Trapping by clusters of traps

Yu. A. Makhnovskii,[1,2] A. M. Berezhkovskii,[3] D.-Y. Yang,[1] S.-Y. Sheu,[4] and S. H. Lin[1]

[1]*Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, Republic of China*

[2]*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Prospekt 29, 117912 Moscow, Russia*

[3]*Karpov Institute of Physical Chemistry, 10 Vorontsovo Pole Street, Moscow 103064, Russia*

[4]*Department of Life Science, National Yang-Ming University, Taipei, Taiwan, Republic of China*

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We study how the trapping kinetics is modified when traps are gathered in clusters. Recently, we have proposed a mean-field theory of trapping by clusters of traps valid at the initial stage of the process [J. Chem. Phys. **111**, 711 (1999)]. Here by using the optimal-fluctuation method we incorporate fluctuation effects in the theory and discuss the manifestation of trap clustering in the kinetics over the entire time domain. Notable observations are that due to trap clustering (1) the trapping kinetics can be significantly modified from the very beginning of the process; (2) the fluctuation-induced kinetics exhibits more rich behavior; (3) the fraction of particles reacting according to a stretched-exponential law can be substantially increased.

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I. INTRODUCTION

The problem of Brownian particle survival in a medium with randomly located killing traps serves as a model for processes occurring in a number of contexts [1–7]. In the simplest case of *noncorrelated* trap medium, in which the traps are distributed in space according to the Poisson law, the decay of the particle species basically follows the Smoluchowski theory [8]. According to this theory, the particle survival probability $P_{nc}(t)$ (here and below, the subscript nc refers to the case of noncorrelated traps) decays exponentially

$$P_{nc}(t) = e^{-ck_D t} \qquad (1)$$

(after some transient period which is of minor importance for the overall rate), where $k_D = 4\pi bD$ is the rate constant, D is the particle diffusion coefficient, b is the radius of trap, and c is the trap concentration. The Smoluchowski approach is based on the mean-field approximation by neglecting the many-body effects due to competition between traps. This competition leads to slow down of the trapping kinetics compared to the Smoluchowski solution, Eq. (1), which in fact is a lower bound for $P_{nc}(t)$ [9]. The slowdown is a very weak effect up to the final stage of the process. At long times the mean-field approach breaks down since the kinetics is dominated essentially by the many-body effects. The asymptotic $(t\to\infty)$ decay exhibits a stretched-exponential behavior [10]

$$P_{nc}(t) \sim \exp[-A(c^{2/3}Dt)^{3/5}], \qquad (2)$$

where $A = (\frac{5}{3})(2\pi^4)^{2/5}$. The physical reason for this behavior of the survival tail, referred to as fluctuation slowdown of the trapping kinetics, is the particle untypical survival in untypically large trap-free regions. For noncorrelated traps, the fraction of particles surviving up to times, where the stretched-exponential law, Eq. (2), holds, is so small that, as far as we are aware, there is no experimental or computer simulation evidence of observation of the fluctuation slowdown in three dimensional systems.

In fact, however, traps are often distributed in space in a correlated manner. So, the problem arises of how the trapping kinetics is altered when traps are *correlated*. This problem has attracted considerable interest in recent years (see Refs. [1], [6], [7], and references therein).

The present work is focused 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 chains [11], ligand-binding to cell-bound receptors [12], absorption of excitations in materials with irradiation-produced defects [4]. The first attempt to incorporate the effect of trap clustering in the theory of diffusion-limited reactions was made in Ref. [13], where it was shown in particular that trapping by noncorrelated clusters of traps proceeds slower than that by noncorrelated traps, no matter what the cluster structure is [14,15], i.e.,

$$P(t) > P_{nc}(t). \qquad (3)$$

In order to understand how the slowdown due to trap cluster formation is manifested, a mean-field theory has been recently developed by the present authors [16]. This theory is a generalization of the Smoluchowski theory to the case of clustered traps. As for noncorrelated traps, the mean-field solution is of limited utility. In particular, it fails at the final stage of the process, where the most if not all of surviving particles is localized in trap-free regions of the fluctuation nature.

