Brownian-particle trapping by clusters of traps

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Brownian-particle trapping is considered in the case when traps are gathered in "clouds" distributed in space in a noncorrelated manner. A general formula for the survival probability is derived. Its analysis shows that the trap-cluster formation leads to a process slowdown (meaning a slowdown in the trapping rate) in comparison with the case of noncorrelated traps. The slowdown is significant from the very beginning of the process or only at its final stage, depending on the cloud structure.

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The problem of Brownian-particle survival among randomly distributed static traps is of unremitting interest due to its close relation to a variety of physical and chemical phenomena [1,2]. The convention theory suggested by Smoluchowski is based on the assumption that traps are distributed in space in a noncorrelated manner [1]. Several attempts to take trap correlations into account were made in the past decade [3–5]. In this paper the problem is considered in the case when traps are correlated in a special manner, viz., they are collected in "clouds" randomly distributed in space. Such a special type of correlation may arise, for example, due to trap binding with a certain supporting object (e.g., to a polymer chain) or as a result of the trap generation (e.g., when traps are created by radiation damage). We show that trap-cluster formation leads to trapping slowdown; however, depending on the cloud structure, this effect may manifest itself at the early stage of the process or only at large times.

As usual, suppose that traps are absorbing spheres and their volume fraction is small. Trap clouds are assumed spatially noncorrelated and statistically similar, i.e., the number of traps and their distribution inside each cloud are the same. In particular, the total trap concentration c is related to the cloud concentration $c_{\rm cl}$ by the equation $c=nc_{\rm cl}$, where n is the number of traps in each cloud. To calculate the survival probability $P(t)$, it is necessary to carry out two procedures of averaging: one over trap configurations and the other over trajectories of a Brownian particle. Following the approach suggested in [6], we start with the first averaging, i.e., find the (conditional) survival probability $P(t|W_t)$ for a particle moving along a fixed Wiener trajectory W_t. Denote by $Q(X|W_t)$ the probability of the annihilation of such a particle on a single cloud centered at a point $\mathbf{X}$. Introducing an auxiliary volume Ω containing $N=c_{\rm cl}\Omega$ clouds centered at $\mathbf{X}_i,\ldots,\mathbf{X}_N$ and passing to the limit $\Omega\to\infty$, we obtain

$$\begin{aligned}P(t|W_t)&=\lim_{\Omega\to\infty}\frac{1}{\Omega^N}\int_\Omega\cdots\int_\Omega\prod_{i=1}^{N}[1-Q(\mathbf{X}_i|W_t)]d\mathbf{X}_i\\&=\lim_{\Omega\to\infty}\left[1-\frac{1}{\Omega}\int_\Omega Q(\mathbf{X}|W_t)d\mathbf{X}\right]^N\\&=\exp\left[-c_{\rm cl}\int Q(\mathbf{X}|W_t)d\mathbf{X}\right].\end{aligned}\tag{1}$$

So, the problem is reduced to that with the presence of only one trap cloud.

In turn, the annihilation probability $Q(\mathbf{X}|W_t)$ equals the fraction of such intracloud trap configurations that at least one trap center occurs at a distance less than the trap radius b from the trajectory W_t, i.e., within the b vicinity of W_t. Such a b-vicinity $\omega_b(W_t)$, known as a "Wiener sausage" [7,8], is the region of space visited by a sphere of the radius b whose center moves along the Wiener trajectory W_t. Using the indicator function $\chi(\mathbf{Z};\omega_b(W_t))$, which is equal to 1 when point $\mathbf{Z}$ belongs to $\omega_b(W_t)$ and 0 otherwise, and denoting an average over intracloud trap configurations by a bar, we can write

$$Q(\mathbf{X}|W_t)=1-\overline{\prod_{j=1}^{n}\{1-\chi(\mathbf{W}+\mathbf{Y}_j;\omega_b(W_t))\}}\ ,\tag{2}$$

