# Trapping kinetics in subthreshold percolation systems

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The trapping kinetics in subthreshold percolation systems is investigated. Expressions are derived in the low-reaction-rate limit for the decrease in the reagent density for neutral and charged particles reacting in an external electric field. The influence of trap diffusion on the reaction kinetics is analyzed.

## I. INTRODUCTION

Diffusion-controlled reactions (DCR), aggregation, and percolation processes are of increased interest today in the physics of disordered media. The two-particle description of the kinetics for diffusion-controlled reactions was first developed by Smoluchowski.[1] According to this theory, the rate of an irreversible bimolecular reaction

$$A + B \xrightarrow{k_s} \text{Product} \tag{1}$$

is given by an analog of the law of mass action:

$$\partial\rho_A/\partial t = \partial\rho_B/\partial t = -k_s(t)\rho_A\rho_B, \tag{2}$$

where $\rho_A$ and $\rho_B$ are the densities of the particles $A$ and $B$. The effective reaction rate constant $k_s(t)$ is taken equal to the density flux $\Phi^{(d)}$ of the reagent $A$ across a reaction sphere of radius $a = R_A + R_B$ toward a particle $B$, where $R_A$ and $R_B$ are the radii of the particles $A$ and $B$. The density $\rho_A(r,t)$ obeys the diffusion equation

$$\partial\rho_A(r,t)/\partial t = D\Delta\rho_A(r,t), \tag{3}$$

where $\Delta$ is the $d$-dimensional Laplace operator, $d$ is the spatial dimension, and $D = D_A + D_B$, where $D_A$ and $D_B$ are the diffusion coefficients for the particles $A$ and $B$. The boundary conditions are of the form

$$\Phi^{(d)}(a,D,t) \equiv S_a^{(d)} D \left.\frac{\partial\rho_A}{\partial r}\right|_{r=a} = -k_r\rho_A(r,t),$$
$$\rho_A(r,0) = \rho_0, \tag{4}$$

where $k_r$ is the rate constant for the chemical reaction, $S_a^{(d)} = 2\pi^{d/2}a^{d-1}/\Gamma(d/2)$ is the area of a $d$-dimensional sphere of radius $a$, and $\Gamma(x)$ is the gamma function. The superscript $(d)$ in (4) and throughout this paper indicates the dimensionality of the system. For $\rho_A \ll \rho_B$, the probability for an $A$ particle to survive for a time $t$ is given by the formula

$$\rho_A(t)/\rho_0 \equiv W^{(d)}(t) = \exp[-\Phi_{Sm}^{(d)}(a,k_r,D,t)], \tag{5}$$

where the Smoluchowski flux $\Phi_{\rm sm}^{(d)}$ for $d = 1,2,3$ is given by

$$\Phi_{Sm}^{(3)} = n_B t \frac{k_r k_D}{k_r + k_D}\left[1 + \frac{k_r}{k_r + k_D}\frac{a}{(\pi D t)^{1/2}}\right], \tag{6}$$

$$\Phi_{Sm}^{(2)} = \begin{cases} k_r n_B t, & t \ll t_+^{(2)} \sim \dfrac{a^2}{D}\exp(4\pi D/k_r), \\ \dfrac{4\pi n_B D t}{\ln(Dt/a^2)}, & t \gg t_+^{(2)}, \end{cases} \tag{7}$$

$$\Phi_{Sm}^{(1)} = \begin{cases} k_r n_B t, & t \ll t_+^{(1)} \sim Dk_r)^{-2}, \\ \dfrac{4n_B}{\pi^{1/2}}(Dt)^{1/2}, & t \gg t_+^{(1)}; \end{cases} \tag{8}$$

$n_B$ is the concentration of the $B$ particles and $k_D = 4\pi aD$. The Smoluchowski theory is valid if the reagents are homogeneously distributed. It has been found[2–14] that in many cases the Smoluchowski solution describes only an intermediate limiting case of the problem, and that the initial ($t = 0$) fluctuations in the reagent density in fact completely determine the DCR kinetics in the limit $t \to \infty$.

The random walk problem was considered in Ref. 10 for a particle migrating in a lattice containing immobile traps. At late times all the particles are trapped, except for those within fairly large regions devoid of traps. Within these regions the motion of the particle is described by the diffusion equation (3) with the boundary condition

$$\rho_A(r,t)|_{r\in\Sigma} = 0, \tag{9}$$

where $\Sigma$ is the boundary of the region. This gives rise to the familiar fluctuation behavior[3,10,11]

$$W^{(d)}(t) = \exp[-qt^{d/(d+2)}], \tag{10}$$

where $q = \text{const}(d,D,a,n_B)$. In Ref. 12 this result was derived by the diagram method, and corrections determining the onset of the asymptotic regime were found.

The DCR kinetics becomes more sensitive to fluctuation effects as the density of the system increases. One anticipates that the fluctuations will be most important when the fraction of the volume filled by the active particles (the gas parameter $\alpha = n_B a^d$) is of the order of unity. However, the kinetics of fast reactions in such systems is clearly difficult to investigate experimentally, since for $\alpha \sim 1$ the diffusion-controlled reaction takes places during an extremely short time interval $\tau \sim 10^{-13}$ s (Ref. 13). Furthermore, most industrial and natural processes occur in dense systems with high reagent concentrations and moderate reaction rate constants. It is therefore of interest to consider slow reactions in dense systems and in systems containing inert barriers and traps.

The vast majority of theoretical papers on DCR kinetics have been concerned with low-density systems. For example, it was shown in Ref. 14 that in systems where not all collisions between the reagents result in reaction, the kinetics is the same as for fast reactions, except that the time and the gas parameter have to be rescaled. Fluctuation effects in these systems are delayed even longer than for DCR reactions, and the fraction of unreacted particles (from the equa-

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tions of formal kinetics) is also less. Dense systems differ fundamentally from dilute ones because in the prepercolation region (large $\alpha$), the particles cannot diffuse over long distances but are instead localized in bounded regions.[15,16] The replica technique was used in Ref. 17 to analyze the trapping kinetics, and it was stated that the fluctuation kinetics in the long-time limit remains the same even beyond the percolation point (when the density of immobile traps is increased).

In the present paper we will show that dense percolation systems, in which the particles react slowly with traps and barriers, and reaction systems containing traps and inert barriers both exhibit various intermediate types of limiting behavior, which in many common cases describe the reaction of nearly all of the reagent. The large number of intermediate fluctuation limits obtained in this paper reflects the multiplicity of the parameters in the model (diffusion coefficients for the various particles, densities, true reaction rate constant, particle dimensions, and also the external field in the case of charged particles).

We mention in particular Refs. 18 and 19, in which estimates are obtained for the observed reaction rate constant in dense systems. Those results rest essentially on the assumption that the reaction kinetics obeys the exponential dependence predicted by the formal kinetic theory. We show below that this is not the case in subthreshold percolation systems, so that the conclusions reached in Refs. 18 and 19 do not apply.

For threshold percolation systems, qualitative scaling estimates for the long-time fluctuation kinetics were derived in Ref. 20.

It is well established experimentally that most reactions in solid and amorphous solutions do not obey the laws of formal kinetics (see, e.g., Refs. 21–26). Instead, one frequently finds

$$\rho_A(t)=\rho_A(0)\exp(-cn_B t^b), \tag{11}$$

where $c,b=\text{const}$, $0<b<1$. The reaction rates given by (11) are slower than those predicted by the equations derived using the formal kinetic theory. Some physical mechanisms leading to a dependence of this type are discussed in Ref. 26.

According to the kinetic theory developed in this paper for reactions in subthreshold percolation systems, the slower kinetics (11) may be attributed to localization of mobile reagent particles within bounded fluctuation cavities. This localization occurs during the entire course of the reaction in disordered systems with a high (subthreshold) density. In view of the similarity of many amorphous and solid solutions to prethreshold percolation systems, our results can also be used to analyze the reaction kinetics in these systems.

In Sec. 1 of this paper we derive some intermediate limiting expressions for neutral particles reacting with immobile traps, $d=2,3$. The same system, but with mobile traps, is considered in Sec. 2. In Sec. 3 we derive the fluctuation kinetic equations for a percolation system that contains, in addition to traps, inert immobile particles (barriers) that restrict the diffusion of the reagent ($d=2,3$). The study of this system is continued in Sec. 4, with the additional complication that the traps are allowed to move. One-dimensional analogs of the systems considered previously are examined in Sec. 5. In Sec. 6 we consider a uniform external field acting on charged particles in the system analyzed in Sec. 1, while in Sec. 7 we do the same for the system treated in Sec. 2. Some of the results in this paper were discussed briefly in a previous publication.[27]

## 1. REACTIONS OF NEUTRAL PARTICLES WITH IMMOBILE TRAPS/BARRIERS IN TWO- AND THREE-DIMENSIONAL SYSTEMS

We consider the density $\rho_A(r,t)$ of particles $A$ diffusing over a lattice. The lattice sites can be occupied independently by immobile neutral particles $B$ (traps through which the $A$ particles cannot pass), with probability $p_B$; we assume that $\rho_B \gg p_A$ always holds. There is a small probability that an $A$ particle will be absorbed (annihilated) upon encountering a $B$ particle. Otherwise, when absorption of $A$ by $B$ does not occur, $A$ is reflected elastically from $B$. In this paper we consider dense percolation systems in which the fraction of empty sites is less than the percolation limit for the lattice; each particle $A$ is consequently localized in a closed region consisting of a single connected component (Fig. 1).