Our aim in this paper is to take into account the fluctuation effects and to show what is introduced by trap cluster formation in the trapping kinetics over the entire time interval. As a result, we present here a picture of trapping by clusters of traps, which is, roughly speaking, of the same level of accuracy as that described above for traps distributed totally at random. By examination of the whole range of the problem parameters, we find that trap clustering can dramatically change the results known in the case of noncorrelated trap medium. In particular, we show that due to trap clustering the fluctuation-induced kinetics exhibits more rich behavior as compared to the case of noncorrelated traps. An-

other important observation is that spatial correlations between traps can lead to a substantial increase of the fraction of particles annihilating via the fluctuation-induced kinetics.

II. THE MODEL

Consider a point Brownian particle moving among randomly distributed static spherical traps of radius b. The traps are supposed to be perfect (the particle is instantaneously absorbed upon hitting a trap) and their volume fraction $\phi = (4/3)\pi c b^3$ is assumed to be small, $\phi \ll 1$ (otherwise the kinetics is very fast and difficult for observation). A special feature of the model under consideration [13] is that the traps are gathered in spherical clusters of radius $R \gg b$. Trap clusters are assumed to be spatially noncorrelated. Each cluster contains n traps. Therefore, the cluster concentration c_{cl} is related to the total trap concentration c by the equation $c_{cl} = c/n$. We also assume that intracluster correlations are absent, i.e., traps are uniformly distributed within the cluster, being independent of each other.

The quantity of interest is the survival probability $P(t)$, defined as the probability for the particle to be untrapped up to time t. When considering noncorrelated traps, the volume fraction of traps ϕ is the only dimensionless parameter of the problem. In the model of clustered traps, there appear two additional parameters R/b and n. To understand the influence of trap correlations on the trapping kinetics, one has to analyze the behavior of $P(t)$ everywhere over the plane $(R/b, n)$.

If the volume fraction of clusters $\Phi = (4/3)\pi c_{cl} R^3 = \phi(R/b)^3/n$ is small, the overwhelming majority of clusters are nonoverlapping, and conversely if Φ is large, the strong overlap between clusters occurs. A conditional border between these two regimes is the line $\Phi = 1$. Qualitatively, we call the clusters nonoverlapping (overlapping), if $\Phi < 1$ ($\Phi > 1$).

To classify the clusters, it is reasonable to introduce another instructive parameter $\alpha = \tau_D/\tau_1 = 3nb/R$, which is the ratio of two characteristic times related to particle passage through a cluster: the diffusion time $\tau_D = R^2/D$ and the life time $\tau_1 = R^3/3nbD$ [the latter is estimated from the Smoluchowski solution, Eq. (1), where c is replaced by the intracluster concentration of traps $c_{in} = 3n/4\pi R^3$]. The parameter α measures the degree to which an individual cluster is absorbing. If it is small, a particle passes through a cluster almost safely. If α is large a particle entering a cluster is most likely eliminated. It is natural to call the clusters with $\alpha < 1$ transparent and those with $\alpha > 1$ absorbing. The line $\alpha = 1$ is a conditional border between transparent and absorbing clusters. We would like to stress that a cluster may be absorbing even if much of the cluster volume is free from traps [17]. This is a manifestation of the peculiar volume-filling property of a diffusing particle [18] due to the fractal nature of the Brownian motion [19].

III. KINETIC REGIMES

A theory developed in Ref. [16] suggests a mean-field solution for $P(t)$ valid for the entire range of problem parameters R/b and n at the initial stage of the process. However, the mean-field arguments are invalid at the final stage of the process. In this section we briefly review the mean-field results and extend the theory by consideration of particle survival in large trap-free regions, which determines the kinetics at long times. We show that for clustered traps the fluctuation-induced kinetics is much different from that for noncorrelated traps. This is a consequence of the fact that trap clustering causes a considerable modification of the size distribution of trap-free voids.

A. Mean-field solution

With the mean-field approximation, the survival probability can be written as

$$P(t) = \exp\left[-c\int_0^t k(t')dt'\right]. \quad (4)$$

According to estimates [16,20], the rate coefficient $k(t)$ monotonically decreases with time from $k(0) = k_D$ to the plateau value k_∞ given by

$$k_\infty = k_D \frac{3}{\alpha}\left(1 - \frac{\tanh\sqrt{\alpha}}{\sqrt{\alpha}}\right). \quad (5)$$

For transparent clusters (overlapping or not) $k_\infty \approx k_D$ and hence $k(t)$ is almost the same as the Smoluchowski rate constant k_D. So in this case, the trapping kinetics is close to that for noncorrelated traps, $P(t) \approx P_{nc}(t)$, and trap clustering does not actually manifest itself in the kinetics. The slowdown predicted by inequality in Eq. (3) is a very weak effect.

