Fluctuation analysis of time-averaged mean-square displacement for the Langevin equation with time-dependent and fluctuating diffusivity

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(Received 19 November 2014; published 29 September 2015)

The mean-square displacement (MSD) is widely utilized to study the dynamical properties of stochastic processes. The time-averaged MSD (TAMSD) provides some information on the dynamics which cannot be extracted from the ensemble-averaged MSD. In particular, the relative standard deviation (RSD) of the TAMSD can be utilized to study the long-time relaxation behavior. In this work, we consider a class of Langevin equations which are multiplicatively coupled to time-dependent and fluctuating diffusivities. Various interesting dynamics models such as entangled polymers and supercooled liquids can be interpreted as the Langevin equations with time-dependent and fluctuating diffusivities. We derive a general formula for the RSD of the TAMSD for the Langevin equation with the time-dependent and fluctuating diffusivity. We show that the RSD can be expressed in terms of the correlation function of the diffusivity. The RSD exhibits the crossover at the long time region. The crossover time is related to a weighted average relaxation time for the diffusivity. Thus the crossover time gives some information on the relaxation time of fluctuating diffusivity which cannot be extracted from the ensemble-averaged MSD. We discuss the universality and possible applications of the formula via some simple examples.

DOI: 10.1103/PhysRevE.92.032140 PACS number(s): 61.20.Lc, 05.10.Gg, 83.80.Sg

I. INTRODUCTION

The mean-square displacement (MSD) is one of the most commonly utilized quantities to characterize the dynamical properties in experiments, theories, and simulations. Because a single-particle trajectory is a stochastic variable, we need to perform averaging operations. As the averaging operation, the ensemble average is widely employed. The ensemble-averaged MSD (EAMSD) is utilized, for example, to characterize the dynamical properties of particles. In many systems, the EAMSD shows a power-law type time dependence, i.e., the anomalous diffusion:

$$\langle [\boldsymbol{r}(\Delta) - \boldsymbol{r}(0)]^2 \rangle \propto \Delta^{\alpha}. \tag{1}$$

Here $\boldsymbol{r}(t)$ is a position of a particle at time t, Δ is the time difference, $\langle \dots \rangle$ represents the ensemble average, and $\alpha > 0$ is the exponent which characterizes the diffusion behavior ($\alpha < 1$, $\alpha = 1$, and $\alpha > 1$ correspond to the subdiffusion, normal diffusion, and superdiffusion, respectively). The anomalous behavior is observed in various systems ranging from a charge carrier transport in amorphous material [1], light diffusion [2], and polymeric materials [3] to biological transports [4–9]. The diffusion behavior will depend on the time scale, and thus the exponent α may take several different values depending on Δ. For example, in entangled polymers, the EAMSD of a segment exhibits four different regions which reflect the crossovers between different characteristic relaxation time scales [3]. In supercooled liquids, the EAMSD of a glass-forming particle strongly depends on the temperature, and it shows a transient plateau. This is considered as evidence of the cage effect, which constrains the motion of the particle into a narrow region [10].

Although the EAMSD provides various useful information on the dynamical properties, some properties cannot be extracted from the EAMSD. For example, nonergodic behavior cannot be analyzed from the EAMSD. For such a purpose, the time-averaged MSD (TAMSD) can be utilized instead. The TAMSD is defined as

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

where Δ and t are the time difference and the observation time, respectively. If the system is ergodic and the time average is taken for a sufficiently long observation time (at the limit of $t \to \infty$), the TAMSD converges to the EAMSD with the equilibrium ensemble [11]. In molecular simulations and single-particle-tracking experiments, it is not easy to calculate the EAMSD. Instead, the TAMSD (or the average of the TAMSD over different realizations and/or particles) is widely used. If the system is nonergodic and/or the observation time is not sufficiently long, the TAMSD does not coincide to the EAMSD. In such a case, the TAMSD can be interpreted as a stochastic variable. In some stochastic models of anomalous diffusion, such a randomness is intrinsic [12–14]. In other words, TAMSDs remain random even when the observation time t goes to infinity. Such an intrinsic randomness of the TAMSDs will be related to large fluctuations of the TAMSDs. (The large fluctuations are actually observed in single-particle-tracking experiments in living cells [5–9].) Thus it is important

to calculate the statistical quantities such as the average and standard deviation of the TAMSD.

The magnitude of the fluctuation of the TAMSD can be quantitatively characterized by the relative fluctuation (RF) [15,16] or the relative standard deviation (RSD) [12,14,17]:

$$R(t;\Delta) \equiv \frac{\langle|\overline{\delta^2(\Delta;t)} - \langle\overline{\delta^2(\Delta;t)}\rangle|\rangle}{\langle\overline{\delta^2(\Delta;t)}\rangle}, \tag{3}$$

$$\Sigma(t;\Delta) \equiv \frac{\sqrt{\langle[\overline{\delta^2(\Delta;t)} - \langle\overline{\delta^2(\Delta;t)}\rangle]^2\rangle}}{\langle\overline{\delta^2(\Delta;t)}\rangle}. \tag{4}$$

The RF and RSD behave in a similar way, and it is reported that these quantities can characterize some dynamical properties of the system [15–17]. (If the second moment of $\overline{\delta^2(\Delta;t)}$ diverges, then the RSD diverges and the RF should be utilized to characterize the fluctuation of the TAMSD [11]. In some literature, the squared RSD is utilized as the ergodicity breaking parameter [14,18–20].) The RF and RSD analyses for the TAMSD are useful if the systems are nonergodic. The t dependence of the RF or RSD can be related to the ergodic property of the system. For example, Deng and Barkai [20] analyzed the RSD of the TAMSD for the fractional Langevin equation and the fractional Brownian motion. They obtained the analytic expression for the RSD and showed that the behavior of the RSD depends on the Hurst parameter in a nontrivial way.

The RF and RSD analyses are also useful to study ergodic systems. In the recent work [15], the authors applied the RF analysis to the center-of-mass (c.m.) motion in entangled polymer systems [3]. In entangled polymer systems, the RF of the TAMSD shows the crossover behavior:

$$R(t;\Delta) \propto \begin{cases} t^{-\beta} & (t \lesssim \tau_c'), \\ t^{-0.5} & (t \gtrsim \tau_c'). \end{cases} \tag{5}$$

Here $\beta < 0.5$ is the constant and τ_c' is the characteristic crossover time. The crossover time τ_c' behaves in the same way as the longest relaxation time (the disengagement time) τ_d. This means that the crossover time τ_c' characterizes the long-time relaxation in entangled polymer systems. (It would be natural to expect that the RSD of the TAMSD also shows the similar crossover behavior, although the data are not shown in the previous work.) Interestingly, the EAMSD does not show such a crossover around the longest relaxation time, and thus we consider that the TAMSD is actually useful for the analysis of the long-time relaxation behavior in ergodic systems. However, the reason why τ_c' characterizes the long-time relaxation behavior has not been theoretically clarified yet.

One possible explanation is that the crossover originates from the coupling between the dynamic equation for the center of mass and the end-to-end vector [3]. In the reptation model, a tagged polymer chain is modeled as a polymer chain confined in a tubelike obstacle. The polymer chain is allowed to move only along the tube. Due to this constraint, the dynamic equation and the relaxation behavior become nontrivial. (The reptation model can qualitatively reproduce the characteristic dynamical properties, such as the relaxation modulus.) The dynamic equation for the center of mass of the chain can be explicitly expressed as [21]

$$\frac{d\boldsymbol{r}_{\mathrm{c.m.}}(t)}{dt} = \sqrt{\frac{6D_{\mathrm{c.m.}}}{\langle \boldsymbol{p}^2\rangle}}\,\boldsymbol{p}(t)w(t). \tag{6}$$

Here $\boldsymbol{r}_{\mathrm{c.m.}}(t)$ and $\boldsymbol{p}(t)$ are the center-of-mass position and the end-to-end vector of an entangled polymer chain, respectively, $D_{\mathrm{c.m.}}$ is the diffusion coefficient for the center of mass, and $w(t)$ is the one-dimensional Gaussian white noise. The first and second moments of $w(t)$ are given as

$$\langle w(t)\rangle = 0, \quad \langle w(t)w(t')\rangle = \delta(t-t'). \tag{7}$$

One important property of Eq. (6) is that the noise $w(t)$ is multiplicatively coupled to another stochastic variable $\boldsymbol{p}(t)$. Due to this multiplicative coupling, the magnitude of the random motion of $\boldsymbol{r}_{\mathrm{c.m.}}(t)$ directly depends on $\boldsymbol{p}(t)$. Although random variables $\boldsymbol{r}_{\mathrm{c.m.}}(t)$ and $\boldsymbol{p}(t)$ are not statistically independent of each other, the coupling between them is expected to be rather weak. (This is because the dynamics of the end-to-end vector strongly depends on the resampling of new segments at chain ends, and this resampling process is not directly coupled to the dynamics of the center of mass.) If we simply assume that they are statistically independent random variables (the decoupling approximation), we can interpret Eq. (6) as the Langevin equation with a time-dependent and fluctuating diffusivity. Naively, we expect that such a multiplicative coupling causes the nontrivial crossover behavior of the RF.

Similar time-dependent and fluctuating diffusivity has been reported for other systems. For example, the diffusion of molecules in supercooled liquids is known to be heterogeneous [22–25]. This "dynamic heterogeneity" can be modeled by employing time-dependent fluctuating diffusion coefficient. The simplest model may be the two-state model [22] in which a tagged particle takes the slow state or fast state, and the diffusion coefficients of the slow and fast states differ. The intermittent search strategies [26] also consist of fast and slow diffusion modes. They are considered to be important for rapid detection of targets in biological systems such as foraging behavior of animals and reaction pathways of DNA-binding proteins to the binding sites [26]. These models can be also interpreted as the Langevin equations with time-dependent and fluctuating diffusivities.

Therefore, the analysis for a class of Langevin equations with time-dependent and fluctuating diffusivity will provide useful information for several different systems. From the RF analysis result for entangled polymers, the RF and RSD of the TAMSD are expected to be especially useful to quantify the dynamical behavior. However, as far as the authors know, theoretical analyses of the TAMSD for systems with time-dependent and fluctuating diffusivities have not been reported. In this work, we first introduce a class of Langevin equations with time-dependent and fluctuating diffusivity. Such a class of Langevin equations has not been studied in detail. Then we analyze the RSD of the TAMSD and derive a general formula for the RSD. We show that the RSD can be related to the time correlation function of the diffusivity. Our formula gives the relation between the crossover time of the RSD and the relaxation time of the diffusivity. The crossover time is expressed in terms of a weighted average relaxation time of the diffusivity. We show the universality of our formula through

some analytically solvable examples, the (pure) reptation model for entangled polymers and the two-state model for the supercooled liquid with the Markovian and non-Markovian transition dynamics. Finally, we compare our analysis method with other analysis methods and discuss the properties of our method. We also discuss the connection between the time-dependent and fluctuating diffusivity and other models.

II. MODEL

In this work, we consider a class of Langevin equations with a time-dependent and fluctuating diffusivity. As we mentioned, both the reptation model and the two-state model can be interpreted as such Langevin equations. In the reptation model [21], the one-dimensional thermal noise is multiplicatively coupled to the three-dimensional end-to-end vector. On the other hand, in the two-state model, the three-dimensional thermal noise is multiplicatively coupled to the scalar diffusion coefficient. Although they are not equivalent, we may interpret these models are special cases of a more general Langevin equation.

We consider a general multiplicatively coupled Langevin equation model in an n-dimensional space [27]. For simplicity, we assume that no external force is applied. The dynamic equation can be expressed as

$$\frac{d\boldsymbol{r}(t)}{dt} = \sqrt{2}\boldsymbol{B}(t)\cdot\boldsymbol{w}(t). \tag{8}$$

Here $\boldsymbol{r}(t)$ is the position, $\boldsymbol{B}(t)$ is the noise coefficient matrix, and $\boldsymbol{w}(t)$ is the Gaussian white thermal noise. The first and second moments of $\boldsymbol{w}(t)$ are

$$\langle\boldsymbol{w}(t)\rangle = 0, \quad \langle\boldsymbol{w}(t)\boldsymbol{w}(t')\rangle = \delta(t-t')\mathbf{1}, \tag{9}$$

where $\langle\dots\rangle$ represents the ensemble average and $\mathbf{1}$ is the n-dimensional unit tensor. We assume that $\boldsymbol{B}(t)$ obeys a stochastic process which is stationary and independent of $\boldsymbol{r}(t)$ and $\boldsymbol{w}(t)$. Therefore, two independent stochastic processes [$\boldsymbol{B}(t)$ and $\boldsymbol{w}(t)$] are multiplicatively coupled in Eq. (8). As we show below, our model does not exhibit the anomalous diffusion process, since $\boldsymbol{B}(t)$ obeys a stationary stochastic process. (A nonstationary process of $\boldsymbol{B}(t)$, such as the process with explicit time dependence, generates anomalous diffusion [28–30]. In the following, we consider only stationary processes.)

The dynamics model for the noise coefficient matrix can be any stochastic processes, such as the Langevin equation and the jump dynamics. The details are not required for the analysis in the next section. We need only several ensemble-averaged correlation functions. For convenience, we define the instantaneous diffusion coefficient matrix $\boldsymbol{D}(t)$ as

$$\boldsymbol{D}(t) \equiv \boldsymbol{B}(t)\cdot\boldsymbol{B}^{\mathrm{T}}(t). \tag{10}$$

Conversely, we may interpret Eq. (10) as the definition of the noise coefficient matrix. That is, if we have the stochastic process for the instantaneous diffusion coefficient $\boldsymbol{D}(t)$, then the noise coefficient matrix can be defined as the matrix square root (such as the Cholesky decomposition). The instantaneous diffusion coefficient matrix $\boldsymbol{D}(t)$ should be positive definite, and this condition guarantees the existence of the matrix square root.

