Fluctuation Analysis of Time-Averaged Mean-Square Displacement for Langevin Equation with Time-Dependent and Fluctuating Diffusivity

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The mean-square displacement (MSD) is widely utilized to study the dynamical properties of stochastic processes. The time-averaged MSD (TAMSD) provides the information on the dynamics which cannot be extracted from the ensemble-averaged MSD. Especially, the relative standard deviation (RSD) or the relative fluctuation of the TAMSD exhibits the crossover behavior at the long time region, which can be related to the long time relaxation. In this work, we consider a class of Langevin equations which are multiplicatively coupled to time-dependent and fluctuation 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. In this work, we derive the general formula for the RSD of the TAMSD for the Langevin equation with the time-dependent and fluctuating diffusivity. We show that the RSD actually exhibits the crossover at the long time region, and give the explicit relation between the crossover time and the relaxation time of the diffusivity for some analytically solvable models.

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 squared displacement of a single-particle trajectory in a system is a stochastic variable, we need to perform averaging operations. The ensemble-averaged MSD (EAMSD) is widely utilized to characterize the dynamical properties of particles. In many systems ranging from a charge carrier transport in amorphous material\cite{1}, light diffusion\cite{2}, polymeric materials\cite{3}, to biological transports\cite{4-7}, it shows a power-law dependence of time, i.e., the anomalous diffusion:

\[ \langle [r(\Delta) - r(0)]^2 \rangle \propto \Delta^\alpha, \quad (1) \]

where \( r(t) \) is a position of a particle at time \( t \), \( \Delta \) is the time difference, \( \langle \ldots \rangle \) 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 diffusion behavior will depend on the time scale, and thus the exponent \( \alpha \) may take several different values depending on \( \Delta \). For example, in entangled polymers, the EAMSD of a segment exhibits four different regions which reflect the crossovers between different characteristic relaxation time scales\cite{3}. In supercooled liquids, the EAMSD of a glass-forming particle strongly depends on the temperature, and it shows a transient plateau, which is considered as one evidence of the cage-effect which constrains the motion of the particle into a narrow region\cite{8}. Although the EAMSD can provide various useful information on the dynamical properties, some properties cannot be extracted from the EAMSD. For example, non-ergodic behavior cannot be analyzed from the EAMSD, and the time-averaged MSD (TAMSD) can be utilized instead. The TAMSD is defined as

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

where \( \Delta \) 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\cite{9}. 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 non-ergodic and/or the time-average is not taken for a sufficiently long time period, 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 \[10, 12\]. 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 observed in single-particle-tracking experiments in living cells \[5, 7\]. 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) \[13, 14\] or the relative standard deviation (RSD) \[10, 12, 13\]:

\[
R(t; \Delta) = \frac{\langle \delta^2(\Delta; t) \rangle - \langle \delta^2(\Delta; t) \rangle}{\langle \delta^2(\Delta; t) \rangle},
\]

\[
\Sigma(t; \Delta) = \sqrt{\frac{\langle \delta^2(\Delta; t) \rangle - \langle \delta^2(\Delta; t) \rangle^2}{\langle \delta^2(\Delta; t) \rangle^2}}.
\]

The RF and RSD behave in a similar way, and it is reported that these quantities can characterize some dynamical properties of the system \[13, 13\]. (In some literature, the squared RSD is utilized as the ergodicity breaking parameter \[12, 16, 17\].) If the second moment of \( \delta^2(\Delta; t) \) diverges, the RSD is not useful while the RF can be utilized to characterize the fluctuation of the TAMSD \[9\].

In the recent work \[13\], the authors applied the RF analysis to the center of mass motion of an entangled polymer \[3\]. In entangled polymer systems, the RF of the TAMSD shows the crossover behavior:

\[
R(t; \Delta) \propto \begin{cases} t^{-\beta} & (t \lesssim \tau'_{c}), \\ t^{-0.5} & (t \gtrsim \tau'_{c}). \end{cases}
\]

(5)

Here \( \beta < 0.5 \) is the constant and \( \tau'_{c} \) is the characteristic crossover time. The crossover time \( \tau'_{c} \) behaves in the same way as the longest relaxation time (the disengagement time) \( \tau_{d} \). This means that the crossover time \( \tau'_{c} \) 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.) However, the reason why \( \tau'_{c} \) 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 in the reptation model \[3\]. In the reptation model, the dynamics of a tagged polymer chain is modelled as the dynamics of a polymer chain confined in a tube-like obstacle. (The reptation model can qualitatively reproduces the characteristic dynamical properties, such as the relaxation modulus.) 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 dynamic equation for the center of mass of the chain can be explicitly expressed as \[18\]

\[
\frac{d\mathbf{r}_{CM}(t)}{dt} = \sqrt{\frac{6D_{CM}}{p^2(w(t))}} \mathbf{p}(t)w(t).
\]

(6)

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

\[
\langle w(t) \rangle = 0, \quad \langle w(t)w(t') \rangle = \delta(t - t').
\]

(7)

One important property of Eq. \(6\) is that the noise \( w(t) \) is multiplicatively coupled to another stochastic variable \( \mathbf{p}(t) \). Due to this multiplicative coupling, the magnitude of the random motion of \( \mathbf{r}_{CM}(t) \) directly depends on \( \mathbf{p}(t) \). Although, random variables \( \mathbf{r}_{CM}(t) \) and \( \mathbf{p}(t) \) are not statistically independent of each other, the coupling between them is expected to be rather weak. If we 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.

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 \[19, 22\]. This “dynamic heterogeneity” can be modelled by employing time-dependent fluctuating diffusion coefficient. The simplest model may be the two-state model \[19\] in which the particle takes the slow state or fast state, and the diffusion coefficients of the slow and fast states are different. The intermittent search strategies \[22\] also consist of fast and slow modes of diffusion. 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 \[22\]. These models can also be interpreted as the Langevin equations with time-dependent and fluctuating diffusivities.
The RF and RSD of the TAMSD are expected to be useful to quantify the time-dependent diffusivity. However, as far as the authors know, theoretical analyses of the TAMSD for systems with time-dependent diffusivities have not been reported. In this work, we analyze the RSD of TAMSD for a general Langevin equation with time-dependent diffusivity, and show the formula for the RSD. Then we apply the obtained formula to some analytically solvable models. We consider the (pure) reptation model for the entangled polymer, and the two-state model for the supercooled liquid with the Markovian and non-Markovian transition dynamics. We show the universality of the time-dependent diffusivity and the method to analyze it through these analytically solvable examples.

II. MODEL

As we mentioned, both the reptation model and the two-state model can be interpreted as the Langevin equation with time-dependent and fluctuating diffusivity. In the reptation model [18], the one-dimensional thermal noise is multiplicatively coupled to the three-dimensional end-to-end vector. 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 as special cases of a more general Langevin equation.

In this work, we consider a class of Langevin equations with such a multiplicative coupling. For simplicity, we assume that no external force is applied. We consider the following general multiplicatively coupled Langevin equation model in an \( n \)-dimensional space [24]:

\[
\frac{d\mathbf{r}(t)}{dt} = \sqrt{2B(t)} \cdot \mathbf{w}(t).
\]

(8)

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

\[
\langle \mathbf{w}(t) \rangle = 0, \quad \langle \mathbf{w}(t)\mathbf{w}(t') \rangle = \delta(t-t')1.
\]

(9)

where \( \langle \ldots \rangle \) represents the ensemble average and \( 1 \) is the \( n \)-dimensional unit tensor. We assume that \( B(t) \) obeys a stochastic process which is independent of \( \mathbf{r}(t) \) and \( \mathbf{w}(t) \). Therefore, two independent stochastic processes \( B(t) \) and \( \mathbf{w}(t) \) are multiplicatively coupled in Eq. (8).

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

\[
\mathbf{D}(t) \equiv \mathbf{B}(t) \cdot \mathbf{B}^T(t).
\]

(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 \( \mathbf{D}(t) \), the noise coefficient matrix can be defined as the matrix square root (such as the Cholesky decomposition). The instantaneous diffusion coefficient matrix \( \mathbf{D}(t) \) should be positive definite, and this condition guarantees the existence of the matrix square root.