The density $\rho_\Omega(r,t)$ of the $A$ particles in the cavity $\Omega$ is governed by the diffusion equation (3) with the boundary condition

$$\left(\frac{\partial\rho_\Omega}{\partial r}\pm h\rho_\Omega\right)_{r\in\Sigma}=0, \tag{12}$$

where $h=k_r(S_a D_A)^{-1}$; $S_a^{(d)}$ is the area of a $d$-dimensional sphere of radius $a$, where $a$ is the reaction radius. The boundary $\Sigma$ may consist of several connected components if some of the $B$ particles lie inside $\Omega$ (Fig. 1). The $+$ and $-$ signs in (12) correspond to the outer (inner) parts of $\Sigma$.

The topology of this region differs from that for the Smoluchowski problem, because here we consider trapping of $A$ particles at an internal multiply connected surface of the cavity, rather than trapping at the outer surface of a sphere of radius $a$ surrounding a given trap $B$. It was shown for similar problems in Ref. 11 that to calculate the mean density $\rho(t)$ of the $A$ particles it suffices to consider only spherical cavities, which give the main contribution to $\rho(t)$ for large $t$.

We thus consider Eq. (3) in a spherical cavity with the boundary condition (12) and the "homogeneous" initial condition

$$\rho(r,t)\,|_{t=0}=\begin{cases}\rho_0, & r\in\Omega\\ 0, & r\notin\Omega\end{cases}$$

The solution is expressible as an expansion in the eigenfunctions of the associated Schrödinger-type equation

$$\Delta\Psi+\lambda\Psi=0. \tag{13}$$

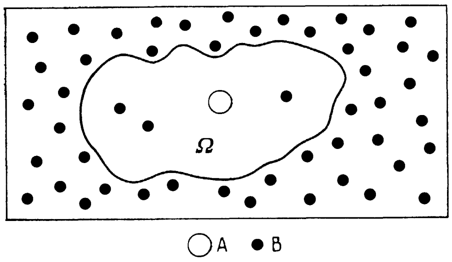


FIG. 1. A fluctuation cavity containing a localized particle $A$ and surrounded by traps.

The eigenfunctions for $d = 2$ and 3 are given by

$$\Psi_n^{(3)}(r)=C_n \sin \lambda_n^{1/2} r/(\lambda_n^{1/2} r), \tag{14}$$

$$\Psi_n^{(2)}(r)=C_n J_0(\lambda_n^{1/2} r). \tag{15}$$

The eigenvalues satisfy the equations

$$\operatorname{tg} x = x(1-hl)^{-1},\ d=3, \tag{16}$$

$$x J_2(x) = hl J_0(x),\ d=2, \tag{17}$$

where $x = \lambda_n^{1/2} l$, $l$ is the radius of the cavity, and $J_0(x)$ and $J_2(x)$ are Bessel functions. The solutions of (16) and (17) are illustrated in Figs. 2 and 3.

We introduce the dimensionless parameters

$$\beta=(k_r/D_A)a^{2-d},\quad \xi=a/l\ll 1,$$

where $\beta$ reflects the relative magnitudes of the chemical and diffusion reaction rate constants, and $\xi$ is the ratio of the particle and cavity dimensions.

For fast reactions ($\beta > \xi$),

$$(\pi n+\pi/2)^2/l^2<\lambda_n<(\pi n+\pi)^2/l^2, \tag{18}$$

where $n \geqslant 0$, $d = 3$. The eigenvalues for the two-dimensional problem are bounded similarly in order of magnitude. For large times the survival probability in a $d$-dimensional cavity is equal to

$$W_\Omega^{(d)}(t)=\exp(-x_1^2 D_A t/l^2), \tag{19}$$

where $x_1$ is the smallest root of the eigenvalue equation. The survival probability $W_\Omega^{(d)}(t)$ can be averaged over the cavity dimensions with the weighting factor $p_\Omega = \exp[-n_B V(\Omega)]$ by using the method of steepest descent; here $V(\Omega)$ is the $d$-dimensional volume of the cavity $\Omega$, $n_B = -\eta \ln(1-p_B)$, and $\eta$ is the density of lattice sites. The radius $l_t^{(d)}$ of an optimal cavity increases with time as $t^{1/(d+2)}$, so that

$$x_1^2|_{t\to\infty} \to \begin{cases} \pi^2, & d=3, \\ k_0, & d=2, \end{cases} \tag{20}$$

where $k_0$ is the square of the first zero of the function $J_0(x)$ (Figs. 2 and 3). From this we recover the well known result (10). The reaction can be said to undergo a transition to the totally diffusion-controlled regime as $t\to\infty$.

In the case of a slow reaction ($\beta \ll \xi$), each of the equations (16), (17) determines a single solution which is close to zero, $0 < x_0^{(d)} \ll 1$. Figure 3 shows a graph for the three-dimensional case, when $\beta(\xi m)^{-1} \to 0$ ($m$ is the area of a $d$-dimensional sphere of unit radius) and the straight line

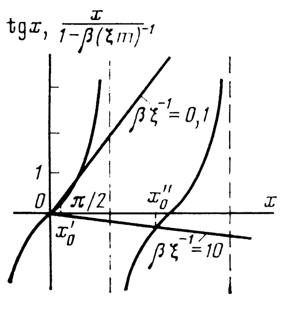


FIG. 2. Graphical solution of the equation $\tan x = x(1-\beta(\xi m)^{-1})^{-1}$ for $\beta\xi^{-1} \gg 1$ and $\beta\xi^{-1} \ll 1$.

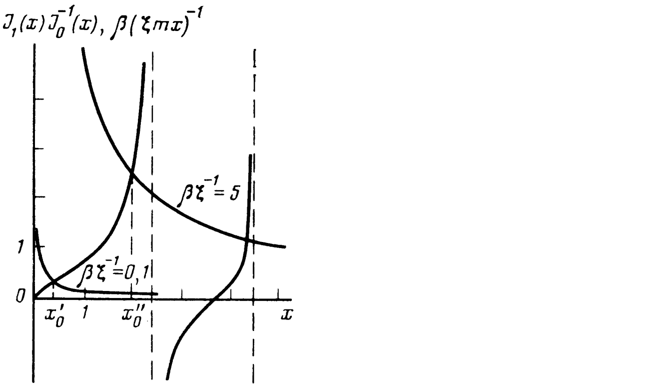


FIG. 3. Graphical solution of the equation $J_1(x)J_0^{-1}(x) = \beta(\xi x m)^{-1}$ for $\beta\xi^{-1} \gg 1$ and $\beta\xi^{-1} \ll 1$.

$x(1-\beta/\xi m)^{-1}$ approaches the tangent to the curve $\tan(x)$ at the point $x = 0$, which ensures the existence of a small root. For the two-dimensional problem, Fig. 3 shows the situation when $\beta(\xi m)^{-1} \to 0$; in this case the hyperbola $\beta(\xi m x)^{-1}$ approaches the coordinate axes and intersects the graph of the function $J_1(x)/J_0(x)$ near the point $x = 0$.

For a three-dimensional system the eigenvalues are given by

$$\lambda_0=\beta\frac{S_\Sigma a^{d-2}}{S_a V}[1+o(\beta\xi^{-1})],$$
$$(\pi n/l)^2<\lambda_n<(\pi n+\pi/2)^2/l^2,\quad n\geqslant 1, \tag{21}$$

where $S_\Sigma$ is the area of the surface $\Sigma$.