where $\mathbf{Y}_j$, $j=1,\ldots,n$ indicates the position of the jth trap center with respect to the cloud center $\mathbf{X}$. Finally, to obtain the desired survival probability $P(t)$, it remains to average the conditional probability (1) over Wiener trajectories, which is denoted by angle brackets:

$$\begin{aligned}P(t)&=\langle P(t|W_t)\rangle\\&=\left\langle\exp\left[-c_{\rm cl}\int Q(\mathbf{X}|W_t)d\mathbf{X}\mathbf{X}\right]\right\rangle.\end{aligned}\tag{3}$$

In the particular case $n=1$,

$$\int Q(\mathbf{X}|W_t)d\mathbf{X}=\overline{\int\chi(\mathbf{X}+\mathbf{Y};\omega_b(W_t))d\mathbf{X}}=\vartheta(\omega_b(W_t))\ ,$$

where $\vartheta(\omega_b(W_t))$ is the volume of the Wiener sausage $\omega_b(W_t)$ and, as should be expected, the survival probability (3) is reduced to that for noncorrelated traps [6]:

$$P_{\rm nc}(t)=\langle \exp[-c\vartheta(\omega_b(W_t))]\rangle \ . \tag{4}$$

To interpret Eq. (3) for $n>1$, let us consider a region $\omega_b^{(n)}(W_t;\{\mathbf{Y}_j\})$ being a unification of n copies of the initial Wiener sausage $\omega_b(W_t)$ shifted at the vectors $\mathbf{Y}_j$, $j=1,\ldots,n$. One can realize such a region as a group of n Wiener sausages generated by the traps of a single cloud as the cloud center moves along the Wiener trajectory. Notice that the concept of the group arises rather naturally if one looks on the process from the "particle's view" when Brownian motion is performed by the cloud center. One can check that the integral in Eq. (3) is equal to the volume of the group $\omega_b^{(n)}(W_t;\{\mathbf{Y}\})$ averaged over intracloud trap configurations $\{\mathbf{Y}_j\}$. Thus, denoting the latter quantity by $\bar{\vartheta}(\omega_b^{(n)}(W_t))$, one can present Eq. (3) in a form analogous to Eq. (4):

$$P(t)=\langle \exp[-c_{\rm cl}\bar{\vartheta}(\omega_b^{(n)}(W_t))]\rangle \ . \tag{5}$$

The general formula (5) enables one to compare the kinetics of trapping on clusters of traps with that in the case of noncorrelated traps, Eq. (4). From the obvious inequality

$$\bar{\vartheta}(\omega_b^{(n)}(W_t))\le n\vartheta(\omega_b(W_t)) \ , \tag{6}$$

it follows immediately that

$$P(t)\le P_{\rm nc}(t) \ . \tag{7}$$

Moreover, because of possible mutual penetration of individual Wiener sausages of the group, the inequalities (6) and (7) are actually strict. Thus, we arrive at the conclusion that the correlations under study result in the process slowdown. Note that the effect is most pronounced in the limiting case when all traps of a cloud are superimposed on one another:

$$P(t)\le \tilde{P}_{\rm nc}(t)=\langle \exp[-c_{\rm cl}\vartheta(\omega_b(W_t))]\rangle \ .$$

Below we show that the trapping slowdown may become considerable either from the very beginning of the process or only at its final stage, depending on the cloud structure.

