Effect of trap clustering on Brownian particle trapping rate

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Brownian particle survival is studied in the case where traps are gathered in clusters. If the number of traps n in a cluster is small, the trap clustering is only manifested at the final stage of the process. In the opposite limit, the clusters are perfectly absorbing and trapping proceeds considerably slower than that by noncorrelated traps from the very beginning. We treat the intermediate case, where n is neither small nor large, and present an approximate expression for the rate constant that connects the two limiting cases. The results are in agreement with computer simulations. [S1063-651X(98)09810-9]

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The idea of Brownian particles trapped by randomly distributed static perfect traps is widely used in theoretical models of different physical and chemical phenomena, exemplified by fluorescence quenching, fast chemical reactions, migration of excitations, etc. [1,2]. An essential point underlying the conventional theory (dating back to Smoluchowski) is the assumption that traps are spatially noncorrelated [1]. In real systems, however, trap correlations are often present either by design or naturally. Several attempts to allow for trap correlations were made [3–8]. Particular emphasis has been placed on the trapping kinetics at the final process stage where closed analytical results are available [3,7].

Our aim in this paper is to handle the correlation effects at times where the majority of particles annihilate. We focus on a specific type of trap correlations, viz., traps are gathered in *clusters*. Trap clustering can play an important role in determining the rates of trapping by segments of polymer chain [9] or ligand binding to cell-bound receptors [10]. A model of trapping by spatially noncorrelated clusters of traps has been proposed by Berezhkovskii *et al.* [6] and discussed in subsequent articles [7,8]. The previous treatments have provided a few general conclusions concerning the trap clustering influence on particle's survival, however, the trapping kinetics at normal (not asymptotically long) times was found only for two limiting cases. If the number of traps n in a cluster is large enough, the clusters by themselves play the role of perfect traps. For such ''*absorbing*'' clusters, the problem is reduced to that with noncorrelated traps whose concentration and size are those of the clusters. In the opposite limit, when n is small enough, a particle passes through a cluster nearly safely. For such ''*transparent*'' clusters, the trap clustering is actually manifested at asymptotically long times only. Here we treat the *intermediate* case, where the clusters are neither transparent nor absorbing, and show how a smooth transition between the two limiting cases occurs. The analytical results are verified by a Brownian dynamics simulation.

A special feature of the model [6] is that each trap is assigned to a certain cluster, so that the trap ensemble can be presented in the form $\{\mathbf{x}_k+\mathbf{y}_i^{(k)},\ i=1,...,n\}$. The points $\{\mathbf{x}_k\}$ have the meaning of cluster ''centers'' and the aggregate of vectors $(\mathbf{y}_1^{(k)},\dots,\mathbf{y}_n^{(k)})$ determines the positions of n spherical traps with respect to the center of kth cluster. Trap clusters are assumed spatially noncorrelated and statistically similar. This implies that the cluster centers are distributed according to the Poisson law and the distribution of traps within each cluster is the same. The trap concentration c and the cluster concentration c_{cl} are related by the equation $c=nc_{\mathrm{cl}}$.

As a beginning, consider a particle moving along a Wiener trajectory W_t in the presence of a single cluster of traps located at given points $\{\mathbf{x}+\mathbf{y}_i,\ i=1,...,n\}$. To characterize the particle's survival, introduce $P(t|W_t|\mathbf{x}|\{\mathbf{y}_i\})$, which equals 1 if the particle survives for a time t and 0 if it is trapped. The condition of survival is formulated especially simply if one looks on the process from the ''particle's point of view.'' Then the particle is stationary at the point $\mathbf{x}$, while the cluster center (initially at the origin) moves along W_t. The ith trap of the cluster describes a tube $\omega_b(W_t-\mathbf{y}_i)$ of radius b, whose centerline is the trajectory W_t shifted at the vector $-\mathbf{y}_i$ with respect to W_t, where $i=1,...,n$. Note that $\omega_b(W_t)$ is known in the literature [11,12] as the *Wiener sausage* (WS). Due to the cluster motion, the traps visit the region $\omega_b^{(n)}(W_t;\{\mathbf{y}_i\})$, which is the union of n identical copies of WS $\omega_b(W_t)$. We will refer to $\omega_b^{(n)}(W_t;\{\mathbf{y}_i\})$, which is a natural generalization of WS to the cluster case, as the *bunch of Wiener sausages* [7,8], or simply the *Wiener bunch* (WB). The particle survives during time t if $\omega_b^{(n)}(W_t;\{\mathbf{y}_i\})$ does not contain the point $\mathbf{x}$. This implies that $P(t|W_t|\mathbf{x}|\{\mathbf{y}_i\})=1-\chi(\mathbf{x};\omega_b^{(n)}(W_t;\{\mathbf{y}_i\}))$, where $\chi(\mathbf{R};\omega)$ is the indicator function, which equals 1 when point $\mathbf{R}$ belongs to ω and 0 otherwise.