For slow reactions ($\beta \ll \xi$), we have $\lambda_n \gg \lambda_0$ for every $n$. The expansion in the eigenfunctions of Eq. (13) is

$$W_\Omega^{(3)}(r,t)=\left[1-\frac{\lambda_0 r^2}{6}+o(\lambda_0^2 r^4)\right] \times\exp\left\{\left(-\frac{k_r S_\Sigma t}{S_a V}\right)[1+o(\beta\xi^{-1})]\right\} +2\beta\frac{a^{d-2} l}{S_a}\sum_{n=1}^{\infty}\frac{(1+\lambda_n l^2)^{1/2}}{\lambda_n l^2}\frac{\sin\lambda_n^{1/2} r}{\lambda_n^{1/2} r}\exp(-\lambda_n D_A t). \tag{22}$$

The terms in the sum in (22) with $n \geqslant 1$ are all small in absolute value compared with the first, and they decrease far more rapidly with time. For $D_A t \gg l^2$ we have

$$W_\Omega^{(3)}(t)=\exp(-k_r S_\Sigma t/S_a V). \tag{23}$$

Using a Hartree-Fock expansion in the small rate constant, it is easy to show that expression (23) for the survival probability holds for all dimensions $d$ and arbitrary cavity shapes if $\beta \ll a/l_{\max}$, where $l_{\max}$ is one-half the maximum diameter of the cavity $\Omega$. Clearly, $W_\Omega^{(d)}(t)$ is largest for spherical cavities.

Averaging the survival probability $W_\Omega^{(d)}(t)$ with weight $p_\Omega(V)$, we find by the method of steepest descent that

$$W^{(3)}(t)=(\pi/2)^{1/4}(3/2)^{3/8}\alpha^{-1/4}(k_r n_B t)^{3/8} \times\exp\left[-\frac{2}{3^{1/4}(\pi\alpha)^{1/2}}(k_r n_B t)^{3/4}\right], \tag{24}$$

$$l_t^{(3)}=a(^3/_8)^{1/4}(\pi\alpha)^{-1/2}(k_r n_B t)^{1/4}; \quad (25)$$

$$W^{(2)}(t)=2(27\alpha)^{-1/6}(\pi k_r n_B t)^{1/3}\exp\left[-\frac{3}{(\pi\alpha)^{1/3}}(k_r n_B t)^{2/3}\right], \quad (26)$$

$$l_t^{(2)}=a(\pi\alpha)^{-2/3}(k_r n_B t)^{1/3}. \quad (27)$$

We remark that in these expressions for $W^{(d)}(t)$ it is the exponentials that are significant, since the coefficients may change when averaged over the cavity shape. For systems of arbitrary dimension

$$W^{(d)}(t)\approx\exp[-ct^{d/(d+1)}], \quad (28)$$

where $c=\text{const}(\alpha,k_r)$.

The radius $l_t^{(d)}$ of an optimum fluctuation cavity $\Omega$ increases with time. On the other hand, the condition that the reaction rate be small is equivalent to the smallness of $l_t^{(d)}$, $l_t^{(d)}\ll a\beta^{-1}$. For $l_t^{(d)}>a\beta^{-1}$ then the smallest eigenvalue of the diffusion operator is given by Eq. (18) (see Figs. 2, 3), so we obtain the asymptotic formula (10). The transition from the intermediate regime (28) to (10) occurs at a time $\tau_2^{(d)}$ equal to $(\alpha a^2/D_A)\beta^{-(d+2)}$. The time to onset of the intermediate fluctuation regime (28) can be found by equating the exponentials in the formal-kinetic result (5) and in (28); one obtains $\tau_1^{(d)}\sim(a^2/D_A)(\beta\alpha^d)^{-1}$. The intermediate regime (28) holds for times $\tau_1^{(d)}<t<\tau_2^{(d)}$, and in dense systems with low reaction rates ($\beta\ll\xi$) we have $\tau_2^{(d)}/\tau_1^{(d)}\sim(\alpha/\beta)^{d+1}\gg1$. The survival probabilities $W^{(d)}(\tau_1)$ and $W^{(d)}(\tau_2)$ determine the fraction of unreacted particles at the corresponding times:

$$W^{(d)}(\tau_1)\sim\exp(-\alpha^{1-d})\sim1,\ W^{(d)}(\tau_2)\sim\exp(-\alpha\beta^{-1})\ll1. \quad (29)$$

In practice, for arbitrary reactions involving trapping in dense systems, the experimental time exceeds $10^{-5}$ s if $\beta^{-1}>10^6$ in liquids (assuming $D_A\sim10^{-5}$ cm$^2$/s) and $\beta^{-1}>10$ in solids (with $D_A\sim10^{-10}$ cm$^2$/s). If the characteristic conversion time for the system exceeds $10^{-5}$ s, then $W^{(d)}(\tau_2)/W^{(d)}(\tau_1)\ll1$ and only the intermediate regime (28) will be observed.

## 2. NEUTRAL PARTICLES AND MOBILE BARRIER TRAPS

### a. Three-dimensional systems

The fluctuation effects are smaller if the traps can move. Following Ref. 28, we can estimate the survival probability for the $A$ particles in the system as follows. When averaging the survival probability in the cavity we multiply $W_\Omega^{(d)}(t)$ by the "survival probability" $p_\Omega(t)$ for the cavity. By definition, $p_\Omega(t)$ is the probability that during the time $t$, the volume of the cavity will not decrease due to trap diffusion. We can find a lower bound for $p_\Omega(t)$ by setting $p_\Omega(t)$ equal to the probability that none of the $B$ particles will ever cross the cavity boundary $\Sigma$ during the time $t$. For spherical regions this probability is equal to

$$p_\Omega(t)=\exp[-\Phi_t^{(d)}(l)], \quad (30)$$

where $\Phi_t^{(d)}(l)$ is the flux across the surface $\Sigma$ found by solving the Smoluchowski problem (6)–(8) for the survival of immobile particles in a medium with diffusing traps. The diffusion coefficient in Eqs. (6)–(8) is equal to the self-diffusion coefficient $D_B$ of the traps in the dense system, and the cavity dimension $l$ appears in place of the particle radius $a$.

The resulting fluctuation-kinetic dependence will correctly describe the reaction kinetics if it predicts a slower time-dependence of the survival probability than given by the formal-kinetic result (5) from the Smoluchowski theory, in which the reaction radius is equal to the sum of the radii of the $A$ and $B$ particles, and the effective diffusion coefficient is equal to the sum of the diffusion coefficient for the $A$ particles, in a medium without traps, plus the self-diffusion coefficient for the $B$ particles in a dense medium.

If the traps are not very mobile ($\gamma\gg\alpha^{-1}$), the above estimate for the survival probability yields a constant value

$$l_t^{(3)}=\frac{a}{\pi}[\gamma(2\alpha)^{-1}]^{1/2} \quad (31)$$

for the radius of an optimal cavity, where $\gamma=(k_r/D_B)a^{2-d}$, as well as an exponential dependence

$$W_t^{(3)}=\exp[-(8(\alpha\gamma)^{-1})^{1/2}k_r n_B t] \quad (32)$$

for the survival probability.

In a three-dimensional medium with diffusing barriers or traps of low mobility, the reaction rate for (1) goes through a sequence of successive intermediate regimes. For fast reactions, for which $\gamma\beta^2>(4\pi)^3$ (and $\tau_2^{(3)}<\tau_*^{(3)}\propto(a^2/D_B)\gamma\alpha^{-1}$), Eq. (28) holds for times $(k_r n_B)^{-1}<t<a^2(\beta k_r n_B)^{-1}$, after which (10) takes over. As shown in Ref. 28, for times $t>(a^2\cdot D\alpha^{2/3})(D_A/D_B)^{5/3}$ the latter is in turn replaced by

$$W_t^{(3)}=\exp[-3\cdot2^{2/3}\cdot\pi^{2/3}(D_A n_B/D_B)^{2/3}Dt]. \quad (33)$$

For slow reactions ($\gamma\beta^2<(4\pi)^3$), expression (28) breaks down for $t>\tau_*^{(3)}$ and is replaced by (32). The survival probability at the transition from (28) to (32) is quite small,

$$-\ln W^{(3)}(\tau_*^{(3)})=(8\gamma^3\alpha^{-1})^{1/2}\gg1. \quad (34)$$

### b. Two-dimensional systems

In two-dimensional systems with relatively immobile traps, so that $\gamma^{-1}\ll1\ll\beta^{-1}$, the intermediate regime (28) discussed above for systems with stationary traps holds for times

$$\tau_1^{(2)}<t<\tau_*^{(2)}\sim(a^2/D_B)(\gamma/\alpha)^2$$

For large times $t\gg\tau_*^{(2)}$, trap diffusion into the fluctuation cavities determines the rate at which the $A$ particles are absorbed. The optimum cavity radius continues to increase as in three-dimensional systems, but more slowly:

$$l_t^{(2)}\approx\frac{a\gamma}{4\pi^2\alpha}\ln^2 pt, \quad (35)$$

so that we get the following expression for the survival probability in two-dimensional systems:

$$W_t^{(2)}=\exp\left[-\frac{4\pi n_B D_B t}{\ln(pt/\ln^4 pt)}\right]\approx\exp\left(-\frac{4\pi n_B D_B t}{\ln pt}\right), \quad (36)$$

where $p=(4\pi^2\alpha/\gamma)^2(D_B/a^2)$. If $\tau_2^{(2)}\ll t_*^{(2)}$ (i.e., $\beta\gamma\gg\alpha$), there is a time interval $\tau_2^{(2)}<t<(Dn_B)^{-1}(D_A/D_B)^2$ during which the trapping of the $A$ particles is given by (10). For $t>(Dn_B)^{-1}(D_A/D_B)^2$ this goes over to

$$W_t^{(2)} = \exp\left[-\frac{4\pi n_B D_B t}{\ln(4\pi n_B D_B^2 t/k_0 D_A)}\right], \tag{37}$$

found in Ref. 28. If $\beta\gamma \ll \alpha$ then (28), which holds for stationary traps, is replaced by (36) when $t > \tau_*^{(2)}$.

