Asymptotic regimes in the loss of particles at trapping centers in dense systems

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(Submitted 23 March 1987)
Pis'ma Zh. Eksp. Teor. Fiz. **45**, No. 9, 443–445 (10 May 1987)

A study is made of the kinetics of the loss at trapping centers of particles which are undergoing a random walk in subthreshold percolation systems. Asymptotic expressions are derived for the survival probability. These expressions determine the kinetics of the disappearance of a significant fraction of the particles. The effect of a uniform external field is studied.

Clustering, the formation of fractal systems, and other diffusion processes have recently attracted increased interest in the physics of disordered systems. One of the few exact results which has been established in this field is that the mean-field dependence

$$c(t) = \exp(-knt) \tag{1}$$

for the survival probability $c(t)$ of a particle A which is diffusing in a d-dimensional medium with immobile trapping centers B (k is the "observable" rate constant of the reaction $A + B \to B$, n is the density of trapping centers, and t is the time) is replaced as $t \to \infty$ by the asymptotic behavior[1,2]

$$\ln c(t) \approx - n^{1/(d+2)} t^{d/(d+2)}, \tag{2}$$

which is related in a definite way to the tail of the state density for an electron in a disordered system.[3]

In this paper we study the behavior of the type in (2) for two percolation systems for which, in the absence of a reaction, particles A are localized in finite volumes. An important point is that, in contrast with most fluctuation effects, the results which are

 0021-3640/87/090567-04$01.00

found describe not only the remote asymptotic behavior but also the kinetics of the conversion of a large fraction of the particles of species A when the parameter values of the problem satisfy a certain relation. In other words, the results derived here can easily be observed experimentally. We study the effect of an external field E on the kinetics of the reaction of charged particles A with neutral particles B.

We consider particles A, each with a charge e, which are diffusing through a lattice whose sites can be occupied by immobile neutral particles B, which are impermeable for particles A. This occupation of sites by the immobile neutral particles B occurs with a probability p in an independent manner for each site. If $1-p$ is below the percolation threshold, each A localizes in a closed, singly connected cavity. When A and B meet, there is a small probability for an annihilation of A (a slow annihilation reaction). The external field E is uniform and parallel to the x axis. For the density of particles A within a cavity Ω we can write the following equation in the continuum limit:

$$\frac{\partial\rho(r,t)}{\partial t} = D\Delta\rho(r,t) + \frac{D}{l}\frac{\partial\rho(r,t)}{\partial x}, \qquad (3)$$

where D is the diffusion coefficient, $l = k_B T(Ee)^{-1}$, k_B is the Boltzmann constant, T is the temperature, and Δ is a d-dimensional Laplacian. Here we have the boundary condition

$$(\Phi = \mp h\rho)|_{r\in\Gamma}, \qquad (4)$$

where Φ is the flux density of ρ across the Ω–Γ boundary (which is not necessarily singly connected); the $-(+)$ corresponds to the exterior (interior) part of Γ; $h = k_p S_a^{-1}$; S_a is the surface area of a d-dimensional sphere whose radius a is equal to the reaction radius; and k_p is the rate constant of the reaction. We also have uniform boundary conditions, $\rho(r,t)|_{t=0} = \rho_0$, within Ω. If $E = 0$ and

$$k_p \ll S_a D R^{-1}, \qquad (5)$$

where R is the maximum diameter of Ω, the survival probability for a particle A in Ω is

$$c_\Omega(t) = \exp(-\lambda t) \qquad (6)$$

where $\lambda = k_p S_\Gamma (S_a V)^{-1}$, S_Γ is the total area of Γ, and V is the volume of Ω. The probability for the formation of a cavity is[4] $\mathscr{P}(V) = \exp(-nV)$, where $n = \eta\ln(1-p)$, and η is the density of lattice sites. At large values of t, the survival probability for a particle A in the system is dominated by spherical cavities with a radius

$$R_t = [k_p t/(\omega_d^2 n)]^{1/(d+1)} \qquad (7)$$

where ω_d is the volume of a d-dimensional unit sphere. When the survival probability is averaged over different cavities, the optimal-fluctuation method[1-3] gives us, correspondingly,

$$\ln c(t) \approx -\omega_d^{-(d-1)/(d+1)} n^{1/(d+1)} (k_p t)^{d/(d+1)} \qquad (8)$$

The corresponding functional dependence for $d=1$ was derived in Refs. 5 and 6. Intermediate asymptotic result (8) gives a correct description of the reaction kinetics as long as (5) holds for R_t from (7). When the opposite inequality holds (as $t\to\infty$), the smallest eigenvalue of the diffusion operator is $\lambda=\pi^2DR^{-2}$, so we find (2).