For absorbing clusters, k_∞ is less than k_D by a factor $3/\alpha$. However, if such clusters are well overlapping, the majority of particles annihilate at times which are small compared to the characteristic time of variation of $k(t)$. Their trapping proceeds in accordance with the Smoluchowski dependence for noncorrelated traps $P_{nc}(t)$, Eq. (1). Significant deviations from the Smoluchowski kinetics occur at long times only, where an application of the mean-field approximation is doubtful. Thus, in this case, as in the case of transparent clusters, $P(t) \approx P_{nc}(t)$.

A different picture takes place when we deal with nonoverlapping absorbing clusters. Here $k(t)$ varies very fast, and the transient period for $k(t)$ is of minor importance in the kinetics. Therefore, the rate coefficient in fact is equal to $k_\infty \approx 3k_D/\alpha = 4\pi DR/n$ and the decay of the survival probability is given by

$$P(t) \approx \exp(-4\pi c_{cl} DRt), \quad (6)$$

i.e., the trapping kinetics is described by the Smoluchowski dependence, Eq. (1), where the trap concentration and size are replaced by those for clusters. This is a consequence of the fact that the clusters by themselves play a role of perfect traps. Only in this case the slowdown due to trap clustering [see Eq. (3)] is significantly manifested from the very beginning of the process.

B. Survival in trap-free voids

At the final stage of the process, the mean-field approach breaks. Here the problem can be treated by recognizing that at long times most if not all of surviving particles is localized in trap-free voids. To find an estimate characterizing the fluctuation-induced behavior of $P(t)$ [more precisely a reasonable lower bound for $P(t)$] we shall use a method similar to the optimal-fluctuation method [21], which underlies the derivation of the asymptotic behavior of $P_{nc}(t)$, Eq. (2), in Ref. [10].

Let us introduce a sphere $V_{\mathcal{R}}$ of radius $\mathcal{R} \gg b$, surrounding the starting point of a particle. Then one can write down the evident inequality

$$P(t) \geqslant P_{\mathcal{R}}(t) g(V_{\mathcal{R}}). \tag{7}$$

Here

$$P_{\mathcal{R}}(t) = \exp(-\pi^2 Dt/\mathcal{R}^2) \tag{8}$$

is the probability of a particle to stay inside $V_{\mathcal{R}}$ during the time $t \gg \mathcal{R}^2/D$ under the condition that the sphere contains no traps; $g(V_{\mathcal{R}})$ is the probability to find the volume $V_{\mathcal{R}}$ free from traps. For noncorrelated traps the emptiness probability $g(V_{\mathcal{R}})$ is given by the Poisson law

$$g_{nc}(V_{\mathcal{R}}) = \exp\left(-\frac{4}{3}\pi c \mathcal{R}^3\right). \tag{9}$$

Then, by substituting Eqs. (8) and (9) into the right side of Eq. (7) and maximizing the resulting product with respect to the unspecified radius $\mathcal{R}$, one arrives at Eq. (2) describing the final stage of trapping by noncorrelated traps [10].

In the considered case of clustered traps, trap-free voids occur both outside and inside the clusters. It is convenient to present the emptiness probability $g(V_{\mathcal{R}})$ as a sum

$$g(V_{\mathcal{R}}) = g_{out}(V_{\mathcal{R}}) + g_{in}(V_{\mathcal{R}}), \tag{10}$$

where $g_{out\,(in)}(V_{\mathcal{R}})$ is the probability to find the void $V_{\mathcal{R}}$ outside (inside) the clusters. Taking into account that the sphere $V_{\mathcal{R}}$ is free from traps if its center and that of the nearest cluster are separated by a distance $(R+\mathcal{R})$ or greater, one can estimate $g_{out}(V_{\mathcal{R}})$ by

$$g_{out}(V_{\mathcal{R}}) = \exp\left[-\frac{4}{3}\pi c_{cl}(R+\mathcal{R})^3\right]. \tag{11}$$