The EAMSD is calculated to be

\[
\langle [\mathbf{r}(\Delta) - \mathbf{r}(0)]^2 \rangle = 2 \int_0^\Delta ds \int_0^\Delta ds' \langle \mathbf{B}(s) \cdot \mathbf{B}^T(s') \rangle : \langle \mathbf{w}(s)\mathbf{w}(s') \rangle = 2tr(\langle \mathbf{D} \rangle)\Delta.
\]

(11)

If we assume \( \langle \mathbf{D} \rangle \) to be isotropic, we can simply express \( \langle \mathbf{D} \rangle \) as

\[
\langle \mathbf{D} \rangle = D_{\text{eff}} 1,
\]

(12)

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

\[
\langle [\mathbf{r}(\Delta) - \mathbf{r}(0)]^2 \rangle = 2nD_{\text{eff}}\Delta,
\]

(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 [25] showed that the GLE with the Gaussian noise can be characterized only by the 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 qualitatively different way from the Gaussian noise.) This means that the simple dynamics models such as the reptation model and the two-state model cannot be expressed as the GLE with the Gaussian noise, which is expected to be applicable for wide class of complex dynamics.

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

$$\frac{dr(t)}{dt} = \Lambda(t) \cdot F(t) + \sqrt{2}B(t) \cdot w(t),$$

where $\Lambda(t)$ 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

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

with $k_B$ and $T$ being the Boltzmann constant and the absolute temperature, respectively. Eqs. (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 well-known dynamics models for some special cases. We consider the case where the noise coefficient matrix is given as follows:

$$B(t) = \sqrt{\frac{nD_{\text{eff}} \langle p(t)p(t) \rangle}{\langle p^2 \rangle}} p(t).$$

If we consider a three-dimensional system ($n = 3$) and interpret $p(t)$ as the end-to-end vector and $D_{\text{eff}}$ as the center of mass diffusion coefficient $D_{\text{CM}}$, Eq. (8) can be rewritten as the following form, which is equivalent to Eq. (6):

$$\frac{dr(t)}{dt} = \sqrt{6D_{\text{eff}} \langle p^2 \rangle} p(t) w'(t).$$

Here, $w'(t)$ is the one-dimensional white Gaussian noise defined by

$$w'(t) = \frac{p(t)}{|p(t)|} \cdot w(t).$$

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

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

If the noise coefficient matrix is given as an isotropic form as

$$B(t) = \sqrt{D(t)} \mathbf{1},$$

Eq. (8) simply reduces to

$$\frac{dr(t)}{dt} = \sqrt{2D(t)} w(t).$$

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 dynamics of 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, and thus we expect that the fluctuation of the TAMSD is mainly governed by the end-to-end vector. In the general multiplicatively coupled Langevin equation model with time-dependent diffusivity in the previous subsection, 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 correlation functions of $D(t)$.

In the following, we assume that the system is in a stationary state. Taking an ensemble average in Eq. (2), we have

$$\langle \delta^2(\Delta;t) \rangle = \langle |\mathbf{r}(\Delta) - \mathbf{r}(0)|^2 \rangle = 2 \text{tr} \, \langle D \rangle \Delta,$$

where we have utilized the time-translational invariance $\langle |\mathbf{r}(t' + \Delta) - \mathbf{r}(t')|^2 \rangle = \langle |\mathbf{r}(\Delta) - \mathbf{r}(0)|^2 \rangle$ and Eq. (1). Then, the RSD of the TAMSD (Eq. (4)) for the model described in the previous section (Eq. (8)) is given by

$$\Sigma(t;\Delta) = \sqrt{\frac{\langle \delta^2(\Delta;t)^2 \rangle}{4 \text{tr} \, (\langle D \rangle)^2 \Delta^2} - 1}. \tag{23}$$

We need the explicit expression of $\langle \delta^2(\Delta;t)^2 \rangle$ to calculate the RSD.

$$\langle \delta^2(\Delta;t)^2 \rangle = \frac{2}{(t - \Delta)^2} \int_0^{t-\Delta} dt' \int_0^{t' - \Delta} dt'' \langle |\mathbf{r}(t' + \Delta) - \mathbf{r}(t'')|^2 \rangle + \frac{16}{(t - \Delta)^2} \int_0^{t-\Delta} dt' \int_0^{t'} dt'' \Theta(t'' - t' + \Delta) \int_0^{t'' + \Delta} ds \int_{t'' + \Delta}^{t' + \Delta} du \langle \text{tr} \, D(s) \text{tr} \, D(u) \rangle \tag{24}$$

where the integrals over $s$, $s'$, $u$ and $u'$ in the last line of Eq. (24) can be calculated as follows. For an arbitrary function $f(s,s',u,u')$, the integrals over $s$ and $u$ become

$$\int_{t'' + \Delta}^{t' + \Delta} ds \int_{t'' + \Delta}^{t' + \Delta} du \, \langle \mathbf{r}(s'') - \mathbf{r}(s) \rangle f(s,s',u,u') = \left\{ \begin{array}{ll} \int_{t'' + \Delta}^{t' + \Delta} ds \, f(s,s',u,u') (t'' + \Delta \geq t'), \\ 0 & (t'' + \Delta < t'). \end{array} \right. \tag{25}$$

Here we have utilized the condition $t' > t''$, which holds for the integrand in (24). The integrals in Eq. (24) become

$$\int_{t'' + \Delta}^{t' + \Delta} ds \int_{t'' + \Delta}^{t' + \Delta} du \, \langle \mathbf{r}(s'') - \mathbf{r}(s) \rangle \text{tr} \, D(s) \cdot D(u) \rangle = \left\{ \begin{array}{ll} \int_{t'' + \Delta}^{t' + \Delta} ds \, \text{tr} \, D(s) \cdot D(u) (t'' + \Delta \geq t'), \\ 0 & (t'' + \Delta < t'). \end{array} \right. \tag{26}$$

Eq. (24) can be rewritten as

$$\langle \delta^2(\Delta;t)^2 \rangle = \frac{8}{(t - \Delta)^2} \int_0^{t-\Delta} dt' \int_0^{t'} dt'' \int_{t'' + \Delta}^{t' + \Delta} ds \int_{t'' + \Delta}^{t' + \Delta} du \, \langle \text{tr} \, D(s) \text{tr} \, D(u) \rangle$$

$$+ \frac{16}{(t - \Delta)^2} \int_0^{t-\Delta} dt' \int_0^{t'} dt'' \Theta(t'' - t' + \Delta) \int_0^{t'' + \Delta} ds \int_{t'' + \Delta}^{t' + \Delta} du \, \langle \text{tr} \, D(s) \text{tr} \, D(u) \rangle \tag{27}$$

$$+ \frac{32}{(t - \Delta)^2} \int_0^{t-\Delta} dt' \int_{\Theta(0,v - \Delta)}^{t'} dt'' \int_{t'' + \Delta}^{t' + \Delta} ds \int_{t'' + \Delta}^{t' + \Delta} du \, \langle \text{tr} \, D(s) \text{tr} \, D(u) \rangle,$$
with $\Theta(t)$ being the Heaviside step function.

We consider the properties of two correlation functions in Eq. \(27\), \(\langle \text{tr } D(s) \text{ tr } D(u) \rangle \) and \(\langle \text{tr } D(s) \cdot D(u) \rangle \). We assume that the stochastic process which $B(t)$ obeys is ergodic, and thus at the limit of $|s-u| \to \infty$, these correlation functions can be decoupled:

\[
\langle \text{tr } D(s) \text{ tr } D(u) \rangle \to \langle \text{tr } (D) \rangle^2,
\]

\[
\langle \text{tr } D(s) \cdot D(u) \rangle \to \text{tr } \langle (D) \cdot (D) \rangle.
\]

(28)

(29)

It would be convenient to rewrite two correlation functions by using Eqs. \(28\) and \(29\), as follows:

\[
\langle \text{tr } D(s) \text{ tr } D(u) \rangle \equiv \text{tr } \langle (D) \rangle^2 \left[ 1 + \psi_1(s-u) \right],
\]

\[
\text{tr } \langle D(s) \cdot D(u) \rangle \equiv n \text{tr } \langle (D) \rangle \left[ \frac{1}{n} + \psi_2(s-u) \right],
\]

(30)

(31)

where $\psi_1(t)$ and $\psi_2(t)$ are four-body two-time correlation functions. Both $\psi_1(t)$ and $\psi_2(t)$ are symmetric in $t$ and approach to zero at $|t| \to \infty$.

