



Role of time scales for the non-Gaussianity of the Brownian motion combined with intermittent adsorption



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ARTICLE INFO

Article history:

Received 30 September 2014
Accepted 15 April 2015
Available online 22 April 2015

Keywords:

Single particle tracking
Single molecule
Brownian motion
Surface
Time series analysis

ABSTRACT

Single-molecule tracking data near solid surfaces contain information on diffusion that is potentially affected by adsorption. However, molecular adsorption can occur in an intermittent manner, and the overall phenomenon is regarded as slower yet normal diffusion if the time scale of each adsorption event is sufficiently shorter than the interval of data acquisition. We compare simple numerical model systems that vary in the time scale of adsorption event while sharing the same diffusion coefficient, and show that the shape of the displacement distribution depends on the time resolution. We also evaluate the characteristics by statistical quantities related to the large deviation principle. We show that the characteristic time scale of the intermittent phenomena is elucidated when the time resolution of the observation is sufficiently fine and the amount of data is sufficiently large to evaluate the intermittency.

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1. Introduction

Diffusion of small objects such as biomolecules in fluid near a solid surface is known to differ from the bulk diffusion [1]. Brownian motion of single-stranded DNA molecules labelled with marker molecules has been experimentally observed by total internal reflection fluorescence microscopy (TIRF) technique [2,3]. Diffusion coefficients near the substrate surfaces were substantially smaller than that expected from bulk consideration [4]. Surface effects such as hydrodynamic wall effects [5–10] and the molecular behaviour of water in the vicinity of the solid surface [11] are thought to contribute to the slow down of diffusion. Furthermore, adsorptive effects may also contribute. Diffusion and adsorption of DNA in solution to the substrate surface has been studied since it is important for the application of self-assembly to the engineering [12–14].

Intuitively, the effect of adsorption of molecules in solution to a solid wall is expected to lead to negligible displacement. However, there can also be the case that the adsorption takes place for short duration compared to the time resolution of observation by high-speed camera mounted onto microscope system. If the duration of adsorption is short, it is usually regarded as negligible. However, the slow down of the diffusion by this adsorption event can be

noticeable if the frequency of the event is sufficiently high. Thus, the adsorptive effect of solid surface on the Brownian motion of molecules is not intrinsically of all-or-nothing nature. In this article, we focus on the intermittency of the adsorption phenomena. We consider simple numerical model to represent the diffusion accompanied by intermittent adsorption events, and show how the time scale of adsorbed and diffusing states affects the displacement at finite frame intervals of observation, while sharing the same diffusion coefficients.

2. Computational model and method

2.1. Model of Brownian motion with intermittent adsorption

We define a one-dimensional model of diffusion combined with intermittent adsorption onto a solid surface. The molecule of interest is either in solution or adsorbed on a flat solid surface. Brownian motion in the direction parallel to the solid surface is discussed. The molecule undergoes a Wiener process in the “diffusing state”:

$$\Delta x = \sqrt{2D_p \Delta t} \cdot \xi, \quad (1)$$

where Δx , D_p , Δt and ξ are the displacement, diffusion coefficient within the diffusing state, time increment of the dynamics and Gaussian random variable with zero mean and unit variance, respectively. On the other hand, the solute molecule does not undergo observable displacement in the “adsorbed state”:

$$\Delta x = 0. \quad (2)$$

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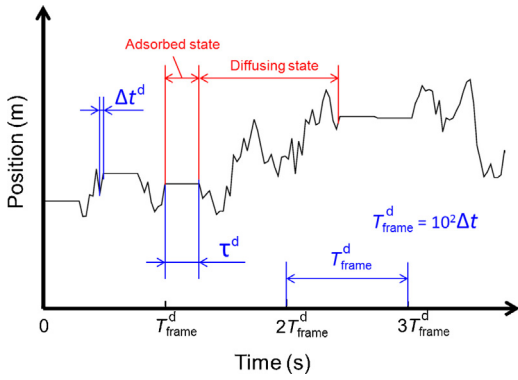


Fig. 1. Schematic graph indicating the time evolution of the position. Molecule of interest is either in the adsorbed or diffusing states, and the state changes stochastically. The duration of a diffusing state is exponentially distributed but the mean duration is τ , which is the same as a continuous adsorbed state. All of the parameters in the figure are displayed with superscript “d”, indicating that they are quantities with dimension. Δt is the time increment to generate the trajectory. The frame interval T_{frame}^d is defined to be $T_{\text{frame}}^d = 10^2 \Delta t$, and three cases $\tau = 10\Delta t$, $10^2 \Delta t$, and $10^3 \Delta t$ of physical systems are considered.

The duration of the diffusing state t_{diffuse} between adsorbed states is defined to be exponentially distributed based on the probability density:

$$p_{\text{Exp}}(t_{\text{diffuse}}) = \frac{1}{\tau} \exp\left(-\frac{t_{\text{diffuse}}}{\tau}\right), \quad (3)$$

where τ is the mean duration of a diffusing state. The duration of a continuous adsorbed state is defined to be constant. It should be noted that we place emphasis on the simplicity here in order to make the essence clear. We do not intend to uncover all of the significant factors for the slow down of diffusion of a molecule in solution in the vicinity of solid surface, but we focus solely on the influence of time scale of intermittent adsorption on the time-series data of displacements that is captured by finite frame intervals.

