges in the distribution as $t \to \infty$ [12,14,16]. Moreover, the PDF of the normalized TMSD, i.e., $\overline{\delta^2(\Delta;t)}/\langle\overline{\delta^2(\Delta;t)}\rangle$, follows a universal distribution called the Mittag-Leffler distribution, which is one of the distributional limit theorems in infinite ergodic theory [17]. This distributional property for a time-averaged observable is called distributional ergodicity in stochastic processes [14,18]. While the generalized Langevin equation is also a model of anomalous diffusion, it has been shown to be ergodic [19,20]. Hence, an anomalous diffusion process does not always imply distributional ergodicity.

Other distributional behaviors have been found in other diffusion processes such as a quenched trap model [21] and stored-energy-driven Levy flight (SEDLF) [18,22], where the PDF of the normalized TMSDs (time-averaged diffusion coefficients) follows other distributions depending on the power-law exponent in the waiting time distribution, the spatial dimension, and parameters controlling jumps of a random walker. It is important to clarify whether fluctuations of time-averaged observables are intrinsic or not, because diffusion coefficients obtained by single-particle-tracking experiments in living cells exhibit large fluctuations [13,23–26]. Such large fluctuations will have relevance to distributional behaviors in stochastic models of anomalous diffusion. Therefore, in this paper we investigate ergodic properties of time-averaged

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diffusivity in temporally heterogeneous diffusion processes related to diffusion in living cells.

II. LANGEVIN EQUATION WITH DICHOTOMOUSLY FLUCTUATING DIFFUSIVITY

To investigate ergodic properties in temporally heterogeneous diffusion processes, we consider the following Langevin equation with fluctuating diffusivity (LEFD):

$$\frac{d\boldsymbol{r}(t)}{dt} = \sqrt{2D(t)}\boldsymbol{w}(t), \tag{4}$$

where $\boldsymbol{w}(t)$ is the d-dimensional white Gaussian noise with $\langle \boldsymbol{w}(t)\rangle = 0$ and $\langle w_i(t)w_j(t')\rangle = \delta_{ij}\delta(t-t')$. On the other hand, the diffusion coefficient $D(t)$ can be a non-Markovian stochastic process. We assume that $D(t)$ and $\boldsymbol{w}(t)$ are statistically independent. Because the diffusion coefficient in Brownian motion is determined by the shape of the particle or the surrounding environment, the LEFD captures the dynamics of a particle changing its shape with time or in a fluctuating environment [27,28]. Such a fluctuating diffusivity was recently observed in peripheral membrane proteins binding specific lipids [29] and a protein crowding environment [30] by molecular simulations. In fact, this model describes the equation of motion for the center of mass of entangled polymer in the reptation model [31] and is related to dynamic heterogeneity in supercooled liquids [32–35]. Moreover, because the stochastic process $D(t)$ is generic, this system includes temporally heterogeneous diffusion models induced by spatial heterogeneity such as the ones studied in [36–38].

In a previous study [39], the relative standard deviation (RSD) of the TMSD in the LEFD was investigated when the stochastic process $D(t)$ is in equilibrium, where the RSD is defined by

$$\Sigma(t;\Delta) \equiv \frac{\sqrt{\langle[\overline{\delta^2(\Delta;t)} - \langle\overline{\delta^2(\Delta;t)}\rangle]^2\rangle}}{\langle\overline{\delta^2(\Delta;t)}\rangle}. \tag{5}$$

In equilibrium processes, the RSD becomes

$$\Sigma^2(t;\Delta) \approx \frac{2}{t^2}\int_0^t ds(t-s)\psi_1(s), \tag{6}$$

where $\psi_1(t)$ is the normalized correlation function of the diffusion coefficients, i.e., $\psi_1(t) \equiv [\langle D(t)D(0)\rangle - \langle D\rangle^2]/\langle D\rangle^2$. Therefore, information on the underlying diffusion coefficient $D(t)$ can be extracted by the RSD analysis [39–41]. Here we investigate ergodic properties of the LEFD especially in nonequilibrium cases. In particular, we consider two-state models for the stochastic process $D(t)$ as studied in [41]. When the mean sojourn time of a state in $D(t)$ diverges, the stochastic process becomes nonstationary, which implies that the system is intrinsically in nonequilibrium. We show normal diffusion yet anomalous fluctuations of the TMSD in the LEFD.