The principal difficulty in analyzing Eq. (5) is related to averaging over Wiener trajectories. It is clear that at the initial stage the main contribution is given by the typical trajectories determining the average volume of the group of Wiener sausages. This suggests employing the mean-field approximation, neglecting the volume fluctuations at such times. Note that at the final stage, such an approach is inapplicable because of the crucial role of the volume fluctuations at asymptotically large times. (The boundary between the initial and final stages of the process is discussed below.) For noncorrelated traps the mean-field approximation is justified at normal (not asymptotically large) times [6]. In particular, in three dimensions due to the time dependence of the average Wiener-sausage volume [9], $\langle \vartheta(\omega_b(W_t))\rangle \simeq 4\pi bDt$, where D is the diffusion coefficient, the survival probability (4) is reduced to the well-known Smoluchowski result

$$-\ln P_{\rm nc}(t)\simeq 4\pi bcDt \ . \tag{8}$$

Similarly, applying the mean-field approximation to Eqs. (3) and (5), we arrive at the following equation for the probability of particle survival among clusters of traps at normal times:

$$P(t)\simeq \exp\left[-c_{\rm cl}\int Q(\mathbf{X};t)d\mathbf{X}\right] =\exp[-c_{\rm cl}\vartheta_{\rm eff}^{(n)}(t)] \ . \tag{9}$$

Here, $Q(\mathbf{X};t)=\langle Q(\mathbf{X}|W_t)\rangle$ is the annihilation probability in the presence of a single cloud centered at $\mathbf{X}$ and $\vartheta_{\rm eff}^{(n)}(t)$ is the volume of the group of Wiener sausages averaged over Wiener trajectories,

$$\vartheta_{\rm eff}^{(n)}(t)=\langle \bar{\vartheta}(\omega_b^{(n)}(W_t))\rangle \ .$$

It should be pointed out that the correlations under consideration may be treated as a combination of correlations of two different types, viz., cluster formation, being responsible for the formation of clouds, and intracloud correlations determining cloud structure. In the case when the latter are absent and traps in a cloud, being independent of each other, are uniformly distributed within the cloud, the correlations may be interpreted as a display of trap attraction. In that sense, the process slowdown predicted by the inequality (7) is in agreement with the general conclusion about the influence of trap correlations on the trapping kinetics [5]. In this case the annihilation probability (2) can be presented in the form

$$Q(\mathbf{X},t)=\langle Q(\mathbf{X}|W_t)\rangle=1-\langle [1-q_1(\mathbf{X}|W_t)]^n\rangle \ , \tag{10}$$

where

$$q_1(\mathbf{X}|W_t)=\overline{\chi(\mathbf{X}+\mathbf{Y},\omega_b(W_t))}$$

is the probability that the trajectory W_t hits a given trap randomly located within the cloud centered at $\mathbf{X}$. Below, we consider the problem in three dimensions assuming that clouds are spheres of radius $R\gg b$. We also restrict ourselves to the case when the number of traps in a cloud is large, $n\gg 1$, and clouds are nonoverlapping, i.e., their volume fraction is small,

$$c_{\rm cl}R^3\ll 1 \ . \tag{11}$$

Before proceeding to an analysis of Eq. (9), let us outline a qualitative picture of the kinetics by heuristic arguments. Begin with a comparison of two characteristic times related to Brownian-particle passage through a cloud: the diffusion time $\tau_d\sim R^2/D$ and the lifetime $\tau_l\sim(c_{\rm in}bD)^{-1}$, where $c_{\rm in}=n/V_R$ is the intracloud trap concentration and V_R is the cloud volume [τ_l is estimated from the Smoluchowski dependence (8) where c is replaced by $c_{\rm in}$]. It is readily seen that if the cloud parameters satisfy the inequality $nb/R\gg 1$, then $\tau_d\gg\tau_l$, and a particle entering such a cloud most likely is annihilated before leaving. In other words, a cloud actually plays the role of a single trap of radius R and hence may be called "absorbing." In this case the kinetics have the usual Smoluchowski form and are controlled by the cloud concentration, but not the total trap concentration [cf. Eq. (8)]:

$$-\ln P(t) \simeq 4\pi R D c_{\rm cl} t \ . \tag{12}$$

In contrast, if $nb/R \ll 1$, then $\tau_d \ll \tau_l$, which means that a particle passes through a cloud nearly "safely." It is natural to call such clouds "transparent." Notice that nonoverlapping clouds [see Eq. (11)] can be transparent only if the number of traps inside a cloud is not too large: $n \ll (cb^3)^{-1/2}$. Due to the cloud transparency, a particle visits a large number of clouds before being annihilated. Since the clouds are nonoverlapping, the time $\tilde{t}$ that a particle spends in the intracloud domains is $\tilde{t} \simeq c_{\rm cl} V_R t$. So, one can effectively realize the process as if it occurs with noncorrelated traps of the concentration $c_{\rm in}$ during the time $\tilde{t}$. Then, in the framework of the Smoluchowski theory, one obtains

$$-\ln P(t) \simeq 4\pi b c_{\rm in} D \tilde{t} \simeq 4\pi n c_{\rm cl} b D t \ ,$$

and the conventional dependence (8) is recovered. Thus, cloud transparency is responsible for the particle being affected by just the total trap concentration c, i.e., the effective averaging of the initially inhomogeneous medium takes place.

So, we arrive at the following simple picture: The cluster-formation influence on the kinetics is characterized by the dimensionless parameter nb/R only. If the parameter is large, $nb/R \gg 1$ (absorbing clouds), then the process is substantially slower than that with noncorrelated traps from the very beginning [cf. Eqs. (8) and (12)]. Note that such an effect was observed in a particular model of trapping by segments of polymer chain [4]. The case of transparent clouds, $nb/R \ll 1$, corresponds to a rather unexpected situation when the slowdown predicted by Eq. (7) is very slight and the trap-cluster formation does not actually manifest itself in the kinetics. This is related to the fact that the slowdown, since it is a very faint effect for transparent clouds, does not appear in the above rough estimations.

Now let us support this picture by an analysis of Eq. (9). First, consider the case of absorbing clouds when $nb/R \gg 1$. It is convenient to present the annihilation probability $Q(\mathbf{X},t)$ (10) in the form reflecting the fact that the particle annihilation implies visiting the cloud:

$$Q(\mathbf{X},t) = Q_R(\mathbf{X},t) - \langle \chi(\mathbf{X},\omega_R(W_t))[1-q_1(\mathbf{X}|W_t)]^n \rangle \ , \tag{13}$$

where

$$Q_R(\mathbf{X},t) = \langle \chi(\mathbf{X},\omega_R(W_t)) \rangle$$

is the probability of annihilation on a trap of radius R and $\omega_R(W_t)$ is a Wiener sausage generated by a spherical Brownian particle of radius R. To estimate the second term in Eq. (13), let us apply a mean-field approximation once more. Then this term is reduced to

$$Q_R(\mathbf{X},t)\{1 - \langle \chi(\mathbf{X},\omega_{\mathbf{R}}(\mathbf{W}_t)) q_1(\mathbf{X}|W_t) \rangle\}^n \ .$$

It can be shown that the expression in the angle brackets is $\sim b/R$. So, the estimated term is small as compared to $Q_R(\mathbf{X},t) \simeq Q_R(\mathbf{X},t)$. Integration of this relation over $\mathbf{X}$ shows that the average group volume $\vartheta_{\rm eff}^{(n)}(t)$ is close to $\langle \vartheta(\omega_R(W_t)) \rangle$ and, as a result, Eq. (9) is reduced to Eq. (12). Note that in this case the group is formed by strongly overlapped Wiener sausages, despite the fact that intracloud volume fraction of traps,

$$\rho_{\rm in} \sim c_{\rm in} b^3 \sim n(b/R)^3 \ ,$$

may be small.