This equation shows two important features of the model. The distribution of large ($\mathcal{R} \gg R$) voids is described by Eq. (9) in which c is replaced by c_{cl}. This means that on large scales the ensemble of clustered traps can be viewed as a Poisson ensemble of noncorrelated traps, whose concentration is c_{cl}. A completely different distribution occurs for small ($\mathcal{R} \ll R$) voids:

$$g_{out}(V_{\mathcal{R}}) = \exp[-\Phi(1+3\mathcal{R}/R)]. \tag{12}$$

Evidently, for nonoverlapping clusters the probability to find a void $V_{\mathcal{R}}$ inside the clusters is small, $g_{in}(V_{\mathcal{R}}) \ll g_{out}(V_{\mathcal{R}})$, and can be neglected. For overlapping clusters, the intracluster concentration c_{in} has to be replaced by the total trap concentration $c = c_{in}\Phi$ and the estimate for $g_{in}(V_{\mathcal{R}})$ is given by

Eq. (9) (for $\mathcal{R} < R$). Noteworthy is that for clustered traps the emptiness probability of any given region is greater than in the case of noncorrelated traps [17,22], i.e., due to trap clustering trap-free regions are more pronounced. The inequality in Eq. (3) is a consequence of this fact.

Then, proceeding in the same manner as in the noncorrelated case, we substitute Eqs. (8) and (10) into the right side of Eq. (7) and maximize the resulting product with respect to the radius $\mathcal{R}$. As a result, we obtain the estimates for the radius of optimal void, $\mathcal{R}(t)$, and the survival probability of the particles localized in trap-free regions. As one might expect, these estimates have different forms according to which kind of voids (inside or outside clusters, small or large) plays the dominant role. At very long, times $t \to \infty$, the main contribution is given by large voids, $\mathcal{R}(t) \gg R$. Here one obtains that

$$P(t) \sim \exp\left[-2.5\Phi\left(\frac{t}{\tau}\right)^{3/5}\right]$$

$$= \exp[-A(c_{cl}^{2/3}Dt)^{3/5}], \quad \mathcal{R}(t) = R\left(\frac{t}{\tau}\right)^{1/5}, \tag{13}$$

where $\tau = (3/2\pi^2)\Phi\tau_D \propto R^5$ is a characteristic time characterizing the particle survival in trap-free voids outside the clusters. Equation (13) provides a reasonable lower bound for $P(t)$ at times $t \gg \tau$. Moreover, it presents the asymptotic ($t \to \infty$) behavior of the exact solution, as it was proved in Ref. [22]. This regime stems from large scale properties of the model (clusters act as noncorrelated absorbing traps regardless of details of their structure). This is why the survival probability, Eq. (13), is similar to that known for noncorrelated traps, Eq. (2). The only difference is that the kinetics is controlled by the cluster concentration c_{cl} rather than the trap concentration c. In agreement with Eq. (3), this decay is substantially slower than $P_{nc}(t)$ given by Eq. (2).

At times $t \ll \tau$, the main contribution to $P(t)$ is given by the particles surviving in small (compared to the correlation length R) voids, $\mathcal{R}(t) \ll R$, which occur both outside and inside the clusters. In the former case, the particle survival is described by

$$P(t) \sim \exp\left[-\Phi\left(1+4.5\left(\frac{t}{\tau}\right)^{1/3}\right)\right], \quad \mathcal{R}(t) = R\left(\frac{t}{\tau}\right)^{1/3}, \tag{14}$$

i.e., the decay proceeds much slower than at long times $t \gg \tau$ [see Eqs. (13) and (14)]. In the latter case (and for overlapping clusters only), the estimate for $P(t)$ is given by Eq. (2) at times, where $\mathcal{R}(t) = (\pi Dt/2c)^{1/5} < R$. Note that for overlapping clusters the particle survival in the intracluster trap-free regions plays the dominant role when $t \ll \tau/n^{2/3}$.