Here we consider dichotomous processes for diffusivity $D(t)$ (see Fig. 1), i.e., $D(t) = D_+$ if the state is positive and $D(t) = D_-$ otherwise (a negative state). Sojourn times for positive and negative states are random variables following different PDFs, $\rho_+(\tau)$ and $\rho_-(\tau)$ for positive and negative states, respectively. We assume that one of the PDFs $\rho_+(\tau)$ follows either a narrow distribution where all moments are finite or a broad distribution of power-law form [Eq. (2)] and that the other PDF follows a power-law distribution whose Laplace transform is given by $\hat{\rho}_-(s) = 1 - a_- s^{\alpha_-} + o(s)$ ($\alpha_- < 1$). In particular, we consider three cases for $\rho_+(x)$: (i) narrow distribution, $\hat{\rho}_+(s) = \sum_{k=0}^{\infty}\frac{m_k}{k!}s^k$; (ii) $\alpha_- < \alpha_+ < 1$, $\hat{\rho}_+(s) = 1 - a_+ s^{\alpha_+} + o(s^{\alpha_+})$; and (iii) $\alpha_- = \alpha_+$, $\hat{\rho}_+(s) = 1 - a_+ s^{\alpha_+} + o(s^{\alpha_+})$, where m_k is the kth moment of sojourn times of the positive state. In what follows we set $\alpha_- = \alpha$. We note that this kind of power-law behavior is observed in supercooled liquids [35]. In two-state processes, one can consider equilibrium and nonequilibrium processes. The PDF of the initial sojourn time is denoted by $\tilde{\rho}^0_\pm(\tau)$, i.e., the probability that the initial sojourn time is in $[\tau,\tau+d\tau]$ under the condition that the initial state is positive is given by $\tilde{\rho}^0_+(\tau)d\tau$. For equilibrium processes, the PDF of the initial sojourn time becomes $\tilde{\rho}^0_\pm(\tau) = \rho^{\rm eq}_\pm(\tau)$, where

$$\rho^{\rm eq}_\pm(\tau) = \frac{1-\hat{\rho}_\pm(s)}{\mu_\pm s}, \tag{7}$$

with $\mu_\pm$ the mean sojourn time for the positive and negative states, respectively. However, we use here $\tilde{\rho}^0_\pm(\tau) = \rho_\pm(\tau)$ as a typical nonequilibrium initial ensemble. Because the PDF in equilibrium exists if and only if both the mean sojourn times $\mu_\pm$ are finite, the process we consider cannot be in equilibrium.

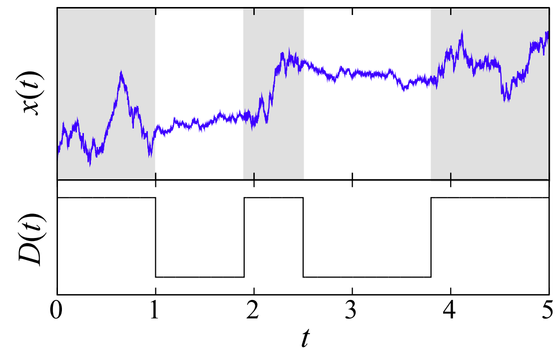

FIG. 1. Trajectory of the Langevin equation with dichotomously fluctuating diffusivity. The lower panel represents the underlying diffusion coefficient.

III. REPRESENTATION OF TIME-AVERAGED MEAN-SQUARE DISPLACEMENT

For $\Delta \ll t$, the TMSD is represented by

$$\overline{\delta^2(\Delta;t)} \underset{\Delta\ll t}{\approx} \frac{\sum_{i=0}^{N_t-1}\int_{t_i}^{t_{i+1}}\delta\boldsymbol{r}^2(\Delta;t')dt' + \int_{t_{N_t}}^{t}\delta\boldsymbol{r}^2(\Delta;t')dt'}{t}, \tag{8}$$

where $\delta\boldsymbol{r}(\Delta;t') \equiv \boldsymbol{r}(t'+\Delta) - \boldsymbol{r}(t')$, t_i is the ith transition time from one state to the other state with $t_0 = 0$, and N_t is the number of transitions up to time t. Since a particle undergoes