By combining Eqs. \(23\), \(27\), \(30\), and \(31\), the square of the RSD is expressed as

\[
\Sigma^2(t; \Delta) = \frac{2}{\Delta^2(t-\Delta)^2} \int_0^{t-\Delta} dt' \int_0^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_s^{t'+\Delta} du \psi_1(s-u)
\]

\[
+ \frac{8C}{\Delta^2(t-\Delta)^2} \int_0^{t-\Delta} dt' \int_{t'}^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_s^{t'+\Delta} du \left[ \frac{1}{n} + \psi_2(s-u) \right],
\]

(32)

where $C$ is defined as

\[
C \equiv n \text{tr } \langle (D) \cdot \langle (D) \rangle \rangle / \langle \text{tr } (D) \rangle^2.
\]

(33)

Note that if the average diffusion coefficient matrix $\langle D \rangle$ is isotropic, we have $C = 1$. For the case where $t \gg \Delta$, which is satisfied in many practical cases, Eq. \(33\) is simplified as follows:

\[
\Sigma^2(t; \Delta) \approx \frac{2}{\Delta^2 t^2} \int_0^t dt' \int_0^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_s^{t'+\Delta} du \psi_1(s-u)
\]

\[
+ \frac{8C}{\Delta^2 t^2} \int_0^t dt' \int_{t'}^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_s^{t'+\Delta} du \left[ \frac{1}{n} + \psi_2(s-u) \right].
\]

(34)

The second term in the right hand side of Eq. \(34\) is modified as

\[
\frac{8}{\Delta^2 t^2} \int_0^t dt' \int_{t'}^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_s^{t'+\Delta} du \left[ \frac{1}{n} + \psi_2(s-u) \right]
\]

\[
= \frac{4}{3n} \frac{\Delta}{t} + \frac{8C}{\Delta^2 t^2} \int_0^t ds \int_0^{s} du (s-u) \psi_2(u).
\]

(35)

The first term in the right hand side of Eq. \(34\) is modified as

\[
\frac{2}{\Delta^2 t^2} \int_0^t dt' \int_0^{t'} dt'' \int_{t'}^{t'+\Delta} ds \int_s^{t'+\Delta} du \psi_1(s-u)
\]

\[
= \frac{2}{\Delta^2 t^2} \int_0^t dv (t-v) \int_0^{\Delta} ds \int_0^{s} du \psi_1(s-u+v),
\]

(36)

and thus we have

\[
\Sigma^2(t; \Delta) \approx \frac{2}{\Delta^2 t^2} \int_0^t dv (t-v) \int_0^{\Delta} ds \int_0^{s} du \psi_1(s-u+v)
\]

\[
+ \frac{4C \Delta}{3n t} + \frac{8C}{\Delta^2 t^2} \int_0^t ds \int_0^{s} du (s-u) \psi_2(u).
\]

(37)
If the characteristic relaxation time of $\psi_1(t)$ and $\psi_2(t)$, $\tau$, is much longer than $\Delta$, Eq. (37) can be further approximated:

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

(38)

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

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

(39)

Eqs. (38) and (39) 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. (38), we find that the $t$-dependence of the RSD is essentially determined only by $\psi_1(t)$, and is independent of $\psi_2(t)$. Therefore the crossover time $\tau_c$ is related only to $\psi_1$. From Eq. (39), the crossover time $\tau_c$ is estimated as:

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

(40)

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

$$\tau_c \approx 2\tau.$$ 

(41)

As expected, the crossover time is proportional to the relaxation time, although they are different by the numerical factor 2. In general, the correlation function $\psi_1(t)$ cannot be expressed as a single exponential relaxation mode 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, if we replace the relaxation time $\tau$ in Eq. (41) by the average relaxation time for multiple relaxation 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 A, the RF behaves in the 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 [13] 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 $\Delta/t$ is not sufficiently small. In such a case, the second and third terms in the right hand side of Eq. (37) cannot be simply neglected. As before, we approximate the integrand in the third term in the right hand side of Eq. (37) by $\psi_2(0)$. Then we have

$$\Sigma^2(t; \Delta) \approx \psi_1(0) + 4C \int_0^\infty ds \psi_1(s).$$

(42)

If $t/\Delta \lesssim 4C[1/n + \psi_2(0)]/3\psi_1(0)$, the contribution of the second term in the right hand side of Eq. (42) 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 $\Delta$ dependence of the RSD is rather simple. We may utilize the RSD data with different values of $\Delta$ 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. (38) and (39) together with Eq. (30)) 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. In the reptation model, the motion of a tagged polymer chain is modelled as one of a polymer chain in a tube-like obstacle. The dynamic
equation is expressed as the one-dimensional Langevin equation, and various dynamical properties can be analytically calculated from the dynamic equation. 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. (3). If we assume that the dynamics of the center of mass are decoupled from the dynamics of the end-to-end vector, then the RSD of the TAMSD can be evaluated analytically. The instantaneous diffusion matrix \( D(t) \) becomes

\[
D(t) = 3D_{CM} \frac{p(t)p(t)}{\langle p^2 \rangle}.
\] (43)

The effective diffusion coefficient \( D_{eff} \) simply coincides with \( D_{CM} \):

\[
D_{eff} = \frac{1}{3} \text{tr}(D) = D_{CM}.
\] (44)

Then the correlation function \( \psi_1(t) \) (Eq. (40)) becomes

\[
\psi_1(t) = \frac{\langle p^2(t)p^2(0) \rangle}{\langle p^2 \rangle^2} - 1.
\] (45)

We need to calculate \( \langle p^2(t)p^2(0) \rangle \) to obtain the explicit expression for the RSD of the TAMSD.

In the reptation model, many of dynamical quantities can be calculated from the tube survival probability, which represents the tube segment with a tube segment at time 0 survive up to time \( t \). The tube survival probability of the segment index \( s \) at time \( t \) can be expressed as

\[
\Psi(s; t) = \sum_{k: \text{odd}} \frac{4}{k\pi} \sin \left( \frac{k\pi s}{Z} \right) \exp \left( -\frac{k^2 t}{\tau_d} \right).
\] (46)

Here \( Z \) is the number of tube segments \((0 \leq s \leq Z)\) and \( \tau_d \) is the disengagement time. Note that the expression of the surviving probability in this work is slightly different from commonly utilized one in the Doi-Edwards textbook \[2\]. (Our definition makes the calculations slightly simple, as shown below.) In this work \( s \) represents the segment index along the tube \((0 \leq s \leq Z)\) whereas in the Doi-Edwards definition \( s \) represents the distance along the tube \((0 \leq s \leq L = Za)\).

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 in a similar way to the calculation of \( \Psi(s, t) \). We consider the case \( s \leq s' \), and set \( \xi \equiv s' - s \). Then \( \Psi(s, s'; t) = \Psi(s + \xi; t) \) obeys the backward Fokker-Planck equation:

\[
\frac{\partial \Psi(s, s + \xi; t)}{\partial t} = \frac{1}{Z\tau_l} \frac{\partial^2 \Psi(s, s + \xi; t)}{\partial s^2},
\] (47)

with \( \tau_l \) being the characteristic time scale of the longitudinal motion of a segment along the tube. The longest relaxation time (the disengagement time) \( \tau_d \) is related to \( \tau_l \) as \( \tau_d = Z^2\tau_l/\pi^2 \). The initial condition is

\[
\Psi(s, s + \xi; 0) = 1,
\] (48)

and the boundary condition is

\[
\Psi(Z - \xi, Z; t) = \Psi(0, \xi; t) = 0.
\] (49)

By solving Eq. (47), we have the following expression for the joint survival probability:

\[
\Psi(s, s + \xi; t) = \sum_{k: \text{odd}} \frac{4}{k\pi} \sin \left( \frac{p\pi s}{Z - \xi} \right) \exp \left[ -\frac{Z^2k^2t}{\langle \xi \rangle^2 \tau_d} \right].
\] (50)

For the case of \( s > s' \), the solution is the same form as Eq. (50) with \( s \) and \( \xi \) replaced by \( s' \) and \( s - s' \), respectively. Combining them and we have

\[
\Psi(s, s'; t) = \sum_{k: \text{odd}} \frac{4}{k\pi} \sin \left( \frac{k\pi \min(s, s')}{Z - |s - s'|} \right) \exp \left[ -\frac{Z^2k^2t}{(Z - |s - s'|)^2 \tau_d} \right].
\] (51)
For the case of $s = s'$, Eq. (51) reduces to $\Psi(s; t)$. Namely,
\[
\Psi(s, s; t) = \Psi(s; t).
\] (52)