We define the typical time scale $T = 10^{-2}$ s in order to use nondimensionalized quantities. We consider the frame interval of $T_{\text{frame}}^d = 1$. The model definition with relevant time scales is schematically shown in Fig. 1. The time step of the dynamics itself is defined as $\Delta t = 10^{-2}$. The total number of steps to generate the trajectory is $n_{\text{total}} = 10^6$. We conduct two series of simulations. In the first series, the duration of a continuous adsorbed state is defined to be the same as the mean duration τ of the diffusing state. In other words, the time fraction R of the adsorbed state in the overall dynamics is 0.5 regardless of τ after sufficient duration of sampling. We keep R fixed, and we consider three physical systems; $\tau = 0.1$, 1, and 10. We study how the difference of τ is reflected on the displacement characteristics at the resolution of T_{frame}^d . The unit of length scale is defined as $L = 10^{-6}$ m, and the nondimensional diffusion coefficient during the diffusing state is defined as $D_p = 1$. In the second series of simulations, we fix τ and vary R . We assign $\tau = 1$, and $R = 0.1$, 0.2, and 0.5. In other words, we vary t_{diffuse} . Furthermore, we vary D_p in order to keep the overall diffusion coefficient D to be a constant value regardless of the variation in R . The specific values are $D_p = 5/9$ and $5/8$ for the cases of $R = 0.1$ and 0.2, which lead to $D = 1/2$ regardless of R . In summary, we examine the influence of τ in the first series of simulations, and R in the second series. The overall diffusion coefficient is always $D = 1/2$.

2.2. Data analysis based on the large deviation principle

The rate function $S(u)$ in the large deviation principle is defined as follows:

$$S(u) = - \lim_{T_{\text{span}} \rightarrow \infty} \frac{1}{T_{\text{span}}} \ln P(\bar{u}(T_{\text{span}}) \in [u, u + du]), \quad (4)$$

where $\bar{u}(T_{\text{span}})$ is the finite-time mean of the stochastic variable of interest for the period of T_{span} , and P is the probability of $\bar{u}(T_{\text{span}})$ taking the values between u and $u + du$. The rate function indicates how fast the probability of $\bar{u}(T_{\text{span}})$ taking the specific values of u other than the expected values converges to zero as the number of samples T_{span} are increased. In case of Gaussian random variable, the rate function is known to take parabolic shape [15]. As we cannot have infinite amount of data, we consider a kind of approximation. First, we consider the absolute value $U_j(i)$ of displacement Δx per time step Δt by splitting the $n_{\text{total}} = 10^6$ sequence of time series data into n_{ens} sets, each of which consists of n_{span} steps and define

$$\bar{u}_j(n_{\text{span}}) = \frac{1}{n_{\text{span}}} \sum_{i=1}^{n_{\text{span}}} U_j(i). \quad (5)$$

The use of absolute value instead of the displacement itself is intended for the ease of distinction of the results between the different conditions of τ . The finite amount of data is processed as follows:

$$\phi(q, n_{\text{span}}, n_{\text{ens}}) \equiv \frac{1}{n_{\text{span}}} \ln \left[\frac{1}{n_{\text{ens}}} \sum_{j=1}^{n_{\text{ens}}} \exp(qn_{\text{span}} \bar{u}_j(n_{\text{span}})) \right], \quad (6)$$

$$u(q, n_{\text{span}}, n_{\text{ens}}) = \frac{d\phi(q, n_{\text{span}}, n_{\text{ens}})}{dq}, \quad (7)$$

$$S(u(q), n_{\text{span}}, n_{\text{ens}}) = qu(q, n_{\text{span}}, n_{\text{ens}}) - \phi(q, n_{\text{span}}, n_{\text{ens}}), \quad (8)$$

$$\chi(q, n_{\text{span}}, n_{\text{ens}}) \equiv \frac{du(q, n_{\text{span}}, n_{\text{ens}})}{dq}. \quad (9)$$

We have previously shown that this analysis uncovers the characteristics of anisotropy in the Brownian motion of prolate particles [16] and the motility of model bacteria [17]. In particular, characteristic time scale of the dynamics can be revealed from $\chi(0, n_{\text{span}}, n_{\text{ens}})$ as a function of n_{span} [17].

3. Results and discussion

The time-series data of displacement per Δt for different conditions of τ are shown in Fig. 2(a). The data are numerically generated by the rule defined in Section 2.1 under the condition that τ is varied while R is kept constant to be 0.5. Namely, the mean duration of continuous diffusing state is defined to be equal to the duration of single adsorption state τ , and each of the diffusion duration is exponentially distributed. Although difference in Fig. 2(a) is qualitatively recognized, the mean square displacements (MSDs) are the same for all of the three cases as shown in Fig. 2(b). It means that the dynamics of $\tau = 0.1$, 1, and 10 share the same one-dimensional diffusion coefficient D since the slope of MSD corresponds to it:

$$D = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle |x(t) - x(0)|^2 \rangle, \quad (10)$$

where $x(t)$ and $\langle \rangle$ are the position at time t and the ensemble average, respectively. Furthermore, the model has a characteristic that displacement distribution at the resolution of $\Delta t = 10^{-2}$ is the same regardless of the adsorption duration as shown in Fig. 3(a). These characteristics are realized by keeping the time fraction of unit adsorption duration R in the overall dynamics to be 0.5 regardless of τ , which leads to the overall diffusion coefficient $D = D_p(1 - R)$.

Whereas the variation of τ does not exhibit the difference in the displacement distribution at the time resolution of Δt , it is reflected on the displacement distribution at coarser time resolution. Fig. 3(b) shows the histogram of displacement per frame interval T_{frame}^d . Whereas the displacement distribution at the resolution Δt shown in Fig. 3(a) is the superposition of Gaussian

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