Brownian motion in each state, the TMSD becomes

$$\sum_{i=0}^{N_t-1}\int_{t_i}^{t_{i+1}} \delta \boldsymbol{r}^2(\Delta;t')dt' + \int_{t_{N_t}}^{t} \delta \boldsymbol{r}^2(\Delta;t')dt' \underset{\Delta\ll\tau_0}{\approx} \int_0^{T_+(t_{N_t})} \delta \boldsymbol{r}_+^2(\Delta;t')dt' + \int_0^{T_-(t_{N_t})} \delta \boldsymbol{r}_-^2(\Delta;t')dt', \tag{9}$$

where $\delta \boldsymbol{r}_\pm(\Delta;t') \equiv \int_{t'}^{t'+\Delta} dt'' \sqrt{2D_\pm}\boldsymbol{w}(t'')$, $T_\pm(t)$ is the occupation time of the positive and negative states, respectively, up to time t [thus $T_+(t)+T_-(t)=t$], and τ_0 is a characteristic time for the transitions of $D(t)$. The condition of $\Delta \ll \tau_0$ validates the approximation that the state in $[t_i, t_i+\Delta]$ does not change. Moreover, we can represent the TMSD as

$$\overline{\delta^2(\Delta;t)} \approx 2d \frac{\overline{D_+(t)}\, T_+(t) + \overline{D_-(t)}\, T_-(t)}{t}\Delta, \tag{10}$$

where we define a time-averaged diffusion coefficient of each state as $\overline{D_\pm(t)} \equiv \int_0^{T_\pm(t)} \delta \boldsymbol{r}_\pm^2(\Delta;t')dt'/(2dT_\pm(t))$. Hence, TMSDs always show normal diffusion and the time-averaged diffusion coefficient defined as $\overline{D(t)} \equiv \overline{\delta^2(\Delta;t)}/(2d\Delta)$ is given by

$$\overline{D(t)} \approx \overline{D_-(t)} + \left[\overline{D_+(t)} - \overline{D_-(t)}\right]\frac{T_+(t)}{t}. \tag{11}$$

The time-averaged diffusion coefficient $\overline{D(t)}$ is determined by three stochastic variables $\overline{D_\pm(t)}$ and $T_+(t)$. As shown below, the RSD of $T_+(t)$ decays as $t^{-\beta}$ with $\beta < 1/2$ in the limit $t \to \infty$, while those of $\overline{D_\pm(t)}$ decay as $t^{-0.5}$. Thus, in the long-time limit, the fluctuation of $T_+(t)$ is dominant over those of $\overline{D_\pm(t)}$ and thus we can approximate it as $\overline{D_\pm(t)} \simeq D_\pm$. In the long-time limit, statistical properties of occupation time $T_+(t)$ determine those of $\overline{D(t)}$. Hence, under the above approximation, we have

$$\overline{\delta^2(\Delta;t)} \approx 2d \frac{D_- + (D_+ - D_-)T_+(t)}{t}\Delta. \tag{12}$$

This is one of the main results in this paper.

Using Eqs. (10) and (11), we have the RSD [Eq. (5)] $\Sigma^2(t;\Delta) \approx \langle[\overline{D(t)} - \langle\overline{D(t)}\rangle]^2\rangle/\langle\overline{D(t)}\rangle^2$. Under the above approximation, we have the asymptotic behavior

$$\Sigma^2(t;\Delta) \sim \frac{\langle T_+^2(t)\rangle - \langle T_+(t)\rangle^2}{\frac{D_-}{(D_+-D_-)^2}t^2 + \langle T_+(t)\rangle^2}. \tag{13}$$

This is another representation of the RSD by the occupation time in LEFD with two-state diffusivity [see Eq. (6), where the RSD is represented by the correlation function of $D(t)$]. We confirmed that the asymptotic behavior is the same as Eq. (6) in equilibrium processes. Since we neglect fluctuations of $\overline{D_\pm(t)}$, this expression for the RSD is valid only when the right-hand side of Eq. (13) decays more slowly than $t^{-0.5}$. Otherwise, the asymptotic behavior of the RSD is the same as that in Brownian motion (see Appendix A):

$$\Sigma^2(t;\Delta) \sim \frac{\langle[\overline{D_-(t)} - D_-]^2\rangle}{D_-^2} \sim \frac{4\Delta}{3dt}. \tag{14}$$