The EAMSD is simply calculated to be

$$\begin{aligned}&\langle[\boldsymbol{r}(\Delta)-\boldsymbol{r}(0)]^2\rangle\\ &= 2\int_0^\Delta ds\int_0^\Delta ds'\,\langle\boldsymbol{B}(s)\cdot\boldsymbol{B}^{\mathrm{T}}(s')\rangle : \langle\boldsymbol{w}(s)\boldsymbol{w}(s')\rangle\\ &= 2\,\mathrm{tr}\langle\boldsymbol{D}\rangle\Delta,\end{aligned} \tag{11}$$

where the symbol ":" means a double dot product of tensors, i.e., $\boldsymbol{X}:\boldsymbol{Y}\equiv\sum_{ij}X_{ij}Y_{ij}$ for second rank tensors $\boldsymbol{X}$ and $\boldsymbol{Y}$. In the last line of Eq. (11), we utilized the fact that the ensemble average of the instantaneous diffusion matrix becomes time-independent due to the time-translational invariance: $\langle\boldsymbol{D}(t)\rangle = \langle\boldsymbol{D}\rangle$. (The ensemble average of the instantaneous diffusion coefficient is independent of time t, due to the stationarity.) If we assume $\langle\boldsymbol{D}\rangle$ to be isotropic, we can simply express $\langle\boldsymbol{D}\rangle$ as

$$\langle\boldsymbol{D}\rangle = D_{\mathrm{eff}}\mathbf{1}, \tag{12}$$

with D_{eff} being the effective diffusion coefficient. Then Eq. (11) is rewritten as:

$$\langle[\boldsymbol{r}(\Delta)-\boldsymbol{r}(0)]^2\rangle = 2nD_{\mathrm{eff}}\Delta, \tag{13}$$

where n is the dimension of the system.

The multiplicatively coupled Langevin equation shown above cannot be expressed as the generalized Langevin equation (GLE) with the Gaussian noise. Fox [31] showed that a GLE with the Gaussian noise can be characterized only by its memory kernel. Therefore, if one obtains the EAMSD, the corresponding GLE is uniquely determined. Because our model gives only the normal diffusion behavior, the corresponding GLE would become a normal Langevin equation with a Gaussian white noise which has no memory effect. This apparent inconsistency comes from the assumption that the noise is Gaussian. (As shown in the next section, the fourth-order moment of the noise behaves in a way that differs qualitatively from the Gaussian noise.) The simple dynamics models such as the reptation model and the two-state model cannot be expressed as the GLE with the Gaussian noise.

If the force is applied, we need to add the term proportional to the force $\boldsymbol{F}(t)$ to the Langevin equation. Then Eq. (8) is modified as

$$\frac{d\boldsymbol{r}(t)}{dt} = \boldsymbol{\Lambda}(t)\cdot\boldsymbol{F}(t) + \sqrt{2}\boldsymbol{B}(t)\cdot\boldsymbol{w}(t), \tag{14}$$

where $\boldsymbol{\Lambda}(t)$ is the time-dependent instantaneous mobility matrix. If we assume that the fluctuation-dissipation relation of the second kind holds for the instantaneous mobility, we have

$$\boldsymbol{\Lambda}(t) = \frac{1}{k_BT}\boldsymbol{D}(t) = \frac{1}{k_BT}\boldsymbol{B}(t)\cdot\boldsymbol{B}^{\mathrm{T}}(t). \tag{15}$$

with k_B and T being the Boltzmann constant and the absolute temperature, respectively. Equations (14) and (15) will be useful to study a particle trapped in a potential or driven by an external force.

Before we proceed to the detailed analysis, we show that our general model reduces to the reptaion and two-state models for some special cases. For a case where $n = 3$ and the noise

coefficient matrix is given as

$$\boldsymbol{B}(t) = \sqrt{\frac{3D_{\mathrm{c.m.}}}{\langle \boldsymbol{p}^2 \rangle}} \frac{\boldsymbol{p}(t)\boldsymbol{p}(t)}{|\boldsymbol{p}(t)|}, \tag{16}$$

Eq. (8) reduces to the reptation model. By introducing the one-dimensional Gaussian white noise $w'(t)$ as

$$w'(t) \equiv \frac{\boldsymbol{p}(t)}{|\boldsymbol{p}(t)|} \cdot \boldsymbol{w}(t), \tag{17}$$

Eq. (8) can be rewritten as follows:

$$\frac{d\boldsymbol{r}(t)}{dt} = \sqrt{\frac{6D_{\mathrm{c.m.}}}{\langle \boldsymbol{p}^2 \rangle}} \boldsymbol{p}(t) w'(t). \tag{18}$$

The first- and second-order moments of $w'(t)$ become

$$\langle w'(t) \rangle = 0, \quad \langle w'(t) w'(t') \rangle = \delta(t - t'). \tag{19}$$

Equations (18) and (19) are equivalent to the reptation model [Eqs. (6) and (7)]. For the case where $n = 3$ and the noise coefficient matrix is isotropic as

$$\boldsymbol{B}(t) = \sqrt{2D(t)}\mathbf{1}, \tag{20}$$

Eq. (8) simply reduces as follows:

$$d\boldsymbol{r}(t)/dt = \sqrt{2D(t)}\boldsymbol{w}(t). \tag{21}$$

This can be interpreted as the two-state model for supercooled liquids or the trap model if it is combined with appropriate transition dynamics for $D(t)$.

III. THEORY

The EAMSD cannot extract the information on the instantaneous diffusion coefficient. As we mentioned, the fluctuation analysis of the TAMSD is useful to characterize the long-time relaxation behavior of entangled polymers. In the reptation model, the end-to-end vector is multiplicatively coupled to the thermal noise in the Langevin equation. Naively, the fluctuation of the TAMSD is expected to be governed by the dynamics of the end-to-end vector. In the general Langevin equation model with time-dependent diffusivity, the fluctuation of the TAMSD can be related to the relaxation behavior of the noise coefficient matrix or the instantaneous diffusion coefficient matrix. In this section, we analyze the RSD of the TAMSD and derive a formula which relates the RSD and the time correlation functions of $\boldsymbol{D}(t)$.

Because we are considering a stationary process for $\boldsymbol{B}(t)$, the ensemble average can be evaluated rather straightforwardly. By taking an ensemble average in Eq. (2), we have

$$\langle \overline{\delta^2(\Delta;t)} \rangle = \langle [\boldsymbol{r}(\Delta) - \boldsymbol{r}(0)]^2 \rangle = 2 \operatorname{tr} \langle \boldsymbol{D} \rangle \Delta, \tag{22}$$

where the time-translational invariance $\langle [\boldsymbol{r}(t'+\Delta) - \boldsymbol{r}(t')]^2 \rangle = \langle [\boldsymbol{r}(\Delta) - \boldsymbol{r}(0)]^2 \rangle$ and Eq. (11) have been utilized. Then the RSD of the TAMSD [Eq. (4)] for the Langevin equation (8) is given by

$$\Sigma(t;\Delta) = \sqrt{\frac{\langle [\overline{\delta^2(\Delta;t)}]^2 \rangle}{4(\operatorname{tr} \langle \boldsymbol{D} \rangle)^2 \Delta^2} - 1}. \tag{23}$$

We need the explicit expression of $\langle [\overline{\delta^2(\Delta;t)}]^2 \rangle$ to calculate the RSD. We can obtain a rather simple expression for $\langle [\overline{\delta^2(\Delta;t)}]^2 \rangle$, although the detailed calculations become lengthy. After straightforward but long calculations, we have

$$\begin{aligned} \langle \overline{[\delta^2(\Delta;t)]}^2 \rangle = {} & \frac{8}{(t-\Delta)^2} \int_0^{t-\Delta} dt' \int_0^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_{t''}^{t''+\Delta} \\ & \times ds' \, \langle \operatorname{tr} \boldsymbol{D}(s) \operatorname{tr} \boldsymbol{D}(s') \rangle \\ & + \frac{32}{(t-\Delta)^2} \int_0^{t-\Delta} dt' \int_{\max(0,t'-\Delta)}^{t'} dt'' \int_{t'}^{t''+\Delta} \\ & \times ds \int_{t'}^{s} ds' \, \operatorname{tr} \langle \boldsymbol{D}(s) \cdot \boldsymbol{D}(s') \rangle. \end{aligned} \tag{24}$$

See Appendix A for detailed calculations. We consider the properties of two correlation functions in Eq. (24), $\langle \operatorname{tr} \boldsymbol{D}(t) \operatorname{tr} \boldsymbol{D}(t') \rangle$ and $\operatorname{tr} \langle \boldsymbol{D}(t) \cdot \boldsymbol{D}(t') \rangle$. We assume that the stochastic process $\boldsymbol{B}(t)$ is ergodic, and thus at the limit of $|t - t'| \to \infty$, these correlation functions can be decoupled:

$$\langle \operatorname{tr} \boldsymbol{D}(t) \operatorname{tr} \boldsymbol{D}(t') \rangle \to (\operatorname{tr} \langle \boldsymbol{D} \rangle)^2, \tag{25}$$

$$\operatorname{tr} \langle \boldsymbol{D}(t) \cdot \boldsymbol{D}(t') \rangle \to \operatorname{tr} (\langle \boldsymbol{D} \rangle \cdot \langle \boldsymbol{D} \rangle). \tag{26}$$

It would be convenient to rewrite two correlation functions by using Eqs. (25) and (26), as follows:

$$\langle \operatorname{tr} \boldsymbol{D}(t) \operatorname{tr} \boldsymbol{D}(t') \rangle \equiv (\operatorname{tr} \langle \boldsymbol{D} \rangle)^2 [1 + \psi_1(t - t')], \tag{27}$$

$$\operatorname{tr} \langle \boldsymbol{D}(t) \cdot \boldsymbol{D}(t') \rangle \equiv n \operatorname{tr} (\langle \boldsymbol{D} \rangle \cdot \langle \boldsymbol{D} \rangle) \left[\frac{1}{n} + \psi_2(t - t') \right], \tag{28}$$

where $\psi_1(t)$ and $\psi_2(t)$ represent four-body two-time correlation functions. Both $\psi_1(t)$ and $\psi_2(t)$ are symmetric in t and approach to zero at $|t| \to \infty$. [For one-dimensional systems ($n = 1$), $\psi_1(t) = \psi_2(t)$. For $n \geqslant 2$, generally $\psi_1(t)$ and $\psi_2(t)$ do not coincide.]

By combining Eqs. (23), (24), (27), and (28), the squared RSD is expressed as

$$\begin{aligned} \Sigma^2(t;\Delta) = {} & \frac{2}{\Delta^2(t-\Delta)^2} \int_0^{t-\Delta} dt' \int_0^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_{t''}^{t''+\Delta} \\ & \times ds' \, \psi_1(s - s') \\ & + \frac{8C}{\Delta^2(t-\Delta)^2} \int_0^{t-\Delta} dt' \int_{\max(0,t'-\Delta)}^{t'} dt'' \int_{t'}^{t''+\Delta} \\ & \times ds \int_{t'}^{s} ds' \left[\frac{1}{n} + \psi_2(s - s') \right], \end{aligned} \tag{29}$$

with C being defined as

$$C \equiv n \frac{\operatorname{tr} (\langle \boldsymbol{D} \rangle \cdot \langle \boldsymbol{D} \rangle)}{(\operatorname{tr} \langle \boldsymbol{D} \rangle)^2}. \tag{30}$$

Note that if the average diffusion coefficient matrix $\langle \boldsymbol{D} \rangle$ is isotropic, we have $C = 1$. In many practical cases, the observation time t is much longer than the time difference

Δ. For such a case ($t \gg \Delta$), Eq. (29) is simplified as follows:

$$\Sigma^2(t;\Delta) \approx \frac{2}{\Delta^2 t^2}\int_0^t ds''\,(t-s'')\int_0^\Delta ds\int_0^\Delta ds'\,\psi_1(s-s'+s'') + \frac{4C}{3n}\frac{\Delta}{t} + \frac{8C}{\Delta^2 t}\int_0^\Delta ds\int_0^s ds'\,(s-s')\psi_2(s'). \tag{31}$$

Moreover, if the characteristic relaxation time of $\psi_1(t)$ and $\psi_2(t)$, τ, is much longer than Δ ($\tau \gg \Delta$), Eq. (31) can be further approximated:

$$\Sigma^2(t;\Delta) \approx \frac{2}{t^2}\int_0^t ds\,(t-s)\psi_1(s). \tag{32}$$

Thus the squared RSD becomes approximately independent of $\psi_2(t)$. If $\psi_1(t)$ decays sufficiently fast as t increases (strictly speaking, if $\psi_1(t)$ decays faster than t^{-1}), then we have the following asymptotic forms:

$$\Sigma^2(t;\Delta) \approx \begin{cases} \psi_1(0) & (t \ll \tau), \\ \frac{2}{t}\int_0^\infty ds\,\psi_1(s) & (t \gg \tau). \end{cases} \tag{33}$$

Equations (32) and (33) are the main result of this section. For the case of $t \gg \tau$, the RSD behaves as $\Sigma(t;\Delta) \propto t^{-1/2}$, which corresponds to the Gaussian fluctuation. From Eq. (32), we find that the t dependence of the RSD is essentially determined only by $\psi_1(t)$. Therefore the crossover time τ_c is related only to ψ_1. From Eq. (33), the crossover time τ_c is estimated as

$$\tau_c \approx \frac{2}{\psi_1(0)}\int_0^\infty ds\,\psi_1(s). \tag{34}$$

For a single exponential type relaxation [$\psi_1(t) = \psi_1(0)e^{-t/\tau}$], this crossover time becomes:

$$\tau_c \approx 2\tau. \tag{35}$$

As expected, the crossover time is proportional to the relaxation time, although they differ by the numerical factor 2. In general, the correlation function $\psi_1(t)$ cannot be expressed as a single exponential form but a sum of multiple exponential relaxation modes. Even in such a case, a similar relation between the relaxation time and the crossover time holds. For such a case, the relaxation time τ in Eq. (35) is replaced by the weighted average relaxation time for multiple exponential relaxation modes (with the weights proportional to the amplitude of modes). This result justifies the use of the crossover time as the characteristic relaxation time for systems with time-dependent diffusivities, as long as $\psi_1(t)$ reflects the characteristic relaxation at the long time scale. As shown in Appendix B, the RF behaves in a similar way to the RSD. Thus we consider that the empirical relation between the crossover time and the longest relaxation time in the entangled polymers in the previous work [15] is theoretically supported by this work.

Before we proceed to calculations for some analytically solvable models, we briefly consider the behavior of the RSD in the case where Δ/t is not sufficiently small. In such a case, the second and third terms in the right-hand side of Eq. (31) are not always negligible. As before, we approximate the integrand in the third term in the right-hand side of Eq. (31) by $\psi_2(0)$. Then we have

$$\Sigma^2(t;\Delta) \approx \psi_1(0) + \frac{4C}{3}\left[\frac{1}{n} + \psi_2(0)\right]\frac{\Delta}{t}. \tag{36}$$

If $t/\Delta \lesssim 4C[1/n + \psi_2(0)]/3\psi_1(0)$, then the contribution of the second term in the right-hand side of Eq. (36) becomes non-negligible. Roughly speaking, this term gives the correction, which is proportional to $(\Delta/t)^{1/2}$, to the RSD. It should be noted here that the Δ dependence of this correction is rather simple. We may utilize the RSD data with different values of Δ to obtain the data at the limit of $\Delta \to 0$ by the extrapolation. In what follows, we will neglect this correction term for simplicity.