In the opposite case of transparent clouds when $nb/R \ll 1$, we proceed from the following expansion of the annihilation probability (10):

$$Q(\mathbf{X},t) = \sum_{i=1}^{n} (-1)^{i-1} Q_i(\mathbf{X},t) \ , \tag{14}$$

where

$$Q_i(\mathbf{X},t) = [n!/i!(n-i)!] \langle q_1^i(\mathbf{X}|W_t) \rangle$$

is the probability that the Wiener trajectory hits i different traps belonging to the cloud centered at $\mathbf{X}$. Observe that retention of only the first term Q_1 leads to the Smoluchowski dependence (8). The second term Q_2 of the alternating expansion (14) bounds the deviation of Q from Q_1. The probability Q_2 can be evaluated via the account of two factors: hitting one of n traps and subsequently hitting some other trap. The probability of the first event is bounded just by Q_1, whereas that of the second one is $\sim nb/R$. So, for transparent clouds, $Q_2 \ll Q_1$, and hence the estimation $Q \simeq Q_1$ is correct. As a result, the average group volume $\vartheta_{\rm eff}^{(n)}(t)$ is close to $n\langle \vartheta(\omega_b(W_t)) \rangle$, i.e., the overlapping of Wiener sausages in the group is small, and the trap-cluster formation does not affect the process kinetics. Note that the above approximation of the annihilation probability Q gives an upper bound and, in fact, the kinetics is slower than that for noncorrelated traps, Eq. (8), in accordance with the inequality (7).

At asymptotically large times, the mean-field approach fails. Fortunately, here the problem can be treated in a different manner. The point is that the majority of particles surviving at such times spend all the time in large spherical cavities free from traps. Such particles move along trajectories that generate Wiener sausages of spherical shape. At every time instant there are cavities of optimal radius growing with time, which give the main contribution to the survival probability [7,10]. When the optimal cavity size becomes greater than the cloud radius, one can treat clouds as absorbing regardless of their structure. This is why the survival probability $P(t)$ (5) has a universal asymptotic behavior controlled by the cloud concentration

$$-\ln P(t) \sim (c_{\rm cl}^{2/3} D t)^{3/5} \ . \tag{15}$$

Thus, at large times the trapping is considerably slower than that in the absence of correlations. In particular, for transparent clouds the slowdown predicted by Eq. (7), being negligible at normal times, is displayed in the long run.

Estimate a fraction a of particles whose annihilation obeys the nonexponential asymptotic law (15). Let t^* be the crossover time separating normal and asymptotically large times. The time instant t^* is found via equating the dependencies describing the kinetics at the initial and final stages. Using Eqs. (8), (12), and (15), one obtains

$$\ln a \sim \begin{cases} \rho_{\rm in}^{1/2}\ln a_{\rm nc} & \text{for absorbing clouds} \\ n_{-1}\ln a_{\rm nc} & \text{for transparent clouds ,} \end{cases}$$

where $a_{\rm nc}$ is the value of a for noncorrelated traps, $-\ln a_{\rm nc} \sim \rho^{-1/2}$, and $\rho \sim cb^3$ is the total volume fraction of traps. One can check that for absorbing clouds the quantity a increases with cloud size and is considerably greater than $a_{\rm nc}$ provided $\rho_{\rm in} < 1$. The maximal value of a is attained for transparent clouds since, due to the condition (8), $\rho_{\rm in}^{1/2} < n^{-1}$. Thus, cluster formation of traps can lead to a substantial increase in the fraction of particles which annihilate according to the asymptotic law (15). A similar effect for a particular model (in fact, corresponding to the case of absorbing clouds) was noted in Ref. [4].

In conclusion, we have studied the trapping problem in the case when traps are gathered in randomly distributed clouds. We have shown that the trap-cluster formation leads to a slowdown of the process [Eq. (7)] regardless of the intracloud structure. The case of the "pure" clusterization has been analyzed in detail for nonoverlapping clouds. We have found that if clouds are absorbing, then the deviations of the trapping kinetics from that with noncorrelated traps are considerable from the very beginning of the process. In contrast, if clouds are transparent, cluster formation does not manifest itself at normal times. So, the cloud transparency "cancels" the correlations. At asymptotically large times, the slowdown effect is strongly pronounced independently of the cloud structure and the kinetics has a universal form [Eq. (15)].

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