IV. OCCUPATION TIME STATISTICS

To investigate fluctuations of the TMSD, we consider the occupation time statics for the three cases. Let $g_n^\pm(y;t)$ be the joint probability distribution of the occupation time $T_+(t)=y$ and the number of renewal $N_t = n$ up to time t under the condition that the initial state is positive or negative. Then, we have

$$g_n^\pm(y;t) = \langle \delta(y - T_+(t)) I(t_n \leqslant t < t_{n+1})\rangle_\pm, \tag{15}$$

where $I(t_n \leqslant t < t_{n+1}) = 1$ if the relation $t_n \leqslant t < t_{n+1}$ is satisfied and otherwise 0. The Laplace transform of $g_n^\pm(y;t)$ with respect to y and t is given by

$$\hat{g}_n^\pm(u;s) = \left\langle \int_{t_n}^{t_{n+1}} e^{-st} e^{-uT_+(t)}dt \right\rangle_\pm, \tag{16}$$

where $n = 1,2,\ldots$. For example, if the initial state is positive and $n = 2k$ or $2k+1$, it can be represented as

$$\hat{g}_{2k}^\pm(u;s) = \left\langle \int_{t_{2k}}^{t_{2k+1}} e^{-st} e^{-u[\tau_1+\tau_3+\cdots+\tau_{2k-1}+(t-t_{2k})]}dt \right\rangle, \tag{17}$$

$$\hat{g}_{2k+1}^\pm(u;s) = \left\langle \int_{t_{2k+1}}^{t_{2k+2}} e^{-st} e^{-u(\tau_1+\tau_3+\cdots+\tau_{2k+1})}dt \right\rangle, \tag{18}$$

where τ_k is the kth sojourn time and thus $t_k = \sum_{i=1}^k \tau_i$. Integrating the above equations and using the interindependence of τ_k and τ_l ($k \neq l$), we have

$$\hat{g}_{2k+1}^+(u;s) = \frac{1-\hat{\rho}_-(s)}{s}\hat{\rho}_-^k(s)\hat{\rho}_+^{k+1}(s+u), \tag{19}$$

$$\hat{g}_{2k}^+(u;s) = \frac{1-\hat{\rho}_+(s+u)}{s+u}\hat{\rho}_-^k(s)\hat{\rho}_+^k(s+u). \tag{20}$$

The cases in which the system starts from the negative state can be calculated in a similar way. Then the PDF of $T_+(t)$ is obtained by summing up $g_n^\pm(y;t)$ in terms of n, $g^\pm(y;t) = \sum_{n=0}^\infty g_n^\pm(y;t)$, and thus we have

$$\hat{g}^+(u;s) = \frac{1-\hat{\rho}_-(s)}{s\hat{\rho}(s,u)}\hat{\rho}_+(s+u) + \frac{1-\hat{\rho}_+(s+u)}{(s+u)\hat{\rho}(s,u)}, \tag{21}$$

$$\hat{g}^-(u;s) = \frac{1-\hat{\rho}_+(s+u)}{(s+u)\hat{\rho}(s,u)}\hat{\rho}_-(s) + \frac{1-\hat{\rho}_-(s)}{s\hat{\rho}(s,u)}, \tag{22}$$

where $\rho(s,u) \equiv 1 - \hat{\rho}_+(s+u)\hat{\rho}_-(s)$. In the small s and u limit,

$$\hat{g}^\pm(u;s) \sim \frac{1-\hat{\rho}_-(s)}{s\hat{\rho}(s,u)} + \frac{1-\hat{\rho}_+(s+u)}{(s+u)\hat{\rho}(s,u)}. \tag{23}$$

V. DISTRIBUTIONAL LIMIT THEOREMS

A. Case (i)

From Eq. (23), the Laplace transform of the PDF of $T_+(t)$ for case (i) is given by

$$\hat{g}^\pm(u;s) \sim \frac{a_- s^{\alpha-1} + \mu}{a_- s^\alpha + \mu(s+u)}, \tag{24}$$

where $\mu = m_1$. Using the relation between the moments of $T_+(t)$ and $\hat{g}^\pm(u;s)$, we have the asymptotic behavior of the

nth moment of $T_+(t)$,

$$\langle T_+^n(t)\rangle_\pm = \mathcal{L}^{-1}\left[(-1)^n \frac{\partial^n \hat{g}^\pm}{\partial u^n}(0;s)\right](t) \sim \left(\frac{\mu}{a_-}\right)^n \frac{n!t^{n\alpha}}{\Gamma(1+n\alpha)}, \tag{25}$$

where $\mathcal{L}^{-1}$ is the inverse Laplace transform. Because the TMSD can be represented by $T_+(t)/t$ through Eq. (10), the ensemble average of the TMSD (ETMSD) shows normal diffusion

$$\langle\overline{\delta^2(\Delta;t)}\rangle \sim 2d\left[D_- + \frac{\mu(D_+ - D_-)}{a_-\Gamma(1+\alpha)}\frac{1}{t^{1-\alpha}}\right]\Delta, \tag{26}$$

where we used $\langle\overline{D_\pm(t)}\rangle \sim D_\pm$ and Eq. (25). Because the TMSD converges to $2dD_-\Delta$ as $t\to\infty$, this process seems to be normal diffusion.