In dense two- and three-dimensional percolation systems, (10) thus fails to hold for certain parameter values.

If the traps are highly mobile ($\gamma \ll 1$) then for $t > (4/\alpha\gamma)^2(a^2/D_B)\exp(4\pi\gamma^{-1})$ the formal kinetic result (5) reduces to (36).

Figures 4 and 5 schematically show the various reaction regimes in the three- and two-dimensional cases.

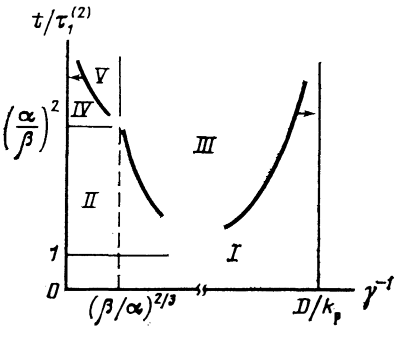


FIG. 5. Various kinetic regimes, corresponding to Eqs. (5) (I), (26) (II), (36) (III), (10) (IV), (37) (V). The curve $t/\tau_1^{(2)} = \gamma^3$ separates regions II and III; IV and V are separated by $t/\tau_1^{(2)} = (\gamma^{-1} + \beta^{-1})^{-1}(\gamma/\beta)^2$, I and III by $t/\tau_1^{(2)} = 16\gamma^{-1}\exp(4\pi/\gamma)$.

## 3. NEUTRAL PARTICLES, INERT BARRIERS, AND STATIONARY TRAPS IN THREE- AND TWO-DIMENSIONAL SYSTEMS

### a. Three-dimensional systems

In this section we analyze the trapping kinetics in a dense percolation lattice whose sites can be occupied (with probability $p_C$), by inert immobile barriers which do not participate in the reaction, and by traps (with probability $p_B \ll p_C$). The mobile $A$ particles are distributed with low density among the sites unoccupied by $B$ or $C$. The quantity $1 - p_C$ is less than the percolation threshold so that, as in the systems considered in the previous sections, the $A$ particles are localized in cavities essentially devoid of $C$ (Fig. 6).

It is obvious that as $t \to \infty$, the survival probability in this system tends to a constant limit $W_\infty$ equal to the fraction of the cavities that do not contain any traps $B$. The rate at which $W(t)$ tends to $W_\infty$ as $t \to \infty$ is determined by the cavities with the fewest traps.

Let us consider the survival probability for an $A$ particle diffusing in a spherical cavity with reflecting walls which contains a spherical trap $B$. The eigenfunctions for the associated boundary-value problem are

$$\Psi_n^{(3)}(r) = C_n \sin[\lambda_n^{1/2}(r-a)]/(\lambda_n^{1/2} r). \tag{38}$$

The eigenvalues $\lambda_n$ are given by the equation

$$\operatorname{tg} x(1-\xi) = x(ha+1+\xi)/(x^2\xi + ha + 1). \tag{39}$$

One finds readily that in this system the survival probability is equal to

$$W_\Omega^{(3)}(t) = \exp(-k_o t/V) \tag{40}$$

if $\xi \ll 1$ and $D_A t \gg l^2$, where $k_o$ is the observed reaction rate constant, $k_o = k_r k_D/(k_r + k_D)$. For a spherical cavity containing $N$ traps, $N \ll \xi^{-3}$, we have

$$W_\Omega^{(3)}(t) = \exp(-Nk_o t/V). \tag{41}$$

The mean survival probability is

$$W(t) = \int_V \sum_{N=0}^{\infty} P_V(N)\exp(-Nk_o t/V)\, p(V)\, dV. \tag{42}$$

Here $P_V(N)$ is the Poisson distribution with mean equal to the expectation of $n_B$, the number of traps in the cavity; $p(V) = \exp(-n_C V)$, where $n_C$ is the concentration of barriers $C$. Adding (42) over $N$ and subtracting $W_\infty^{(3)}$, we get

$$\Delta W^{(3)}(t) = W^{(3)}(t) - W_\infty^{(3)}$$

$$= \int_V \exp[-(n_B+n_C)V]\{\exp[n_B V \exp(-k_o t/V)] - 1\}\, dV. \tag{43}$$

For small $t$, expression (43) leads to the formal kinetic dependence (5) for any distribution $p(V)$ which is normalized to unity. For $t \to \infty$ the method of steepest descent gives

$$\ln \Delta W^{(3)}(t) = -2(k_o(n_B+n_C)t)^{1/2}. \tag{44}$$

The transition from (5) to (44) occurs when $t > \tilde{\tau}_1^{(3)} \sim (n_B + n_C)/k_r n_B^2$.

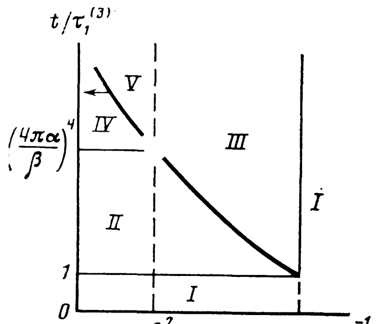


FIG. 4. Various kinetic regimes, corresponding to Eqs. (5) (region I), (24) (II), (32) (III), (10) (IV), (33) (V). The curve $t/\tau_1^{(3)} = (4\pi)^{-2}(\alpha\gamma)^2$ separates regions II and III, the curve $t/\tau_1^{(3)} = \alpha^{10/3}(\gamma^{-2} + \beta^{-1})^{-1}(\gamma/\beta)^{5/3}$ regions IV and V.

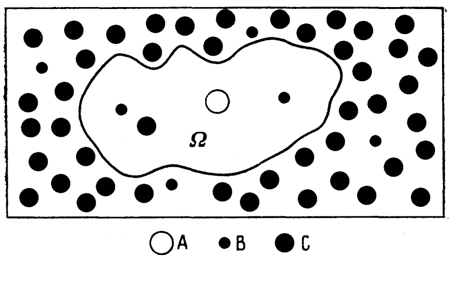


FIG. 6. A fluctuation cavity surrounded by barrier particles $C$ and containing a localized $A$ particle and two traps $B$.

## b. Two-dimensional systems

The eigenfunctions of the diffusion equation (3), with boundary conditions analogous to those used in the three-dimensional case, are equal to

$$\Psi_n^{(2)}(r)=C_{n1}J_0(\lambda_n^{1/2}r)+C_{n2}N_0(\lambda_n^{1/2}r), \quad (45)$$

where $N_0(x)$ is the zeroth-order Neumann function. The equation for the eigenvalues is

$$N_1(x)[xJ_1(x\xi)+hlJ_0(x\xi)]-J_1(x)[xN_1(x\xi)+hlN_0(x\xi)]=0, \quad (46)$$

where $x=\lambda_n^{1/2}l$. The smallest eigenvalue is

$$\lambda_0=\frac{1}{V}\frac{\beta}{1+(\beta/\pi)(b\ln\xi^{-1}-c)}, \quad (47)$$

where $b\approx2.00$ and $c\approx0.25$ (Ref. 29). The survival probability for the $A$ particles in a cavity $\Omega$ with $N$ traps is given by

$$W_\Omega^{(2)}(t)=\exp(-\lambda_0 ND_A t) \quad (48)$$

when $N\ll\xi^{-2}$, $D_A t\gg l^2$. Averaging (48) over $N$ and $V$ by the method of steepest descent, we find that the optimum cavity radius $l_t^{(2)}$ increases:

$$l_t^{(2)}\approx\left(\frac{k_r t}{\pi^2(n_B+n_C)}\right)^{1/4}\left\{1+\frac{\beta}{\pi}\left(b\ln\left[\frac{1}{a}\left(\frac{k_r t}{\pi^2(n_B+n_C)(1+\beta)}\right)^{1/4}\right]-c\right)\right\}^{-1/4}, \quad (49)$$

where $t\gg a_c(1+\beta)a^2/k_r$, $\alpha_c=(n_B+n_C)a^d\sim1$; the relaxation of $W^{(2)}(t)$ to $W_\infty^{(2)}$ is given by

$$\ln\Delta W^{(2)}(t)|_{t\to\infty}\approx-2(k_r(n_B+n_C)t)^{1/2}\left[1+\frac{\beta}{\pi}\left(b\ln\left[\frac{1}{a}\left(\frac{k_r t}{\pi^2(n_B+n_C)(1+\beta)}\right)^{1/4}\right]-c\right)\right]^{-1/2}. \quad (50)$$

Expression (50) replaces the formal kinetic result (5) when

$$t>\tilde{\tau}_1^{(2)}\sim\frac{n_B+n_C}{k_r n_B^2}\frac{1+(k_r/D)^2}{1+\beta}.$$

The fraction of unreacted $A$ particles at time $t=\tilde{\tau}_1^{(2)}$ is small and proportional to the factor $\exp(-n_C/n_B)$. For sufficiently large times $t>\alpha_c\beta^{-1}(1+\beta)^{-1}(a^2/D_A)$, the relaxation expression for $\Delta W^{(2)}(t)$ becomes

$$\ln\Delta W^{(2)}(t)|_{t\to\infty}\infty\left(\frac{t}{\ln t}\right)^{1/2}. \quad (51)$$

The survival probability in two-dimensional systems thus decays more slowly than in three-dimensional systems. Significantly, the kinetics in both cases $d=2,3$ differs from that given by the formal kinetic expression (5).