Thus, the decay of the particle survival probability in trap-free voids involves two or (for overlapping clusters) three stages. At times $t \gg \tau$, the decay is governed by the time dependence in Eq. (13). At shorter times $t \ll \tau$ (for overlapping clusters $\tau/n^{2/3} \ll t \ll \tau$), the decay proceeds in accordance with Eq. (14). At times $t \ll \tau/n^{2/3}$ (for overlapping clusters only) there exists a regime, where the effects due to trap clustering are of minor importance and the decay form is the same as that for noncorrelated traps, Eq. (2).
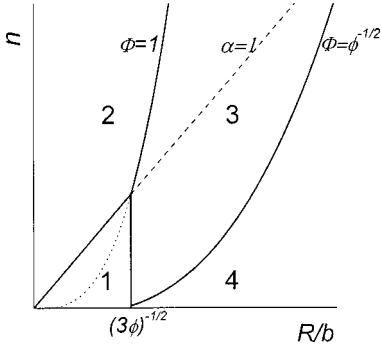
FIG. 1. Schematic representation of the domains in the plane of the problem parameters $(R/b, n)$, corresponding to different kinetic scenarios. Domain 1 represents nonoverlapping and weakly overlapping transparent clusters. Domain 2 represents nonoverlapping absorbing clusters. Domains 3 and 4 represent moderately and strongly overlapping clusters, respectively.

IV. DISCUSSION

We are now in a position to discuss different manifestations of trap clustering in the kinetics over the entire time domain. To understand better what is introduced by trap clustering in the trapping kinetics, it is reasonable to start by recalling the kinetic scenario for noncorrelated traps. This scenario is based on the two lower bounds for the survival probability given by Eqs. (1) and (2). At times $t > t_{nc}^* = A_1 \phi^{-1/2} (4\pi bcD)^{-1}$, where $(4\pi bcD)^{-1}$ is the Smoluchowski life time [see Eq. (1)] and $A_1 = 5^{5/2}\pi^3/54$, the lower bound, Eq. (2), resulting from the optimal-fluctuation method, offers a better estimate for $P_{nc}(t)$ than the Smoluchowski result, Eq. (1). Thus t_{nc}^* can be considered as a conditional border between the mean-field and the fluctuation regimes: at times $t < t_{nc}^*$ the kinetics is single-exponential while at times $t > t_{nc}^*$ it exhibits a stretched-exponential behavior. The fraction of particles $\varepsilon_{nc} = P_{nc}(t_{nc}^*)$ annihilating according to the stretched exponential law, Eq. (2), is a negligibly small quantity

$$\varepsilon_{nc} = \exp(-A_1 \phi^{-1/2}) \qquad (15)$$

and trapping of the overwhelming majority of particles is well described by the Smoluchowski dependence, Eq. (1).

When considering the model of clustered traps, we also have at hand the mean-field and the fluctuation estimates of the survival probability (see Sec. III). The corresponding kinetic scenario is arrived at by comparison these lower bounds for $P(t)$. A new factor is that the estimates obtained in Sec. III are determined by the two additional dimensionless parameters R/b and n appearing in the problem. Therefore, such a comparison should be carried out everywhere over the plane $(R/b, n)$. As a result we arrive at the more rich picture than that known for noncorrelated traps. Noteworthy also is at times when the fluctuation slowdown does occur, the neglect of the survival of particles which have left a void is justified, since $\mathcal{R}(t)$ is large compared with the characteristic length over which a particle is trapped outside a void.

Schematic representation of domains in the plane $(R/b, n)$, corresponding to different kinetic scenarios, is shown in Fig. 1. Let us consider the trapping kinetics for

these domains in order. For transparent ($\alpha < 1$) nonoverlapping ($\Phi < 1$) and weakly overlapping ($\alpha\Phi < 1$) clusters (domain 1 in Fig. 1), $R/b < (3\phi)^{-1/2}$, $1 < n < (\frac{1}{3})R/b$, and absorbing nonoverlapping ($\alpha > 1$, $\Phi < 1$) clusters (domain 2), $n > \max[(\frac{1}{3})R/b, \phi(R/b)^3]$, a general behavior of $P(t)$ is reminiscent of that for noncorrelated traps. At times $t < t^*$, the survival probability decays exponentially

$$P(t) = \exp(-ck_\infty t), \qquad (16)$$

while after t^* its time behavior is governed by the asymptotic dependence in Eq. (13), associated with the particle survival in large, compared to the correlation length R, trap-free voids. The crossover time $t^* = n^{-1}(k_\infty/k_D)^{-5/2}t_{nc}^*$ is found via equating the survival probabilities given by Eqs. (13) and (16). In the case of transparent clusters (domain 1), $k_\infty \approx k_D$ and Eq. (16) is reduced to Eq. (1). Therefore, the slowdown due to trap clustering [see Eq. (3)] is manifested only at the final stage of the process [see Eqs. (2) and (13)] due to the existence of the large trap-free regions. The fraction of particles annihilating in the fluctuation regime is given by

$$\varepsilon = P(t^*) = \exp(-A_1 n^{-1}\phi^{-1/2}) = (\varepsilon_{nc})^{1/n}. \qquad (17)$$