In Brownian motion, $\overline{D(t)}$ converges to a constant and the distribution of $\overline{D(t)}$ follows a Gaussian one. Therefore, deviation from Gaussian detects an anomaly of the process. Since $\overline{D(t)}$ is given by Eq. (11) and $\overline{D(t)} \to D_-$, we consider the deviation, i.e., $\delta D_t \equiv \overline{D(t)} - D_-$.

By Eq. (11) we have

$$\frac{\delta D_t}{\langle \delta D_t\rangle} \cong \frac{(\overline{D_-(t)} - D_-)t}{(D_+ - D_-)\langle T_+(t)\rangle} + \frac{T_+(t)}{\langle T_+(t)\rangle}. \tag{27}$$

Here the first term on the right-hand side can be neglected if $\langle[\overline{D_-(t)} - D_-]^2 t^2\rangle = o(\langle T_+(t)^2\rangle - \langle T_+(t)\rangle^2)$. Note that this condition is satisfied when $\alpha > 0.5$ [see Eq. (25)]. By Eq. (25), moments of the normalized occupation time defined by $T_\alpha(t) \equiv T_+(t)/\langle T_+(t)\rangle$ become

$$\langle T_\alpha(t)^n\rangle \sim \frac{n!\Gamma(1+\alpha)^n}{\Gamma(1+n\alpha)} \quad (t\to\infty). \tag{28}$$

When the PDF of a random variable M_α follows the Mittag-Leffler distribution of order α, the Laplace transform is given by

$$\langle e^{-zM_\alpha}\rangle = \sum_{k=0}^{\infty} \frac{\Gamma(1+\alpha)^k z^k}{\Gamma(1+k\alpha)}. \tag{29}$$

Therefore, the distribution of $\delta D_t/\langle\delta D_t\rangle$ is not Gaussian but converges to the Mittag-Leffler distribution when $\alpha > 0.5$ [see Fig. 2(a)]. For $\alpha < 0.5$, the first term in Eq. (27) becomes the leading term and the distribution of $\delta D_t/\langle\delta D_t\rangle$ becomes Gaussian with a mean 0 and variance $2\Delta D_-^2 a_-^2\Gamma(1+\alpha)^2 t^{1-2\alpha}/d(D_+ - D_-)^2\mu^2$. For $\alpha > 0.5$, using Eq. (13) yields

$$\Sigma^2(t;\Delta) \sim \frac{\mu^2(D_+ - D_-)^2 A(\alpha)}{a_-^2 D_-^2 \Gamma(1+\alpha)^2} t^{-2(1-\alpha)}, \tag{30}$$

where $A(\alpha) = \frac{2\Gamma(\alpha+1)^2}{\Gamma(2\alpha+1)} - 1$. This result is consistent with that in [41]. When $D_- = 0$, the RSD does not decay but converges to $\sqrt{A(\alpha)}$, which is exactly the same as that in the CTRW model [12].

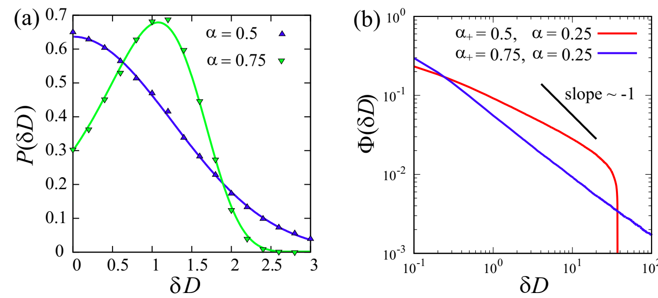

FIG. 2. Distribution of deviations of the time-averaged diffusivity $\delta D \equiv \delta D_t/\langle D_t\rangle$ in (a) case (i) and (b) case (ii) ($D_- = 1$, $D_+ = 10$, and $t = 10^4$). In (a) the Mittag-Leffler distributions are drawn by solid lines. In (b) the vertical axis is the survival probability $\Psi(\delta D) = \int_{\delta D}^{\infty} P(\delta D')\delta D'$ and $\Psi(\delta D) \propto \delta D^{-1}$ is drawn for reference. Squares with colors are the results of numerical simulations. The power-law distributions we used in numerical simulations are described in Appendix B. In case (i), we used the exponential distribution $\rho_+(\tau) = e^{-\tau/\mu}/\mu$ with $\mu = 10^{-2}$.