## 4. NEUTRAL PARTICLES, INERT BARRIERS, AND DIFFUSING TRAPS

If the traps $B$ in the system described in Sec. 3 have a small but infinite mobility, the kinetics is more complicated. The survival probability $W(t)$ for a particle in the system is again equal to $W_\infty(t)$, the survival probability in cavities devoid of traps, plus $\Delta W(t)$, the survival probability in cavities containing $N\geqslant1$ traps.

Due to the diffusion of traps into the cavity, $W_\infty^{(d)}(t)$ for $d=2,3$ tends to zero as $t\to\infty$, and the decay is given by the formal kinetic equations:

$$W_\infty^{(3)}(t)=\exp(-4\pi n_B D_B lt),$$

$$W_\infty^{(2)}(t)=\exp\left[-\frac{4\pi n_B D_B t}{\ln(D_B t/l^2)}\right]. \quad (52)$$

### a. Three-dimensional systems

The relaxation of $\Delta W^{(3)}(t)$ to zero is determined by fluctuation effects when the trap mobility is small, $\gamma\gg\alpha_c^{1/3}$. In this case, trap diffusion does not play a significant role during the time interval

$$\tilde{\tau}_1^{(3)}<t<\tilde{\tau}_*^{(3)}\approx\frac{3a^2}{D_B}(\gamma(4\pi\alpha_c)^{-1})^{1/2}$$

and $\Delta W^{(3)}(t)$ decays to zero according to Eq. (44). The optimum cavity radius $l_t^{(3)}$ increases as $t^{1/6}$, and at time $t=\tilde{\tau}_*^{(3)}$ reaches its maximum value $l_*^{(3)}\approx a\gamma^{1/4}(9/16\pi^2\alpha_c)^{1/4}$, at which trap diffusion into the cavity becomes substantial. For $t\gg\tilde{\tau}_*^{(3)}$ the trap diffusion completely dominates the kinetics; in this case $l_t^{(3)}\approx l_*^{(3)}=\text{const}$ and

$$\ln\Delta W^{(3)}(t)=-\frac{2(2\pi)^{1/2}}{(\alpha_c\gamma^3)^{1/4}}k_p n_B t. \quad (53)$$

### b. Two-dimensional systems

For low trap mobilities ($\gamma\gg1+\beta$), the formal kinetic result (5) is valid for times $a^2/D\ll t<\tilde{\tau}_1^{(2)}$. The trapping then obeys (50) for times

$$\tilde{\tau}_1^{(2)}<t<\tilde{\tau}_*^{(2)}\approx\frac{a^2}{D_B}\frac{\gamma(n_B+n_C)}{n_B^2a^2(1+\beta)}.$$

Trap diffusion starts to dominate the kinetics when $t\sim\tilde{\tau}_*^{(2)}$, at which the optimum cavity radius $l_t^{(2)}$ reaches the value

$$l_*^{(2)}=a(\gamma\ln^2[4\pi^2\gamma^{-2}(1+\beta)k_r n_B t])^{1/2}\left\{4\pi^2 n_B a^2\left[1+\frac{\beta}{\pi}\left(b\ln\left[\frac{1}{2\pi}\left(\frac{\gamma}{n_B a^2(1+\beta)}\right)^{1/2}\right]-c\right)\right]\right\}^{-1/2}, \quad (54)$$

where $t\gg\gamma^2(4\pi^2(1+\bar{\beta})/k_r n_B)^{-1}$. For $t>\tilde{\tau}_*^{(2)}$ we have $l_t^{(2)}\approx l_*^{(2)}(t)$, and the relaxation of $\Delta W^{(2)}(t)$ to zero is given by

$$\ln\Delta W^{(2)}(t)=-\frac{4\pi\gamma^{-1}k_r n_B t}{\ln[4\pi^2\gamma^{-2}(1+\beta)k_r n_B t]}. \quad (55)$$

If the traps are highly mobile ($\gamma\ll1+\beta$) then the formal kinetic dependence (5) is replaced by (55) when

$$t\gg\frac{a^2}{D}\left(\frac{2\beta}{\gamma}p_0\ln p_0\right)^{2(1+\beta/\gamma)},$$

where

$$p_0=\frac{2\pi}{\gamma}\left[\frac{\beta(1+\beta)n_B a^2}{1+\beta/\gamma}\right]^{1/2}.$$

## 5. NEUTRAL PARTICLES DIFFUSING IN A ONE-DIMENSIONAL CHAIN CONTAINING INERT BARRIERS AND TRAPS

In Refs. 30 and 31, the trapping kinetics was analyzed for one-dimensional systems with barriers $C$ and nonideal traps $B$. The survival probability for a reagent particle $A$ traveling along paths bounded at either end by barriers and/or traps was calculated by a nonrigorous approximate method, in which the motion of $A$ was modeled as a series of hops occurring at a rate $\omega$, the trapping rate $\omega'$ being arbitrary. In this section we will find an exact solution of the corresponding diffusion problem.

In the continuous limit, Eq. (3) with the boundary conditions

$$\left(\frac{\partial\rho_\Omega}{\partial x}-h\rho_\Omega\right)_{x=0}=0,\quad \left(\frac{\partial\rho_\Omega}{\partial x}+h\rho_\Omega\right)_{x=l}=0 \qquad (56)$$

or

$$\left.\frac{\partial\rho_\Omega}{\partial x}\right|_{x=0}=0,\quad \left(\frac{\partial\rho_\Omega}{\partial x}+h\rho_\Omega\right)_{x=l}=0 \qquad (57)$$

holds for an $A$ particle diffusing over a distance $l$; (56) is appropriate for the case when the path begins and ends at traps, (57) when the path is bounded at one end by a trap and at the other by a barrier. Here we have written $h=\beta/a$. The corresponding equations for the eigenvalues are

$$\operatorname{tg} x=\frac{2hlx}{x^2-h^2l^2} \qquad (58)$$

for boundary conditions (56) and

$$\operatorname{tg} x=hl/x \qquad (59)$$

for (57), where $x=\lambda_n^{1/2}l$.

If the reaction rate constant is large ($\beta>\xi$) then

$$(\pi n-\pi/2)^2/l^2<\lambda_n<(\pi n/l)^2,\ n\geqslant1. \qquad (60)$$

For large times the survival probability $W_\Omega^{(1)}(t)$ is determined by the smallest root $x_1$ of Eqs. (58) or (59),

$$W_\Omega^{(1)}(t)=\exp[-(x_1/l)^2D_At], \qquad (61)$$

where

$$x_1|_{t\to\infty}\to\begin{matrix}\pi & \text{for } (58),\\ \pi/2 & \text{for } (59).\end{matrix} \qquad (62)$$

The usual relation (10) for the relaxation of $W^{(1)}(t)$ to $W_\infty^{(1)}$ follows by averaging (61) over $l$ with weight $\exp[-(n_B+n_C)l]$ equal to the probability for the diffusion path to be of length $l$.