When there are many clusters and the positions of all traps are fixed, the survival of a particle moving along W_t is characterized by

$$\prod_k P(t|W_t|\mathbf{x}_k|\{\mathbf{y}_i^{(k)}\})=\prod_k [1-\chi(\mathbf{x}_k;\omega_b^{(n)}(W_t;\{\mathbf{y}_i^{(k)}\}))]. \tag{1}$$

What is really needed is the particle survival probability $P(t)$, which is the average of the product in Eq. (1), taken over trap configurations and particle (Wiener) trajectories. Following the approach proposed in [13], we start with the first averaging, which is carried out in two separate stages. First, we make the partial average over trap configurations inside each cluster for the fixed positions of clusters centers, which is denoted below by a bar. Then, the average over the Poisson ensemble of trap centers is made. This can be conveniently done by introducing an auxiliary volume Ω with $N=c_{\mathrm{cl}}\Omega$ cluster centers and passing to the limit $\Omega\to\infty$ in the final result. In so doing, we obtain for the (conditional) survival probability

$$\begin{aligned} P(t|W_t) &= \lim_{\Omega\to\infty}\frac{1}{\Omega^N}\int_\Omega\cdots\int_\Omega \overline{\prod_{k=1}^{N}[1-\chi(\mathbf{x}_k;\omega_b^{(n)})]d\mathbf{x}_k} \\ &= \lim_{\Omega\to\infty}\left[1-\frac{1}{\Omega}\,\overline{\int_\Omega \chi(\mathbf{x};\omega_b^{(n)}(W_t;\{\mathbf{y}_i\}))d\mathbf{x}}\right]^N \\ &= \exp\left[-c_{\mathrm{cl}}\int\overline{\chi(\mathbf{x};\omega_b^{(n)}(W_t;\{\mathbf{y}_i\}))}d\mathbf{x}\right]. \end{aligned} \tag{2}$$

Let us define the volume of WB corresponding to a given trajectory W_t and a fixed intracluster configuration of traps $\{\mathbf{y}_i\}$ as $v_b^{(n)}(W_t;\{\mathbf{y}_i\})\equiv v[\omega_b^{(n)}(W_t;\{\mathbf{y}_i\})]=\int\chi(\mathbf{x};\omega_b^{(n)}(W_t;\,\{\mathbf{y}_i\}))d\mathbf{x}$, and denote the WB volume averaged over intracluster configurations by $\overline{v_b^{(n)}}(W_t)$. Finally, it remains to average $P(t|W_t)$, Eq. (2), over Wiener trajectories, which is denoted by angular brackets. Taking into account the definition of the WB volume, we arrive at the following expression for the survival probability [6]:

$$P(t)=\langle\exp[-c_{\mathrm{cl}}\overline{v_b^{(n)}}(W_t)]\rangle. \tag{3}$$

In the particular case $n=1$, the volume of WB is simply the volume $v_b(W_t)$ of single WS and the representation of the survival probability (3) is reduced to that obtained earlier [13] for noncorrelated traps

$$P_{\mathrm{nc}}(t)=\langle\exp[-cv_b(W_t)]\rangle. \tag{4}$$

The formal analogy between Eqs. (3) and (4) is noteworthy. The presence of the cluster concentration c_{cl}, in place of the trap concentration c, reflects the fact that here we deal with an ‘‘ideal gas’’ of clusters instead of an ideal gas of traps in the conventional model. The volume of WS is replaced by the volume of WB because the clusters have a certain inner structure.