Note that $\varepsilon > \varepsilon_{nc}$ and the difference $(\varepsilon - \varepsilon_{nc})$ increases with n. However, because n is bound by $\phi^{-1/2}$ in this domain, the quantity ε remains negligibly small.

A distinctive feature of the kinetics of trapping by nonoverlapping absorbing clusters (domain 2) is that the trap clustering manifests itself from the very beginning of the process. Indeed, in this domain $k_\infty \approx 3k_D/\alpha \ll k_D$. Therefore Eq. (16) is reduced to Eq. (6). This implies that the clusters by themselves play a role of perfect traps and the problem is reduced to that of noncorrelated traps whose concentration and size are those of the clusters. Thus in domain 2, the fraction of particles $\varepsilon = P(t^*)$ reacting in the fluctuation-induced regime, Eq. (13), is given by Eq. (15) in which one has to replace the volume fraction of traps ϕ by the volume fraction of clusters Φ

$$\varepsilon = \exp(-A_1 \Phi^{-1/2}) = (\varepsilon_{nc})^{\sqrt{nb^3/R^3}}. \qquad (18)$$

In the trivial case of trap-filled clusters, $nb^3/R^3 > 1$, the quantity ε is smaller than ε_{nc}. If, however, $nb^3/R^3 < 1$ and hence $\phi < \Phi$, then $\varepsilon > \varepsilon_{nc}$. The more the cluster volume free of traps, the more this difference. The estimate Eq. (18) is obtained under the condition $\Phi < 1$, so in domain 2 the quantity ε is bound by its value near the border $\Phi = 1$, where $\varepsilon = \exp(-A_1)$. Attention is drawn to the fact that for absorbing clusters ε declines with n, which is quite in contrast to what one has for transparent clusters. Thus the dependence $\varepsilon(n)$ exhibits a nonmonotonic behavior. The maximum is located near the region of transition from transparent to absorbing clusters, where $n \sim R/b$.

Domain 3 corresponds to moderately overlapping, $\max(1, 1/\alpha) < \Phi < \phi^{-1/2}$, clusters, $R/b > (3\phi)^{-1/2}$, $\max[(27\phi)^{-1/2}, \phi(R/b)^3] > n > \phi^{3/2}(R/b)^3$. In this case the kinetic scenario involves three stages. The first one is well described by the Smoluchowski solution, Eq. (1), which is justified here up to time $\tau_1 = \tau_D/\alpha$. At the time interval τ_1

$<t<\tau$, the decay is governed by the time dependence given by Eq. (14). This intermediate asymptotic behavior is associated with roaming of particles within small (compared to the cluster size R) trap-free cavities between the clusters. At last, at times $t>\tau$ the survival probability takes its universal asymptotic form, Eq. (13). Thus in domain 3 the whole distribution of voids outside the clusters, and not just that of large voids, is of importance in explaining the fluctuation-induced kinetics. Note that in this case the total fraction of particles reacting in the two fluctuation regimes (mainly in the first one) is

$$\varepsilon = e^{-\Phi}. \tag{19}$$

This fraction falls off as the volume fraction of clusters increases.