To obtain the correlation functions of the end-to-end vector, we need the expression of the end-to-end vector in terms of the bond vectors of segments. We can express the end-to-end vector as
\[
p(t) = \int_0^Z ds \mathbf{u}(s, t).
\] (53)

where $\mathbf{u}(s, t)$ 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
\[
\langle \mathbf{u}(s) \rangle = 0, \quad \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \frac{1}{3} a^2 \delta(s - s').
\] (54)

Here $a$ is the tube segment size. The average end-to-end vector size can be calculated straightforwardly:
\[
\langle p^2 \rangle = Za^2.
\] (55)

We consider the four-body two-time correlation function $\psi_1(t)$. The correlation function can be evaluated if we know whether the bonds at time $0$ still survive at time $t$ or not. There are three possible cases. The first case is where two original 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
\[
\langle p^2(t)p^2(0) \rangle = \int_0^Z ds \int_0^Z ds' \int_0^Z dv \int_0^Z dv' \langle [\mathbf{u}(s, t) \cdot \mathbf{u}(s', t)][\mathbf{u}(v, 0) \cdot \mathbf{u}(v', 0)] \rangle
\]
\[= \int_0^Z ds \int_0^Z dv \int_0^Z dv' \left[ \langle [\mathbf{u}(s) \cdot \mathbf{u}(s')][\mathbf{u}(v) \cdot \mathbf{u}(v')])\Psi(s, s; t) \right.
\]
\[+ \langle [\mathbf{u}(s')] \cdot [\mathbf{u}(v) \cdot \mathbf{u}(v')]\rangle(\Psi(s; t) - \Psi(s, s'; t))
\]
\[+ \langle [\mathbf{u}(s)] \cdot [\mathbf{u}(s')][\mathbf{u}(v) \cdot \mathbf{u}(v')]\rangle(\Psi(s'; t) - \Psi(s, s'; t))
\]
\[+ \langle [\mathbf{u}(s) \cdot \mathbf{u}(s')]\langle [\mathbf{u}(v) \cdot \mathbf{u}(v')],(1 - \Psi(s; t) - \Psi(s'; t) + \Psi(s, s'; t)) \rangle
\]
\[= \int_0^Z ds \int_0^Z dv \int_0^Z dv' \langle [\mathbf{u}(s) \cdot \mathbf{u}(s')][\mathbf{u}(v) \cdot \mathbf{u}(v')])\Psi(s, s'; t) \rangle
\]
\[+ Z^2 a^4 + Za^4 \int_0^Z ds (\Psi(s, s; t) - 2\Psi(s; t)).
\] (56)

By using the Wick’s theorem, the average for the bond vectors in Eq. (56) can be decomposed as follows:
\[
\langle [\mathbf{u}(s) \cdot \mathbf{u}(s')][\mathbf{u}(v) \cdot \mathbf{u}(v')] \rangle
\]
\[= \langle [\mathbf{u}(s) \cdot \mathbf{u}(s')]\rangle\langle [\mathbf{u}(v) \cdot \mathbf{u}(v')] \rangle + \langle [\mathbf{u}(s)]\rangle\mathbf{u}(v) \cdot \langle [\mathbf{u}(v')] \rangle + \langle [\mathbf{u}(s')]\rangle\mathbf{u}(v) \cdot \langle [\mathbf{u}(v')] \rangle + \langle [\mathbf{u}(s)]\rangle\mathbf{u}(v) \cdot \langle [\mathbf{u}(v')] \rangle
\]
\[= a^4 \delta(s - s')\delta(v - v') + \frac{a^4}{3}(s - v)\delta(s' - v') + \frac{a^4}{3}(s - v')\delta(s' - v).
\] (57)

The first term in the last line of Eq. (56) is calculated to be
\[
\int_0^Z ds \int_0^Z dv \int_0^Z dv' \langle [\mathbf{u}(s) \cdot \mathbf{u}(s')][\mathbf{u}(v) \cdot \mathbf{u}(v')] \rangle \Psi(s, s'; t)
\]
\[= Za^4 \int_0^Z ds \Psi(s, s; t) + \frac{2a^4}{3} \int_0^Z ds \int_0^Z ds' \Psi(s, s'; t).\] (58)

From Eqs. (55), (56), and (58), $\psi_1(t)$ can be expressed in terms of the survival probabilities:
\[
\psi_1(t) = \int_0^Z ds [\Psi(s, s; t) - \Psi(s; t)] + \frac{2}{3Z^2} \int_0^Z ds \int_0^Z ds' \Psi(s, s'; t)
\]
\[= \frac{2}{3Z^2} \int_0^Z ds \int_0^Z ds' \Psi(s, s'; t),
\] (59)
where we have used \( \Psi(s, s'; t) = \Psi(s; t) \).

Eq. (50) can be further modified by substituting Eq. (51) into it:

\[
\psi_1(t) = \frac{8}{3\pi Z^2} \sum_{k \text{ odd}} \frac{1}{k} \int_0^Z ds \int_0^Z ds' \sin \left[ \frac{k\pi \min(s, s')}{Z - |s - s'|} \right] \exp \left[ -\frac{Z^2 k^2 t}{(Z - |s - s'|)^2 \tau_d} \right]
\]

\[
= \frac{16}{3\pi Z^2} \sum_{k \text{ odd}} \frac{1}{k} \int_0^Z ds \int_0^s ds' \sin \left[ \frac{k\pi s'}{Z - (s - s')} \right] \exp \left[ -\frac{Z^2 k^2 t}{(Z - (s - s'))^2 \tau_d} \right].
\]

By introducing the variable transform \( w = s - s' \), Eq. (60) can be integrated over \( s \) as

\[
\psi_1(t) = \frac{16}{3\pi Z^2} \sum_{k \text{ odd}} \frac{1}{k} \int_0^Z dw \int_w^Z ds \sin \left[ \frac{k\pi (s - w)}{Z - w} \right] \exp \left[ -\frac{Z^2 k^2 t}{(Z - w)^2 \tau_d} \right]
\]

\[
= \frac{32}{3\pi Z^2} \sum_{k \text{ odd}} \frac{1}{k^2} \int_0^Z dw (Z - w) \exp \left[ -\frac{Z^2 k^2 t}{(Z - w)^2 \tau_d} \right].
\]

We introduce another variable transform \( x = Z/(Z - w) \) to make the integral simple:

\[
\psi_1(t) = \frac{16}{3\pi^2} \sum_{k \text{ odd}} \frac{1}{k^2} \int_1^\infty dx x^{-2} \exp \left( -\frac{k^2 t}{\tau_d} \right)
\]

\[
= \frac{16}{3\pi^2} \sum_{k \text{ odd}} \frac{1}{k^2} E_2(k^2 t/\tau_d).
\]

Here \( E_m(z) \) is the (generalized) exponential integral of the \( m \)-th order [26].

At \( t = 0 \), \( \psi_1(t) \) reduces to the simple form:

\[
\psi_1(0) = \frac{16}{3\pi^2} \sum_{k \text{ odd}} \frac{1}{k^2} = \frac{2}{3}.
\]

Here we used \( E_2(0) = 1 \). On the other hand, the integral of \( \psi(t) \) over \( t \) is calculated as

\[
\int_0^\infty dt \psi_1(t) = \sum_{k \text{ odd}} \frac{16 \tau_d}{3\pi^2 k^4} \int_0^\infty dz E_2(z) = \frac{8 \tau_d}{3\pi^2} \sum_{k \text{ odd}} \frac{1}{k^4} = \frac{\pi^2 \tau_d}{36},
\]

where we used the integral formula for the exponential integral [26]:

\[
\int_0^\infty dz E_2(z) = E_2(0) = \frac{1}{2}.
\]

Finally, we have the following asymptotic forms of the RSD of the TAMSD:

\[
\Sigma^2(t; \Delta) \approx \begin{cases} 
\frac{2}{\pi^2 \tau_d} (t \ll \tau_d), \\
\frac{\pi^2 \tau_d}{18 t} (t \gg \tau_d).
\end{cases}
\]

The crossover time \( \tau_c \) is then estimated as

\[
\tau_c \approx \frac{\pi^2 \tau_d}{12} \approx 0.822 \tau_d.
\]

Thus we find that \( \tau_c \) is closer to \( \tau_d \) than the case of the single relaxation time. This result is consistent with our previous simulation results for the reptation model. (The crossover time of the RF is almost the same as the disengagement time.)