The representation (3) of the survival probability enables us to draw an important conclusion. Since for $t>0$ the volume of WB is smaller than the sum of the volumes of n individual WS forming WB, a comparison of Eqs. (3) and (4) shows that for $t>0$

$$P(t)>P_{\mathrm{nc}}(t). \tag{5}$$

Thus, trapping by clusters of traps proceeds slower than that by noncorrelated traps no matter what the cluster structure is [6]. Note that the correlations featuring the model can be treated as a combination of grouping correlations responsible for the cluster formation and intracluster correlations determining the structure of cluster. The former can be interpreted as a display of some specific trap attraction and hence facilitate the particle's survival, according to the general conclusion concerning the trap correlation influence on the trapping rate [5]. The latter can be of arbitrary nature so that their influence on the kinetics is ambiguous. The inequality (5) points to the decisive role of the grouping correlations.

Another appropriate estimate of $P(t)$ is obtained from Eq. (3) on the relevant assumption that the clusters are spheres of radius R. Then, from the evident inequality $\overline{v_b^{(n)}}(W_t)\leqslant v_R(W_t)$, where $v_R(W_t)\equiv v[\omega_R(W_t)]$ is the volume of WS generated by a spherical Brownian particle of radius R, immediately follows that

$$P(t)\geqslant\langle\exp[-c_{\mathrm{cl}}v_R(W_t)]\rangle=\tilde{P}_{\mathrm{nc}}(t). \tag{6}$$

$\tilde{P}_{\mathrm{nc}}(t)$ is the survival probability of a particle among noncorrelated traps of radius R, whose concentration is c_{cl} [cf. Eq. (4)]. So, trapping by clusters of traps runs slower than that by clusters playing the role of traps. At asymptotically long times, when the majority of surviving particles spend all the time in large trap-free regions [14], the inequality (6) passes into equality and the long-time decay of $P(t)$ in d dimensions (regardless of the cluster structure) exhibits Donsker-Varadhan behavior [12] controlled by the cluster concentration [7]

$$-\ln P(t)\sim(c_{\mathrm{cl}}^{2/d}Dt)^{d/(d+2)}. \tag{7}$$

To find $P(t)$ at normal times, a recourse to approximations making Eq. (3) analytically treatable is required. At the initial stage, the main contribution is given by the Wiener trajectories determining the average (over W_t) volume of WB, $\overline{v_b^{(n)}}(t)\equiv\langle\overline{v_b^{(n)}}(W_t)\rangle$. This suggests use of the mean-field approximation neglecting the WB volume fluctuations. For noncorrelated traps, a similar approach [13] well describes trapping of the bulk of particles provided (as usual in the trapping problem) that the volume fraction of traps is small. One might expect that an employment of the mean-field approximation to the problem under study offers the greatest promise, when the volume fraction of clusters is small, $c_{\mathrm{cl}}R^d\ll 1$ (nonoverlapping clusters). With this approximation, the survival probability (3) is given by

$$P(t)\simeq\exp[-c_{\mathrm{cl}}\overline{v_b^{(n)}}(t)]. \tag{8}$$

By setting $n=1$, the model is reduced to that of noncorrelated traps, the volume $\overline{v_b^{(1)}}(t)$ is the average WS volume $v_b(t)$, and Eq. (8) leads to the conventional trapping kinetics. In particular in three dimensions [15],

$$v_b(t)=4\pi bDt(1+2b/\sqrt{\pi Dt}) \tag{9}$$

and the kinetics (8) takes its familiar Smoluchowski form

$$-\ln P_{\mathrm{nc}}(t)=k_{\mathrm{nc}}ct(1+2b/\sqrt{\pi Dt}), \tag{10}$$

where D is the particle diffusion coefficient and $k_{\mathrm{nc}}=4\pi bD$ is the rate constant describing trapping by noncorrelated traps. Note that at asymptotically long times the mean-field approximation fails because of the crucial role of the WB volume fluctuations at these times and the survival probability (7) decays considerably slower than the mean-field estimate (8) predicts.

By definition, the average volume of WB is $\overline{v_b^{(n)}}(t) = \int \overline{Q(t;\mathbf{x})} d\mathbf{x}$, where $\overline{Q(t;\mathbf{x})} = \overline{Q(t;\mathbf{x},\{\mathbf{y}_i\})}$ and $Q(t;\mathbf{x},\{\mathbf{y}_i\}) = \langle \chi(\mathbf{x};\omega_b^{(n)}(W_t;\{\mathbf{y}_i\}))\rangle$. The latter is the fraction of the trajectories starting at $\mathbf{x}$, which have visited at least one of n traps located at the points $\{\mathbf{y}_i\}$ during time t at least once, i.e., the death probability of a particle initially at point $\mathbf{x}$ in the presence of a single cluster centered at the origin. Thus, the mean-field approximation reduces the problem to that of particle survival in the presence of only one cluster of traps. In the following, we treat the latter problem in three dimensions, assuming that $R \gg b$, $n \gg 1$, and intracluster correlations are absent, i.e., traps, being independent of each other, are uniformly distributed within the cluster.