For slow reactions ($\beta\ll\xi$), Eqs. (58) and (59) each give a single eigenvalue $\lambda_0$ which is close to zero, and for any $n\geqslant1$ we have $\lambda_n\gg\lambda_0=(f\beta\xi/a^2)(1+o(\beta\xi^{-1}))$, where $f$ is the number of traps at the ends of the path. For $D_At\gg l^2$ the survival probability is given by the relation

$$W_\Omega^{(1)}(t,f)=\exp\left(-f\frac{k_rt}{l}\right). \qquad (63)$$

The kinetics in the overall system depends on the ratios of the numbers of paths with zero, one, or two traps at the ends[31]:

$$W^{(1)}(t)=\sum_{f=0}^{2}p_fW^{(1)}(t,f), \qquad (64)$$

where $p_f$ is the corresponding probability. In the two extreme cases

$$f=\begin{cases}1, & n_B\ll n_C\\ 2, & n_B\gg n_C\end{cases}, \qquad (65)$$

we have the expressions

$$l_t^{(1)}=[fk_rt(n_B+n_C)]^{1/2}, \qquad (66)$$

$$\ln\Delta W^{(1)}(t)=-2[fk_r(n_B+n_C)t]^{1/2} \qquad (67)$$

for the relaxation of $\Delta W(t)$ to zero and for the optimum path, of length $l_t^{(1)}$ (found by the method of steepest descent). Equation (67) replaces the formal kinetic dependence (5) for times $t>\tau_1^{(1)}\sim(n_B+n_C)/k_rn_B^2$. Because $l_t^{(1)}$ is larger, for $t>\tau_2^{(1)}\sim a^2\alpha_c/D_A\beta^3$ the quantity $\beta$ exceeds $\xi_t$ and (67) is replaced by (10). We note that the intermediate regime (67) holds only for small $\beta$ with $\beta\ll n_Ba$, so that the inequality $\tau_2^{(1)}\gg\tau_1^{(1)}$ is satisfied.

According to (67), the fraction of absorbed particles is proportional to $\exp[-(1+n_C/n_B)]$, which is largest at high relative trap concentrations $n_B\gg n_C$. At time $t=\tau_2^{(1)}$ nearly all the $A$ particles are absorbed by the traps: $\Delta W^{(1)}(\tau_2)\propto\exp(-2f^{1/2}\alpha_c/\beta)\ll1$.

### a. Mobile traps

Now suppose that the traps move with a diffusion coefficient $D_B$. A similar problem was considered in Ref. 28 for systems in which the kinetics is controlled by the diffusion of the $A$ particles. In this section we consider the case when the kinetics is controlled by a chemical reaction, for a one-dimensional system in which the traps can diffuse.

The relation

$$\ln\Delta W^{(1)}(t)=-2[fk_r(n_B+n_C)t]^{1/2}-\frac{4n_B}{\pi^{1/2}}(D_Bt)^{1/2} \qquad (68)$$

gives a lower bound for the survival probability $\Delta W^{(1)}(t)$, where the second term corresponds to the "survival" probability along the path and is equal to the Smoluchowski flux (8) with diffusion coefficient $D_B$.

If the trap mobility is small, so that

$$\gamma^{-1}<\gamma_*^{-1}\approx\frac{\pi f(n_B+n_C)}{16n_B^2a}\left[\frac{4n_B^2a}{\pi f(n_B+n_C)}-1\right]^2, \qquad (69)$$

then Eq. (68) replaces the formal kinetic result (5) for times

$$t>\tau_*^{(1)}\approx(k_rn_B)^{-1}\{2[f(1+n_C/n_B)]^{1/2}+4(n_Ba/\pi\gamma)^{1/2}\}^2 \qquad (70)$$

The relaxation of $\Delta W^{(1)}(t)$ to zero depends on the ratio of the terms in (68):

$$\ln\Delta W^{(1)}(t)\approx-\begin{cases}2[fk_r(n_B+n_C)t]^{1/2}, & \gamma^{-1}\ll(n_B+n_C)/n_B^2a, \quad (71a)\\ 4n_B(D_Bt)^{1/2}/\pi^{1/2}, & (n_B+n_C)/n_B^2a\ll\gamma^{-2}<\gamma_*^{-1}, \quad (71b)\end{cases}$$

For highly mobile traps ($\gamma<\gamma^*$), the formal kinetic formula (5) is valid at least to $t\sim\tau_2^{(1)}$.

For times $t>\tau_2^{(1)}$ this estimate for $\Delta W^{(1)}(t)$ is superseded by[28]

$$\ln\Delta W^{(1)}(t)=-\frac{3\pi}{4}(D_A\tau/D)^{1/2}+(D_B\tau/D)^{1/2},$$
$$\tau=16n_B^2Dt/\pi. \qquad (72)$$

Trap diffusion thus retards the absorption of the $A$ particles for all $D_B$; however, for $D_B\to0$ or $D_B\to D$ this fluctuational retardation begins only for very large times $t\to\infty$.

## 6. NEUTRAL STATIONARY TRAPS AND CHARGED PARTICLES IN A UNIFORM EXTERNAL FIELD

In this section we consider the trapping of $A$ particles with charge $q$ by neutral immobile traps $B$ in the presence of a uniform external electric field for systems of dimension $d = 1,2,3$. The force $q\mathbf{E}$ causes the $A$ particles to move toward the boundaries of the cavities in which they are localized, and the optimum cavity is thus an elongated cylinder extending along the field. In Ref. 32 time-dependent effects were considered for a one-dimensional chain in which the hopping probabilities from one lattice site to another were random in the presence of an electric field. The behavior of the current $j(t)$ at large times $t\to\infty$ is sensitive to the strength of the field.

The density of the $A$ particles in a cylindrical cavity $\Omega$ of radius $l_1$ and length $l$ obeys the Smoluchowski equation

$$\frac{\partial\rho_\Omega(\mathbf{r},t)}{\partial t}=\operatorname{div}D_A\left(\operatorname{grad}\rho_\Omega-\frac{q\mathbf{E}}{k_BT}\rho_\Omega\right). \qquad (73)$$

We write $\rho_\Omega$ in the form

$$\rho_\Omega(\mathbf{r},t)=\rho_1(x,t)\rho_2(r,t), \qquad (74)$$

where $\rho_1$ and $\rho_2$ are the solutions of the boundary-value problems (76) and (75):

$$\partial\rho_2/\partial t=D_A\Delta\rho_2,\quad [\partial\rho_2/\partial r+h\rho_2]_{r=l_1}=0,\quad \rho_2(r,0)=1 \qquad (75)$$

(Eq. (75) was solved in Sec. 1 of this paper),

$$\frac{\partial\rho_1}{\partial t}=D_A\frac{\partial^2\rho_1}{\partial x^2}+v\frac{\partial\rho_1}{\partial x},$$

$$\left[\frac{\partial\rho_1}{\partial x}+\left(\frac{v}{D_A}-h\right)\rho_1\right]_{x=0}=0,$$

$$\left[\frac{\partial\rho_1}{\partial x}+\left(\frac{v}{D_A}+h\right)\rho_1\right]_{x=l}=0,\qquad \rho_1(x,0)=\rho_0, \qquad (76)$$

where $v=qED_A/k_BT=bF$, where $b$ is the mobility of the particles, and $D_A/v=k_BT/qE=L$, where $L$ is the effective longitudinal dimension of the cavity, along which the field varies appreciably. The eigenfunctions for (76) are equal to

$$\Psi(x)=\begin{cases}\exp(-x/2L)\,(C_1\operatorname{ch}\theta x+C_2\operatorname{sh}\theta x), & (77)\\ \exp(-x/2L)\,(C_1\cos\theta x+C_2\sin\theta x). & (78)\end{cases}$$

where $\theta=[(2L)^{-2}-|\lambda|D_A^{-1}]^{1/2}$. We will call (77) and (78) the decaying and oscillating modes, respectively.

We first examine the decaying mode. The boundary conditions give

$$\Psi(x)=C\exp(-x/2L)[\theta\operatorname{ch}\theta x-(1/2L-h)\operatorname{sh}\theta x],$$

$$\operatorname{th}x=\frac{2hlx}{(l/2L)^2-h^2l^2-x^2}=f_1(x), \qquad (79)$$

where $x=\theta l$. Equation (79) has a unique nontrivial solution if

$$f_1'(0)<(\operatorname{th}x)'|_{x=0}=1. \qquad (80)$$

This existence condition for the decaying mode restricts the range over which the characteristic parameters of the problem can vary:

$$E>E_{cr}=\left(\frac{2h}{l}+h^2\right)^{1/2}\frac{2k_BT}{q}\bigg|_{l\to\infty}\approx\frac{2k_BT}{q}h,$$

$$\beta<\beta_{cr}=a\{[l^{-2}+(2L)^{-2}]^{1/2}-l^{-1}|_{l\to\infty}\approx a/2L,$$

$$l>l_{cr}=2h[(2L)^{-2}+h^{-2}]^{-1}. \qquad (81)$$

Let us consider the strong-field case $l/L\gg1$, so that the behavior of the reaction at large times is determined by the survival of the $A$ particles localized in the largest cavities.