An important point is that at small values of k_p most of the reactant is lost according to (8). This behavior is correct in a certain time interval $t_1 \ll t \ll t_2$; for the corresponding extents of reaction with $d=3$ we have $\ln c(t_1) = -(na^3)^{-2}$ and $\ln c(t_2) = -na^3(Da/k_p)^3$. The time for a real experiment, $\tau \approx (k_p n)^{-1} = (a^2/D)(Da/k_p)(1/na^3)$, would be greater than 10^{-5} s in a dense system ($na^3 \approx 1$) if the condition $Da/k_p > 10^6$ holds in a liquid ($D \approx 10^{-5}$ cm^2/s) or if the condition $Da/k_p > 10$ holds in a solid ($D \approx 10^{-10}$ cm^2/s). Consequently, if the typical reaction time exceeds 10^{-5} s in these systems, only behavior (8) will be observable.

In an electric field $E\neq 0$ at a large value of t, at which the relation $R_t > l$ holds, the optimal cavity becomes a cavity which is stretched out along x, and λ becomes independent of the dimensions of the cavity. As a result, there is a change in the asymptotic behavior after a long time. For strong fields (small values of k_p), under the condition $k_p \ll S_a DEe(k_BT)^{-1}$, we have the following result as $t\to\infty$:

$$\ln c(t) \approx -k_p Ee(S_a k_B T)^{-1} t.$$

In the opposite limit, $k_p \gg S_a DEe(k_BT)^{-1}$, we have the following result as $t\to\infty$:

$$\ln c(t) \approx -D(Ee)^2(k_BT)^{-2} t.$$

Let us consider the second case, in which the particles of species B, which are blocking the diffusion of A, are neutral with respect to the reaction, and the vanishing of reactant A occurs in an encounter with particles of a third species: trapping centers C, which are distributed in a random way among the sites which are not occupied by particles B. In the limit $t\to\infty$, $c(t)$ tends toward a finite limit c_∞, which is equal to the fraction of localization cavities which contain not a single trapping center C. The relaxation of $c(t)$ toward c_∞ is determined by the kinetics of the loss of particles A which are diffusing in closed cavities with a random number of trapping centers N. The density A in each of the cavities obeys (3) with a boundary condition of the type in (4), in which we have $h=0$ at the boundary of the cavity and $h=k_pS_a$ at the reaction surface of the trapping centers. Under the conditions $R\gg a$, $Dt\gg R^2$, $N\ll R^3\eta$, $E=0$, and $d=3$, relation (6) with $\lambda = kN(\omega_d R^d)^{-1}$ and $k=4\pi Dak_p(4\pi Da+k_p)^{-1}$ holds. The average survival probability in the system is

$$c(t) = \int_0^\infty \sum_{N=0}^\infty \mathcal{P}_V(N)\, e^{-kNt/V}\, \mathcal{P}(V)\, dV,$$

where $\mathcal{P}_V(N)$ is a Poisson distribution with a mean value of n_cV, and n_c is the density of trapping centers C. Summing over N, and subtracting c_∞, we find

$$c(t) - c_\infty = \int dV \left[\exp\left(nV\exp\left(-\frac{kt}{V}\right)\right) - 1\right]\mathcal{P}(V). \qquad (9)$$

At small values of t, expression (9) for any normalized $\mathscr{P}(V)$ to unity leads to (1). In the limit $t \to \infty$, we find by the method of steepest descent

$$\ln[c(t) - c_\infty] \approx -2\sqrt{k(n+n_c)t}.$$

In the case $E \neq 0$, the long-term relaxation of $c(t)$ is determined by cylindrical cavities which are stretched out along x and which have a single trapping center at one base of the cylinder. In this case, calculations by the method of steepest descent yield the power law

$$\ln[c(t) - c_\infty] \approx -\frac{na^2k_BT}{Ee}\ln\left[\frac{k(Ee)^2t}{na^4(kT)^2}\right].$$

We wish to thank A. I. Onipko for pointing out the existence of an intermediate asymptotic behavior of the type in (8) in one-dimensional systems; we also thank O. F. Ivanov for a useful discussion.

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Translated by Dave Parsons