An approximate treatment presented here is based on the simple idea similar to that used in the theory of ligand binding to receptors on cell surfaces [10]. In fact, we need the integral of the probability $\overline{Q(t;\mathbf{x})}$ taken over different particle starting points $\mathbf{x}$ rather than the probability itself. At times, $t \gg \tau_D$ ($\tau_D = R^2/D$ is the characteristic time of Brownian-particle passage through a cluster), the main contribution comes from $x \gg R$. A particle initially far from a cluster does not ''feel'' fine details of the cluster structure. For such a particle, the cluster appears to be uniform but neither perfectly absorbing nor perfectly transparent. This suggests replacement of the cluster of traps (sphere with ''black holes'') by a uniform partially absorbing (''gray'') sphere of radius R, in which the particle can be absorbed at any point with a fixed rate. With this approximation, the problem becomes spherically symmetric and $\overline{Q(t;x)} = 1 - 4\pi \int_0^\infty G(t,r;x) r^2 dr$, where $G(t,r;x)$ is the probability density that the particle initially at distance x will be at distance r after time t, which satisfies the diffusion equation with a sink term

$$\frac{\partial G}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial G}{\partial r}\right) - \frac{1}{\tau} H(R-r) G, \tag{11}$$

the initial condition $G(0,r;x) = (4\pi x^2)^{-1}\delta(r-x)$, and the boundary condition that $G(t,r;x) \to 0$ when $r \to \infty$. Here $H(z)$ is the Heaviside step function and τ is the characteristic particle lifetime in a cluster. Applying the Laplace transformation, Eq. (11) is easily solved and the Laplace transforms of the death probability and the average volume of WB are successively found. The final result is

$$\overline{v_b^{(n)}}(s) = \int_0^\infty e^{-st} \overline{v_b^{(n)}}(t) dt = \frac{4\pi R^3}{3s(1+s\tau)} \times \left[1 + \frac{3(1+z)}{z^2(1+s\tau)} \frac{\sqrt{z+\alpha}\coth\sqrt{z+\alpha} - 1}{\sqrt{z+\alpha}\coth\sqrt{z+\alpha} + z}\right], \tag{12}$$

where $z = \sqrt{s\tau_D}$ and the dimensionless parameter $\alpha = \tau_D/\tau$ measures the degree to which a cluster is absorbing. If α is small, a particle passes through a cluster nearly safely (the case of transparent clusters). If α is large, a particle entering a cluster most likely is eliminated before leaving (the case of absorbing clusters). It is natural to call α the absorption coefficient.

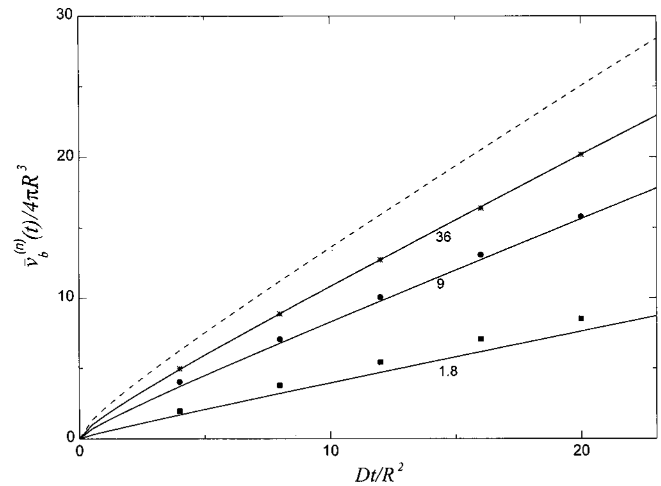

FIG. 1. Comparison of the analytical solution [Eq. (9) with b replaced by $R^\star$] for the average volume of WB (solid lines with the numbers showing the values of α) with simulation data [$R/b = 5$, $n = 3$ (squares), 15 (circles), 60 (stars)]. The dashed line is the time dependence of the average volume visited by a Brownian particle of radius R.