For slow reactions ($\beta\ll\beta_{cr}$), we find from (79) that

$$\lambda_0=\frac{hD_A}{L}[1+2\exp(-l/L)]. \qquad (82)$$

For $\beta\lesssim\beta_{cr}$ (so that $hl\gg1$, since $l/L\gg1$), we have

$$\lambda_0=D_A/(2L)^2+5/2l^2\approx D_A/(2L)^2. \qquad (83)$$

The eigenfunctions and the eigenvalue equation for the oscillating mode are of the form

$$\Psi(x)=C\exp\left(-\frac{x}{2L}\right)\left[\theta\cos\theta x-\left(\frac{1}{2L}-h\right)\sin\theta x\right],$$

$$\operatorname{tg}x=\frac{2hlx}{(l/2L)^2-h^2l^2+x^2}. \qquad (84)$$

For arbitrary $\beta$, the eigenvalues $\lambda_n$ obtained from (84) are given by

$$\lambda_n=\frac{D_A}{(2L)^2}\{1+o[(4l)^2]\},\qquad n\geqslant\begin{cases}1, & \beta<\beta_{cr}\\ 0, & \beta\geqslant\beta_{cr}\end{cases}. \qquad (85)$$

The mean survival probability for the $A$ particles in a cavity $\Omega$ is given by

$$W_\Omega(t)=\sum_{n=0}^{\infty}f_n\exp(-\lambda_nt), \qquad (86)$$

where $f_n=I_n^2(J_nl)^{-1}$, $I_n=\int_0^l\Psi_n dx$, $J_n=\int_0^l\Psi_n^2dx$. The coefficients $f_n$ are equal to

$$f_0\approx\begin{cases}2l/L, & \beta\ll\beta_{cr}\\ 4l/L, & \beta\approx\beta_{cr},\\ 0, & \beta\gg\beta_{cr},\end{cases}\qquad f_n=\frac{8L}{l}h^2l^2\frac{1}{x_n^2+(l/2L)^2},\quad n\geqslant1 \qquad (87)$$

where the $x_n$ are the roots of (84).

For slow reactions ($\beta\ll\beta_{cr}$), if $D_At\gg L^2$ holds then the first term in the expansion in (86) gives the dominant contribution:

$$W_\Omega(t)\approx\frac{2L}{l}\exp\left\{-\frac{hD_At}{L}[1+2\exp(-l/L)]\right\}, \qquad (88)$$

since for every $n\geqslant1$ we have $f_0\gg f_n$ and $\lambda_0\ll\lambda_n$.

For large reaction constants ($\beta\gtrsim\beta_{cr}$), the $f_n$ and $\lambda_n$ all have roughly the same order of magnitude, and for $t\to\infty$ the term with the smallest $\lambda_n$ dominates in (86):

$$W_\Omega(t)\approx\exp[-D_At/(2L)^2-(m_0/l)^2D_At], \qquad (89)$$

where $m_0|_{l\to\infty}\to\pi$ is the smallest root of Eq. (84).

The mean survival probability for this system is given by the relation

$$W(t)=\int dVW_\Omega(t)\varphi(t)p(V), \qquad (90)$$

where $p(V)=\exp(-n_BV)$ and $\varphi(t)$ is given by the appropriate limiting expression for the problem (75) corresponding to a given $\beta$.

For a slow reaction ($\beta \ll a/L$), the logarithm of the survival probability is

$$\ln W^{(d)}(t)\,|_{t\to\infty} \approx -\frac{k_p qEt}{S_a k_B T}\,(1+\Delta^{(d)}(t)), \tag{91}$$

where $\Delta^{(d)}(t)$ decreases as a power of $t$ when $t\to\infty$. For $d=1,2,3$ the function $\Delta^{(d)}(t)$ is given by

$$\Delta^{(3)}(t)=\begin{cases}\left(\dfrac{9\pi n_B S_a L^4}{k_r t}\ln\dfrac{8k_r t}{\pi n_B S_a L^4}\right)^{1/3}, & t\ll\tau_e^{(3)},\\[2ex] \left(\dfrac{2\pi k_0 n_B S_a^2 L^3}{a\beta k_r t}\ln\dfrac{4a\beta k_r t}{\pi k_0 n_B S_a^2 L^3}\right)^{1/2}, & t\gg\tau_e^{(3)},\end{cases}$$

$$\Delta^{(2)}(t)=\begin{cases}2\left(\dfrac{n_B S_a L^3}{k_r t}\ln\dfrac{2k_r t}{n_B S_a L^3}\right)^{1/2}, & t\ll\tau_e^{(2)},\\[2ex] \dfrac{3^{1/2}\pi n_B S_a^{3/2} L^{5/2}}{(a\beta)^{1/2}k_r t}\ln\dfrac{2(a\beta)^{1/2}k_r t}{\pi n_B S_a^{3/2} L^{5/2}}, & t\gg\tau_e^{(2)},\end{cases}$$

$$\Delta^{(1)}(t)=\frac{n_B L^2}{k_r t}\ln\frac{2e k_r t}{n_B L^2}, \tag{92}$$

where $\tau_c^{(d)} \sim \alpha a^{d-1} L/\beta^d k_r$. The change in the form of $\Delta^{(d)}(t)$ for $d=2,3$ for times $t\sim\tau_c^{(d)}$ reflects the change in the fluctuation asymptotics for the problem (75).

For a fast reaction with $\beta \gg a/L$, the logarithm of the survival probability is given by

$$\ln W^{(d)}(t)\,|_{t\to\infty} \approx -\frac{D_A (qE)^2 t}{(2k_B T)^2}\,[1+\chi^{(d)}(t)], \tag{93}$$

where $\chi^{(d)}(t)$ has the form

$$\chi^{(3)}(t)=20(\pi^2 k_0 n_B L^5/4D_A t)^{2/5},$$
$$\chi^{(2)}(t)=12\pi L^2 (n_B/D_A t)^{1/2},$$
$$\chi^{(1)}(t)=3(4\pi n_B L^3/D_A t)^{1/3}. \tag{94}$$

The decaying mode (77) in the solution of (76) thus determines the long-time behavior of the conversion of the reagent $A$ for slow reactions with $\beta \ll \beta_{cr}$. For fast reactions ($\beta \gg \beta_{cr}$), this behavior is determined by the largest term in the oscillating mode (78) in the expansion (86).

## 7. NEUTRAL IMMOBILE TRAPS AND INERT BARRIERS FOR THE CASE OF CHARGED PARTICLES IN A UNIFORM EXTERNAL FIELD

In this section we analyze the kinetics for the system described in Sec. 2 when a uniform electric field is present. The $A$ particles have the charge $q$, while the traps $B$ and barriers $C$ are electrically neutral. Let $N$ traps be present inside the cavity $\Omega$. The survival probability for the $A$ particles will be greatest in those cylindrical cavities where the traps lie on one of the end faces and the field causes the $A$ particles to drift toward the opposite face. These cavities determine $\rho_\Omega(x,t)$, the density of the $A$ particles at large times. The density $\rho_\Omega(x,t)$ is a solution of the following system of equations:

$$\frac{\partial\rho_\Omega}{\partial t}=D_A\frac{\partial^2\rho_\Omega}{\partial x^2}+\bar v\frac{\partial\rho_\Omega}{\partial x},$$
$$\left[\frac{\partial\rho_\Omega}{\partial x}+\frac{\bar v}{D_A}\rho_\Omega\right]_{x=0}=0,$$
$$\left[\frac{\partial\rho_\Omega}{\partial x}+\left(h^*+\frac{\bar v}{D_A}\right)\rho_\Omega\right]_{x=l}=0,$$
$$\rho_\Omega(x,\,0)=\rho_0, \tag{95}$$

where $h^* = k_r N/D_A S_b$, and $S_b$ is the cross-sectional area of the cavity normal to the field. As with (76), the solution of (95) again consists of a decaying and an oscillating mode.