Although the expression becomes complicated, the integral in Eq. (58) can be calculated. After long but straightforward calculations, we have the following explicit expression for the squared RSD:

\[
\Sigma^2(t; \Delta) = \frac{32}{3\pi^2 t^2} \sum_{k \text{ odd}} \frac{1}{k^2} \int_0^t ds (t - s) E_2(k^2 t/\tau_d)
\]

\[
= \frac{\pi^2 \tau_d}{18 t} - \frac{\pi^4 \tau_d^2}{270 t^2} + \frac{32 \tau_d^2}{3\pi^2 t^2} \sum_{k \text{ odd}} \frac{1}{k^2} E_4(k^2 t/\tau_d).
\]
This reduces to two asymptotic forms shown in Eq. (66), 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 CM. (The details of the model and simulation method are described in the previous work \[13\].) We show the RSD of the TAMSD for the number of tube segments per chain \( Z = 80 \) in Figure 1. The time difference \( \Delta \) is taken to be \( \Delta = 10 \tau_l \) where \( \tau_l \) is the characteristic time scale for the longitudinal motion of a segment along the tube. We observe that our analytical expression (Eq. (68)) and its asymptotic forms (Eq. (66)) are in good agreement with the simulation result except for the small \( t \) region. This result supports the validity of our general formula (Eq. (38)) and its asymptotic forms (Eq. (39)).

B. Two-state Model for Supercooled Liquid

The dynamics of supercooled liquids have been extensively studied by experiments, theories, and simulations \[19–22\]. The molecular dynamics (MD) simulations allow us to directly observe the motion of each particle and calculate various statistical quantities. One important finding by the MD simulations is the “dynamic heterogeneity \[27, 28\].” 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 \[19\].

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

\[
\frac{d\mathbf{r}(t)}{dt} = \sqrt{2D(t)}w(t). \tag{69}
\]

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

\[
D(t) = \begin{cases} 
D_f & \text{(for } h(t) = f), \\
D_s & \text{(for } h(t) = s). 
\end{cases} \tag{70}
\]

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 state \( h \) at time \( t \) as \( P_h(t) \).

1. Markovian case

We consider the simplest case where the transition dynamics is Markovian. We assume that the transition dynamics between the fast and slow states can be described by the following master equation:

\[
\frac{d}{dt} \begin{bmatrix} P_f(t) \\ P_s(t) \end{bmatrix} = \begin{bmatrix} -k_f & k_s \\ k_f & -k_s \end{bmatrix} \cdot \begin{bmatrix} P_f(t) \\ P_s(t) \end{bmatrix}. \tag{71}
\]

where \( k_f \) and \( k_s \) are the transition rates from the fast to slow and from the slow to fast states, respectively. Despite its simplicity, the Markovian two-state model can reproduce some interesting dynamic properties which reflect the dynamic heterogeneity in supercooled liquids.

The set of equations (69)–(71) can be solved analytically. The equilibrium probabilities of the fast and slow states, which corresponds to the equilibrium fractions, become

\[
\phi_f = \frac{k_s}{k_f + k_s}, \quad \phi_s = \frac{k_f}{k_f + k_s}. \tag{72}
\]

The effective diffusion coefficient is

\[
D_{\text{eff}} = \langle D \rangle = D_f \phi_f + D_s \phi_s, \tag{73}
\]

and \( \psi_1(t) \) is given by

\[
\psi_1(t) = \frac{\langle D(t)D(0) \rangle}{\langle D \rangle^2} - 1. \tag{74}
\]
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. (71).

$$\begin{bmatrix} W_{ff}(t) & W_{fs}(t) \\ W_{sf}(t) & W_{ss}(t) \end{bmatrix} = \exp \begin{bmatrix} -k_f t & k_s t \\ k_f t & -k_s t \end{bmatrix} = \begin{bmatrix} \phi_f(t) + \phi_s e^{-t/\tau} & \phi_f(1 - e^{-t/\tau}) \\ \phi_s(1 - e^{-t/\tau}) & \phi_s + \phi_f e^{-t/\tau} \end{bmatrix}.$$  

(75)

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

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

(76)

From Eqs. (75) and (76), the explicit form of $\psi_1(t)$ becomes

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

(77)

By substituting Eq. (74) into Eq. (58), finally we have the explicit expression for the RSD:

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

(78)

The asymptotic forms are

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

(79)

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

We perform the simulations and compare the simulation results with the theoretical prediction (Eq. (78) or Eq. (79)). We perform simulations with $D_s = 1$, $D = 10$, $k_f = 1$, and several different values of $k_s$ ($k_s = 0.1, 1,$ and $10$). Figure 2 shows the simulation results together with the theoretical prediction (Eq. (78)) and the asymptotic forms (Eq. (79)). We observe that the theoretical prediction agrees well with the simulation data, except the small $t$ region, as the case of the reptation model. (The deviation from the theory at the small $t$ regions is due to the correction term, as mentioned.) Therefore, we find that our general formula (Eqs. (58) and (79)) 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.

2. Non-Markovian case

A simple extension of the two state model described in the previous subsection is obtained by incorporating non-Markovian transition processes between the fast and slow states. Since, in general, Markovian models are derived for ideal situations where the memory effects are negligible, an extension to the non-Markovian dynamics will be important when comparing the model with experimental data. In this subsection, we consider the two-state model defined by Eq. (69) with non-Markovian transition processes between fast and slow states. To handle these non-Markovian processes, we use the renewal theoretic approach [29, 30]. 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 the following, we use the same notations as the previous subsection.

We express the trapping-time distributions of the fast and slow states as $\rho_f(\tau)$ and $\rho_s(\tau)$, respectively. Similarly, we express the equilibrium trapping-time distributions as $\rho_f^{(\text{eq})}(\tau)$ and $\rho_s^{(\text{eq})}(\tau)$. For example, if a particle is in the fast state at time $t = 0$, this particle became that state at some time $t = t_0 < 0$. Therefore, if $t_1$ is the time when first transition (to the slow state) occurs, $\tau_1 = t_1 - t_0$ obeys the distribution $\rho_f(\tau_1)$, but $t_1$ itself does not necessarily obey $\rho_f(t_1)$. (We note that the time $t_1$ is called the forward recurrence time in renewal theory [30].) $\rho_h^{(\text{eq})}(\tau) (h = f, s)$ is the distribution of the first trapping time $\tau$ (if the particle starts with the state $h$ at $t = 0$). The explicit expression for $\rho_h^{(\text{eq})}$ is [29, 30]

$$\rho_h^{(\text{eq})}(\tau) = \frac{1}{(\tau)_h} \int_\tau^\infty d\tau' \rho_h(\tau'),$$  

(80)
where \( \langle \tau \rangle_h \) is the average trapping time of the state \( h \), defined as

\[
\langle \tau \rangle_h \equiv \int_0^\infty d\tau \, \tau \rho_h(\tau).
\] (81)

(For the exponential distribution, two distributions \( \rho_h(\tau) \) and \( \rho_h^{(\text{eq})}(\tau) \) coincide.) The (unilateral) Laplace transform of Eq. (80) is given as

\[
\hat{\rho}_h^{(\text{eq})}(u) = \frac{1 - \hat{\rho}_h(u)}{u \langle \tau \rangle_h},
\] (82)

where the functions with hats (such as \( \hat{\rho}_h \) and \( \hat{\rho}_h^{(\text{eq})} \)) represent the Laplace transformed functions. (For the exponential distribution, \( \hat{\rho}_h(u) = \hat{\rho}_h^{(\text{eq})}(u) = 1/(u\langle \tau \rangle_h + 1) \).) Equilibrium fractions of each state, \( \hat{\phi}_f \) and \( \hat{\phi}_s \), are given by

\[
\hat{\phi}_f = \frac{\langle \tau \rangle_f}{\langle \tau \rangle_f + \langle \tau \rangle_s}, \quad \hat{\phi}_s = \frac{\langle \tau \rangle_s}{\langle \tau \rangle_f + \langle \tau \rangle_s}.
\] (83)