B. Case (ii)

In this case, Eq. (23) yields the Laplace transform of the PDF of $T_+(t)$:

$$\hat{g}^\pm(u;s) \sim \frac{a_+(s+u)^{\alpha_+-1} + a_- s^{\alpha-1}}{a_+(s+u)^{\alpha_+} + a_- s^\alpha}. \tag{31}$$

The Laplace transform of the first moment $\langle T_+(t)\rangle$ is scaled as

$$\langle \hat{T}_+(s)\rangle = -\left.\frac{\partial \hat{g}^\pm(u;s)}{\partial u}\right|_{u=0} \sim \frac{a_+}{a_-}\frac{1}{s^{2-\delta\alpha}}, \tag{32}$$

where $\delta\alpha = \alpha_+ - \alpha$. Thus, the asymptotic behavior of $\langle T_+(t)\rangle$ becomes

$$\langle T_+(t)\rangle \sim \frac{a_+}{a_-\Gamma(2-\delta\alpha)} t^{1-\delta\alpha}. \tag{33}$$

Moreover, the second moment of $T_+(t)$ is scaled as

$$\langle T_+(t)^2\rangle \sim \frac{2a_+(1-\alpha_+)}{a_-\Gamma(3-\delta\alpha)} t^{2-\delta\alpha}. \tag{34}$$

It follows that the second moment of $T_+(t)/\langle T_+(t)\rangle$ diverges for $t\to\infty$. Using Eqs. (11) and (33) yields the ETMSD

$$\langle\overline{\delta^2(\Delta;t)}\rangle \sim 2d\left[D_- + \frac{a_+(D_+ - D_-)}{a_-\Gamma(2-\delta\alpha)}\frac{1}{t^{\delta\alpha}}\right]\Delta. \tag{35}$$

As in the previous case, TMSD converges to $2dD_-\Delta$ as $t\to\infty$. By Eq. (13) the RSD decays as

$$\Sigma^2(t;\Delta) \sim \frac{2a_+(D_+ - D_-)^2(1-\alpha_+)}{a_- D_-^2\Gamma(3-\delta\alpha)} t^{-\delta\alpha}. \tag{36}$$

This result is also consistent with that in [41].

Although we do not have the limit distribution of $T_+(t)/\langle T_+(t)\rangle$, the tail should be a heavy tail (power-law distribution) because the second moment of $T_+(t)/\langle T_+(t)\rangle$ diverges. By the relation between δD_t and $T_+(t)$, i.e., Eq. (27), we find that the deviations of the time-averaged diffusion coefficient $\delta D_t/\langle\delta D_t\rangle$ are random and the distribution is a nontrivial distribution characterized by a power law [see