Domain 4 represents strongly overlapping, $\Phi > \phi^{-1/2}$, clusters, $R/b > (3\phi)^{-1/2}$, $n < \phi^{3/2}(R/b)^3$. One can expect that strong overlapping of clusters effectively cancels the trap correlations. Our estimates of the trapping kinetics in domain 4 support these expectations. Here the kinetic scenario involves four stages. At the first two stages, the decay basically does not differ from the kinetics inherent in the case of noncorrelated traps: when $t < t_{nc}^*$, it follows mean-field predictions, Eq. (1), while when $\tau/n^{2/3} > t > t_{nc}^*$ the survival probability decays according to the stretched-exponential law, Eq. (2), associated here with the particle survival in intracluster trap-free voids. Thus, the correlations effects do not disturb the trapping kinetics over a long period of time even when survival strategy in trap-free regions becomes advantageous. This is quite in contrast to what we have seen in all cases discussed above. Only at very long times $t > \tau/n^{2/3}$, the trap correlations manifest themselves: first $P(t)$ decays in accordance with Eq. (14) and finally, when $t > \tau$, the universal asymptotic behavior, Eq. (13), takes place. When $\Phi \to \infty$ the four stage kinetic scenario is reduced to the two stage kinetic scenario for noncorrelated traps. Evidently, in this domain $\varepsilon = \varepsilon_{nc}$ (the contribution of the third and the fourth stages is negligibly small).

Our last remark concerns the effect of trap clustering on the fraction of particles ε annihilating via the fluctuation-induced decay forms. As is seen from the estimates above, the quantity ε can be significantly increased when we deal with clustered traps. The estimate for ε (in domain 3) given by Eq. (19) appears to be promising. It predicts values of ε much greater than ε_{nc}, Eq. (15), if the volume fraction of clusters Φ is not too large. As is seen from Eq. (19), the function $\varepsilon(\Phi)$ monotonically decreases with Φ when $\Phi > 1$. On the other hand, the estimate for ε obtained in domain 2, Eq. (18), shows a monotonic increase with Φ, when $\Phi < 1$. This suggests that the dependence $\varepsilon(\Phi)$ exhibits a nonmonotonic behavior with a maximum located near the border line $\Phi = 1$ between overlapping and nonoverlapping absorbing clusters (domains 2 and 3). One can expect that trap clusters, parameters of which are in this optimal region, are best suited to exhibit the fluctuation effects in the trapping kinetics. Nevertheless, even under such optimal conditions it

is unlikely that the bulk of particles is trapped following the fluctuation decay laws. The point is that the fluctuation slow-down is originated from the particle untypical survival in untypically large trap-free regions [see Eq. (7)]. In the case of clustered traps, the probability to find trap-free voids [the emptiness probability $g(V_{\mathcal{R}})$] can be much greater than when traps are noncorrelated, however, the probability $P_{\mathcal{R}}(t)$, Eq. (8), of a Brownian particle staying inside $V_{\mathcal{R}}$ during the time $t \gg \mathcal{R}^2(t)/D$ remains small.

V. CONCLUSIONS

This paper treats the trapping kinetics in the case when traps are gathered in spherical clusters which are uniformly distributed in space. By consideration of the whole range of the cluster parameters, we have discussed both the mean-field and the fluctuation-induced regimes determining the initial and the final stage of the process, respectively. Thus, we extend the theory of diffusion-limited reactions to the case of clustered traps over the entire time interval.

The following important observations related to the manifestation of trap clustering in the trapping kinetics may be deduced from our analysis: (i) The effect of trap correlations is strong from the very beginning of the process only for nonoverlapping absorbing clusters (domain 2 in Fig. 1). In all other cases, the slowdown due to trap cluster formation [see Eq. (3)] becomes significant only at asymptotically long times. (ii) Due to trap clustering, the fluctuation-induced kinetics exhibits more rich behavior as compared to the case of noncorrelated traps. In particular, there exists the intermediate asymptotic dependence, Eq. (14), which decays considerably slower than the long-time decay law, Eq. (13), predicts. (iii) Due to trap clustering, the fraction of particles reacting according to nonexponential kinetics can be significantly increased. Moreover, there exists a region of cluster parameters, where the effect takes its maximal value. This region, presumably near the border between overlapping and nonoverlapping absorbing clusters (the curve $\Phi = 1$ in the Fig. 1), is best suited to exhibit the fluctuation effects in the trapping kinetics. (iv) Strong overlapping of clusters effectively cancels the trap correlation effects in the kinetics.

As a final remark, we conjecture that qualitatively similar results should be obtained when considering more general models of clustered traps (such as, for example, clusters of nonspherical shape), where analytical treatments seems to be much more difficult. Therefore, though the model discussed here is highly simplified, it can be taken as a useful guide in the analysis of the trap clustering influence on the trapping kinetics in more realistic cases.

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