IV. EXAMPLES

In this section, we apply the general formula [Eqs. (32) and (33) together with Eq. (27)] obtained in the previous section to some analytically solvable models. We show the explicit forms of the RSD and discuss how we can relate the long-time relaxation behavior of systems to time-dependent diffusivity from the fluctuation of the TAMSD.

A. Reptation model for entangled polymer

As a simple model of entangled polymers, we consider the (pure) reptation model [3]. In the reptation model, the motion of a tagged polymer chain is modeled as one of a polymer chain in a tubelike obstacle. The dynamic equation is expressed as a one-dimensional Langevin equation, and various dynamical properties can be analytically calculated. For example, we can calculate the shear relaxation modulus, the end-to-end vector relaxation function, and the EAMSD.

As we mentioned, the dynamic equation for the center of mass in the reptation model is given as Eq. (6). The instantaneous diffusion matrix $\boldsymbol{D}(t)$ becomes

$$\boldsymbol{D}(t) = 3D_{\text{c.m.}}\frac{\boldsymbol{p}(t)\boldsymbol{p}(t)}{\langle \boldsymbol{p}^2\rangle}. \tag{37}$$

The effective diffusion coefficient D_{eff} simply coincides with $D_{\text{c.m.}}$:

$$D_{\text{eff}} = \frac{1}{3}\,\text{tr}\langle \boldsymbol{D}\rangle = D_{\text{c.m.}}. \tag{38}$$

Under the decoupling approximation, the reptation model reduces to the Langevin equation with the time-dependent and flucuating diffusivity, and the general formula can be utilized. The correlation function $\psi_1(t)$ [Eq. (27)] becomes

$$\psi_1(t) = \frac{\langle \boldsymbol{p}^2(t)\boldsymbol{p}^2(0)\rangle}{\langle \boldsymbol{p}^2\rangle^2} - 1. \tag{39}$$

We need to calculate $\langle \boldsymbol{p}^2(t)\boldsymbol{p}^2(0)\rangle$ to obtain the explicit expression for the RSD of the TAMSD. The four-body two-time correlation function $\psi_1(t)$ can be analytically evaluated. After long but straightforward calculations, we have the following form for $\psi_1(t)$:

$$\psi_1(t) = \frac{16}{3\pi^2}\sum_{k:\text{odd}}\frac{1}{k^2}E_2(k^2 t/\tau_d). \tag{40}$$

Here $E_m(z)$ is the (generalized) exponential integral of the m-th order [32], and τ_d is the disengagement time [3] which corresponds to the longest relaxation time in the reptation model. The detailed calculations are summarized in Appendix C.

The behavior of the RSD of the TAMSD in the reptation model can be calculated from Eqs. (32), (33), and (40). The asymptotic forms can be calculated as follows. At $t = 0$, $\psi_1(t)$ simply becomes

$$\psi_1(0) = \frac{16}{3\pi^2} \sum_{k:\text{odd}} \frac{1}{k^2} = \frac{2}{3}. \tag{41}$$

Here we have used $E_2(0) = 1$. The integral of $\psi_1(t)$ over t is calculated as

$$\int_0^\infty dt\, \psi_1(t) = \sum_{k:\text{odd}} \frac{16\tau_d}{3\pi^2 k^4} \int_0^\infty dz\, E_2(z) = \frac{\pi^2 \tau_d}{36}, \tag{42}$$

where we have used the integral formula for the exponential integral [32]:

$$\int_0^\infty dz\, E_2(z) = E_3(0) = \frac{1}{2}. \tag{43}$$

From Eqs. (41) and (42), we have the following asymptotic forms for the RSD of the TAMSD:

$$\Sigma(t;\Delta) \approx \begin{cases} \sqrt{\frac{2}{3}} & (t \ll \tau_d), \\ \sqrt{\frac{\pi^2 \tau_d}{18t}} & (t \gg \tau_d). \end{cases} \tag{44}$$

The crossover time τ_c is then estimated as

$$\tau_c = \frac{\pi^2 \tau_d}{12} \approx 0.822 \tau_d. \tag{45}$$

Thus we find that τ_c is actually proportional to τ_d. Moreover, τ_c is closer to τ_d than the case of the single relaxation time. This result is consistent with our previous simulation results for the reptation model [15]. (The crossover time of the RF, τ_c', is almost the same as the disengagement time.) The analytic results shown above are obtained under the decoupling approximation, which we employed without any justifications. The decoupling approximation can be justified for the calculation of the RSD of the TAMSD, and thus Eqs. (44) and (45) can be also justified. See Appendix D.

Here it would be worth noting that the integral in Eq. (32) can be analytically evaluated (although the obtained expression becomes complicated). After straightforward calculations, we have the following explicit expression for the squared RSD:

$$\Sigma^2(t;\Delta) = \frac{\pi^2 \tau_d}{18t} - \frac{\pi^4 \tau_d^2}{270t^2} + \frac{32\tau_d^2}{3\pi^2 t^2} \sum_{k:\text{odd}} \frac{1}{k^6} E_4(k^2 t/\tau_d). \tag{46}$$

This reduces to two asymptotic forms shown in Eq. (44) at $t \ll \tau_d$ and $t \gg \tau_d$.

To validate our result, we perform a simulation for the discretized version of the reptation model (the discrete reptation model) and calculate the RSD of the TAMSD of the center of mass. The dynamics of an entangled polymer is modeled by a stochastic jump process. A polymer chain is expressed as a series of discrete tube segments which have the constant size. The chain randomly moves inside the tube (the reptation motion), and the end segments are stochastically resampled. (The details of the model and simulation method are described in the previous work [15].) We show the RSD of the TAMSD for the number of tube segments per chain $Z = 80$ in Fig. 1. The time difference Δ is taken to be $\Delta = 10\tau_l$, where τ_l is the characteristic time scale for the longitudinal motion of a segment along the tube. We observe that our analytic expression [Eq. (46)] and its asymptotic forms [Eq. (44)] are in good agreement with the simulation result except for the small t region. This result supports the validity of our general formula [Eq. (32)] and its asymptotic forms [Eq. (33)].

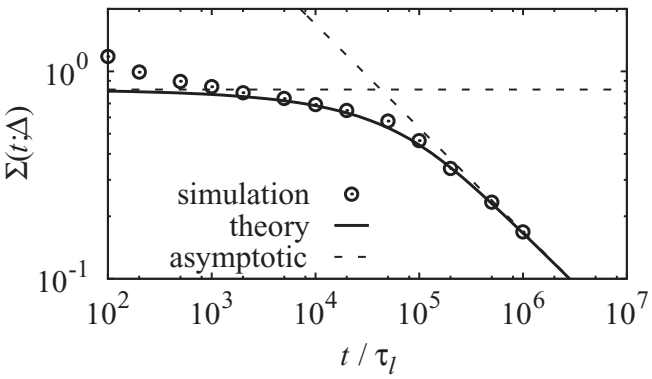

FIG. 1. The RSD of the TAMSD of a center of mass in the discrete reptation model. The number of tube segments Z is $Z = 80$ and the time difference Δ is $\Delta = 10\tau_l$. τ_l is the characteristic time of the longitudinal motion of a segment along the tube. Symbols represent the kinetic Monte Carlo simulation data. The dotted and dashed curves represent the theoretical prediction [Eq. (46)] and its asymptotic forms [Eq. (44)].

B. Two-state model for supercooled liquid

The dynamics of supercooled liquids have been extensively studied by experiments, theories, and simulations [22–25]. In the molecular dynamics (MD) simulations, the motion of each particle can be observed and various statistical quantities can be calculated. One important finding by the MD simulations is the "dynamic heterogeneity" [33,34]. The mobility or the diffusivity of a particle strongly fluctuates spatially and temporally. The dynamic heterogeneity is considered as a characteristic property of supercooled or glassy liquids. Many theoretical and experimental studies have been conducted to observe and characterize the dynamic heterogeneity. The two-state model is a simple and analytically solvable theoretical model which takes into account the dynamic heterogeneity [22].

In the two-state model, dynamics of a tagged particle is considered. The position of the tagged particle at time t, $\boldsymbol{r}(t)$, obeys the following Langevin equation:

$$\frac{d\boldsymbol{r}(t)}{dt} = \sqrt{2D(t)}\boldsymbol{w}(t). \tag{47}$$

Here $D(t)$ is the time-dependent diffusion coefficient. The particle has a state and the state is time dependent. We express the state of the particle at time t as $h(t)$, and this $h(t)$ can take either the fast (f) or slow (s) state. The fast and slow states have different diffusion coefficients, and thus the diffusion

coefficient $D(t)$ is expressed as

$$D(t) = \begin{cases} D_f & (\text{for } h(t) = f), \\ D_s & (\text{for } h(t) = s). \end{cases} \tag{48}$$

Here D_f and D_s are diffusion coefficients of the fast and slow states ($D_f > D_s$). We describe the probability that the particle is at the state h at time t as $P_h(t)$. The four-body two-time correlation function $\psi_1(t)$ is given by

$$\psi_1(t) \equiv \frac{\langle D(t)D(0)\rangle}{\langle D\rangle^2} - 1. \tag{49}$$

We express equilibrium fraction (equilibrium probability) of the state h as ϕ_h ($\phi_h \equiv \langle P_h\rangle$). Then the effective diffusion coefficient can be expressed as

$$D_{\text{eff}} = \langle D\rangle = D_f\phi_f + D_s\phi_s. \tag{50}$$

1. Markovian case

We consider the simplest case where the transition dynamics is Markovian. (Even in the Markovian case, the two-state model can reproduce some interesting dynamic properties which reflect the dynamic heterogeneity.) In this case, we can describe the transition dynamics between the fast and slow states by the following master equation:

$$\frac{d}{dt}\begin{bmatrix} P_f(t) \\ P_s(t) \end{bmatrix} = \begin{bmatrix} -k_f & k_s \\ k_f & -k_s \end{bmatrix}\begin{bmatrix} P_f(t) \\ P_s(t) \end{bmatrix}. \tag{51}$$

where k_f and k_s are the transition rates from the fast to slow states and from the slow to fast states, respectively. The set of Eqs. (47)–(51) can be solved analytically.

The equilibrium probabilities (equilibrium fractions) of the fast and slow states, become

$$\phi_f = \frac{k_s}{k_f + k_s}, \quad \phi_s = \frac{k_f}{k_f + k_s}. \tag{52}$$

The joint probability to find the particle at the state h' at time 0 and at the state h at time t (the transition probability), $W_{hh'}(t)$, can be calculated straightforwardly from the coefficient matrix in Eq. (51). The explicit expression becomes

$$\begin{bmatrix} W_{ff}(t) & W_{fs}(t) \\ W_{sf}(t) & W_{ss}(t) \end{bmatrix} = \begin{bmatrix} \phi_f + \phi_s e^{-t/\tau} & \phi_f(1 - e^{-t/\tau}) \\ \phi_s(1 - e^{-t/\tau}) & \phi_s + \phi_f e^{-t/\tau} \end{bmatrix}, \tag{53}$$

where we have defined the characteristic relaxation time as $\tau \equiv 1/(k_f + k_s)$. The four-body two-time correlation function $\psi_1(t)$ can be expressed by using $W_{hh'}(t)$ and ϕ_h as

$$\psi_1(t) = \frac{1}{D_{\text{eff}}^2} \sum_{h,h'=f,s} D_h D_{h'} W_{hh'}(t)\phi_{h'} - 1. \tag{54}$$

From Eqs. (53) and (54), the explicit form of $\psi_1(t)$ becomes

$$\psi_1(t) = \frac{\phi_s\phi_f(D_f - D_s)^2}{D_{\text{eff}}^2} e^{-t/\tau}. \tag{55}$$

By substituting Eq. (55) into Eq. (32), finally we have a simple expression for the squared RSD:

$$\Sigma^2(t;\Delta) = \frac{\phi_s\phi_f(D_f - D_s)^2}{D_{\text{eff}}^2} \frac{2\tau^2}{t^2}\left(e^{-t/\tau} - 1 + \frac{t}{\tau}\right). \tag{56}$$

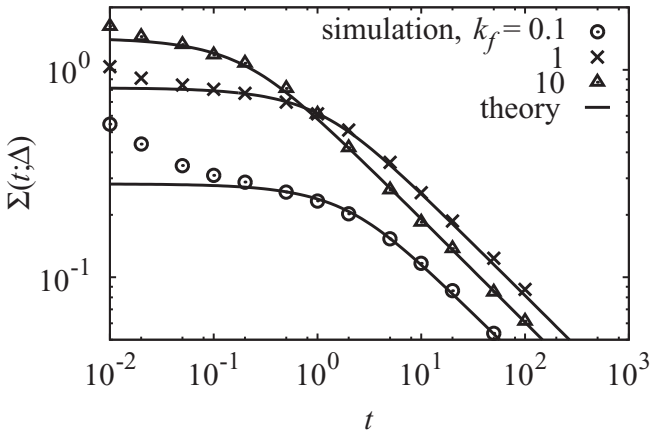

FIG. 2. The RSD of the TAMSD of the Markovian two-state model. The diffusion coefficients and transition rates are $D_s = 1$, $D_f = 10$, $k_s = 1$, and $k_f = 0.1, 1$, and 10. The time difference is $\Delta = 0.001$. Symbols represent the simulation results and solid curves represent the theoretical prediction.

The asymptotic forms for $t \ll \tau$ and $t \gg \tau$ are

$$\Sigma(t;\Delta) = \begin{cases} \frac{\sqrt{\phi_s\phi_f}(D_f - D_s)}{D_{\text{eff}}} & (t \ll \tau), \\ \frac{\sqrt{\phi_s\phi_f}(D_f - D_s)}{D_{\text{eff}}}\sqrt{\frac{2\tau}{t}} & (t \gg \tau). \end{cases} \tag{57}$$

From these asymptotic forms, the crossover time τ_c is estimated as $\tau_c = 2\tau$. As expected, the crossover time is twice of the relaxation time τ.