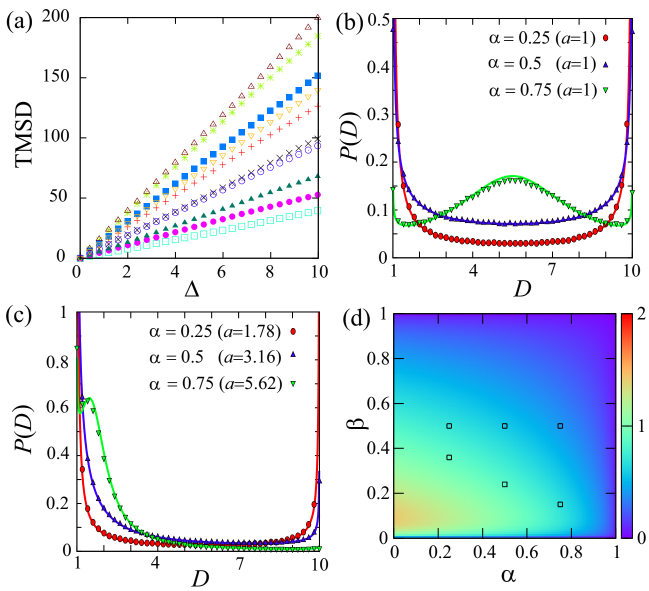

FIG. 3. Anomalous fluctuations of time-averaged diffusivity in case (iii) ($D_- = 1$ and $D_+ = 10$). (a) TMSDs for ten different realizations ($\alpha = 0.5$ and $t = 10^4$). (b) and (c) Distribution of time-averaged diffusion coefficients ($t = 10^3$). Symbols are the results of numerical simulations and solid curves are the theoretical ones. (d) RSD as a function of α and β ($t = 10^5$). Squares with colors are the results of numerical simulations. In numerical simulations, we used the same power-law distribution as in Fig. 2.

Fig. 2(b)]. The situation is similar for the PDF of time-averaged diffusion coefficients in some parameter region of the SEDLF [22].

C. Case (iii)

Contrary to the previous two cases, TMSDs do not converge to a constant in case (iii), whereas TMSD shows normal diffusion [see Eq. (10) and Fig. 3(a)]. Equation (23) yields the Laplace transform of the PDF of $T_+(t)$:

$$\hat{g}^{\pm}(u;s) \sim \frac{a_+(s+u)^{\alpha-1} + a_- s^{\alpha-1}}{a_+(s+u)^{\alpha} + a_- s^{\alpha}}. \tag{37}$$

By Appendix B in [3], Eq. (37) implies that the limit distribution of $T^+(t)/t$ exists,

$$\lim_{t\to\infty} g_{T^+/t}(x) = g_{\alpha,\beta}(x), \tag{38}$$

and the distribution is given by

$$g_{\alpha,\beta}(x) = \frac{(a\sin\pi\alpha/\pi)x^{\alpha-1}(1-x)^{\alpha-1}}{a^2x^{2\alpha} + 2a\cos\pi\alpha(1-x)^{\alpha}x^{\alpha} + (1-x)^{2\alpha}}, \tag{39}$$

where $g_{T^+/t}(x)$ is the PDF of $T_+(t)/t$, $a = a_-/a_+$, and $\beta \equiv 1/(1+a)$. This is the Lamperti generalized arcsine law [2], which is observed for time-averaged drift in superdiffusion [42]. By Eq. (11) the distribution of the time-averaged diffusion coefficient is given by that of $T_+(t)/t$,

$$\Pr[\overline{D(t)} \leqslant x] = \Pr\left(\frac{T_+(t)}{t} \leqslant \frac{x - D_-}{D_+ - D_-}\right). \tag{40}$$

Because the PDF of $T_+(t)/t$ follows the Lamperti generalized arcsine law (39), the PDF of $\overline{D(t)}$ is given by $P_D(x) = g_{\alpha,\beta}(\frac{x-D_-}{D_d})/D_d$, where $D_d = D_+ - D_-$. Figures 3(b) and 3(c) show that the generalized arcsine distribution describes clearly the PDF of the time-averaged diffusion coefficients. Because the mean and second moment of $T_+(t)/t$ are given by $\langle T_+(t)/t\rangle = \beta$ and $\langle (T_+/t)^2\rangle = m(\alpha,\beta) \equiv \beta(\alpha\beta + 1 - \alpha)$, respectively [3], we have the RSD

$$\Sigma(t;\Delta) \sim \sqrt{\frac{D_-^2 + 2D_-D_d\beta + D_d^2 m(\alpha,\beta)}{(D_- + D_d\beta)^2} - 1}. \tag{41}$$

As shown in Fig. 3, theory is in good agreement with numerical results. This fluctuation analysis extracts information on the underlying diffusion process $D(t)$ from single-particle-tracking trajectories, e.g., the power-law exponent α and the asymmetric parameter a.

VI. CONCLUSION

We have shown three distributional limit theorems for time-averaged observables related to diffusivity in the Langevin equation with dichotomously fluctuating diffusivity, where the mean sojourn time of one of the states diverges. By the fluctuation analysis of the TMSD, i.e., RSD analysis and the distribution of the TMSD, one can extract information on statistical properties of the underlying diffusion process, i.e., fluctuating diffusivity. In general, it is difficult to obtain such information from single-particle-tracking trajectories because the ETMSD shows only normal diffusion. Since our analysis can be conducted in all single-particle-tracking experiments, our results are useful for understanding anomalous diffusion properties hidden in usual MSD analysis.