An approximation for τ is derived on the assumption that the mutual influence of intracluster traps on the particle death can be neglected. This suggests use of the Smoluchowski dependence (10), where c is replaced by the intracluster trap concentration $c_{\mathrm{in}} = 3n/4\pi R^3$. Following this way, we have $\tau \simeq \tau_{\mathrm{Sm}} = (R/3nb)\tau_D$ and

$$\alpha = 3nb/R. \tag{13}$$

The approximation made is good if traps are far apart enough, i.e., the volume fraction of traps in clusters, $\rho_{\mathrm{in}} \sim n(b/R)^3$, is small. Even if ρ_{in} is not small, this also seems to be reasonable. The point is that $\alpha \gg \rho_{\mathrm{in}}$ and the volume $\overline{v_b^{(n)}}$ as a function of α approaches the limiting value $v_R(t) = \langle v_R(W_t)\rangle$ [given by Eq. (9) with b replaced by R] even if much of the cluster volume is free from traps. So, Eqs. (12) and (13) provide the simplest possible solution for the average volume of WB.

In calculating $\overline{v_b^{(n)}}$ we assume that $t \gg \tau_D$. So, converting Eq. (12) we retain only the first two terms of the long-time expansion. In so doing, we obtain that at $t \gg \tau$ the average volume of WB is presented by Eq. (9) for the average volume of WS, where the radius b is replaced by $R^\star = R(1 - \tanh\sqrt{\alpha}/\sqrt{\alpha})$. To verify the analytical solution we compare it with the results of computer simulations. We have simulated stochastic trajectories [16] of a cluster, counted directly the volume visited by spherical particles randomly distributed within the cluster, and averaged this volume over trajectories and particle configurations [17]. As Fig. 1 shows, the simulated and the analytical results for the average volume of WB are in close agreement. Marked deviations (~14%) occur only for $\alpha = 1.8$ ($n = 3$), where both n and R/b are not sufficiently large and our theory is too crude.

Substituting the expression for $\overline{v_b^{(n)}}$ into Eq. (8) we arrive at the Smoluchowski kinetics corrected for the trap clustering [cf. Eq. (10)]

$$-\ln P(t) \simeq ck(\alpha)t(1+2R^{\star}/\sqrt{\pi Dt}), \qquad (14)$$

where the time-independent rate constant is given by

$$k(\alpha)=k_{\mathrm{nc}}\frac{3}{\alpha}\left(1-\frac{\tanh\sqrt{\alpha}}{\sqrt{\alpha}}\right). \qquad (15)$$

Equations (14) and (15) are the main results of this work. They show how the trap clustering (represented by the absorption coefficient) modifies the course of the process. If α is small, $\alpha \ll 1$, then $k(\alpha)\simeq k_{\mathrm{nc}}(1-0.4\alpha)$. The main term coincides with the rate constant for noncorrelated traps. For transparent clusters, Eq. (14) in fact is reduced to Eq. (10) and trap-cluster formation manifests itself very slightly. The rate constant $k(\alpha)$ monotonously decreases with a rise in the absorption coefficient despite the absorption by a single cluster increases with α. The slowdown due to trap clustering, predicted by inequality (5) is most pronounced when α is large and the clusters become absorbing. In this case, $k(\alpha) \simeq (\tilde{k}_{\mathrm{nc}}/n)(1-\alpha^{-1/2})$, where $\tilde{k}_{\mathrm{nc}}=4\pi DR$ is the rate constant for noncorrelated traps of radius R, and the kinetics (14) is controlled by the cluster concentration and size. In accordance with the general theory, for any α trapping by clusters of traps runs slower than that by both noncorrelated traps [cf. Eq. (5)] and perfectly absorbing clusters [cf. Eq. (6)].

Finally, we emphasize that our treatment of the problem provides an intermediate asymptotic behavior of the survival probability. At small times, $t \leqslant \tau_D$, the method of calculation of the average WB volume is inapplicable. At very long times, the mean field approximation breaks down. For the considered case of nonoverlapping clusters, Eqs. (14) and (15) give a satisfactory description of the trapping kinetics at times where the overwhelming majority of particles annihilate.

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[17] The procedure for the volume calculation was tested by known analytical results for the WS volume [15]. The simulation data were generated from 100 trajectories for each intracluster configuration, and averaged over 30, 20, and 10 configurations for $n=3$, 15, and 60. The algorithm used here will be described elsewhere.