For the case of the exponential trapping-time distribution, \( \langle \tau \rangle_h = 1/k_h \) and we recover Eq. (72). We also 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 \( \rho_s(\tau) \),

\[
\rho(\tau) \equiv \rho_f \ast \rho_s(\tau) = \rho_s(\tau) = \int_0^\tau d\tau' \rho_f(\tau - \tau')\rho_s(\tau').
\] (84)

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

\[
\hat{\rho}(u) = \hat{\rho}_f(u)\hat{\rho}_s(u).
\] (85)

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

\[
If(t) = \int_0^\infty dt'f(t').
\] (86)

Then, \( Q_{h,n}(t) \) can be expressed as \( 29 \)

\[
Q_{h,n}(t) = \begin{cases} 
I\rho_h^{(\text{eq})}(t) & (n = 0), \\
\rho_h^{(\text{eq})} \ast \rho \ast \rho \ast \cdots \ast \rho \ast (I\rho_h)(t) & (n = 1, 3, 5, \ldots), \\
\rho_h^{(\text{eq})} \ast \rho \ast \rho \ast \cdots \ast \rho \ast \rho \ast \rho \ast (I\rho_h)(t) & (n = 2, 4, 6, \ldots).
\end{cases}
\] (87)

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

\[
\hat{Q}_{h,n}(u) = \begin{cases} 
\langle \tau \rangle_h u - 1 + \hat{\rho}_h(u) & (n = 0), \\
\langle \tau \rangle_h u^2 \frac{1 - \hat{\rho}_h(u)(1 - \hat{\rho}_h(u))}{\langle \tau \rangle_h u^2} & (n = 1, 3, 5, \ldots), \\
\langle \tau \rangle_h u^2 \frac{1 - \hat{\rho}_h(u)^2}{\langle \tau \rangle_h u^2} & (n = 2, 4, 6, \ldots).
\end{cases}
\] (88)

Using these probabilities, the probability of being at state \( h \) at time \( t \), starting from at state \( h' \) at time 0, \( W_{hh'}(t) \), is expressed as

\[
W_{hh'}(t) = \sum_{n=0}^{\infty} Q_{h,2n}(t) \quad (h' = h), \\
\sum_{n=0}^{\infty} Q_{h,2n+1}(t) \quad (h' = \hat{h}).
\] (89)
The correlation function $\psi_1(t)$ can be calculated in the same way as the Markovian case:

$$\psi_1(t) = \frac{1}{D_{\text{eff}}^2} \sum_{h,h'=f,s} D_h D_{h'} [W_{hh'}(t) - \phi_h] \phi_{h'}.$$  \hfill (90)

Here $D_{\text{eff}} = D_f \phi_f + D_s \phi_s$ is the effective diffusion coefficient. Although it is difficult to derive the explicit expression of $\psi_1(t)$ by calculating the sum in Eq. (59), we can obtain the explicit forms at some asymptotic limits.

For $t = 0$, $W_{hh'}(0) = \delta_{hh'}$ and thus we have

$$\psi_1(0) = \frac{\phi_f \phi_s (D_f - D_s)^2}{D_{\text{eff}}^2}. \hfill (91)$$

Eq. (91) has formally the same form as the Markovian case (Eq. (77) 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. Since $W_{hh'}(t)$ converges to $\phi_h$ for $t \to \infty$, it would be convenient to consider $W_{hh'}(t) - \phi_h$. The Laplace transform of $W_{hh'}(t) - \phi_h$ has the following asymptotic form for small $u$:

$$\tilde{W}_{hh'}(u) - \frac{\phi_h}{u} \approx \sigma_{hh'} \frac{\langle \tau^2 \rangle_s \langle \tau \rangle^2_f + \langle \tau^2 \rangle_f \langle \tau \rangle^2_s - 2 \langle \tau \rangle^2_s \langle \tau \rangle^2_f}{2 \langle \tau \rangle_{h'} \langle \tau \rangle_s + \langle \tau \rangle_f^2}, \hfill (92)$$

where $\sigma_{hh'} = 1$ or $-1$ for $h' = h$ and $h' = \bar{h}$, respectively, and we have utilized the expansion of the $\tilde{\rho}_h(u)$ for small $u$, $\tilde{\rho}_h(u) = 1 - \langle \tau \rangle u + \langle \tau \rangle^2 u^2/2 + \cdots$. For convenience, we define the characteristic relaxation time scale of the non-Markovian two-state model, $\tilde{\tau}$, as

$$\tilde{\tau} \equiv \left( \frac{\langle \tau^2 \rangle_s - \langle \tau \rangle^2_s}{\langle \tau \rangle^2_s} + \frac{\langle \tau^2 \rangle_f - \langle \tau \rangle^2_f}{\langle \tau \rangle_f^2} \right) \frac{\langle \tau \rangle_f \langle \tau \rangle_s}{2 \langle \tau \rangle_{h'} \langle \tau \rangle_s + \langle \tau \rangle_f^2}. \hfill (93)$$

(For the exponential trapping-time distribution, we simply have $\tilde{\tau} = \tau$.) By using Eqs. (92) and (93), we have the following relation for the transition probability:

$$\int_0^\infty dt \left[ W_{hh'}(t) - \phi_h \right] = \lim_{u \to 0} \left[ \tilde{W}_{hh'}(u) - \frac{\phi_h}{u} \right] = \left\{ \begin{array}{ll} \tilde{\tau} \phi_h & (h' = h), \\ -\tilde{\tau} \phi_h & (h' = \bar{h}). \end{array} \right. \hfill (94)$$

Then, from Eqs. (90) and (94), we have the following simple expression for the integral of $\psi_1(t)$:

$$\int_0^\infty dt \psi_1(t) = \frac{\phi_f \phi_s (D_f - D_s)^2}{D_{\text{eff}}^2} \tilde{\tau}. \hfill (95)$$

Finally, from Eqs. (59), (91), and (95), we have the following crossover again:

$$\Sigma(t; \Delta) \approx \left\{ \begin{array}{ll} \frac{\sqrt{\phi_f \phi_s (D_f - D_s)}}{D_{\text{eff}}} \left( t \ll \tilde{\tau} \right), \\ \frac{D_{\text{eff}}}{\sqrt{\phi_f \phi_s (D_f - D_s)}} \sqrt{\frac{2\tilde{\tau}}{t}} & \left( t \gg \tilde{\tau} \right). \end{array} \right. \hfill (96)$$

Eq. (96) has almost the same form as Eq. (76) ($\tau$ in Eq. (76) is replaced by $\tilde{\tau}$), and 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. Thus the crossover time becomes twice of the average relaxation time $\tilde{\tau}$ (Eq. (93)), as we mentioned.

To examine the validity of Eq. (96), we perform simulations for the non-Markovian two-state model and compare the simulation results with Eq. (96). In this work, we employ the exponential distribution for the fast state and a non-exponential distribution for the slow state, as follows:

$$\rho_f(t) = k_f e^{-k_f t}, \hfill (97)$$

$$\rho_s(t) = \int_{k_{s,0}}^{k_{s,1}} dk_s k_s e^{-k_s t} q_s(k_s). \hfill (98)$$
Here \( k_{s,0} \) and \( k_{s,1} \) are the lower and upper limits for the transition probabilities 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 \( q_s(k_s) \),

\[
q_s(k_s) = \frac{\alpha - 1}{k_{s,1} - k_{s,0}} k_s^{\alpha - 2},
\]

with \( 0 \leq \alpha \leq 1 \) being the power-law exponent. We set parameters as \( D_s = 1, \ D_f = 10, \ k_f = 1, \ k_{s,1} = 1, \ \alpha = 0.2, \) and 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 9 shows the simulation results together with the theoretically derived asymptotic forms. The simulation data show clear crossovers for the RSD, as the case of the Markovian two-state model. We observe the asymptotic forms by our theory (Eq. 99) agree with the simulation data. Unlike the case of the Markovian two-state model, the transition from the small to large \( t \) regions is relatively broad. Especially, for the case of \( k_{s,0} = 0.001, \) we observe a deviation of the simulation data from the theory. This may be due to the combination of the broadening of the transition region and the correction at the small \( t \) region. Although the agreement between the simulation and theory is not perfect, we consider that our theory can be applied to non-Markovian dynamics without serious problems.