When one of the diffusivity states is zero ($D_- = 0$) in case (i), statistical properties of the TMSD are exactly the same as those in the CTRW model. Therefore, this model is a generalization of the CTRW model. When both diffusion coefficients in the LEFD are not zero, the TMSD asymptotically shows normal diffusion in all cases, whereas fluctuations of the TMSD (deviations of time-averaged diffusion coefficients) are intrinsically random even in the long-time limit of the measurement time. Especially in case (iii), time-averaged diffusion coefficients are intrinsically random and the distribution follows the generalized arcsine law. Therefore, we have found anomalous fluctuations in apparently normal diffusion processes. These anomalous fluctuations are reminiscent of distributional limit theorems in infinite ergodic theory [5–8].

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APPENDIX A: DERIVATION OF EQ. (14)

Here we derive the RSD in Brownian motion with the diffusion coefficient D. Since this process is described by Brownian motion, displacement $\delta\boldsymbol{r}(\Delta;t) \equiv \boldsymbol{r}(\Delta + t) - \boldsymbol{r}(t)$

follows a Gaussian distribution with a mean 0 and variance $2dD\Delta$. The mean TMSD is straightforwardly calculated as $\langle\{\overline{\delta^2(\Delta;t)}\}\rangle = 2nD\Delta$. The second moment of TMSD can be calculated as follows:

$$\begin{aligned}
\langle\{\overline{\delta^2(\Delta;t)}\}^2\rangle &\sim \frac{2}{t^2}\int_0^t dt'\int_{t'}^t dt''\langle\delta\boldsymbol{r}^2(\Delta;t')\delta\boldsymbol{r}^2(\Delta;t'')\rangle\\
&= \frac{2}{t^2}\int_0^t dt'\int_{t'}^{t'+\Delta} dt''\langle\delta\boldsymbol{r}^2(\Delta;t')\delta\boldsymbol{r}^2(\Delta;t'')\rangle + \frac{2}{t^2}\int_0^t dt'\int_{t'+\Delta}^t dt''\langle\delta\boldsymbol{r}^2(\Delta;t')\rangle\langle\delta\boldsymbol{r}^2(\Delta;t'')\rangle\\
&= \frac{2}{t^2}\int_0^t dt'\int_{t'}^{t'+\Delta} dt''\{\langle\delta\boldsymbol{r}^2(t''-t';t')\rangle\langle\delta\boldsymbol{r}^2(\Delta;t'')\rangle + \langle\delta\boldsymbol{r}^4(t'+\Delta-t'';t'')\rangle\\
&\quad + \langle\delta\boldsymbol{r}^2(t'+\Delta-t'';t'')\rangle\langle\delta\boldsymbol{r}^2(t''-t';t'+\Delta)\rangle\} + \frac{2}{t^2}\int_0^t dt'(t-t'-\Delta)(2dD\Delta)^2\\
&= (2dD\Delta)^2\left(1+\frac{4\Delta}{3dt}\right).
\end{aligned} \tag{A1}$$

It follows that the RSD decays as

$$\Sigma^2(t;\Delta) \sim \frac{4\Delta}{3dt} \quad (t\to\infty). \tag{A2}$$

APPENDIX B: NUMERICAL SIMULATION

In numerical simulations we used 10^5 trajectories to calculate the PDFs of δD for cases (i) and (ii) and D for case (iii). To solve the Langevin equation (4) numerically, we used the Euler method, where the time step is $\Delta t = 10^{-3}$. For the stochastic process $D(t)$, we assume that the first sojourn time is also drawn from the same sojourn time distribution, that is, an ordinary renewal process [43]. In other words, we do not consider an equilibrium renewal process. This is because there are no finite relaxation times in all cases we considered. To generate random variables following a power-law distribution, we used a uniform random variable U on $[0,1]$ and transformed it to $\tau_0 U^{-1/\alpha}$, where τ_0 is a cutoff for the smallest value. Thus, we used $\rho_\pm(\tau) = \alpha_\pm\tau^{-1-\alpha_\pm}/\tau_0^{\alpha_\pm}$ for $\tau \geqslant \tau_0$ and 0 for $\tau < \tau_0$, where $\tau_0 = 10^{-3}$. In case (i), we used the exponential distribution for $\rho_+(\tau)$.

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