The eigenfunctions and the eigenvalue equation for the decaying mode are

$$\Psi(x)=C\exp(-x/2L)\,[\operatorname{ch}\theta x-(2L\theta)^{-1}\operatorname{sh}\theta x],$$
$$\operatorname{th} x=\frac{h^* l x}{(l/2L)(l/2L+h^* l)-x^2}=f_2(x). \tag{96}$$

Equation (96) has a (unique) nonzero solution if $f_2'(0)<1$. This condition restricts the parameters of the problem as follows:

$$E>E_{cr}^*=\frac{k_B T}{ql}\,[(h^{*2}l^2+4h^* l)^{1/2}-hl]=\frac{k_B T}{ql}\varphi(h^* l), \tag{97}$$

$$\beta<\beta_{cr}^*=\begin{cases}\dfrac{a}{l}\,\dfrac{l/2L}{1-l/2L}, & \dfrac{l}{2L}<1\\[2ex] \infty, & \dfrac{l}{2L}\geqslant 1\end{cases}, \tag{98}$$

$$l/2L>\varphi(h^* l), \tag{99}$$

where

$$\varphi(x)\approx\begin{cases}2x^{1/2}, & x\ll 1,\\ 2[1-2/x+o(1/x^2)], & x\gg 1.\end{cases} \tag{100}$$

We see from (98) and (99) that Eq. (96) always has a unique solution provided that $l/2L \gg 1$. When (97)–(99) are satisfied, the solution of (96) has the form

$$\lambda_0=\frac{h^* D_A\exp(-l/L)}{L(1+h^* L)}\left[1-\frac{h^* L\exp(-l/L)}{1+h^* L}\right]$$
$$\approx\frac{h^* D_A\exp(-l/L)}{L(1+h^* L)}. \tag{101}$$

For the oscillating mode we have

$$\Psi(x)=C\exp(-x/2L)(\cos\theta x-(2L\theta)^{-1}\sin\theta x),$$
$$\operatorname{tg} x=h^* l x\Big/\left[\frac{l}{2L}\left(\frac{l}{2L}+h^* l\right)+x^2\right]. \tag{102}$$

When $E>E_{cr}^*$, the eigenvalues found from (102) are equal to

$$\lambda_n\,|_{t\to\infty}=\frac{D_A}{(2L)^2}+\left(\frac{\pi n}{l}\right)^2 D_A,\quad n\geqslant 0. \tag{103}$$

If $E<E_{cr}^*$ and $h^* l \ll 1$ (i.e., when $\beta\xi^{-1}\ll 1$) we have a minimum eigenvalue:

$$\lambda_0=\frac{h^* D_A}{l}\,[1+o(4l)]. \tag{104}$$

Expression (103) is valid for $\lambda_n$ with $n\geqslant 1$, as well as for the case when $E<E_{cr}^*$ and $h^* l>1$ (i.e., $\beta\xi^{-1}>1$).

The expansion coefficients $f_n$ in (86) are given by

$$f_n=\begin{cases}\dfrac{2l}{L}\exp(-l/L)\,\dfrac{\sin^2 x_n}{x_n^2}, & n\geqslant 1,\quad E>0,\\[2ex] 2\exp(-l/L)\,[\operatorname{ch}(2x_0)-1], & n=0,\quad E>E_{cr}^*,\end{cases} \tag{105}$$

where the $x_n$ ($n\geqslant 1$) are the roots of Eq. (102), and $x_0$ satisfies (96). In particular, for $1/2L > 1$ we have

$$f_0 = 1 + o[(l/L)^2 \exp(-l/L)]. \quad (106)$$

It is easy to see that for $E \ll E^*_{cr}$, the survival probability $\Delta W^{(d)}(t)$ for the $A$ particles is given either by Eqs. (44), (50), and (67) with $d = 1, 2, 3$, or by (10) with $d = 1$. The optimum cavity is then a $d$-dimensional sphere of radius $l_t^{(d)}$. However, because $l_t^{(d)}$ increases with time we will eventually have $E > E^*_{cr}$ for any nonzero field, and the remaining $A$ particles will vanish in the field-induced fluctuation regime, for which the optimum cavity is a cylinder elongated along the field.

For $E \lesssim E^*_{cr}$, the $L$-dependent terms in (103) and (104) are comparable in order of magnitude to the terms depending on $l$. If we average (86) over $V$ with the weight $\exp[-(n_B + n_C)V]$, where $V \sim a^{d-1} l$, i.e., over the cylindrical cavities, we get an intermediate large-time formula for the survival probability which breaks down when $E > E^*_{cr}$.

We now consider the strong-field case $E \gg E^*_{cr}$. The fluctuation cavities are now large, and for every $n \gg 1$ we have $f_0 \gg f_n$, $\lambda_0 \ll \lambda_n$. The survival probability for the $A$ particles in the cavity $\Omega$ is

$$W_\Omega^{(d)}(t) = \exp\left[-\frac{h' D_A t \exp(-l/L)}{L(1 + h' L)}\right]. \quad (107)$$

The mean probability $\Delta W^{(d)}(t) = W^{(d)}(t) - W_\infty^{(d)}$ is given by (90), with $p(V) = \exp[-(n_B + n_C)V]$, $\phi(t) \equiv 1$ (because the $A$ particles are absorbed only at one end of the cylindrical cavity).

For a fast reaction ($\beta \gg a/L$), the survival probability in the cavity $\Omega$ is equal to

$$W_\Omega^{(d)}(t) = \exp[-D_A t L^{-2} \exp(-l/L)], \quad (108)$$

which averaged over $l$ gives

$$\ln \Delta W^{(d)}(t)\,|_{t\to\infty} \approx -\frac{S(d) k_B T(n_B + n_C)}{qE} \ln\left[\frac{e D_A (qE)^3 t}{S(d)(n_B + n_C)(k_B T)^3}\right], \quad (109)$$

where $S(3) = \pi a^2$, $S(2) = a$, $S(1) = 1$.

If the reaction is slow ($\beta \ll a/L$) then

$$W_\Omega^{(d)}(t) = \exp\left[-N \frac{k_p t}{V_c^{(d)}} \exp(-l/L)\right], \quad (110)$$

where $V_e^{(3)} = \pi L l_1^2$. For $t \to \infty$ we find, after averaging (110) over $N$ and $V$, that most of the contribution to $\Delta W^{(d)}(t)$ comes from cavities containing just one trap, and the dimensions of the optimum cavity are approximately equal: $l_1 \approx a$, $l \sim L \ln t$. Therefore,

$$\ln \Delta W^{(d)}(t)\,|_{t\to\infty} \approx -\frac{S(d) k_B T(n_B + n_C)}{qE} \ln\left[\frac{e (qE)^2 k_r t}{S^2(d)(n_B + n_C)(k_B T)^2}\right]. \quad (111)$$

The survival probability $\Delta W^{(d)}(t)$ for this system thus decreases as a power of $t$ when $t \to \infty$.

## 8. DISCUSSION AND CONCLUSIONS

In this paper we have investigated the kinetics of processes of the annihilation type involving nonideal (mobile) traps for two types of subthreshold percolation lattice systems, in which the active particles $A$ are localized in bounded cavities in the absence of a reaction. In the first case, the $A$ particles are localized by the traps themselves, and if the reaction is slow enough a significant percentage of the $A$ particles are absorbed, as given by the expression $\ln W(t) \sim -t^{d/(d+1)}$ for the survival probability in the intermediate regime. In the second case, the $A$ particles are localized due to blocking of the lattice sites by inert, immobile barriers $C$. The explicit relations $\ln \Delta W(t) \sim -(t/\ln t)^{1/2}$ and $\ln \Delta W(t) \sim -t^{1/2}$ were obtained for $d = 2$ and 3, respectively. According to these relations, the percentage of the $A$ particles absorbed is relatively low and proportional to $\exp(-n_C/n_B)$.

One-dimensional systems with randomly distributed traps $B$ and inert barriers were considered in a separate section. If the reaction is sufficiently slow the $A$-particle concentration, which is proportional to $\exp[-(1 + n_C/n_B)]$, vanishes in the fluctuation regime $\ln \Delta W(t) \sim -t^{1/2}$. This concentration is greatest for high trap concentrations $n_B \gg n_C$.

For the case of diffusing traps in either type of system, we analyzed the successive onset of the various fluctuation stages in the reaction as a function of the parameters of the problem. If the traps $B$ are highly mobile, the fluctuation effects are suppressed due to mixing in the system, and the reaction kinetics is described by the formal kinetic equations.

We also studied the influence of a uniform external field on the reaction kinetics for mobile charged particles $A$ and immobile neutral particles $B$ and $C$. The survival probability for the $A$ particles decays exponentially: $\ln W(t) \sim -E^n t$, where $n = 1$ for $\beta \ll a/L$, $n = 2$ for $\beta \gg a/L$ in a system containing only $A$ and $B$ particles, and as a power of $t$: $\ln \Delta W(t) \sim -(1/E) \ln t$ in a system containing $A$, $B$, and $C$ particles.

We emphasize that our formulas predict reaction rates slower than those given by the formal kinetic theory. Moreover, and unlike the situation with most fluctuation effects, the effects studied here determine not only the limiting behavior in the remote future but also the trapping kinetics for a large fraction of the $A$ particles, i.e., they can be observed experimentally.

We note that the survival probability $W(t)$ for the reagent particles was defined as an average $W(t) = \int W_\Omega(t) p_\Omega(V)$, where $W_\Omega(t)$ is the survival probability in the cavity $\Omega$ and $p_\Omega(V)$ is the cavity formation probability; $W_\Omega(t)$ depends on the reaction rate constant and the density of the system. A Poisson distribution for $p_\Omega(V)$ is realistic for a wide class of problems in which the interaction among the particles composing the matrix is negligible. In the general case, surface tension forces at the cavity boundaries will alter the form of the dependence $p_\Omega(V)$ (there will be more large cavities) and the fluctuation effects will be enhanced.

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