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 \cite{27, 28} showed that the van Hove correlation function can resolve the dynamic heterogeneity. The van Hove self-correlation function is defined as

\[
G_s(r, \Delta) = \langle \delta(r - r(\Delta) + r(0)) \rangle.
\]

For a relatively short time scale, \( G_s(r, \Delta) \) shows non-Gaussian behavior, due to the dynamic heterogeneity. For a relatively long time scale, \( G_s(r, \Delta) \) approaches to 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, so-called the non-Gaussianity parameter has been utilized. The non-Gaussianity parameter is defined as \cite{31, 32}

\[
A(\Delta) = \frac{n\langle [r(\Delta) - r(0)]^4 \rangle}{(n + 2)\langle [r(\Delta) - r(0)]^2 \rangle^2} - 1.
\]

This parameter becomes non-zero 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 B.

Recent simulation and theoretical works show that the four-point time-space correlation function is an important quantity in supercooled liquids \cite{34, 37}. The four-point dynamic correlation function is defined as

\[
\chi_4(r, r', \Delta) = \langle \delta \rho(r, \Delta) \delta \rho(r, 0) \delta \rho(r', \Delta) \delta \rho(r', 0) \rangle - \langle \delta \rho(r, \Delta) \delta \rho(r, 0) \rangle \langle \delta \rho(r', \Delta) \delta \rho(r', 0) \rangle,
\]

where \( \delta \rho(r, t) \) is the density fluctuation at position \( r \) 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 \( \alpha \)-relaxation time) will be interesting.
B. Time-Dependent Diffusivity Model and Other Models

As we have shown, 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 and other dynamics models.

Luczka, Niemiec and Piotrowski \cite{38,39} 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 \cite{40} 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 virtual time. The use of the virtual time may be interpreted as the use of the time-dependent and fluctuating diffusivity. Thus, we can interpret the Fogedby model as a special case of the time-dependent and fluctuating mobility model. We note that the Fogedby model is designed to reproduce the Lévy flight, and thus the dynamics of the virtual time can be non-ergodic, which is different from our model. Recently, Jeon, Chechkin and Metzler \cite{41} 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 $\alpha$ being an exponent). Namely, the dynamics of the instantaneous diffusion coefficient matrix is deterministic. Such a dynamics model also reproduces the anomalous diffusion behavior. Using non-ergodic 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 in Section IV.B.2). Such jump dynamics is often modeled as the CTRW \cite{42}. 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 \cite{13}. 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. In other words, if the particle is in the slow state, it is trapped. The particle can move freely in the fast state. If the average sojourn time in the fast state is very short, the movement of the particle looks like the instantaneous and discrete jump. Thus, at the limit of $\langle \tau_f \rangle \to 0$ with $D_f(\tau_f) = \text{(const.)}$, the trajectory of the Brownian particle with the time-dependent diffusivity reduces to the trajectory of the CTRW. The step size distribution for the CTRW is determined from the sojourn time distribution 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 the difference between the Langevin equation with the time-dependent and fluctuating diffusivity and the CTRW. The RF and RSD in the CTRW \cite{12,13} also show the crossover behavior similar to one in the Langevin equation in this work. However, in the CTRW, the RSD in the short $t$ region $(t \ll \tau_c)$ shows the power-law type behavior $\Sigma(t; \Delta) \propto t^{-\alpha}$ (with $\alpha > 0$ being a power-law exponent). (The constant RSD can be observed only for nonequilibrium initial ensembles.) This is because the plateau of the RSD at the small $t$ region (Eq. \ref{eq:rf}) diverges at $\langle \tau_f \rangle \to 0$. Thus the crossover from the plateau $(\Sigma(t; \Delta) \propto t^0)$ to Gaussian decay $(\Sigma(t; \Delta) \propto t^{-1/2})$ disappears. This implies that the crossover behavior in the Langevin equation with the time-dependent and fluctuation diffusivity is qualitatively different from one 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 measurement 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 observed 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. Applying the formula to the reptation model and two-state models, and comparing the theoretical predictions with numerical simulation data, we have shown that the crossover time can actually characterize the relaxation times of the diffusivities. Our result justifies our previous study \cite{13} 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 is qualitatively different from one of the Langevin equation
model. We expect 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.

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Appendix A: 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. Thus 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 ($t \ll \tau$), from Eq. (39), the RSD becomes constant. It can be rewritten as

$$\Sigma(t; \Delta) \approx \sqrt{\psi_1(0)} = \sqrt{\langle (\text{tr} D)^2 \rangle - (\text{tr} \langle D \rangle)^2}.$$  \tag{A1}

From Eq. (A1), we find that $\Sigma(t; \Delta)$ is expressed as the relative standard deviation of $\text{tr} D$ 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 $D(0)$, and the TAMSD of each realization can be reasonably approximated as

$$\delta^2(\Delta; t) \approx 2 \text{tr} D(0) \Delta.$$  \tag{A2}

If we use Eq. (A2), the RSD of the TAMSD can be approximated as the RSD of $2 \text{tr} D(0) \Delta$, which is equivalent to Eq. (A1). In a similar way, the RF can be approximately expressed as the RF of $2 \text{tr} D(0) \Delta$. Thus we have the following expression for the RF:

$$R(t; \Delta) \approx \frac{\langle |\text{tr} D - \text{tr} \langle D \rangle| \rangle}{\sqrt{\langle (\text{tr} D)^2 \rangle - (\text{tr} \langle D \rangle)^2}} \Sigma(t; \Delta).$$  \tag{A3}

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

$$R(t; \Delta) \approx \frac{\langle |\text{tr} D - \text{tr} \langle D \rangle| \rangle}{\sqrt{\langle (\text{tr} D)^2 \rangle - (\text{tr} \langle D \rangle)^2}} \Sigma(t; \Delta).$$  \tag{A4}

For the large $t$ case ($t \gg \tau$), from Eq. (39), we have the relation $\Sigma(t; \Delta) \propto t^{-1/2}$. This behavior 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:

$$P\left(\delta^2(\Delta; t)\right) \approx \frac{1}{\sqrt{2\pi} \Sigma(t; \Delta) \langle \delta^2(\Delta; t) \rangle} \exp \left[ - \frac{\left[ \delta^2(\Delta; t) - \langle \delta^2(\Delta; t) \rangle \right]^2}{2\Sigma(t; \Delta) \langle \delta^2(\Delta; t) \rangle^2} \right].$$  \tag{A5}

The RF can be then calculated as

$$R(t; \Delta) \approx \frac{1}{\langle \delta^2(\Delta; t) \rangle} \int \frac{d\delta^2(\Delta; t)}{\delta^2(\Delta; t)} \left| \delta^2(\Delta; t) - \langle \delta^2(\Delta; t) \rangle \right| \left[ P\left(\delta^2(\Delta; t)\right) \right]^{\frac{1}{2}} \Sigma(t; \Delta).$$  \tag{A6}

By combining Eqs. (A1) and (A6), we have the asymptotic forms of $R(t; \Delta)$ as

$$R(t; \Delta) \approx \begin{cases} \frac{\langle |\text{tr} D - \text{tr} \langle D \rangle| \rangle}{\sqrt{\langle (\text{tr} D)^2 \rangle - (\text{tr} \langle D \rangle)^2}} \Sigma(t; \Delta) & (t \ll \tau), \\ \frac{\langle |\text{tr} D - \text{tr} \langle D \rangle| \rangle}{\sqrt{2} \Sigma(t; \Delta)} & (t \gg \tau). \end{cases}$$  \tag{A7}
From Eq. (A7), we find that the RF behaves qualitatively in the same way as the RSD. The crossover time determined by the RF, \( \tau'_c \), is different from \( \tau_c \) in Eq. (10) by the constant factor:

\[
\tau'_c = \frac{2[(\langle \text{tr} D \rangle)^2] - (\langle \text{tr} (D) \rangle)^2]}{\pi[\langle \text{tr} D - \text{tr}(D) \rangle]^2} \tau_c.
\]  

(A8)

In most practical cases, the ratio of \( \tau'_c \) and \( \tau_c \) 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 by using the equilibrium distribution for the end-to-end vector \( p \) [9]:

\[
P^{(\text{eq})}(p) = \left( \frac{3}{2\pi Z a^2} \right)^{3/2} \exp \left( -\frac{3p^2}{2Z a^2} \right).
\]  

(A9)

Finally we have the following asymptotic forms for \( R(t; \Delta) \) as

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

(A10)

This gives the crossover time \( \tau'_c \approx 0.918 \tau_d \). (In the previous work, we reported \( \tau'_c \approx \tau_d \) [13]. This small discrepancy may be due to the accuracy of the fitting for the plateau region.) To check whether Eq. (A7) works well for the data in our previous work [13] or not, 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 CM in the reptation model for \( Z = 80 \) and \( \Delta = 10\tau_l \) in Figure 3. We also show the asymptotic forms of the RF calculated from the asymptotic forms of the RSD by Eq. (A10) in Figure 4. From Figure 4, we find that the prediction by our theory agrees well with the asymptotic behavior of the RF calculated from the simulation. Thus we conclude that both the RSD and RF of the TAMSD can be utilized to study the long time relaxation behavior.