We perform the simulations and compare the simulation results with the theoretical prediction [Eq. (56) or Eq. (57)]. We show the simulation method later, because the simulation for the Markovian two-state model can be performed as a special case of the non-Markovian two-state model. We perform simulations with $D_s = 1$, $D_f = 10$, $k_f = 1$, and several different values of k_s ($k_s = 0.1, 1$, and 10). Figure 2 shows the simulation results together with the theoretical RSD [Eq. (56)] and its asymptotic forms [Eq. (57)]. We observe that the theoretical prediction agrees well with the simulation data, except for the small-t region. (The deviations at the small-t region are similar to the case of the reptation model.) Therefore, we find that our general formula [Eqs. (32) and (33)] can be applied to the Markovian two-state model, where the dynamics of the instantaneous diffusivity is described by the Markovian transition dynamics between two states. The deviation from the theory at the small t regions is due to the correction term. From Eq. (36), the relative contribution of the correction term increases as the plateau value of the RSD [$\psi_1(0)$] decreases. Actually, we observe that the deviation is especially large for the case of $k_f = 0.1$, in which the plateau value is small.

2. Non-Markovian case

Markovian models are varied for ideal systems where the memory effects are negligible. If the memory effects are not negligible, the dynamics should be non-Markovian. In this subsection, we consider the two-state model defined by Eq. (47) with non-Markovian transition processes between fast and slow states. Such non-Markovian dynamics will be

important when comparing the model with experimental data. To handle non-Markovian processes, we use the renewal theoretic approach [35,36]. We assume that the system is initially in the equilibrium state. In other words, we assume that the mean trapping time does not diverge and the the system is well equilibrated. In what follows, we mainly use the same notations as the Markovian case.

We express the trapping-time distribution of the state h as $\rho_h(\tau)$. Also, we express the equilibrium trapping-time distribution as $\rho_h^{(\mathrm{eq})}(\tau)$. For example, if a particle is in the fast state at time $t=0$, then this particle became the fast state at some time $t=t_0<0$. If t_1 is the time when first transition (to the slow state) occurs, then $\tau_1=t_1-t_0$ obeys the distribution $\rho_f(\tau_1)$, but t_1 itself does not necessarily obey $\rho_f(t_1)$. Instead, t_1 obeys $\rho_f^{(\mathrm{eq})}(\tau)$. (We note that the time t_1 is called the forward recurrence time in renewal theory [36].) The explicit expression for $\rho_h^{(\mathrm{eq})}$ is [35,36]

$$\rho_h^{(\mathrm{eq})}(\tau)=\frac{1}{\langle\tau\rangle_h}\int_\tau^\infty d\tau'\,\rho_h(\tau'), \tag{58}$$

where $\langle\tau\rangle_h$ is the average trapping time of the state h, defined as

$$\langle\tau\rangle_h\equiv\int_0^\infty d\tau\,\tau\rho_h(\tau). \tag{59}$$

[For the exponential distribution, two distributions $\rho_h(\tau)$ and $\rho_h^{(\mathrm{eq})}(\tau)$ coincide.] Equilibrium fractions of each state, ϕ_f and ϕ_s, are given by

$$\phi_f=\frac{\langle\tau\rangle_f}{\langle\tau\rangle_f+\langle\tau\rangle_s},\quad \phi_s=\frac{\langle\tau\rangle_s}{\langle\tau\rangle_f+\langle\tau\rangle_s}. \tag{60}$$

For the case of the exponential trapping-time distribution, $\langle\tau\rangle_h=1/k_h$ and we recover Eq. (52).

The four-body two-time correlation function $\psi_1(t)$ can be calculated in a similar way to the Markovian case. Using the joint probability of being at state h at time t, starting from at state h' at time 0, $W_{hh'}(t)$, $\psi_1(t)$ can be expressed as

$$\psi_1(t)=\frac{1}{D_{\mathrm{eff}}^2}\sum_{h,h'=f,s}D_hD_{h'}[W_{hh'}(t)-\phi_h]\phi_{h'}. \tag{61}$$

Here D_{eff} is the effective diffusion coefficient defined by Eq. (50).

Although it is difficult to obtain the explicit expression of $\psi_1(t)$, we can obtain the asymptotic forms. For $t=0$, the transition probability simply becomes $W_{hh'}(0)=\delta_{hh'}$ and thus we have

$$\psi_1(0)=\frac{\phi_f\phi_s(D_f-D_s)^2}{D_{\mathrm{eff}}^2}. \tag{62}$$

Equation (62) has formally the same form as the Markovian case [Eq. (55) with $t=0$]. This result is physically natural because we have no transition at $t=0$ and the details of the transition dynamics do not affect $\psi_1(0)$, as long as the system is in equilibrium.

The integral of $\psi_1(t)$ becomes as follows:

$$\int_0^\infty dt\,\psi_1(t)=\frac{\phi_f\phi_s(D_f-D_s)^2}{D_{\mathrm{eff}}^2}\tilde{\tau}. \tag{63}$$

Here $\tilde{\tau}$ is the characteristic relaxation time of the non-Markovian two-state model and is defined as

$$\tilde{\tau}\equiv\left(\frac{\langle\tau^2\rangle_s-\langle\tau\rangle_s^2}{\langle\tau\rangle_s^2}+\frac{\langle\tau^2\rangle_f-\langle\tau\rangle_f^2}{\langle\tau\rangle_f^2}\right)\frac{\langle\tau\rangle_f\langle\tau\rangle_s}{2(\langle\tau\rangle_f+\langle\tau\rangle_s)}. \tag{64}$$

(For the exponential trapping-time distribution, we simply have $\tilde{\tau}=\tau$.) The detailed calculations for Eq. (63) are summarized in Appendix E.

From Eqs. (33), (62), and (63), we have the following asymptotic forms for the RSD:

$$\Sigma(t;\Delta)\approx\begin{cases}\frac{\sqrt{\phi_f\phi_s}(D_f-D_s)}{D_{\mathrm{eff}}} & (t\ll\tilde{\tau}),\\ \frac{\sqrt{\phi_f\phi_s}(D_f-D_s)}{D_{\mathrm{eff}}}\sqrt{\frac{2\tilde{\tau}}{t}} & (t\gg\tilde{\tau}).\end{cases} \tag{65}$$

Equation (65) has almost the same form as the Markovian case, Eq. (57) [τ in Eq. (57) is replaced by $\tilde{\tau}$]. Thus our theory predicts similar crossover behavior as the Markovian case. The crossover time is estimated as $\tau_c=2\tilde{\tau}$. Here it should be emphasized that the correlation function $\psi_1(t)$ of the non-Markovian two-state model is not a single exponential form. The crossover time depends on the average relaxation time $\tilde{\tau}$ defined in Eq. (64) and thus is not a simple arithmetic nor harmonic averages of $\langle\tau\rangle_f$ and $\langle\tau\rangle_s$. Equation (65) gives only the asymptotic forms for the RSD. The detailed transition behavior from the constant RSD [$\Sigma(t;\Delta)\propto t^0$] to the Gaussian decay [$\Sigma(t;\Delta)\propto t^{-1/2}$] can qualitatively differ from the Markovian case.

To examine the validity of Eq. (65), we perform simulations for the non-Markovian two-state model and compare the simulation results with Eq. (65). The simulation scheme consists of two steps. First, we sample the waiting time τ at the current state from the waiting time distribution. Second, we integrate the Langevin equation (47) until the sampled waiting time. Then we change the state and go back to the first step and iterate the same procedure. (This simulation scheme can be applied for the Markovian two-state model if we use the exponential distribution functions both for the fast and slow states.)

In this work, we employ the exponential distribution for the fast state and a nonexponential distribution for the slow state as follows:

$$\rho_f(\tau)=k_fe^{-k_f\tau}, \tag{66}$$

$$\rho_s(\tau)=\int_{k_{s,0}}^{k_{s,1}}dk_s\,k_se^{-k_s\tau}q_s(k_s). \tag{67}$$

Here $k_{s,0}$ and $k_{s,1}$ are the lower and upper limits for the transition rate at the slow state, and $q_s(k_s)$ is the distribution of the transition rate. We employ the following power-law type distribution for $q_s(k_s)$,

$$q_s(k_s)=\frac{\alpha-1}{k_{s,1}^{\alpha-1}-k_{s,0}^{\alpha-1}}k_s{}^{\alpha-2}, \tag{68}$$

with $0\leqslant\alpha\leqslant1$ being the power-law exponent. As a result, the distribution for the slow state obeys a power law for small τ and exponential distribution for large τ. (The transition from a power law to the exponential occurs at $\tau\approx k_{s,0}^{-1}$.) We set parameters as $D_s=1$, $D_f=10$, $k_f=1$, $k_{s,1}=1$,

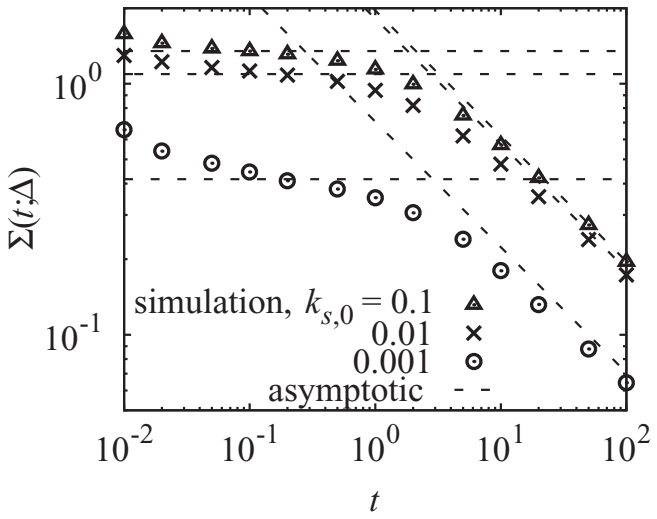

FIG. 3. The RSD of the TAMSD of the non-Markovian two-state model. The diffusion coefficients are $D_s = 1$ and $D_f = 10$. The waiting time distribution for the fast state is given by the exponential distribution with $k_f = 1$, and the waiting time distribution for the slow state is given by the power-law type distribution with $k_{s,1} = 1$ and $k_{s,0} = 0.1, 0.01$, and 0.001. The time difference is $\Delta = 0.001$. Symbols represent the simulation results and dashed curves represent the theoretically predicted asymptotic forms.

$\alpha = 0.2$. We vary the value of $k_{s,0}$ as $k_{s,0} = 0.1, 0.01$, and 0.001 to control the non-Markovian transition dynamics. Figure 3 shows the simulation results together with the theoretically derived asymptotic forms. The simulation data show clear crossovers for the RSD, as in the case of the Markovian two-state model. We observe the asymptotic forms by our theory [Eq. (65)] agree with the simulation data.

However, because $\psi_1(t)$ is not a single exponential form and has rather broad distribution of relaxation times, the crossover region becomes broad compared with the Markovian case. This means that there is some deviations from the asymptotic form Eq. (33), at the intermediate t region. Especially for the case of $k_{s,0} = 0.001$, the deviation from two asymptotic forms is relatively large. (Also, as the case of the Markovian case, the contribution of the correction term is relatively large for $k_{s,0} = 0.001$. This is another reason why the deviation from the theoretical form is relatively large for $k_{s,0} = 0.001$.)

V. DISCUSSIONS

A. Comparison with other analysis methods

We have shown that our general formula for the RSD of the TAMSD works well for several analytically solvable systems. Here we compare our analysis method with other methods. For supercooled liquids, so far, several different quantities have been employed to analyze the dynamic heterogeneity.

Yamamoto and Onuki [33,34] showed that the van Hove correlation function can resolve the dynamic heterogeneity. The van Hove self-correlation function is defined as

$$G_s(\boldsymbol{r},\Delta) \equiv \langle \delta[\boldsymbol{r} - \boldsymbol{r}(\Delta) + \boldsymbol{r}(0)] \rangle. \tag{69}$$

For a relatively short time scale, $G_s(\boldsymbol{r},\Delta)$ shows non-Gaussian behavior, due to the dynamic heterogeneity. For a relatively long time scale, $G_s(\boldsymbol{r},\Delta)$ approaches the Gaussian behavior, which corresponds to the ergodic state. Although the van Hove correlation is useful to qualitatively observe the dynamic heterogeneity, it is not easy to quantitatively determine, for example, the crossover time directly from the van Hove correlation function. For such a purpose, scalar quantities are preferred than distribution functions. To quantify the non-Gaussian behavior, the so-called non-Gaussianity parameter has been utilized. The non-Gaussianity parameter is defined as [37–39]

$$A(\Delta) \equiv \frac{n\langle [\boldsymbol{r}(\Delta) - \boldsymbol{r}(0)]^4 \rangle}{(n+2)\langle [\boldsymbol{r}(\Delta) - \boldsymbol{r}(0)]^2 \rangle^2} - 1. \tag{70}$$

This parameter becomes nonzero if the distribution of the displacement (the van Hove correlation function) is not Gaussian. Although the non-Gaussianity parameter can characterize the long-time relaxation behavior, its explicit expression for the time-dependent diffusivity model is not simple compared with our general formula for the RSD, as shown in Appendix F.

Recent simulation and theoretical works show that the four-point time-space correlation function is an important quantity in supercooled liquids [25,40–42]. The four-point dynamic correlation function is defined as

$$\begin{aligned}\chi_4(\boldsymbol{r},\boldsymbol{r}',\Delta) \equiv\ & \langle \delta\rho(\boldsymbol{r},\Delta)\delta\rho(\boldsymbol{r},0)\delta\rho(\boldsymbol{r}',\Delta)\delta\rho(\boldsymbol{r}',0)\rangle \\ & - \langle \delta\rho(\boldsymbol{r},\Delta)\delta\rho(\boldsymbol{r},0)\rangle\langle \delta\rho(\boldsymbol{r}',\Delta)\delta\rho(\boldsymbol{r}',0)\rangle,\end{aligned} \tag{71}$$

where $\delta\rho(\boldsymbol{r},t)$ is the density fluctuation at position $\boldsymbol{r}$ and time t. The four-point correlation function can also quantify the dynamic heterogeneity and was analyzed in detail in recent works. Although the RSD of the TAMSD is not equivalent to the four-point correlation function, nor the non-Gaussianity parameter, the RSD of the TAMSD can be utilized in a similar way to these quantities. As far as the authors know, the RSD or RF analysis is not performed for MD data of supercooled liquids. The application of the TAMSD analysis to the MD simulation data of the supercooled liquids is an interesting future work. In particular, the comparison of the crossover time determined from the RSD of the TAMSD with other characteristic times (such as the α relaxation time) will be interesting.

Garrahan, Chandler, and coworkers [43–45] analyzed the "activity" to study the dynamics of supercooled liquids. The activity is defined as:

$$K[x] \equiv \Delta \sum_{t'=0}^{t} [\boldsymbol{r}(t'+\Delta) - \boldsymbol{r}(t')]^2. \tag{72}$$

Here $x(t)$ represents the point in the configuration space, and Δ and t are the time step size and the observation time, respectively. $\boldsymbol{r}(t)$ represents the trajectory of a particle and it depends on $x(t)$. The summation over t' in Eq. (72) represents the sum taken for every Δ within the observation time window $(0 < t' < t)$. The activity is essentially the same as the TAMSD. [The summation over t' may be replaced by the integral over t', and then the activity reduces to the TAMSD except the normalization factor $1/(t-\Delta)$.] Thus the activity can be interpreted as a stochastic variable just like the TAMSD. [The activity is a time-averaged quantity but explicitly depends on the position in the configuration space. Naively, we expect that $x(t)$ contains the same information as $\boldsymbol{B}(t)$ in our model.] Hedges *et al.* [43] showed that the

ensemble average of the activity can be utilized as the order parameter and the glass transition can be interpreted in analogy to the first-order phase transition. Although their approach differs from ours, we consider that the fluctuation analysis of the TAMSD in this work can also provide useful information for the dynamics of supercooled liquids.

There are other analysis methods which do not utilize the MSD. For example, to analyze the longest relaxation time in entangled polymers, the relaxations of the stress and the end-to-end vector are simple and useful [3]. As already pointed out in previous work [15], the RF and RSD analyses give qualitatively similar long-time relaxation behavior as other analysis methods. Our general formula [Eq. (34)] or the analytic result for the reptation model [Eq. (45)] gives the relation between the relaxation time distribution and the crossover time τ_c. In general, if the relaxation is not a single exponential type, τ_c becomes differ quantitatively from the characteristic relaxation times determined by other analysis methods. Thus, the comparison of τ_c with other relaxation time data can provide the information on the relaxation time distribution. For example, in the case of entangled polymers, the ratio τ_c/τ_d (τ_d is determined from the stress relaxation) can be utilized as an index for the contribution of nonreptation type relaxation mechanisms.

The advantage of the RSD analysis is that it directly reflects the dynamics of the instantaneous diffusivity. From Eq. (32), the RSD can be directly related to the correlation function $\psi_1(t)$. From Eqs. (27) and (32), we have the following relation:

$$\frac{\langle \mathrm{tr}\, \boldsymbol{D}(t)\, \mathrm{tr}\, \boldsymbol{D}(0)\rangle}{\langle \mathrm{tr}\, \boldsymbol{D}\rangle^2} \approx \frac{1}{2}\frac{\partial^2}{\partial t^2}[t^2\Sigma^2(t;\Delta)]. \tag{73}$$

Equation (73) means that if we have the RSD of the TAMSD for several different observation times, we can calculate the correlation function for the time-dependent and fluctuating diffusivity. As far as the authors know, there is no such analysis method which gives the correlation function of the diffusivity. Equation (73) will be especially useful for the analysis of experimental data, because we cannot directly observe the diffusivity from the trajectories.

B. Time-dependent diffusivity model and other models

As shown in Sec. II, various dynamics models can be expressed as the Langevin equation with time-dependent and fluctuating diffusivity. Here we discuss the relation between the time-dependent diffusivity model (described in Sec. II) and other dynamics models.

Łuczka, Niemiec, and Piotrowski [46,47] considered the randomly interrupted diffusion model, in which the strength of the noise in the Langevin equation depends on another stochastic process. The time-dependent diffusivity model reduces to the randomly interrupted diffusion model by tuning the dynamics of the noise coefficient matrix. Fogedby [48] considered two coupled Langevin equations. Fogedby replaced the time in a usual Langevin equation by the virtual time and introduced another Langevin equation for the evolution of the virtual time. The virtual time may be interpreted as the time-dependent and fluctuating diffusivity. Thus, we can interpret the Fogedby model as a special case of the time-dependent and fluctuating diffusivity model. However, we should note that the Fogedby model is designed to reproduce the Lévy flight, and thus the dynamics of the virtual time is assumed to be nonergodic, which differs from our model. Recently, Jeon, Chechkin, and Metzler [49] considered a time-dependent diffusion coefficient model. In their model, the diffusion coefficient simply depends on time t as $D(t) \propto t^{\alpha-1}$ (with α being an exponent). Namely, the dynamics of the instantaneous diffusion coefficient matrix is deterministic. Such a dynamics model reproduces the anomalous diffusion behavior. Using nonergodic dynamics to the noise coefficient matrix or the instantaneous diffusion coefficient matrix, we have anomalous diffusion in the time-dependent and fluctuating diffusivity model.

When the noise coefficient matrix or the instantaneous diffusion coefficient matrix obeys the discrete jump dynamics, the diffusion behavior strongly depends to the properties of the jump dynamics (as shown for the non-Markovian two-state model in Sec. IV B 2). Such jump dynamics is often modeled as the continuous-time random walk (CTRW) [50]. The CTRW is used, for example, as the diffusion model on the random potential landscape. Klafter and Silbey derived the CTRW for the diffusion model on randomly occupied lattices by using the projection operator technique [51]. Here we show that the two-state model reduces to the CTRW at a certain limit.

We start from the non-Markovian two-state model. In general, the non-Markovian two-state model does not reduce to the CTRW, although some aspects of the model are similar to the CTRW. We consider the special case where $D_s = 0$. In this case, the particle does not move when it is in the slow state. The particle can move freely in the fast state, whereas the particle is trapped and cannot move in the slow state. If the average sojourn time in the fast state, $\langle\tau\rangle_f$, is very short, then the movement of the particle looks like the instantaneous and discrete jump. Thus, at the limit of $\langle\tau_f\rangle \to 0$ with $D_f\langle\tau_f\rangle = (\mathrm{const})$, the trajectory of the Brownian particle reduces to that of the CTRW. The step size distribution for the CTRW is determined from the sojourn time distribution and the diffusion coefficient of the fast state. The trapping-time distribution for the slow state directly corresponds to the waiting time distribution for the CTRW. This can be interpreted as a simple and complementary derivation of the CTRW from a microscopic dynamics model.

It would be informative to mention a connection between the Langevin equation with the time-dependent and fluctuating diffusivity and the CTRW in the fluctuation analysis. If we take the limit of $\langle\tau_f\rangle \to 0$, then the crossover of the RSD disappears because the crossover time $\tau_c = 2\tilde{\tau}$ goes to zero at this limit. Actually, in the CTRW, the RSD does not show the plateau at the short-time region. (The constant RSD can be observed only for nonequilibrium initial ensembles.) However, the RF and RSD in the CTRW [17,52] also show the crossover behavior somewhat similar to one in the Langevin equation in this work. As we mentioned, the crossover time τ_c goes to zero at the limit, and thus this crossover behavior of the RSD in the CTRW has a qualitatively different origin from one in the Langevin equation with the time-dependent and fluctuating diffusivity. The crossover in the CTRW is related to the cutoff time of the waiting time distribution [17,52], not to τ_c in our analysis. When the waiting time distribution in the CTRW obeys a power law with an exponential cutoff, the RSD in the short-t region shows a power-law type behavior $\Sigma(t;\Delta) \propto t^{-(1-\alpha)/2}$ (with

$\alpha > 0$ being the power-law exponent). This behavior reflects the information on the trapping-time distribution, and such a behavior is not considered in the analysis in this work. A power-law type behavior of the RSD will be observed in our Langevin model, if the waiting time has the power-law form in a rather wide range [$k_{s,1}/k_{s,0} \gg 1$ in Eq. (67)]. In fact, as shown in Fig. 3, the crossover behavior becomes rather broad in the case of $k_{s,0} = 0.001$. Such t dependence is somewhat similar to one observed in the CTRW.

VI. CONCLUSIONS

We have derived the formula for the RSD of the TAMSD (which quantifies the fluctuation of the TAMSD) as a function of the observation time, in the Langevin equation with the time-dependent and fluctuating diffusivity. From the asymptotic behavior, a crossover from a constant RSD [$\Sigma(t;\Delta) \propto t^0$] to a Gaussian decay [$\Sigma(t;\Delta) \propto t^{-1/2}$] is predicted if there is a characteristic relaxation time of the fluctuating diffusivity. The asymptotic forms of our formula give the relation between the crossover time and the relaxation time. The crossover time is given as the weighted average relaxation time for the fluctuating diffusivity. Such a characteristic time cannot be calculated from the EAMSD. Applying the formula to the reptation model and the two-state models, we have shown that the crossover time can actually characterize the relaxation times of the diffusivities. This is because the RSD reflects the dynamcis of the time-dependent and fluctuating diffusivity. Our result justifies our previous study [15] in which we have numerically found that the crossover time can characterize the long-time relaxation behavior. We also showed that the (non-Markovian) two-state model reduces to the CTRW at a certain limit. However, this does not mean that the Langevin equation with the time-dependent and fluctuating diffusivity is equivalent to the CTRW. Actually, the behavior of the RSD of the CTRW differs qualitatively from one of the Langevin equation models. The RSD analysis extracts important information for underlying fluctuating diffusion processes. The RSD can be directly related to the correlation function of the instantaneous diffusivity, which is difficult to directly extract from the trajectories. We expect that the analysis of the RSD of the TAMSD is also useful for more complex systems such as MD simulations for entangled polymers and supercooled liquids, single-particle-tracking experiments, and diffusion in confined systems [53]. The RSD analysis together with other analysis methods will also give important information.

ACKNOWLEDGMENTS

T.U. thanks Professor Koh-hei Nitta for helpful comments and supports. The authors thank Eli Barkai, Juan P. Garrahan, and Ralf Metzler for helpful comments and informing some information on their publications. T.U. was supported by Grant-in-Aid (KAKENHI) for Young Scientists B (Grant No. 25800235) from Ministry of Education, Culture, Sports, Science, and Technology (MEXT). T.A. was supported by Grant-in-Aid (KAKENHI) for Young Scientists B (Grant No. 26800204) from Ministry of Education, Culture, Sports, Science, and Technology (MEXT).

APPENDIX A: DETAILED CALCULATIONS FOR ENSEMBLE AVERAGE OF SQUARED TIME-AVERAGED MEAN-SQUARE DISPLACEMENT

In this Appendix, we show the detailed calculations for the ensemble average of the squared TAMSD, $\langle[\overline{\delta^2(\Delta;t)}]^2\rangle$. From Eq. (2), $\langle[\overline{\delta^2(\Delta;t)}]^2\rangle$ can be explicitly written in terms of the noise $\boldsymbol{w}(t)$ and the noise coefficient matrix $\boldsymbol{B}(t)$:

$$\begin{aligned}\langle[\overline{\delta^2(\Delta;t)}]^2\rangle &= \frac{2}{(t-\Delta)^2}\int_0^{t-\Delta} dt' \int_0^{t'} dt'' \,\langle[\boldsymbol{r}(t'+\Delta)-\boldsymbol{r}(t')]^2[\boldsymbol{r}(t''+\Delta)-\boldsymbol{r}(t'')]^2\rangle \\ &= \frac{8}{(t-\Delta)^2}\int_0^{t-\Delta} dt' \int_0^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_{t'}^{t'+\Delta} ds' \int_{t''}^{t''+\Delta} du \int_{t''}^{t''+\Delta} du' \\ &\quad \times \langle w_i(s) w_j(s') w_k(u) w_l(u')\rangle \langle B_{mi}(s) B_{mj}(s') B_{nk}(u) B_{nl}(u')\rangle. \end{aligned} \tag{A1}$$

Here we have employed the Einstein summation convention. By utilizing the Wick's theorem [3], Eq. (A1) can be rewritten as

$$\begin{aligned}\langle[\overline{\delta^2(\Delta;t)}]^2\rangle = \frac{8}{(t-\Delta)^2}\int_0^{t-\Delta} dt' \int_0^{t'} dt'' \Bigg[&\int_{t'}^{t'+\Delta} ds \int_{t''}^{t''+\Delta} du \,\langle \mathrm{tr}\, \boldsymbol{D}(s)\, \mathrm{tr}\, \boldsymbol{D}(u)\rangle \\ &+ 2\int_{t'}^{t'+\Delta} ds \int_{t''}^{t''+\Delta} du \int_{t'}^{t'+\Delta} ds' \int_{t''}^{t''+\Delta} du'\, \delta(s-u')\delta(s'-u)\, \mathrm{tr}\langle \boldsymbol{D}(s)\cdot\boldsymbol{D}(u)\rangle \Bigg]. \end{aligned} \tag{A2}$$

The integrals over s, s', u, and u' in the last line of Eq. (A2) can be calculated as follows. For an arbitrary function $f(s,s',u,u')$, we have the following relation for the integrals over s and u':

$$\int_{t'}^{t'+\Delta} ds \int_{t''}^{t''+\Delta} du'\, \delta(s-u') f(s,s',u,u') = \begin{cases} \int_{t'}^{t''+\Delta} ds\, f(s,s',u,s) & (t''+\Delta \geqslant t'), \\ 0 & (t''+\Delta < t'). \end{cases} \tag{A3}$$

Here we have utilized the condition $t' > t''$, which holds for the integrand in (A2). Then the integrals in Eq. (A2) become

$$\int_{t'}^{t'+\Delta} ds \int_{t''}^{t''+\Delta} du \int_{t'}^{t'+\Delta} ds' \int_{t''}^{t''+\Delta} du'\, \delta(s-u')\delta(s'-u)\, \mathrm{tr}\langle \boldsymbol{D}(s)\cdot\boldsymbol{D}(u)\rangle$$

$$= \begin{cases} \int_{t'}^{t''+\Delta} ds \int_{t''}^{t''+\Delta} du \int_{t'}^{t'+\Delta} ds'\, \delta(s'-u)\, \mathrm{tr}\langle \boldsymbol{D}(s)\cdot\boldsymbol{D}(u)\rangle & (t''+\Delta \geqslant t'), \\ 0 & (t''+\Delta < t'), \end{cases}$$

$$= \begin{cases} \int_{t'}^{t''+\Delta} ds \int_{t'}^{t''+\Delta} du\ \mathrm{tr}\langle \boldsymbol{D}(s)\cdot\boldsymbol{D}(u)\rangle & (t''+\Delta \geqslant t'), \\ 0 & (t''+\Delta < t'). \end{cases} \tag{A4}$$

By using Eq. (A4), Eq. (A2) can be rewritten as

$$\begin{aligned} \langle[\overline{\delta^2(\Delta;t)}]^2\rangle &= \frac{8}{(t-\Delta)^2}\int_0^{t-\Delta} dt' \int_0^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_{t''}^{t''+\Delta} du\, \langle \mathrm{tr}\,\boldsymbol{D}(s)\,\mathrm{tr}\,\boldsymbol{D}(u)\rangle \\ &\quad + \frac{16}{(t-\Delta)^2}\int_0^{t-\Delta} dt' \int_0^{t'} dt''\, \Theta(t''-t'+\Delta) \int_{t'}^{t''+\Delta} ds \int_{t'}^{t''+\Delta} du\ \mathrm{tr}\langle \boldsymbol{D}(s)\cdot\boldsymbol{D}(u)\rangle \\ &= \frac{8}{(t-\Delta)^2}\int_0^{t-\Delta} dt' \int_0^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_{t''}^{t''+\Delta} du\, \langle \mathrm{tr}\,\boldsymbol{D}(s)\,\mathrm{tr}\,\boldsymbol{D}(u)\rangle \\ &\quad + \frac{32}{(t-\Delta)^2}\int_0^{t-\Delta} dt' \int_{\max(0,t'-\Delta)}^{t'} dt'' \int_{t'}^{t''+\Delta} ds \int_{t'}^{s} du\ \mathrm{tr}\langle \boldsymbol{D}(s)\cdot\boldsymbol{D}(u)\rangle, \end{aligned} \tag{A5}$$

with $\Theta(t)$ being the Heaviside step function. This gives Eq. (24).

APPENDIX B: RELATION BETWEEN RELATIVE FLUCTUATION AND RELATIVE STANDARD DEVIATION

In this Appendix, we consider the relation between the RF and the RSD for the TAMSD. Due to the nature of the absolute value, the analytic treatment of the RF is not easy compared with the RSD. We consider two asymptotic limits of the RF, which can be calculated straightforwardly.

As the case of the calculation for the RSD, we assume $\Delta \ll t$. For the small-t case ($t \ll \tau$) the RSD becomes constant as given by Eq. (33). It can be rewritten as

$$\Sigma(t;\Delta) \approx \sqrt{\psi_1(0)} = \frac{\sqrt{\langle(\mathrm{tr}\,\boldsymbol{D})^2\rangle - (\mathrm{tr}\langle\boldsymbol{D}\rangle)^2}}{\mathrm{tr}\langle\boldsymbol{D}\rangle}. \tag{B1}$$

From Eq. (B1), we find that $\Sigma(t;\Delta)$ is expressed as the relative standard deviation of $\mathrm{tr}\,\boldsymbol{D}$ for the equilibrium distribution. This can be understood as follows. In the case of $t \ll \tau$, we can approximate the instantaneous diffusion coefficient matrix by its initial value $\boldsymbol{D}(0)$, and the TAMSD of each realization can be reasonably approximated as

$$\overline{\delta^2(\Delta;t)} \approx 2\,\mathrm{tr}\,\boldsymbol{D}(0)\Delta. \tag{B2}$$

If we use Eq. (B2), the RSD of the TAMSD can be approximated as the RSD of $2\,\mathrm{tr}\,\boldsymbol{D}(0)\Delta$, which is equivalent to Eq. (B1). In a similar way, the RF can be approximately expressed as the RF of $2\,\mathrm{tr}\,\boldsymbol{D}(0)\Delta$. Thus we have the following expression for the RF:

$$R(t;\Delta) \approx \frac{\langle|\,\mathrm{tr}\,\boldsymbol{D} - \mathrm{tr}\langle\boldsymbol{D}\rangle|\rangle}{\mathrm{tr}\langle\boldsymbol{D}\rangle}. \tag{B3}$$

Unfortunately, we cannot calculate $R(t;\Delta)$ further without the explicit form of the equilibrium distribution for $\mathrm{tr}\,\boldsymbol{D}$. Nevertheless, we can formally relate $R(t;\Delta)$ to $\Sigma(t;\Delta)$ as

$$R(t;\Delta) \approx \frac{\langle|\,\mathrm{tr}\,\boldsymbol{D} - \mathrm{tr}\langle\boldsymbol{D}\rangle|\rangle}{\sqrt{\langle(\mathrm{tr}\,\boldsymbol{D})^2\rangle - (\mathrm{tr}\langle\boldsymbol{D}\rangle)^2}}\Sigma(t;\Delta). \tag{B4}$$

For the large t case ($t \gg \tau$), we have the relation $\Sigma(t;\Delta) \propto t^{-1/2}$ from Eq. (33). This means that the distribution of the TAMSD is given as a Gaussian with the aid of the central limit theorem. We can explicitly write the distribution of the TAMSD as follows:

$$\begin{aligned} P(\overline{\delta^2(\Delta;t)}) \approx{}& \frac{1}{\sqrt{2\pi}\,\Sigma(t;\Delta)\langle\overline{\delta^2(\Delta;t)}\rangle} \\ &\times \exp\left[-\frac{[\overline{\delta^2(\Delta;t)} - \langle\overline{\delta^2(\Delta;t)}\rangle]^2}{2[\Sigma(t;\Delta)\langle\overline{\delta^2(\Delta;t)}\rangle]^2}\right]. \end{aligned} \tag{B5}$$

The RF can be then calculated to be

$$\begin{aligned} R(t;\Delta) &\approx \frac{1}{\langle\overline{\delta^2(\Delta;t)}\rangle}\int d\overline{\delta^2(\Delta;t)}\,|\overline{\delta^2(\Delta;t)} \\ &\quad - \langle\overline{\delta^2(\Delta;t)}\rangle|\,P(\overline{\delta^2(\Delta;t)}) \\ &\approx \sqrt{\frac{2}{\pi}}\Sigma(t;\Delta). \end{aligned} \tag{B6}$$

By combining Eqs. (B4) and (B6), we have the asymptotic forms of $R(t;\Delta)$:

$$R(t;\Delta) \approx \begin{cases} \frac{\langle|\,\mathrm{tr}\,\boldsymbol{D}-\mathrm{tr}\langle\boldsymbol{D}\rangle|\rangle}{\sqrt{\langle(\mathrm{tr}\,\boldsymbol{D})^2\rangle-(\mathrm{tr}\langle\boldsymbol{D}\rangle)^2}}\Sigma(t;\Delta) & (t \ll \tau), \\ \sqrt{\frac{2}{\pi}}\Sigma(t;\Delta) & (t \gg \tau). \end{cases} \tag{B7}$$

From Eq. (B7), we find that the RF behaves qualitatively in the same way as the RSD. The crossover time determined by the RF, τ_c', differs from τ_c in Eq. (34) by a constant factor:

$$\tau_c' = \frac{2[\langle(\mathrm{tr}\,\boldsymbol{D})^2\rangle - (\mathrm{tr}\langle\boldsymbol{D}\rangle)^2]}{\pi\,\langle|\,\mathrm{tr}\,\boldsymbol{D} - \mathrm{tr}\langle\boldsymbol{D}\rangle|\rangle^2}\tau_c. \tag{B8}$$

In most practical cases, the ratio of τ_c' and τ_c is of the order of unity, and thus both $R(t;\Delta)$ and $\Sigma(t;\Delta)$ can be utilized to analyze the long-time relaxation behavior.

In the case of the reptation model, the explicit asymptotic forms can be calculated from the equilibrium distribution for the end-to-end vector $\boldsymbol{p}$ [3]:

$$P^{(\mathrm{eq})}(\boldsymbol{p}) = \left(\frac{3}{2\pi\langle\boldsymbol{p}^2\rangle}\right)^{3/2}\exp\left(-\frac{3\boldsymbol{p}^2}{2\langle\boldsymbol{p}^2\rangle}\right). \tag{B9}$$

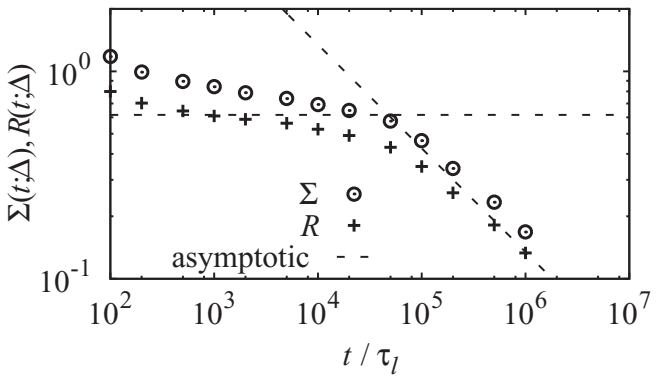

FIG. 4. The RSD and RF of the TAMSD of a center of mass in the discrete reptation model. (The RF data are taken from Ref. [15].) The number of tube segments $Z = 80$ and the time difference $\Delta = 10\tau_l$, where τ_l is the characteristic time of the longitudinal motion of a segment along the tube. Dashed curves represent the asymptotic forms for the RF [Eq. (B10)].

The asymptotic forms of $\Sigma(t;\Delta)$ is given by Eq. (44). Finally, we have the following asymptotic forms for $R(t;\Delta)$:

$$R(t;\Delta) \approx \begin{cases} 2e^{-3/2}\sqrt{6/\pi} & (t \ll \tau), \\ \sqrt{\pi\tau_d/9t} & (t \gg \tau). \end{cases} \tag{B10}$$

This gives the crossover time $\tau_c' \approx 0.918\tau_d$. (In the previous work, we reported $\tau_c' \approx \tau_d$ [15]. This small discrepancy may be due to the accuracy of the fitting for the short observation time region.) To check whether Eq. (B7) actually holds, here we examine the RSD and RF data obtained by the discrete reptation model. We show the RSD and RF of the TAMSD of a center of mass in the reptation model for $Z = 80$ and $\Delta = 10\tau_l$ (τ_l is the characteristic time of the longitudinal segmental motion) in Fig. 4. We also show the asymptotic forms of the RF calculated from the asymptotic forms of the RSD by Eq. (B10) in Fig. 4. From Fig. 4, we find that our theoretical prediction agrees well with the asymptotic behavior of the simulation data. Thus we conclude that the RF shows qualitatively the same behavior as the RSD. Both the RSD and RF of the TAMSD can be utilized to study the long-time relaxation behavior.

APPENDIX C: DETAILED CALCULATIONS FOR REPTATION MODEL

In this Appendix, we show the detailed calculation for the correlation function $\psi_1(t)$ in the reptation model. In the reptation model, many of dynamical quantities can be calculated from the tube survival probability, which represents the probability of a tube segment at time 0 survives up to time t [3]. The tube survival probability of the segment index s at time t can be expressed as

$$\Psi(s;t) = \sum_{k:\text{odd}} \frac{4}{k\pi} \sin\left(\frac{k\pi s}{Z}\right) \exp\left(-\frac{k^2 t}{\tau_d}\right). \tag{C1}$$

Here Z is the number of tube segments ($0 \leqslant s \leqslant Z$) and τ_d is the disengagement time. Note that the expression of the surviving probability in this work differs slightly from commonly utilized one in the Doi-Edwards textbook [3]. In this work s represents the segment index along the tube ($0 \leqslant s \leqslant Z$), whereas in the Doi-Edwards definition s represents the distance along the tube ($0 \leqslant s \leqslant Za$). (Our definition makes the calculations slightly simple, as shown below.)

To calculate the higher-order correlation functions, we need the joint survival probability $\Psi(s,s';t)$ of two segment indices s and s'. $\Psi(s,s';t)$ represents the probability that both of segments s and s' at time 0 survive up to time t. $\Psi(s,s';t)$ can be obtained by solving the first-passage type problem. [This is similar to the calculation of $\Psi(s,t)$.] We consider the case $s \leqslant s'$ and set $\xi \equiv s' - s$. Then $\Psi(s,s';t) = \Psi(s,s+\xi;t)$ obeys the backward Fokker-Planck equation:

$$\frac{\partial\Psi(s,s+\xi;t)}{\partial t} = \frac{1}{Z\tau_l}\frac{\partial^2\Psi(s,s+\xi;t)}{\partial s^2}, \tag{C2}$$

with τ_l being the characteristic time scale of the longitudinal motion of a segment along the tube. The initial condition for Eq. (C2) is

$$\Psi(s,s+\xi;0) = 1, \tag{C3}$$

and the boundary condition for Eq. (C2) is

$$\Psi(Z-\xi,Z;t) = \Psi(0,\xi;t) = 0. \tag{C4}$$

The disengagement time (the longest relaxation time) τ_d is related to τ_l as $\tau_d = Z^3\tau_l/\pi^2$. By solving Eq. (C2), we have the following expression for the joint survival probability:

$$\Psi(s,s+\xi;t) = \sum_{k:\text{odd}} \frac{4}{k\pi} \sin\left(\frac{p\pi s}{Z-\xi}\right) \exp\left[-\frac{Z^2k^2t}{(Z-\xi)^2\tau_d}\right]. \tag{C5}$$

For the case of $s > s'$, the solution is the same form as Eq. (C5) with s and ξ replaced by s' and $s - s'$, respectively. Combining them we have

$$\Psi(s,s';t) = \sum_{k:\text{odd}} \frac{4}{k\pi} \sin\left(\frac{k\pi \min(s,s')}{Z-|s-s'|}\right) \times \exp\left[-\frac{Z^2k^2t}{(Z-|s-s'|)^2\tau_d}\right]. \tag{C6}$$

For the case of $s = s'$, Eq. (C6) reduces to $\Psi(s;t)$:

$$\Psi(s,s;t) = \Psi(s;t). \tag{C7}$$

We consider the four-body two-time correlation function $\psi_1(t)$. From Eq. (39), we need to calculate the correlation function of the end-to-end vector, $\langle \boldsymbol{p}^2(t)\boldsymbol{p}^2(0)\rangle$. It can be calculated by utilizing the joint survival probability $\Psi(s,s';t)$, because the end-to-end vector can be expressed in terms of the bond vectors of segments. The end-to-end vector at time t can be expressed as

$$\boldsymbol{p}(t) = \int_0^Z ds\, \boldsymbol{u}(s,t), \tag{C8}$$

where $\boldsymbol{u}(s,t)$ is the bond vector at the segment index s at time t. The bond vector obeys the Gaussian statistics in equilibrium. The first and second moments in equilibrium are given as

$$\langle \boldsymbol{u}(s)\rangle = 0, \quad \langle \boldsymbol{u}(s)\boldsymbol{u}(s')\rangle = \tfrac{1}{3}a^2\mathbf{1}\delta(s-s'). \tag{C9}$$

Here a is the tube segment size. The average end-to-end vector size can be calculated straightforwardly:

$$\langle \boldsymbol{p}^2 \rangle = Za^2. \tag{C10}$$

The correlation function $\psi_1(t)$ can be evaluated if we know whether two bonds at time 0 still survive at time t. There are three possible cases. The first case is where both two bonds (s and s') survive, and the probability for this case is given as $\Psi(s,s';t)$. The second case is where only one bond (s or s') survives, and the probabilities are given as $\Psi(s;t) - \Psi(s,s';t)$ or $\Psi(s';t) - \Psi(s,s';t)$, respectively. The third case is where none of two bonds survives, and the probability for this case is $1 - \Psi(s;t) - \Psi(s';t) + \Psi(s,s';t)$. Thus we have

$$\begin{aligned}\langle \boldsymbol{p}^2(t)\boldsymbol{p}^2(0)\rangle = &\int_0^Z ds \int_0^Z ds' \int_0^Z dv \int_0^Z dv' \{\langle [\boldsymbol{u}(s)\cdot\boldsymbol{u}(s')][\boldsymbol{u}(v)\cdot\boldsymbol{u}(v')]\rangle \Psi(s,s';t) \\ &+ \langle \boldsymbol{u}(s')\rangle \cdot \langle \boldsymbol{u}(s)[\boldsymbol{u}(v)\cdot\boldsymbol{u}(v')]\rangle [\Psi(s;t) - \Psi(s,s';t)] + \langle \boldsymbol{u}(s)\rangle \cdot \langle \boldsymbol{u}(s')[\boldsymbol{u}(v)\cdot\boldsymbol{u}(v')]\rangle [\Psi(s';t) - \Psi(s,s';t)] \\ &+ \langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle \langle \boldsymbol{u}(v)\cdot\boldsymbol{u}(v')\rangle [1 - \Psi(s;t) - \Psi(s';t) + \Psi(s,s';t)]\} \\ = &\int_0^Z ds \int_0^Z ds' \int_0^Z dv \int_0^Z dv' \langle [\boldsymbol{u}(s)\cdot\boldsymbol{u}(s')][\boldsymbol{u}(v)\cdot\boldsymbol{u}(v')]\rangle \Psi(s,s';t) + Z^2a^4 + Za^4 \int_0^Z ds\, [\Psi(s,s;t) - 2\Psi(s;t)].\end{aligned} \tag{C11}$$

By using the Wick's theorem [3], the average for the bond vectors in Eq. (C11) can be decomposed as follows:

$$\begin{aligned}\langle [\boldsymbol{u}(s)\cdot\boldsymbol{u}(s')][\boldsymbol{u}(v)\cdot\boldsymbol{u}(v')]\rangle &= \langle \boldsymbol{u}(s)\cdot\boldsymbol{u}(s')\rangle \langle \boldsymbol{u}(v)\cdot\boldsymbol{u}(v')\rangle + \langle \boldsymbol{u}(s)\boldsymbol{u}(v)\rangle : \langle \boldsymbol{u}(s')\boldsymbol{u}(v')\rangle + \langle \boldsymbol{u}(s)\boldsymbol{u}(v')\rangle : \langle \boldsymbol{u}(s')\boldsymbol{u}(v)\rangle \\ &= a^4\delta(s-s')\delta(v-v') + \frac{a^4}{3}\delta(s-v)\delta(s'-v') + \frac{a^4}{3}\delta(s-v')\delta(s'-v).\end{aligned} \tag{C12}$$

The first term in the last line of Eq. (C11) is calculated to be

$$\begin{aligned}&\int_0^Z ds \int_0^Z ds' \int_0^Z dv \int_0^Z dv' \langle [\boldsymbol{u}(s)\cdot\boldsymbol{u}(s')][\boldsymbol{u}(v)\cdot\boldsymbol{u}(v')]\rangle \Psi(s,s';t) \\ &\quad = Za^4 \int_0^Z ds\, \Psi(s,s;t) + \frac{2a^4}{3}\int_0^Z ds \int_0^Z ds'\, \Psi(s,s';t).\end{aligned} \tag{C13}$$

From Eqs. (39), (C11), and (C13), $\psi_1(t)$ can be simplified:

$$\begin{aligned}\psi_1(t) &= \frac{2}{Z}\int_0^Z ds\, [\Psi(s,s;t) - \Psi(s;t)] + \frac{2}{3Z^2}\int_0^Z ds \int_0^Z ds'\, \Psi(s,s';t) \\ &= \frac{2}{3Z^2}\int_0^Z ds \int_0^Z ds'\, \Psi(s,s';t),\end{aligned} \tag{C14}$$

where we have used Eq. (C7).

Equation (C14) can be further modified by substituting Eq. (C6) into it:

$$\begin{aligned}\psi_1(t) &= \frac{8}{3\pi Z^2}\sum_{k:\text{odd}} \frac{1}{k}\int_0^Z ds \int_0^Z ds'\, \sin\left[\frac{k\pi \min(s,s')}{Z - |s-s'|}\right] \exp\left[-\frac{Z^2k^2t}{(Z-|s-s'|)^2\tau_d}\right] \\ &= \frac{16}{3\pi Z^2}\sum_{k:\text{odd}} \frac{1}{k}\int_0^Z ds \int_0^s ds'\, \sin\left[\frac{k\pi s'}{Z-(s-s')}\right] \exp\left[-\frac{Z^2k^2t}{(Z-(s-s'))^2\tau_d}\right].\end{aligned} \tag{C15}$$

By introducing the variable transform $w \equiv s - s'$, Eq. (C15) can be integrated over s as

$$\begin{aligned}\psi_1(t) &= \frac{16}{3\pi Z^2}\sum_{k:\text{odd}} \frac{1}{k}\int_0^Z dw \int_w^Z ds\, \sin\left[\frac{k\pi(s-w)}{Z-w}\right] \exp\left[-\frac{Z^2k^2t}{(Z-w)^2\tau_d}\right] \\ &= \frac{32}{3\pi^2 Z^2}\sum_{k:\text{odd}} \frac{1}{k^2}\int_0^Z dw\, (Z-w) \exp\left[-\frac{Z^2k^2t}{(Z-w)^2\tau_d}\right].\end{aligned} \tag{C16}$$

We introduce another variable transform $x \equiv Z^2/(Z-w)^2$ to make the integral simple and tractable:

$$\begin{aligned}\psi_1(t) &= \frac{16}{3\pi^2}\sum_{k:\text{odd}} \frac{1}{k^2}\int_1^\infty dx\, x^{-2} \exp\left(-\frac{k^2t}{\tau_d}x\right) \\ &= \frac{16}{3\pi^2}\sum_{k:\text{odd}} \frac{1}{k^2} E_2(k^2t/\tau_d).\end{aligned} \tag{C17}$$

In the last line of Eq. (C17), we have utilized the definition of the (generalized) exponential integral [32]. Thus we have the explicit expression for the correlation function $\psi_1(t)$ in the main text, Eq. (40).

APPENDIX D: DECOUPLING APPROXIMATION FOR REPTATION MODEL

In the main text, we employed the decoupling approximation for the reptation model without any justifications. The dynamics of the end-to-end vector depends on the one-dimensional white noise $w(t)$, and thus the decoupling approximation seems not to be fully justified. Here we discuss the validity of the decoupling approximation for the reptation model and show that the decouplilng approximation is reasonable for our calculations.

We consider the EAMSD [Eq. (11) for the reptation model without the decoupling approximation:

$$\langle [\boldsymbol{r}(\Delta)-\boldsymbol{r}(0)]^2\rangle = \frac{6D_{\mathrm{c.m.}}}{\langle \boldsymbol{p}^2\rangle}\int_0^t ds\int_0^t ds'\langle \boldsymbol{p}(s)\cdot\boldsymbol{p}(s')w(s)w(s')\rangle. \quad \text{(D1)}$$

The integrand in the right-hand side of Eq. (D1) can be rewritten as

$$\langle \boldsymbol{p}(s)\cdot\boldsymbol{p}(s')w(s)w(s')\rangle = \langle\langle \boldsymbol{p}(s)\cdot\boldsymbol{p}(s')\rangle_{w(s),w(s')}w(s)w(s')\rangle, \quad \text{(D2)}$$

where $\langle\dots\rangle_{w(s),w(s')}$ represents the ensemble average under given values of $w(s)$ and $w(s')$. Without loss of generality, we consider the case of $s \geqslant s'$. The correlation function $\langle \boldsymbol{p}(s)\cdot\boldsymbol{p}(s')\rangle_{w(s),w(s')}$ can be expressed in terms of the fraction of the surviving tube segments at time s'. The fraction of surviving tube segments is related to the minimum and maximum values of the displacement of the chain along the tube. Therefore, the correlation function can be calculated as follows:

$$\langle \boldsymbol{p}(s)\cdot\boldsymbol{p}(s')\rangle_{w(s)w(s')} = \langle \boldsymbol{p}\rangle^2\left\langle \max\left[0, Z + \min_{\substack{s'' \\ (s'<s''<s)}} W(s'',s') - \max_{\substack{s'' \\ (s'<s''<s)}} W(s'',s')\right]\right\rangle_{w(s),w(s').} \quad \text{(D3)}$$

Here $W(s,s')$ is the one-dimensional displacement of the chain along the tube, at time s starting from time s'. $W(s,s')$ can be expressed as a time integral of the one-dimensional noise $w(t)$:

$$W(s,s') \equiv \sqrt{\frac{2}{Z\tau_l}}\int_{s'}^{s} du\, w(u). \quad \text{(D4)}$$

The contributions of $w(s)$ and $w(s')$ to $W(s,s')$ are infinitesimally small and thus from Eq. (D3), $\langle \boldsymbol{p}(s)\cdot\boldsymbol{p}(s')\rangle_{w(s)w(s')}$ becomes statistically independent of $w(s)$ and $w(s')$. Finally, Eq. (D2) becomes

$$\langle \boldsymbol{p}(s)\cdot\boldsymbol{p}(s')w(s)w(s')\rangle = \langle \boldsymbol{p}(s)\cdot\boldsymbol{p}(s')\rangle\langle w(s)w(s')\rangle. \quad \text{(D5)}$$

From the symmetry, Eq. (D5) also holds for $s < s'$. Equation (D5) justifies the decoupling approximation for the calculation of the EAMSD.

For the calculation of the RSD of the TAMSD, we have a similar correlation function [see Eq. (A1) in Appendix A]:

$$\langle \boldsymbol{p}(s_1)\cdot\boldsymbol{p}(s_2)\boldsymbol{p}(s_3)\cdot\boldsymbol{p}(s_4)w(s_1)w(s_2)w(s_3)w(s_4)\rangle = \langle\langle \boldsymbol{p}(s_1)\cdot\boldsymbol{p}(s_2)\boldsymbol{p}(s_3)\cdot\boldsymbol{p}(s_4)\rangle_{w(s_1),w(s_2),w(s_3),w(s_4)} \times w(s_1)w(s_2)w(s_3)w(s_4)\rangle. \quad \text{(D6)}$$

Here $\langle\dots\rangle_{w(s_1),w(s_2),w(s_3),w(s_4)}$ represents the ensemble average under given $w(s_1), w(s_2), w(s_3)$, and $w(s_4)$. The correlation function $\langle \boldsymbol{p}(s_1)\cdot\boldsymbol{p}(s_2)\boldsymbol{p}(s_3)\cdot\boldsymbol{p}(s_4)\rangle_{w(s_1),w(s_2),w(s_3),w(s_4)}$ depends only on the one-dimensional displacement along the tube. (The explicit expression becomes quite complicated.) The contributions of $w(s_1), w(s_2), w(s_3)$, and $w(s_4)$ to the one-dimensional displacement are infinitesimally small, as in the previous case. Therefore we find that Eq. (D6) can be rewritten as the following decoupled form:

$$\langle \boldsymbol{p}(s_1)\cdot\boldsymbol{p}(s_2)\boldsymbol{p}(s_3)\cdot\boldsymbol{p}(s_4)w(s_1)w(s_2)w(s_3)w(s_4)\rangle = \langle \boldsymbol{p}(s_1)\cdot\boldsymbol{p}(s_2)\boldsymbol{p}(s_3)\cdot\boldsymbol{p}(s_4)\rangle\langle w(s_1)w(s_2)w(s_3)w(s_4)\rangle. \quad \text{(D7)}$$

This justifies the use of the decoupling approximation for the calculation of the RSD of the TAMSD.

APPENDIX E: DETAILED CALCULATIONS FOR NON-MARKOVIAN TWO-STATE MODEL

In this Appendix, we show the detailed calculations for the RSD of the TAMSD in the non-Markovian two-state model. The (unilateral) Laplace transform is convenient to calculate some quantities for such a non-Markovian model. For example, the Laplace transform of the equilibrium trapping-time distribution $\rho_h^{(\mathrm{eq})}(t)$ [Eq. (58)] simply becomes

$$\hat{\rho}_h^{(\mathrm{eq})}(u) = \frac{1-\hat{\rho}_h(u)}{u\langle\tau\rangle_h}. \quad \text{(E1)}$$

Here the functions with hats (such as $\hat{\rho}_h$ and $\hat{\rho}_h^{(\mathrm{eq})}$) represent the Laplace transformed functions. We define the distribution for the sum of two successive trapping times as $\rho(\tau)$. $\rho(\tau)$ can be expressed as the convolution of $\rho_f(\tau)$ and $\rho_s(\tau)$,

$$\rho(\tau) \equiv \rho_f * \rho_s(\tau) = \rho_s * \rho_f(\tau) = \int_0^\tau d\tau'\,\rho_f(\tau-\tau')\rho_s(\tau'). \quad \text{(E2)}$$

The Laplace transform of $\rho(\tau)$ simply becomes

$$\hat{\rho}(u) = \hat{\rho}_f(u)\hat{\rho}_s(u). \quad \text{(E3)}$$

We express the probabilities of having n transitions up to time t starting from the state h at time 0, as $Q_{h,n}(t)$ $(h = f,s)$. For convenience, we introduce the following integral operator $\mathcal{I}$:

$$\mathcal{I}f(t) \equiv \int_t^\infty dt'\, f(t'). \quad \text{(E4)}$$

Then $Q_{h,n}(t)$ can be expressed as [35]

$$Q_{h,n}(t) = \begin{cases} \mathcal{I}\rho_h^{(\mathrm{eq})}(t) & (n=0), \\ \rho_h^{(\mathrm{eq})} * \overbrace{\rho * \rho * \cdots * \rho}^{(n-1)/2} * (\mathcal{I}\rho_{\bar{h}})(t) & (n = 1,3,5,\dots), \\ \rho_h^{(\mathrm{eq})} * \overbrace{\rho * \rho * \cdots * \rho}^{n/2-1} * \rho_{\bar{h}} * (\mathcal{I}\rho_h)(t) & (n = 2,4,6,\dots). \end{cases} \tag{E5}$$

where $\bar{h} = s$ and f for $h = f$ and s, respectively. The Laplace transform of $Q_{h,n}(t)$ becomes

$$\hat{Q}_{h,n}(u) = \begin{cases} \frac{\langle\tau\rangle_h u - 1 + \hat{\rho}_h(u)}{\langle\tau\rangle_h u^2} & (n=0), \\ \frac{[1-\hat{\rho}_h(u)][1-\hat{\rho}_{\bar{h}}(u)]}{\langle\tau\rangle_h u^2}\hat{\rho}^{(n-1)/2}(u) & (n = 1,3,5,\dots), \\ \frac{[1-\hat{\rho}_h(u)]^2}{\langle\tau\rangle_h u^2}\hat{\rho}_{\bar{h}}(u)\hat{\rho}^{n/2-1}(u) & (n = 2,4,6,\dots). \end{cases} \tag{E6}$$

The transition probability $W_{hh'}(t)$ can be expressed in terms of $Q_{h,n}(t)$ as

$$W_{hh'}(t) = \begin{cases} \sum_{n=0}^{\infty} Q_{h,2n}(t) & (h' = h), \\ \sum_{n=0}^{\infty} Q_{\bar{h},2n+1}(t) & (h' = \bar{h}). \end{cases} \tag{E7}$$

We calculate the asymptotic form of the correlation function $\psi_1(t)$ in the long-time region. The long-time asymptotic behavior can be calculated from the small-u limit for the Laplace transform. Since $W_{hh'}(t)$ converges to ϕ_h at the limit of $t \to \infty$, it is convenient to consider $W_{hh'}(t) - \phi_h$ rather than $W_{hh'}(t)$ itself. From Eqs. (E6) and (E7), we obtain the following asymptotic form for the Laplace transform of $W_{hh'}(t) - \phi_h$ for small u:

$$\hat{W}_{hh'}(u) - \frac{\phi_h}{u} \approx \sigma_{hh'} \frac{\langle\tau^2\rangle_s\langle\tau\rangle_f^2 + \langle\tau^2\rangle_f\langle\tau\rangle_s^2 - 2\langle\tau\rangle_s^2\langle\tau\rangle_f^2}{2\langle\tau\rangle_{h'}(\langle\tau\rangle_s + \langle\tau\rangle_f)^2}, \tag{E8}$$

where $\sigma_{hh'} = 1$ or -1 for $h' = h$ or $h' = \bar{h}$, respectively, and we have utilized the expansion of $\hat{\rho}_h(u)$ around $u = 0$,

$$\hat{\rho}_h(u) = 1 - \langle\tau\rangle_h u - \langle\tau^2\rangle_h u^2/2 + \cdots. \tag{E9}$$

From Eq. (E8), we have the following simple relation for the transition probability:

$$\int_0^{\infty} dt\,[W_{hh'}(t) - \phi_h] = \lim_{u\to 0}\left[\hat{W}_{hh'}(u) - \frac{\phi_h}{u}\right] = \begin{cases} \tilde{\tau}\phi_{\bar{h}} & (h' = h), \\ -\tilde{\tau}\phi_h & (h' = \bar{h}), \end{cases} \tag{E10}$$

where $\tilde{\tau}$ is the characteristic relaxation time defined by Eq. (64). By combining Eqs. (61) and (E10), finally we have Eq. (63).

APPENDIX F: NON-GAUSSIANITY PARAMETER

The non-Gaussianity parameter [37–39] is widely employed to investigate the non-Gaussian properties of the diffusion processes. In this Appendix, we calculate the expression for the non-Gaussianity parameter $A(\Delta)$ [Eq. (70)] in terms of the four-body two-time correlation functions. Then we compare it with the RSD of the TAMSD.

The ensemble average of quartic displacement can be calculated in the same way as Eq. (A2),

$$\begin{aligned} &\langle[\boldsymbol{r}(\Delta) - \boldsymbol{r}(0)]^4\rangle \\ &= 4\int_0^{\Delta} ds \int_0^{\Delta} ds' \int_0^{\Delta} du \int_0^{\Delta} du'\, \langle w_i(s) w_j(s') w_k(u) w_l(u')\rangle \\ &\quad \times \langle B_{mi}(s) B_{mj}(s') B_{nk}(u) B_{nl}(u')\rangle \\ &= 8\int_0^{\Delta} ds \int_0^{s} du\, \langle \mathrm{tr}\,\boldsymbol{D}(s)\,\mathrm{tr}\,\boldsymbol{D}(u)\rangle \\ &\quad + 16\int_0^{\Delta} ds \int_0^{s} du\, \mathrm{tr}\langle \boldsymbol{D}(s)\cdot\boldsymbol{D}(u)\rangle. \end{aligned} \tag{F1}$$

By using the correlation functions $\psi_1(t)$ and $\psi_2(t)$ defined in Eqs. (27) and (28), Eq. (F1) can be rewritten as

$$\begin{aligned} &\langle[\boldsymbol{r}(\Delta) - \boldsymbol{r}(0)]^4\rangle \\ &= 4\left(1 + \frac{2C}{n}\right)[\mathrm{tr}\langle\boldsymbol{D}\rangle]^2\Delta^2 + 8[\mathrm{tr}\langle\boldsymbol{D}\rangle]^2 \\ &\quad \times \int_0^{\Delta} ds \int_0^{s} du\,[\psi_1(s-u) + 2C\psi_2(s-u)]. \end{aligned} \tag{F2}$$

From Eqs. (70) and (F2), finally we have the following formula for the non-Gaussianity parameter:

$$\begin{aligned} A(\Delta) = \frac{2(C-1)}{n+2} + \frac{2n}{(n+2)\Delta^2}\int_0^{\Delta} ds \\ \times \int_0^{s} du\,[\psi_1(s-u) + 2C\psi_2(s-u)]. \end{aligned} \tag{F3}$$

Equation (F3) contains both $\psi_1(t)$ and $\psi_2(t)$. Because these correlation functions exhibit the characteristic long time relaxation, the non-Gaussianity parameter can be utilized to analyze the characteristic relaxation at the long time scale. The short- and long-time asymptotic forms are calculated to be

$$A(\Delta) \approx \begin{cases} \frac{2(C-1)}{n+2} + \frac{n}{n+2}[\psi_1(0) + 2C\psi_2(0)] & (\Delta \ll \tau), \\ \frac{2(C-1)}{n+2} + \frac{2n}{(n+2)\Delta}\int_0^{\infty} dv\,[\psi_1(v) + 2C\psi_2(v)] & (\Delta \gg \tau). \end{cases} \tag{F4}$$

Equation (F4) has somewhat similar properties to the squared RSD, Eq. (33). However, the bahavior of $A(\Delta)$ qualitatively differs from one of the squared RSD. $A(\Delta)$ approaches to the constant $2(C-1)/(n+2)$ at the limit of $\Delta \to \infty$, whereas $\Sigma^2(t;\Delta)$ approaches to zero at the limit of $t \to \infty$. Such a property of $A(\Delta)$ makes the numerical analysis difficult. [We need to determine the constant $2(C-1)/(n+2)$ and then subtract it from $A(\Delta)$.] In the case of the isotropic systems, $C=1$ and this constant vanishes. Then Eq. (F4) reduces to

$$A(\Delta) \approx \begin{cases} \frac{n}{n+2}[\psi_1(0)+2\psi_2(0)] & (\Delta \ll \tau), \\ \frac{2n}{(n+2)\Delta}\int_0^\infty dv\,[\psi_1(v)+2\psi_2(v)] & (\Delta \gg \tau). \end{cases} \tag{F5}$$

Even in this simple case, $A(\Delta)$ depends on both $\psi_1(t)$ and $\psi_2(t)$. Also $A(\Delta)$ explicitly depends on the dimension of the system. On the other hand, the explicit expression for the squared RSD [Eq. (32)] and its asymptotic forms [Eq. (33)] are simple and common for isotropic and anisotropic systems. [As mentioned in the main text, $\Sigma^2(t;\Delta)$ essentially depends only on $\psi_1(t)$.] Thus we consider that the RSD would be more suitable than the non-Gaussianity parameter to characterize the long-time relaxation behavior of time-dependent and fluctuating diffusivities.

[1] H. Scher and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975).
[2] P. Barthelemy, J. Bertolotti, and D. S. Wiersma, Nature **453**, 495 (2008).
[3] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
[4] A. Caspi, R. Granek, and M. Elbaum, Phys. Rev. Lett. **85**, 5655 (2000).
[5] I. Golding and E. C. Cox, Phys. Rev. Lett. **96**, 098102 (2006).
[6] A. Weigel, B. Simon, M. Tamkun, and D. Krapf, Proc. Natl. Acad. Sci. USA **108**, 6438 (2011).
[7] S. A. Tabei, S. Burov, H. Y. Kim, A. Kuznetsov, T. Huynh, J. Jureller, L. H. Philipson, A. R. Dinner, and N. F. Scherer, Proc. Natl. Acad. Sci. USA **110**, 4911 (2013).
[8] J.-H. Jeon, V. Tejedor, S. Burov, E. Barkai, C. Selhuber-Unkel, K. Berg-Sørensen, L. Oddershede, and R. Metzler, Phys. Rev. Lett. **106**, 048103 (2011).
[9] J.-H. Jeon, N. Leijnse, L. B. Oddershede, and R. Metzler, New J. Phys. **15**, 045011 (2013).
[10] F. Sciortino, P. Gallo, P. Tartaglia, and S. H. Chen, Phys. Rev. E **54**, 6331 (1996).
[11] T. Akimoto and T. Miyaguchi, J. Stat. Phys. **157**, 515 (2014).
[12] T. Miyaguchi and T. Akimoto, Phys. Rev. E **83**, 031926 (2011).
[13] T. Akimoto and T. Miyaguchi, Phys. Rev. E **87**, 062134 (2013).
[14] Y. He, S. Burov, R. Metzler, and E. Barkai, Phys. Rev. Lett. **101**, 058101 (2008).
[15] T. Uneyama, T. Akimoto, and T. Miyaguchi, J. Chem. Phys. **137**, 114903 (2012).
[16] T. Akimoto, E. Yamamoto, K. Yasuoka, Y. Hirano, and M. Yasui, Phys. Rev. Lett. **107**, 178103 (2011).
[17] T. Miyaguchi and T. Akimoto, Phys. Rev. E **83**, 062101 (2011).
[18] S. Burov, J.-H. Jeon, R. Metzler, and E. Barkai, Phys. Chem. Chem. Phys. **13**, 1800 (2011).
[19] A. G. Cherstvy, A. V. Chechkin, and R. Metzler, New J. Phys. **15**, 083039 (2013).
[20] W. Deng and E. Barkai, Phys. Rev. E **79**, 011112 (2009).
[21] M. Doi and S. F. Edwards, J. Chem. Soc. Farady Trans. 2 **74**, 1789 (1978).
[22] H. Sillescu, J. Non-Cryst. Solids **243**, 81 (1999).
[23] W. Gotze and L. Sjogren, Rep. Prog. Phys. **55**, 241 (1992).
[24] R. Richert, J. Phys. Cond. Matt. **14**, R703 (2002).
[25] L. Berthier and G. Biroli, Rev. Mod. Phys. **83**, 587 (2011).
[26] O. Bénichou, C. Loverdo, M. Moreau, and R. Voituriez, Rev. Mod. Phys. **83**, 81 (2011).
[27] C. W. Gardiner, *Handbook of Stochastic Methods*, 3rd ed. (Springer, Berlin, 2004).
[28] A. Fuliński, Phys. Rev. E **83**, 061140 (2011).
[29] A. Fuliński, J. Phys. Chem. **138**, 021101 (2013).
[30] P. Massignan, C. Manzo, J. A. Torreno-Pina, M. F. García-Parajo, M. Lewenstein, and G. J. Lapeyre, Phys. Rev. Lett. **112**, 150603 (2014).
[31] R. F. Fox, J. Math. Phys. **18**, 2331 (1977).
[32] F. W. J. Olver, D. W. Lozier, R. F. Boisvert, and C. W. Clark (eds.), *NIST Handbook of Mathematical Functions* (Cambridge University Press, Cambridge, 2010).
[33] R. Yamamoto and A. Onuki, Phys. Rev. Lett. **81**, 4915 (1998).
[34] R. Yamamoto and A. Onuki, Phys. Rev. E **58**, 3515 (1998).
[35] C. Godrèche and J. M. Luck, J. Stat. Phys. **104**, 489 (2001).
[36] D. R. Cox, *Renewal Theory* (Methuen, London, 1962).
[37] A. Rahman, Phys. Rev. **136**, A405 (1964).
[38] D. Ernst, J. Köhler, and M. Weiss, Phys. Chem. Chem. Phys. **16**, 7686 (2014).
[39] A. G. Cherstvy and R. Metzler, Phys. Rev. E **90**, 012134 (2014).
[40] S. C. Glotzer, V. N. Novikov, and T. B. Schrøder, J. Chem. Phys. **112**, 509 (2000).
[41] N. Lačević, F. W. Starr, T. B. Schrøder, and S. C. Glotzer, J. Chem. Phys. **119**, 7372 (2003).
[42] H. Mizuno and R. Yamamoto, Phys. Rev. E **84**, 011506 (2011).
[43] L. O. Hedges, R. L. Jack, J. P. Garrahan, and D. Chandler, Science **323**, 1309 (2009).
[44] D. Chandler and J. P. Garrahan, Annu. Rev. Phys. Chem. **61**, 191 (2010).
[45] G. Biroli and J. P. Garrahan, J. Chem. Phys. **138**, 12A301 (2013).
[46] J. Łuczka, M. Niemiec, and E. Piotrowski, Phys. Lett. A **167**, 475 (1992).
[47] J. Łuczka, M. Niemiec, and E. Piotrowski, J. Math. Phys. **34**, 5357 (1993).
[48] H. C. Fogedby, Phys. Rev. E **50**, 1657 (1994).
[49] J.-H. Jeon, A. V. Chechkin, and R. Metzler, Phys. Chem. Chem. Phys. **16**, 15811 (2014).
[50] R. Metzler and J. Klafter, Phys. Rep. **339**, 1 (2000).
[51] J. Klafter and R. Silbey, Phys. Rev. Lett. **44**, 55 (1980).
[52] T. Miyaguchi and T. Akimoto, Phys. Rev. E **87**, 032130 (2013).
[53] T. Akimoto and K. Seki, Phys. Rev. E **92**, 022114 (2015).