Appendix B: Non-Gaussianity Parameter

The non-Gaussianity parameter [31, 32] is widely employed to investigate the non-Gaussian properties of the diffusion processes. In this appendix, we calculate the expression for the non-Gaussian parameter \( A(\Delta) \) (Eq. (101)) and compare it with the RSD of the TAMSD in the main text.

The ensemble average of quartic displacement can be calculated in the same way as Eq. (24):

\[
\langle |r(\Delta) - r(0)|^4 \rangle = 4 \int_0^\Delta ds \int_0^\Delta ds' \int_0^\Delta du \int_0^\Delta du' \langle w_i(s)w_j(s')w_k(u)w_l(u') \rangle \times \langle B_{mi}(s)B_{mj}(s')B_{nk}(u)B_{nl}(u') \rangle
\]

\[
= 8 \int_0^\Delta ds \int_0^s du \langle \text{tr} D(s) \cdot D(u) \rangle \times \text{tr} D(s) \cdot D(u)
\]

\[
+ 16 \int_0^\Delta ds \int_0^s du \langle \text{tr} D(s) \cdot D(u) \rangle.
\]

(B1)

By using the correlation functions \( \psi_1(t) \) and \( \psi_2(t) \) defined in Eqs. (30) and (31), Eq. (B1) can be rewritten as

\[
\langle |r(\Delta) - r(0)|^4 \rangle = 4 \left( 1 + \frac{2C}{n} \right) [\text{tr} (D)]^2 \Delta^2
\]

\[
+ 8[\text{tr} (D)]^2 \int_0^\Delta ds \int_0^{s*} du [\psi_1(s - u) + 2C\psi_2(s - u)].
\]

(B2)

From Eqs. (101) and (B2), finally we have the following formula for the non-Gaussianity parameter:

\[
A(\Delta) = \frac{2(C - 1)}{n + 2} + \frac{2n}{(n + 2)\Delta^2} \int_0^\Delta ds \int_0^{s*} du [\psi_1(s - u) + 2C\psi_2(s - u)].
\]  

(B3)
Eq. (B3) 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

$$A(\Delta) \approx \begin{cases} \frac{2(C - 1)}{n + 2} + \frac{n}{2(n + 2)} \left[ \psi_1(0) + 2C\psi_2(0) \right] & (\Delta \ll \tau), \\ \frac{n}{2(n + 2)} \int_0^\infty ds \left[ \psi_1(s) + 2C\psi_2(s) \right] & (\Delta \gg \tau). \end{cases} \quad (B4)$$

Eq. (B4) has somewhat similar properties to Eq. (39). However, $A(\Delta)$ behaves in the qualitatively different way to the RSD, $A(\Delta)$ approaches to the constant $2(C - 1)/(n + 2)$ at the limit of $\Delta \to \infty$, whereas $\Sigma(t; \Delta)$ 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. (B4) reduces to

$$A(\Delta) \approx \begin{cases} \frac{n}{2(n + 2)} \left[ \psi_1(0) + 2\psi_2(0) \right] & (\Delta \ll \tau), \\ \frac{n}{2(n + 2)} \int_0^\infty ds \left[ \psi_1(s) + 2\psi_2(s) \right] & (\Delta \gg \tau). \end{cases} \quad (B5)$$

Even in this simple case, $A(\Delta)$ depends both on $\psi_1(t)$ and $\psi_2(t)$. On the other hand, the explicit expression for the RSD (Eq. (38)) and its asymptotic forms (Eq. (39)) are simple and common for isotropic and anisotropic systems. (As mentioned in the main text, $\Sigma(t; \Delta)$ essentially depends only on $\psi_1(t)$.) Thus we consider that the RSD would be more suitable than the non-Gaussianity parameter, for characterizing the long time relaxation behavior for the diffusion processes with time-dependent diffusivities.

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[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] P. Sciortino, P. Gallo, P. Tartaglia, and S. H. Chen, Phys. Rev. E 54, 6331 (1996).
[9] T. Akimoto and T. Miyaguchi, J. Stat. Phys. 157, 515 (2014).
[10] T. Miyaguchi and T. Akimoto, Phys. Rev. E 83, 031926 (2011).
[11] T. Akimoto and T. Miyaguchi, Phys. Rev. E 87, 062134 (2013).
[12] Y. He, S. Burov, R. Metzler, and E. Barkai, Phys. Rev. Lett. 101, 058101 (2008).
[13] T. Uneyama, T. Akimoto, and T. Miyaguchi, J. Chem. Phys. 137, 114903 (2012).
[14] T. Akimoto, E. Yamamoto, K. Yasuoka, Y. Hirano, and M. Yasui, Phys. Rev. Lett. 107, 178103 (2011).
[15] T. Miyaguchi and T. Akimoto, Phys. Rev. E 83, 062101 (2011).
[16] S. Burov, J.-H. Jeon, R. Metzler, and E. Barkai, Phys. Chem. Chem. Phys. 13, 1800 (2011).
[17] A. G. Cherstvy, A. V. Chechkin, and R. Metzler, New J. Phys. 15, 083039 (2013).
[18] M. Doi and S. F. Edwards, J. Chem. Soc. Faraday Trans. 2 74, 1789 (1978).
[19] H. Sillescu, J. Non-Cryst. Solids 243, 81 (1999).
[20] W. Gotze and L. Sjogren, Rep. Prog. Phys. 55, 241 (1992).
[21] R. Richert, J. Phys. Cond. Matt. 14, R703 (2002).
[22] A. Bouchard and G. Biroli, Rev. Mod. Phys. 83, 587 (2011).
[23] O. Bénichou, C. Loverdo, M. Moreau, and R. Voituriez, Rev. Mod. Phys. 83, 81 (2011).
[24] C. W. Gardiner, Handbook of Stochastic Methods, 3rd ed. (Springer, Berlin, 2004).
[25] R. F. Cox, Renewal theory (Methuen, London, 1962).
[26] A. Rahman, Phys. Rev. 136, A405 (1964).
[27] D. Ernst, J. Köhler, and M. Weiss, Phys. Chem. Chem. Phys. 16, 7686 (2014).
Figure Captions

Figure 1: The RSD of the TAMSD of a CM in the discrete reptation model. The number of tube segments $Z$ is $Z = 80$ and the time difference $\Delta$ is $\Delta = 10 \tau_l$. $\tau_l$ 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. (68)) and its asymptotic forms (Eq. (66)).

Figure 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 $k_f = 0.1, 1, \text{and} 10$. The time difference is $\Delta = 0.001$. Symbols represent the simulation results and solid curves represent the theoretical prediction.

Figure 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 $k_{s,0} = 0.1, 0.01, \text{and} 0.001$. The time difference is $\Delta = 0.001$. Symbols represent the simulation results and dashed curves represent the theoretically predicted asymptotic forms.

Figure 4: The RSD and RF of the TAMSD of a CM in the discrete reptation model. (The RF data are taken from Ref [13].) The number of tube segments $Z = 80$ and the time difference $\Delta = 10 \tau_l$, where $\tau_l$ is the characteristic time of the longitudinal motion of a segment along the tube. Dashed curves represent the asymptotic forms calculated from the RF, calculated by Eqs. (66) and (A10).
Figures

FIG. 1:

\[ \Sigma(t; \Delta) \]

\( t / \tau_l \)

simulation, \( k_f = 0.1 \)

theory

asymptotic

FIG. 2:
FIG. 3:

FIG. 4: