Effect of reactant-fluctuation density on the kinetics of recombination, multiplication, and trapping processes

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A number of diffusion processes in which fluctuation effects are decisive is investigated. A new perturbation-theory variant is proposed for the problem of annihilation of a diffusing particle by immobile traps. This variant yields, in first order in the gas parameter (at low trap density), both the intermediate Smoluchowski asymptote and the asymptote at $t \to \infty$. Corrections that determine the rate of the establishment of the asymptotic regimes are obtained. It is shown that in systems with multiplication and annihilation by immobile traps, the density increases exponentially over long times at arbitrarily low rate of multiplication and finite trap density. An asymptotically exact equation is obtained for the density evolution in a system with multiplication and annihilation in which the density of the quenching agent obeys the diffusion equation with Gaussian random initial distribution. It is shown that the previously obtained power-law asymptotes for reactions of the recombination times are asymptotically exact.

Interest in the influence of fluctuations on the kinetics of diffusively controllable processes has increased substantially of late. The range of applications of the theory of diffusely controllable processes is quite large. It includes research into the kinetics of excitation damping and recombination of carriers or defects in solids, a large class of rapid reactions in solids, liquids, and glasses, a number of biological processes related to population survival, and of the aggregation and coagulation type.

A two-particle description of the kinetics of a diffusely controllable reaction was first formulated by Smoluchowski.[1] According to his theory, the rate of an irreversible bimolecular reaction $A + B \to C$ is determined by the law of effective masses

$$\frac{dC_A}{dt}=\frac{dC_B}{dt}=-k_s C_A C_B,$$

in which the "observable reaction-rate constant" $k_s(t)$ is assumed equal to the flux Φ of the density $n(r,t)$ of the reactant B through a reaction sphere of radius $a = R_A + R_B$, where R_A and R_B are the radii of particles A and B, and $n(r,t)$ obeys the diffusion equation

$$\partial n(r,t)/\partial t = D\Delta n(r,t), \tag{1}$$

where Δ is the d-dimensional Laplace operator, d is the dimensionality of the reacting system, $D = D_A + D_B$, D_A and D_B are the diffusion coefficients of particles A and B, respectively. The boundary conditions for Eq. (1) are expressed in the form

$$\Phi \equiv 4\pi a^2 \frac{\partial n(r,t)}{\partial r}\bigg|_{r=a} = -kn(a,t); \qquad n(r,t)\,|_{t=0} = C_B, \tag{2}$$

where k is the true rate constant of the reaction. At $t \gg a^2/D$, $k \gg 4\pi aD$ and $d = 3$ we have

$$k_s = 4\pi aD[1 + a(\pi Dt)^{-1/2}]. \tag{3}$$

Smoluchowski's theory was extended in Ref. 2 to include the case of reversible bimolecular reactions, and in Ref. 3 to include trimolecular reactions. It was shown in Refs. 4–7 that Smoluchowski's solution describes in a number of important cases an intermediate asymptote of the problem, whereas the time dependence of the reagent concentration as $t \to \infty$ is determined completely by the fluctuations of the density of the initial distribution (prior to the start of the reaction) of the reagents.

In three-dimensional systems, at $C_A \ll C_B = n$, $D_B = 0$, the transition from Smoluchowski's intermediate asymptote to the fluctuation regime occurs for $\tau \gg \alpha^{-1/2}$, where $\tau = 4\pi aDnt$, $\alpha = 4\pi na^d$. For reactions of the recombination type for which $C_A(t) = C_B(t)$ we have $\alpha = 4\pi C_A(0)a^d$. Since the parameter α in liquid-phase systems is as a rule small, the fraction of reactants that vanish in accordance with the fluctuational asymptotic laws is also small and are therefore difficult to investigate in experiment. In Ref. 8 are pointed out polymer systems in which the bulk of the reactant vanishes in the fluctuation regime.

Diagram expansions were used in Refs. 9–13 to obtain corrections to Smoluchowski's solution. Kinetics of processes of the multiplication type, $A + B \to kA + B, k > 1$, were investigated in Ref. 14.

We investigate here a number of situations in which the fluctuation effects are decisive and can be observed in experiment. Foremost are diffusion-controllable reactions such as quenching the excited state (annihilation in traps), which occurs in systems with homogeneous multiplication of the reactant (a process that can be used by the presence of chain processes, etc.). In the first section we formulate the problem of evolution of the reactant density in such systems. In the second we develop a perturbation theory corresponding to fluctuation times $\tau \ll \alpha^{-1/2}$ for which the Smoluchowski theory is valid to first order in α. We discuss the connection with motion, in a random medium, of a particle having an energy close to the mobility threshold,[15,16] and with the percolation problem.[17] A nontrivial dependence of the rms displacement of the particles on the time is obtained. In the third section we develop a modified perturbation theory that yields both Smoluchowski's intermediate asymptote and the long-time fluctuation asymptote, and we determine the corrections on which the rate of convergence of the process to an asymptotic relation depends. Analysis of the diagram-

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matic expansions for small α and for $d = 3$ provides a description, in the entire time interval, of the reaction kinetics in systems with multiplication. We show that at an arbitrarily small average multiplication rate the average reactant density in a system with immobile traps increases exponentially as $t \to \infty$, and the induction transition corresponds to an explosive process and depends on α and d.

The long-time asymptote in a system with immobile traps is determined by the Poisson fluctuations of the trap density. In the case of mobile particles B, their diffusion smoothens the Poisson fluctuations, and small Gaussian density fluctuations become decisive at $t \to \infty$. The most clearly pronounced is the influence of Gaussian density fluctuations in the kinetics of a reaction of the recombination type. In Sec. 4 is analyzed the influence of the Gaussian fluctuations on the kinetics of a diffusely controllable reaction $A + B +$ Product, and the fifth section deals with the static-recombination kinetics. It is shown that the relations obtained in Refs. 4–7 by various methods are asymptotically accurate.

An interesting situation occurs in a system with moving traps if the average rate of multiplication of particles A is equal to the rate of their annihilation in the traps. The two-particle approximation predicts in this case a slow decrease of the density of A on account of the second (nonstationary) term in the expression for the effective rate constant of the reaction (3). We show in Sec. 6 that Gaussian fluctuations of the density of B lead in such a system to a slow growth of the density of A, and the corresponding asymptotic relations are derived.

1. ANNIHILATION IN IMMOBILE TRAPS IN A SYSTEM WITH MULTIPLICATION. FORMULATION OF THE PROBLEM

Consider a system in which N immobile traps of radius a each are randomly (with a Poisson distribution) placed uniformly over a volume V. We designate the radius vector of the jth trap by R_j, with $j = 1, 2, \ldots, N$. Let, in parallel with the diffusion and vanishing in the traps, the particles A also multiply via some arbitrary chain process. In this case the equation for the generating function $F(r,t,\theta)$ of the density distribution of A at the point r is given by[18]

$$\partial F(r,t,\theta)/\partial t = D_A \Delta F(r,t,\theta) + f[F(r,t,\theta)]. \quad (4)$$

By definition, $F(r,t,\theta) = \Sigma_m P_m \theta^m$, where $P_m = P_m(r,t)$ is the probability of a particle initially at a point with a radius vector r becoming transformed after a time t into m particles, and $f(\theta)$ is the generating function of the distribution of the number of descendants in a single branching act. If A has initially a uniform distribution, the boundary and initial conditions for Eq. (4) take the form

$$F(r,t,\theta)|_{r\in\Sigma} = 1, \quad F(r,0,\theta) = c_0\theta. \quad (5)$$

The multiply connected surface Σ is a union of all the reaction surfaces $|r - R_j| = a$, $R_j = 1, 2, \ldots N$. The mathematical expectation value of the density $C_A(r,t) = (\partial F/\partial\theta)|_{\theta=1}$ of the particles A obeys the equation

$$\partial C_A/\partial t = D_A \Delta C_A + k_p C_A, \quad k_p = (\partial f(\theta)/\partial\theta)|_{\theta=1} \quad (6)$$

with boundary and initial conditions

$$C_A(r,t)|_{t=0} = C_0, \quad C_A(r,t)|_{r\in\Sigma} = 0.$$

Consequently

$$C_A = \exp(k_p t) \int dr \rho(r,t,r'), \quad (7)$$

where $\rho(r,t,r')$ is the Green's function of a diffusion equation of type (1) with zero boundary conditions on Σ: $\rho(r,t,r')|_{r\in\Sigma} = 0$ and with the initial condition $\rho(r,t,r')|_{t=0} = \delta(r - r')$.

The optimal-fluctuation method[20] was used in Ref. 19 to obtain a lower bound of the function ρ. It was shown in Ref. 21 that this estimate yields an exact result as $t \to \infty$.

The presence of an asymptotically exact result notwithstanding, we investigate in the next section the function $\rho(r,t,r')$ once more, to enable us to determine the variation of ρ in the entire time interval for small values of the parameter α.

2. PERTURBATION THEORY FOR SHORT TIMES

We write down an expression for the Laplace transform, with respect to time, of the function $\rho(r,t,r')$:

$$\rho(r,\lambda,r') = \det\|F\|/\det\|E\|, \quad (8)$$

where

$$\rho(r,\lambda,r') = \int_0^\infty \exp(-\lambda t)\rho(r,t,r')\,dt,$$

F_{lm} is an $(N+1)\times(N+1)$ matrix, E_{ij} is an $N \times N$ matrix,

$$F_{00} = G(\varkappa, r-r'),\ F_{0j} = G(\varkappa, r-R_j),\ F_{i0} = G(\varkappa, R_i - r'),$$

$$F_{ij} = E_{ij} \text{ for } j, i > 0,\ E_{ij} = G(\varkappa, R_i - R_j) \text{ for } i \neq j,$$

$$E_{ii} = G(\varkappa, a),\ \varkappa^2 = D/\lambda,$$

$G(\varkappa,r)$ is the Cauchy function of the operator $(\varkappa^2 - \Delta)$, $(\varkappa^2 - \Delta)G(\varkappa r) = \delta(r)$. The function $\rho(r,\lambda,r')$ satisfies the equation $(\varkappa^2 - \Delta)\rho = 0$, since it is a linear combination of its solutions. If $|r - R_i| = a$, two columns in the matrix F_{ij} become nearly equal to within the small corrections in $|R_i - R_j|/a$, i.e., in the case of small n $\det\|F_{ij}\|$ is equal to zero for $r\in\Sigma$ for an overwhelming majority of the $\{R_i\}$ configurations. The fluctuating clusters of sinks add to operator introduced below corrections that are small in terms of α. These corrections make a contribution that is not singular at large t (small λ), since the long-time asymptote of the problem is determined by regions with increased rather than decreased trap density. A solution obtained without this restriction, for example by a path-integral expansion [see Eq. (42) below] or by the t-matrix method[15] leads, after averaging over $\{R_i\}$, to constants k_s, c_2 and ρ_0 obtained in the present paper, which are accurate to small corrections in terms of the parameter α, do not change the analytic structure of the perturbation-theory series, and do not affect the conclusions of the paper.

Expanding the determinant $\det\|F\|$ in terms of the elements of the zeroth row and zeroth column, using the expression for the inverse matrix E^- in terms of the minors of the determinant of the matrix E, and finally expanding in terms of $\tilde{E}$ the matrix $[G(\varkappa,a)I + \tilde{E}]^{-1}$ (in which I is a unit $N \times N$ matrix, $\tilde{E}_{ij} = E_{ij}$ at $i \neq j$ and $E_{ij} = 0$ at $i = j$), we get

$$\rho(r,\lambda,r') = G(\varkappa, r-r') - \sum_{i=1}^{N}\sum_{j=1}^{N} G(\varkappa, r-R_i)[\Gamma_{ij} + I]G(\varkappa, R_j - r'), \quad (9)$$

where

$$\Gamma_{ij}=\sum_{k=1}^{\infty}(-1)^k\|E_{ij}\|^k[G(\varkappa,a)]^{(k+1)}.$$

Correspondingly,

$$\rho(\lambda)=\frac{1}{\lambda}\Big\{1-\sum_{i=1}^{N}\sum_{j=1}^{N}G(\varkappa,r-R_i)\,[I+\Gamma_{ij}]\Big\},\qquad(10)$$

where

$$\rho(\lambda)=\int\rho(r,\lambda,r')\,dr'=\int\rho(r,\lambda,r')\,dr.$$

The function $\rho(\lambda)$ averaged over the random distribution of the vectors R_i in $3D$ space can be written in the form (we neglect the intersection of the absorption spheres)

$$\rho(\lambda)=\frac{1}{\lambda}\Big\{1-x\int G(y_0)\,dy_0\Big[1+\sum_{k=1}^{\infty}(-x)^k\rho_k\Big]\Big\},\qquad(11)$$

where

$$\rho_k=\sum_{0\leqslant d\leqslant k-1}(a/x)^d\rho_{kd},$$

$$\rho_{kd}=\int\dots\int\sum_{i_l=1}^{k}\sum_{j_l=1}^{i_l-2}\Big[\prod_{l=1}^{d}\delta(y_{i_l}-y_{j_l})\prod_{m=1}^{k}G(y_m-y_{m-1})\Big]dy_m,\qquad(12)$$

$$x=4\pi aDn\exp(\varkappa a)/\lambda,\quad G(y)=y^{-1}e^{-y}.$$

The expression for ρ_{kd} can be represented graphically by a diagram consisting of k points corresponding to k-fold integration with respect to the variables y_m that correspond to the radius vectors of the traps. Each point (except the first and last) is joined by a straight-line segment to the preceding and succeeding points. (The first point is joined only to the preceding one.) A straight-line segment corresponds to a factor $G(y_m-y_{m-1})$ (free propagator) in the integrand. On the obtained chain of k points it is necessary to place d braces, with the lth dashed-line brace, the lth brace corresponding to the factor $\delta(y_{i_l}-y_{i_l})$ in the integrand of (12), where $l=1,2,\dots d$. To calculate ρ_{kd} it is necessary to sum all the diagrams with different placements of d braces on k points; the braces are assumed indistinguishable and each can join together any two points except neighboring ones. Figure 1 shows a typical diagram which contributes to ρ_{kd} at $k=21$ and $d=5$.

It is easy to sum in explicit form over all the diagrams that differ from one another only in the number of points between the nearest (dashed) vertical lines on the diagram. For the diagram shown in Fig. 1 this corresponds to summation over the number of points located between the first and second, fifth and eighth, eighth and tenth, tenth and eleventh, eleventh and thirteenth, thirteenth and sixteenth, sixteenth and nineteenth, and nineteenth and twenty-fourth points.

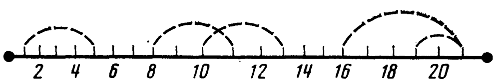

FIG. 1. Example of diagram that contributes to ρ_{kd}.

Summing, we obtain the series

$$\rho(\lambda)=\frac{1}{\lambda}\Big\{1-x\int G(y_0)\,dy_0\Big[1+\sum_{d=0}^{\infty}\Big(\frac{\varkappa a}{x}\Big)^d\rho_d\Big]\Big\},\qquad(13)$$

where ρ_0 is a sum of diagrams, each of which consists of a straight-line segment on which d braces—dashed lines—are placed. To each straight-line segment between nearest intersections of the straight line and a dashed brace or between the end of the straight-line segment and the adjacent intersection with the dashed brace there corresponds a factor $-xG_q(\Delta y)$, $\Delta y=y_m-y_{m-1}$, if the given straight-line segment is not spanned by any brace or is spanned by a brace that intersects with other braces (at least one of them). The segment spanned by a brace that does not intersect with any other brace corresponds to a factor $-x[G_q(\Delta y)-G(y)]$, where $G_q(y)$ is a renormalized propagator. In the k-representation we have $G_q=(k^2+q^2)^{-1}$, and in the r-representation $G_q(r)=e^{-qr}/r$ at $d=3$ and $G_q(r)=K_0(qr)$ at $d=2$, where $K_0(y)$ is a modified Bessel function of imaginary argument and $q^2=x+1$. Just as before, the mth point on the diagram corresponds to the mth-trap radius vector y_m over the values of which the integration is carried out, while the brace is a δ function of the appropriate arguments. Figure 2 shows a typical renormalized diagram.

Summing all the diagrams that break up, on cutting one of the straight-line segments, into a product of diagrams not connected by dashed lines, it can be shown[9] that in systems of any dimensionality we have

$$\rho(\lambda)=\{\lambda[1+x(1+g(\lambda))]\}^{-1},\qquad(14)$$

where $x=4\pi aDne^{\varkappa a}/\lambda$ in 3D systems and $x=2\pi nD/\lambda K_0(\varkappa a)$ in planar systems, while the function $g(\lambda)$ is equal to the sum over the irreducible diagrams, which is calculated in accordance with the rules set forth above.

In 3D systems, the summation corresponds to a change to a new variable $\lambda'=\lambda+s$, where s is a pole of the function $\rho(\lambda)$ calculated in the Smoluchowski approximation.

The functions $g(\lambda)$ contains corrections, small together with the parameter α, to the Smoluchowski solution. The Appendix contains the first five irreducible diagrams that contribute to $g(\lambda)$. It can be seen that each succeeding correction is small in terms of α and is at the same time more singular as $\lambda'\to 0$ compared with the preceding one. In first-order approximation in α we have at $\varkappa a\ll 1$

$$\rho(\lambda)=\{\lambda+4\pi aDn+4\pi a^2n[D(4\pi aDn+\lambda)]^{1/2}\}^{-1}\qquad(15a)$$

and accordingly

$$\rho(\tau)=e^{-\tau(1-\alpha)}\operatorname{erfc}[(\alpha\tau)^{1/2}]\qquad(15b)$$

in 3D systems and

$$\rho(\lambda)=\Big\{\lambda+\frac{2\pi nD}{K_0(\varkappa a)}\Big[1+\frac{\ln(1+2\pi nD/\lambda K_0(\varkappa a))}{2K_0(\varkappa a)}\Big]\Big\}^{-1}\qquad(16)$$

in planar systems. Expressions (15) and (16) were obtained in Ref. 9.

FIG. 2. Example of renormalized graph.

Analysis of the general structure of the perturbation-theory series leads thus to the conclusion that in 3D systems expression (15a), which was obtained in first-order in α, is meaningful at $(\lambda - s)/s \gg \alpha$. The sum of the contributions from the simplest loop-free diagrams correspond to the Smoluchowski theory, which is an an analog of a certain variant of the mean-field theory, and the first correction g to the "mass operator" is the sum of the single-loop diagrams.

It must be noted that the singularities in the higher terms of the perturbation-theory series for $g(\lambda)$ become substantial at $|\lambda - s|/s \approx \alpha$, which corresponds to the time interval $\tau > \alpha^{-1}$. At $d = 3$ and $(\lambda - s)/s \gg \alpha$ the perturbation-theory series yields converging corrections to the rate constant calculated by Smoluchowski, the first of which is negative and has an absolute value $4\pi aDn\alpha$.

The Green's function in first order in α is equal to

$$\rho(k, \lambda) = [k_2 + \bar{\lambda} + (\alpha\bar{\lambda})^{1/2}]^{-1}, \tag{17}$$

where $\bar{\lambda} = (\lambda - s)/s$. Consequently, in this approximation the mean-squared displacement $\langle r^2(t)\rangle$ is equal to $\langle r^2(t)\rangle \sim t^{1/2}$ as $t \to \infty$. A similar dependence was obtained in Ref. 22 for the problem of the mean squared displacement of a particle that wanders over a lattice with blocked sites whose concentration is equal to the uncorrelated mobility threshold. In the approximation corresponding to (17), an infinite cluster at the critical point constitutes a linear chain that is randomly distributed in space. The number of unblocked neighbors of an unblocked site is assumed to be identically equal to unity—the average number of unblocked neighbors of an unblocked site, i.e., branchings are neglected. The average mean squared displacement of a particle along such a chain is equal to $\langle l^2\rangle \sim t$. The mean squared distance between the ith and jth sites is equal to $\langle (r_i - r_j)^2\rangle \approx |i - j| = l$. Accordingly, $\langle r^2(t)\rangle \sim l \sim t^{1/2}$.

The problem of calculating $\rho(\lambda)$ is very close to the problem of the spectrum of a particle in a random potential of repelling impurities.[15] The perturbation theory set forth above describes well the continuous spectrum far from the boundary $\lambda = s$. We modify below the perturbation theory so as to obtain a description of $\rho(t)$ at arbitrary t. The contribution of the states close to the boundary $\lambda = s$, which in principle cannot be described by a theory of the perturbation-theory type, made to the expression for $\rho(t)$ in 3D systems, turns out to be small for all t if $\alpha \ll 1$.

3. MODIFIED PERTURBATION THEORY. ASYMPTOTE AS $t \to \infty$

We change the order of the averaging over the trap positions R_i in expression (10) for $\rho(\lambda)$ in the following manner. We fix the distance between the origin (the starting point of particle A) and the nearest trap B, i.e., we fix $|R_k| = R$, where k is such that $|R_k| = \min|R_i|$, $i = 1, 2, \ldots N$. The distribution over R in a Poisson ensemble was investigated in detail in Ref. 23. We denote the result of averaging the function $\rho(\lambda, r, [R_i])$ over all R_i such that $|R_i| > R$ at a fixed value $|R_k| = R - \rho(\lambda, R)$. Retaining the zero-loop diagrams in the expansion of $\rho(\lambda, R)$ in terms of α, we get

$$\rho(\lambda, R) = \sum_{n=0}^{\infty} \int Q_n(y, \lambda)\, dy, \tag{18}$$

where

$$Q_0 = \rho_0, \quad Q_{n+1}(y, \lambda) = -4\pi Dan \int dy\, Q_n(y, \lambda) G(y - x, \lambda) \eta(x)\, dx,$$
$$G(y, \lambda) = |y|^{-1} \exp(-\lambda^{1/2} y D^{-1/2}),$$
$$\eta(x) = \begin{cases} 1 & \text{if} \quad |x| \geqslant R \\ 0 & \text{if} \quad |x| \leqslant R \end{cases}. \tag{19}$$

It is shown in Ref. 24 that the sum of the series (18) coincides with the solution of the equation

$$\rho_0 + D\Delta\rho - [\lambda + 4\pi Dan\eta(r)]\rho = 0. \tag{20}$$

Generally speaking, the potential in (20) should be supplemented by a term $\delta(|r - R| - a)$, which corresponds to a selected trap B (closest to the origin). It is easy to show, however, that at $\tau \gg \alpha$ or, equivalently, $t \gg a^2/D$, the potential of the separated particles has practically no effect on $\rho(\lambda)$.

Equation (20) is similar to the Schrödinger equation for an electron in a potential well. At $d = 3$ its spectrum has at least one discrete level if $16\pi^{-1} naR^2 \geqslant 1$. The corresponding well width $R_0 = a(16\pi^{-1} na^3)^{-1/2}$ exceeds substantially the average distance between the traps

$$\langle l\rangle \approx (3/4\pi) n^{-1/3}, \qquad R_0/\langle l\rangle \sim \alpha^{-1/6}. \tag{21}$$

With logarithmic accuracy, the density of the fluctuation wells of this distance is equal to $\gamma = \exp(-\pi^3/24\alpha^{1/2})$. The inverse Laplace transform of the solution of Eq. (20) is

$$\rho(t) = I_1(t) + I_2(t), \tag{22}$$

where

$$I_1(t) = 4\pi \int dr \int_{R_0}^{\infty} R^{d-1}\, dR\, W(R) \sum_{\lambda_i} \exp(-\lambda_i t) \psi_i(0) \psi_i(r),$$

$$I_2(t) = 4\pi \int_0^{R_0} W(R) L^{-1}[\rho(\lambda, R)] R^{d-1}\, dR;$$

here $W(R)$ is the distribution function of the distance to the nearest neighbor in the Poisson ensemble, the summation is over the discrete spectrum of the eigenvalues λ_i of the equation conjugate to (20), ψ_i are the corresponding eigenfunctions, and $L^{-1}[\ldots]$ is the inverse Laplace transform. At $\tau \ll \alpha^{-1}$ and $\alpha \ll 1$ the function $I_2(t)$ coincides with the Smoluchowski solution. The corresponding corrections to the mass operator $g(\lambda)$ are small, since the corresponding region of λ is determined by the inequality $(\lambda - s)/s \gg \alpha$. At $t \gg \alpha^{-1}$ an important role is assumed by the nonanalytic solution $\rho(\lambda, R)$ near the pole $\lambda = s$. However, the presence of the factor e^{-st} in the expression for $I_2(t)$ causes $I_1(t)$ to decrease at large t much more slowly than $I_2(t)$, while $I_1(t)$ becomes leading in the sum (22) at $\tau > \alpha^{-1/2}$, i.e., at times much shorter than those at which the non-analytic character of $\rho(\lambda, R)$ becomes substantial.

The smallest eigenvalue $\lambda_{\min}$ in (22) is equal to the solution of the equation[25]

$$\sin[(\lambda/D)^{1/2} R] = \pm(4\pi na^3)^{-1/2} (\lambda/D)^{1/2} a. \tag{23}$$

At $4\tau \gg 1$, the main contribution to $I_1(t)$ is made by the term with $\lambda_{\min}$. At $R \gg R_0$ we have

$$\lambda_{min}=\frac{\pi^2 D}{R^2}-\frac{2R_0 D}{R^3}+\ldots o\left(\frac{R_0}{R}\right). \qquad (24)$$

In this limit the integral with respect to R in the expression for $I_1(t)$ can be calculated by the saddle-point method. Recognizing that $\ln W(R) = -4/3\pi n R^3$, we get

$$-\ln\rho(\tau)=c_1\tau^{3/5}\alpha^{-1/5}[1-c_2(\alpha\tau^2)^{-1/10}+\ldots],$$
$$c_1=\frac{5}{3}\left(\frac{4}{\pi^6}\right)^{-1/5},\quad c_2=\frac{3}{5}\left(\frac{4}{\pi}\right)^{2/5}. \qquad (25)$$

The value of R that maximizes the integrand, viz.,

$$R_m=(\pi Dt/2n)^{1/5}, \qquad (26)$$

is the region of localization of the particle A.

The first term of (25), which is the leading one for long times, is the known asymptotic expression $\ln\rho(t)\approx n^{2/(d+2)}t^{d/(d+2)}$, first obtained in Refs. 19 and 5. The second is a correction for the finite depth of the well. Similar corrections were obtained by the replica method in Refs. 26 and 27.

The density of the reactant A in a three-dimensional system, in which uniform multiplication of A takes place at a rate constant k_m, in parallel with a vanishing in the traps, of the immobile particles B, varies with time in the following fashion (see Fig. 3). If $k_m > 4\pi a n D$, an increase of the density is observed, viz., $C_A(t) = C_0\exp[(k_m - 4\pi RDn)t]$. In the opposite case $4\pi a n D > k_m$, the density of A increases during the initial stage in accordance with the relation

$$C_A(t)=C_0(1-\gamma)\exp[-(4\pi anD-k_m)t]+C_0\gamma,$$

where C_0 is the initial density of the reactant, γ is a small quantity, $\ln\gamma = -\pi^3/24\alpha^{-1/2}$. Complete fading $C_A(t)\approx\gamma$ is observed in the system in a wide time interval $1\ll\tau\ll\alpha^{-1/2}$. (At small α, the quantity γ can as a rule not be recorded in experiment; see Ref. 28, however.) At arbitrarily small k_m but sufficiently long time, an exponential increase of the density of A is observed in the system: $C_A(t) = \gamma\exp(k_m t)$.

It should be noted that the survival time of a given particle A, equal to $\partial F/\partial\theta|_{\theta=1}$ [see Eq. (4)], varies at $\tau\ll\alpha^{-1/2}$ in analogy with the function $C_A(t)$ with $C_0 = 1$, but does not increase at $\tau > \alpha^{-1/2}$ and tends instead to a constant value γ. Consequently, the fluctuation effects cited in the present paper can be observed only in sufficiently large systems for which $C_0 V \gg \exp\alpha^{-1/2}$, where V is the total volume of the reaction system. A transition to the thermodynamic limit in the derivation of the fluctuation asymptotes is valid only for such systems.

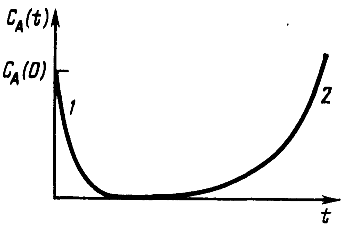

FIG. 3. Density evolution in a system with average multiplication rate k_m smaller than the average rate $4\pi naD$ of annihilation by immobile traps: 1—$\exp[-(4\pi Dan - k_m)t]$, 2—$\gamma\exp(k_m t)$.

We note also that the point $\lambda = \lambda_{\min}(R)$, where R depends parametrically on the time in accordance with (26), is not "dangerous" from the standpoint of the diagrammatic expansion. The propagator of the localized particle decreases exponentially over distances larger than R, and the corrections to the zero-loop diagrams are not singular.

It will be shown below that the singularities of the kinetics in a system with multiplying particles A, which react with mobile traps B, are determined by the Gaussian fluctuations of the density of B if the average rates of multiplication and annihilation are equal. The influence of the fluctuations on the reaction kinetics manifest themselves in reactions such as recombination of particles of two types.

4. DIFFUSION-CONTROLLED REACTION $A+B\to$ PRODUCT AT EQUAL AVERAGE CONCENTRATIONS OF A and B

The concentrations of the reactants A and B (C_A and C_B, respectively), satisfy in the system considered the equations

$$\partial C_A(r,t)/\partial t=-kC_A(r,t)C_B(r,t)+D_A\Delta C_A(r,t), \qquad (27a)$$
$$\partial C_B(r,t)/\partial t=-kC_A(r,t)C_B(r,t)+D_B\Delta C_B(r,t). \qquad (27b)$$

At $D_A = D_B = D_0/2$, following Refs. 4–6, we subtract (27b) from (27a). We obtain for the difference $Z(r,t) = C_A(r,t) - C_B(r,t)$

$$\partial Z(r,t)/\partial t=D_0\Delta Z(r,t). \qquad (28)$$

The initial distributions $C_A(r,0)$, $C_B(r,0)$ and accordingly $Z(r,0)$ are random functions whose properties are determined by the method of preparing the reacting system. In the case of instantaneous generation of the reactants, the distribution can be approximated for a large number of systems by a Gaussian-correlated one. The case of generation by a stationary Poisson source was investigated theoretically in Ref. 29. The average density $C_A(t) = \langle C_A(r,t)\rangle = \langle C_B(r,t)\rangle = C_B(t)$ as $t\to\infty$ was calculated in Ref. 5 to be

$$C_A(t)\approx C^l(t)=\langle|Z(r,t)|\rangle/2. \qquad (29)$$

In Ref. 7, by breaking the chain of linked diffusion-kinetic equations for the central moments of fourth order of the distributions $C_A(r,t)$ and $C_B(r,t)$, a similar result was obtained, which duplicates the intermediate Smoluchowski asymptote

$$C_A(t)=C_0(1+kC_0t)^{-1},$$

and yields as $t\to\infty$

$$C_A(t)\approx C^u(t)=\langle Z^2(r,t)\rangle^{1/2}/2. \qquad (30)$$

We shall show that Eq. (29) gives the lower bound of $C(t)$, and Eq. (30) gives the corresponding upper bound, i.e., $C^u(t) > C(t) > C^l(t)$. Since the ratio $\langle|Z|\rangle/\langle Z^2\rangle^{1/2}$ for a Gaussian distribution is the constant $(\pi/2)^{1/2}$, the results of Refs. 5, 7, and 29 yield the exact relation $C_A(t)\sim t^{-d/4}$ for instantaneous generation and $C_A(t)\sim t^{-1/4}$ at $d=3$ for generation by a stationary source.

The lower bound is obtained right away. Obviously,

$$|C_A(r,t)-C_B(r,t)|\leqslant|C_A(r,t)|+|C_B(r,t)|.$$

Consequently

$$2C_A(t)=\langle C_A(r,t)\rangle+\langle C_B(r,t)\rangle\geqslant\langle|Z(r,t)|\rangle.$$

To obtain the upper bound we substitute the definition $Z(r,t)$ in Eq. (27a):

$$\partial C_A(r,t)/\partial t = D\Delta C_A(r,t) - k[C_A^2(r,t) - C_A(r,t)Z(r,t)]. \quad (31)$$

Averaging both sides of (31) over r, we get

$$dC/dt = -kS[C_A(r,t), Z(r,t)], \quad (32)$$

where

$$S = \frac{1}{V}\int dr[C_A^2(r,t) - C_A(r,t)Z(r,t)]dr. \quad (33)$$

The operator $D_A\Delta$ does not alter the average density in a closed system (at zero fluxes through the boundary), but does affect the correlators $\langle C_A(r,t)Z(r,t)\rangle$ and $[C_A(r,t) - \overline{C}(t)]^2$, influencing thereby the reaction kinetics.

Obviously, $C_A(t) \leqslant C^u(t)$ if $C_A(0) = C_B^u(0)$ and $dC^u/dt = -kS^u[C^u]$, with $S^u[C(t)] \leqslant S[C_A(r,t), Z(r,t)]$ for any distribution $C_A(r,t)$ that meets the condition

$$C_A(t) = C(t) = \frac{1}{V}\int C_A(r,t)\,dr. \quad (34)$$

The functional $S^u[C(t)]$ is equal to the rate of the reaction in a system in which the total number of particles A, equal to $C(t)$, is so distributed that the reaction rate is a minimum at a given distribution $Z(r,t)$. Minimizing the functional (33) with the additional condition (34), taking the identity $\int Z(r,t)dr = 0$ into account, we get

$$C_A(r,t) = C(t) + Z/2, \quad (35)$$

and consequently

$$dC^u/dt = -k\{[C^u(t)]^2 - \overline{Z^2(r,t)}/4\}. \quad (36)$$

Since $|\overline{dZ^2}/dt| \leqslant k(\overline{Z^2})^{3/2}$ as $t\to\infty$ for the systems considered in Refs. 5, 7, and 29, the asymptotic solution of (36) is determined by the function

$$C^u(t) = [\overline{Z^2(r,t)}]^{1/2}/2. \quad (37)$$

5. STATIC RECOMBINATION

An interesting particular case of the influence of fluctuations on the reaction kinetics is that of the kinetics of the static recombination of unlike particles. This problem is of importance in many applications, particularly for the investigation of the kinetics of annealing of point defects in solids. The process of static recombination is defined as follows. Let N particles A be initially located at the points R_i, and N particles B at the points $R_j, i,j = 1,2,...N$. After a short time interval $t \leqslant t' \leqslant t + dt$ each particle A (B) that has not reacted by the instant of time can react with a probability, with a particle B (A) that has not yet entered into a reaction, provided the distance between these particles is in the interval $l \leqslant l' \leqslant l + dl$. The reacting particles are removed from the system. We define τ_i (τ_j) as equal to unity if the particle A (B) initially located at the point R_i (R_j) had not reacted by the instant of time t, and as equal to zero if it did react. The probability that $\tau_i > 0$ ($\tau_j > 0$), which is the mean value of τ_i (τ_j) over the realizations of the random process of annihilation at fixed R_i and R_j, is equal to

$$\tau_i(t) = \exp\left(-\int_0^t dt' \sum_{j=1}^N \tau_j(t')\sigma[R_i - R_j]dt'\right), \quad (38a)$$

$$\tau_j(t) = \exp\left(-\int_0^t dt' \sum_{i=1}^N \tau_i(t')\sigma[R_j - R_i]dt'\right). \quad (38b)$$

In problems dealing with static annihilation at a sufficiently rapidly decreasing function $\sigma(l)$ [for example, in the most prevalent case of the exponential decrease $\sigma(l) = \sigma_0 e^{-l/a}$] an effective approximation is the so-called black-sphere approximation.[30,31] In the framework of this approximation, two particles A and B that have not entered into a reaction by the instant t and have respective centers at the points R_i and R_j, will react with each other within a time interval $t \leqslant t' \leqslant t + dt$ with unity probability if $|R_i - R_j| \leqslant R_t$, and will not react in the opposite case. The effective radius R_t of the black sphere is determined from the relation $t\sigma(R_t) = 1$.

An approximation of the mean-field type is equivalent for this problem to the assumption that the distribution of the reagent particles remains of the Poisson type during the reaction, (i.e., the correlations are neglected). In this approximation, the average density of the reagent obeys the equation

$$C_A(t) = C_A(0)\exp(-4\pi C_A R_t^d/3),$$

where $C_A(0)$ is the initial concentration. At large R_t, such that $C_A(0)R_t^d \gg 1$, we have in this approximation, with logarithmic accuracy,

$$C_A(t) \sim C_A(0)/R_t^d, \quad (39)$$

i.e., one reactant particle remains on the average in a volume with a linear dimension R_t. For an exponential decrease of $\sigma(l)$ we have

$$R_t \approx a\ln(\sigma_0 t), \qquad C_A(t) \approx [a\ln(\sigma_0 t)]^{-d}.$$

It can be shown that expression (39) describes correctly the asymptotic behavior of the annihilation of particles of like type, $A + A \to$ Product, whereas allowance for the fluctuations of the density in the case of a reaction between the particles A and B leads to a slower dependence. The random excess of one of the reactants in a d-dimensional sphere of radius R_t is proportional to $[V_d R_t^d \times C_A(0)]^{1/2}$, where V_d is the volume of the unit d-dimensional sphere. Reasoning similar to that presented above yields

$$C_A(t) \approx \frac{C_0^{1/2}}{R^{d/2}} \approx \frac{C_0^{1/2}}{[a\ln(\sigma_0 t)]^{d/2}} \quad (40)$$

in the limit $C_0[a\ln(\sigma_0 t)]^d \gg 1$.

6. REACTION OF THE A-MULTIPLICATION TYPE, OCCURRING IN A SYSTEM WITH DIFFUSING TRAPS

It is customarily assumed that in a system with a small parameter α the reaction of the particles A with mobile sinks B, for which $(D_B/D_A) \gg \alpha^{1/2}$, are correctly described in the Smoluchowski two-particle approximation. In this approximation, the density A in a system with multiplication and annihilation is given by

$$\rho(t) = \rho_0\exp[-(k_m - 4\pi aDn)t - (4\pi aDn\alpha t)^{1/2}] \quad (41)$$

accurate to terms small compared with Dt/a^2 in the argument of the exponential.

If the average multiplication rate k exceeds the average rate of annihilation in the traps, multiplication and an exponential growth of A take place in the system. Conversely, if the average annihilation rate is larger, the average density of A decreases exponentially. A nontrivial situation arises when the average annihilation rate is exactly equal to the average multiplication rate: $k_m = 4\pi Dan$. Expression (41) predicts in this situation a slower than the exponential, $\rho(t) = \rho_0 \exp[-(\alpha\tau)^{1/2}]$ particle vanishing. By analogy with the preceding sections, one should expect allowance for the fluctuations of the density of B to lead to an effective increase of the survival probability. It must be noted that fluctuations of the multiplication rate cannot compensate for the influence of the fluctuations of the annihilation rate, since they act on the asymptote $\rho(t)$ in one and the same direction. The probability of observing an A particle is higher in those sections of the system where the fluctuations lead to local increase of the multiplication rate and to local decrease of the annihilation rate.

In a system with mobile traps B, their diffusion causes the fluctuations of the density of B to become smeared out in a volume with linear dimension $l \sim (D_B t)^{1/2}$. The effective excess of the rate constant is therefore $4\pi aDn(\delta n/n)$, where $\delta(n)/n$ is the characteristic relative fluctuation of the density of B, equal on the average to $\delta(n)/n \sim (nl^d)^{-1/2}$ and having a Gaussian distribution. One can accordingly expect the effective annihilation rate constant to vary like $4\pi aDn[1-(\alpha/\tau)^{1/2}]$, and this will lead to a situation that is the converse of that predicted by (41), viz., a slow growth of the density of A is expected in a system with equal rates of multiplication and annihilation. We report below a more rigorous investigation of this situation.

A formally exact expression for the average density A in a system with mobile traps B (without multiplication) can be expressed in the form

$$\rho(t) = \rho_0 \left\langle E_A{}^0 \left\{ \prod_{j=1}^{N} E_B{}^{R_j} \left\{ \exp\left[-\int_0^t dt'\, V[x_A(t') - x_j(t')] \right]\right\}\right\}\right\rangle, \tag{42}$$

where $E_A^0\{F\}$ is an integral of the functional $F[x(t)]$, in a Wiener measure, of the trajectories of the particle A, with a diffusion coefficient D_A. The trajectories begin at the origin $x(0) = 0$, $E_B^{R_j}$ is an integral over the trajectories $x_j(t)$ of the jth B trap and start out from the point R_j, $x_j(0) = R_j$, and the angle brackets denote averaging over the Poisson distribution of the initial positions R_j of the traps, a distribution characterized by an average density n, ρ_0 is the initial density of A, $V(r) = 0$ at $|r| > a$, and $V(r) = \infty$ at $|r| < a$.

Averaging over the Poisson distribution for R_j yields

$$\rho(t) = \rho_0 E_A{}^0 \left\{ \exp\left(-nE_B \left\{ \int \left(\exp\left[-\int_0^t dt' V(x_A(t') - x_B(t') - R) \right] - 1 \right) dR \right\}\right)\right\}. \tag{43}$$

A very simple estimate with the aid of a Peierls-type inequality leads to the following inequality for $\rho(t)$:

$$\rho(t) \geqslant \rho_0 \exp\left[-nE_B{}^0 \left\{ E_A{}^0 \left\{ \int \left[\exp\left(-\int_0^t dt'\, V(x_A(t') - x_B(t') - R) \right) - 1 \right] dR \right\}\right\}\right]. \tag{44}$$

It can be shown with the aid of the Feynman-Kac formula that

$$E_A{}^0 \left\{ \mathbb{E}_B{}^0 \left\{ \exp\left[-\int_0^t V(x_A(t') - x_B(t') - R)\, dt' \right]\right\}\right\} = \int G(0, R; r, t)\, dr, \tag{45}$$

where $G(0,R; r,t)$ is the Green's function of Eq. (1) with corresponding boundary conditions and with the initial condition $\rho(r,t)|_{t=0} = \delta(r-R)$. It follows from the Gauss theorem and Eq. (45) that

$$E_A{}^0 \left\{ E_B{}^0 \left\{ \int \left[\exp\left[-\int_0^t dt'\, V(x_A(t') - x_B(t') - R) \right] - 1 \right] dR \right\}\right\} = \int_0^t dt'\, k(t'), \tag{46}$$

where $k(t')$ is the reaction rate constant calculated in accordance with the Smoluchowski procedure. Thus, the obtained Smoluchowski (mean-field) solution gives the lower bound of $\rho(t)$. It is of interest to note that in the limit as $D_A \to 0$ the path integral $E_A\{F[x_A(t)]\}$ tends to $f[x(0)]$ and the inequality (46) turns into an equality, i.e., in this limit the Smoluchowski solution yields the exact answer. In this limit, the fluctuations become equalized within a time t in a volume having a linear dimension $l \sim (D_B t)^{1/2}$, which is exactly equal to the linear dimension over which, according to Smoluchowski, an equilibrium effective depletion of the particles of one reactant takes place near a particle of the second reactant. At $D_A \neq 0$ there appears a second characteristic linear dimension, equal to $(D_A t)$. In the limit $D_A/D_B \to \infty$ the fluctuations of the density of B alter substantially the $\rho(t)$ asymptote as $t \to \infty$. In the intermediate situation $1 > D_B/D_A \gg \alpha^{1/2}$ large-scale small (Gaussian) fluctuations with characteristic dimension $(D_B t)^{1/2}$ become substantial.

The reaction rate in a system with traps whose density varies on account of diffusion processes is determined by the following system of equations:

$$\partial\rho(r,t)/\partial t = D\Delta\rho(r,t) - k_s\rho(r,t)C_B(r,t), \quad \partial C_B(r,t)/\partial t = D_B\Delta C_B(r,t), \tag{47a}$$

$$\rho(r,t)|_{t=0} = \delta(r), \quad C_B(r,t)|_{t=0} = n_0(r), \tag{47b}$$

where $n_0(r)$ is a Gaussian δ-correlated field with mean value n. Equation (47a) with a static Gaussian potential $C_B(r)$ and a Gaussian potential that evolves in accordance with laws that differ from (47b) was recently investigated in Refs. 32 and 33.

The solution of the set (47) can be expressed with the aid of the following integral over the paths of the particle A:

$$\rho(t)=\overline{\rho(r,t)}=\exp\left(-n\int_0^t k_s\,dt\right)C(t),$$

$$C(t)=E_A{}^0\left\{\exp\left[k_s{}^2n\int_0^t dt_1\int_0^{t_1} dt_2\,G_B(x_A(t_1)-x_2(t_2),t_1+t_2)\right]\right\},\tag{48}$$

where

$$G_B(r,t)=e^{-r^2/4D_Bt}[2(\pi D_Bt)^{1/2}]^{-1}.$$

The simplest lower-bound estimate for $C(t)$ is obtained with the aid of an inequality of the Peierls type:

$$C(t)\geqslant\exp\left\{k_s{}^2nE_A{}^0\left[\int_0^t dt_1\int_0^{t_1} dt_2\,G_2(x_A(t_1)-x_A(t_2),t_1+t_2)\right]\right\},$$

and consequently, at $k_s=4\pi a(D_A+D_B)$ we have

$$\ln C(t)\geqslant\frac{2an(D_A+D_B)^2}{D_B-D_A}\left(\frac{t}{\pi}\right)^{1/2}\left[\frac{1}{(D_A+D_B)^{1/2}}-\frac{1}{(2D_B)^{1/2}}\right].\tag{49}$$

The estimate (49 is quite crude, but it does indicate the range of parameters in which the system (47) with constant reaction-rate constants describes satisfactorily the kinetics of the investigated reaction. The nonstationary term in the right-hand side of (49) exceeds the stationary term in the Smoluchowski expression (3) for the rate constant at $D_A>D_B$, i.e., one should expect the sytem (47) to be correct if the diffusion coefficient of the particles A is not less than the diffusion coefficient of the traps.

An exact lower bound for $C(t)$ can be obtained with the aid of the variational inequality

$$C(t)\geqslant E_A{}^0\{\exp(-H_t[x_A(t)])\}\exp(-\langle\Delta H\rangle),\tag{50}$$

$$\langle\Delta H\rangle=E_A{}^0\left\{\exp\left(-H_t[x_A(t)]\right)\left[k_s{}^2n\int_0^t dt_1\int_0^{t_1} dt_2\,G_B(x_A(t_1)-x_A(t_2),t_1+t_2)-H_t[x_A(t)]\right]\right\}.$$

Choosing the trial Hamiltonian in the form

$$H_t=\sigma_t{}^{-1}\int_0^t x_A{}^2(t')\,dt',$$

where σ_t has a parametrically monotonic dependence on the time, such that

$$\lim_{t\to\infty}\frac{D_Bt}{\sigma_t^2}=\infty,\qquad\lim_{t\to\infty}\frac{\sigma_t^2}{D_At}(k_st)^{\varepsilon}=\infty\qquad\text{for any}\qquad\varepsilon>0,$$

we obtain

$$\langle H_t[x_A(t)]\rangle+\ln E_A\{\exp(-H_t[x_A(t)])\}\approx D_At/\sigma_t{}^2,$$

$$k_s{}^2n\left\langle\int_0^t dt_1\int_0^{t_1} dt_2\,G_B(x_A(t_1)-x_A(t_2),t_1+t_2)\right\rangle=8(\pi/2)^{1/2}(2^{1/2}-1)a^2(D_A+D_B)^2D_B^{-3/2}t^{1/2},$$

and consequently

$$\ln C(t)\geqslant2\frac{2^{1/2}-1}{2}\left(\frac{D_A+D_B}{D_B}\right)^{3/2}\left(\frac{\alpha\tau}{\pi}\right)^{1/2},$$

$$\text{where}\quad\tau=4\pi(D_A+D_B)ant.\tag{51}$$

The upper-bound estimate is obtained directly. Obviously,

$$G_B[x_A(t_1)-x_A(t_2),t_1+t_2]\leqslant G_B(0,t_1+t_2)$$

and consequently

$$C(t)\leqslant\exp\left[k_s{}^2n\int_0^t dt_1\int_0^{t_1} dt_2\,G_B(0,t_1+t_2)\right]=\exp\left[2\frac{2^{1/2}-1}{D_B}\left(\frac{D_A+D_B}{D_B}\right)^{3/2}\left(\frac{\alpha\tau}{\pi}\right)^{1/2}\right].\tag{52}$$

The estimates (51) and (52) coincide; consequently the function

$$\rho(t)=\exp\left[-\tau+(2-2^{1/2})\left(\frac{D_A+D_B}{D_B}\right)^{3/2}\left(\frac{\alpha\tau}{\pi}\right)^{1/2}\right]\tag{53}$$

is an asymptotically exact solution of the system (47), a solution of independent interest regardless of the problem considered here. If the average rates of multiplication and annihilation by the traps are equal, $k_mt=\tau$, the average density of the particles A in the system is determined by the second term in the argument of the exponential of Eq. (53).

CONCLUSION

In the first three sections of this paper we constructed a perturbation theory that describes the survival probability of a particle diffusing in a system with immobile traps. The Smoluchowski intermediate asymptotic corresponds to free diffusion of particles with mean-squared displacement $R^2\sim D_At$ or else to a continuous spectrum in the language of the problem of an electron in a random medium with repelling impurities. The long-time asymptotic is determined by localized states with $R^2\sim(D_At)^{2/(d+2)}$ [see Eq. (26)]. These states correspond to a particle A that did not leave even once a spherical region having a size R and containing not even one trap. The perturbation theory developed in the paper for small α converges both in the region of deep local levels and in a continuous spectrum far from its boundary. The region in which the perturbation theory diverges is a narrow interval near the boundary of the continuum—the mobility threshold. The states close to the threshold at small α make a small contribution to the survival probability in the entire time interval. The rate of establishment of the asymptotic regime is given by the expression

$$\ln\rho(\tau)=-c_1\tau^{3/5}\alpha^{-1/5}[1-c_2(\alpha\tau^2)^{-1/10}].$$

The region of Gaussian fluctuations on the boundary of the continuous and discrete spectra is important not for the problem of survival in a medium with traps, but for the localization problem. In terms of the latter, the perturbation theory developed in the first section predicts a nontrivial time dependence of the mean squared displacement of a particle having an energy equal to the mobility threshold, $R^2\sim(D_At)^{1/2}$. This dependence is not an exact answer, but points to the existence of a scaling region and has a lucid physical meaning.

For the problem of diffusion with multiplication and annihilation by immobile traps, the diagram technique developed in this paper makes it possible to express in explicit form the time dependence of the reagent density accurate in first order in α. If the average multiplication rate is less than the average rate of annihilation in traps, $k_m < 4\pi D_A a n$, this dependence is not monotonic. During the initial stage, the density decreases to a small value $\gamma = \exp(-\pi^3/24\alpha^{1/2})$ that obeys the formally kinetic law

$$C(t) = C(0)\exp[-(4\pi a D_A n - k_p)t].$$

After long times, a "burst" takes place in the system, an exponential increase of the density in the form $C(t) = \gamma\exp(k_m t)$, and the corresponding li induction time T_1 is long in systems with small α: $T_1 = (4\pi a D_A n \alpha^{1/2})^{-1}$.

The possibility of a nontrivial change of the reaction kinetics with temperature must also be pointed out. If the activation energy of the diffusion coefficient of particles A is much lower than the activation coefficient of the diffusion of particles B, it may turn out that $D_A/D_B \ll \alpha^{-1/2}$ at high temperatures and $D_A/D_B \gg \alpha^{-1/2}$ at low ones. If $k_m < 4\pi a D_A n$, the trap diffusion at high temperatures will smooth out the fluctuation effects, and only an exponential decrease of the density of the particles A will be observed in the system. At low temperatures, when the particles B can be regarded as immobile, a "burst" at long times should be observed in the system at the same ratio of the average multiplication energy and average annihilation rate. Note that at $D_A \gg D_B$ the quantity D_B does not enter at all in the formal-kinetics equations.

In contrast to the reaction in a system with immobile traps, for which an important role is played at long times by the Poisson character of the distribution of one of the reactants, in a system with diffusing traps $D_A/D_B \ll \alpha^{-1/2}$ the decisive role is played by Gaussian density functions. Reactions of the recombination type do not alter the local concentration difference $Z(r,t)$ of A and B (Refs. 4 and 5), and this difference evolves only as a result of diffusion processes. For a number of cases of practical importance,[4–7,29,34] the moments of the distribution $Z(r,t)$ can be accurately calculated in explicit form. In Sec. 4 of this paper we have shown that if the derivative

$$|\overline{dZ^2(r,t)}/dt| \ll [\overline{Z^2(r,t)}]^{1/2} \text{ and } |\overline{Z(r,t)}/[\overline{Z^2(r,t)}]^{1/2}| = \text{const}$$

as $t \to \infty$, the function $C(t) \approx [Z^2(r,t)]^{1/2}/2$ describes asymptotically correctly the kinetics of the reaction. For the problems investigated in Refs. 4–7, 29, and 34, this condition is met. For instantaneous independent generation of A and B we have $C(t) \sim t^{-d/4}$ (Refs. 4–7), and in the case of generation by a stationary source[29] we have $C(t) \sim t^{-1/4}$ at $d = 3$. The analysis, presented in Sec. 5, of the asymptote of the reaction of static recombination, with an exponential distribution of the reaction probability over the distances, yields $C(t) \sim (\ln t)^{-d/2}$.

In the sixth section, the average density $\rho(t)$ of a reactant diffusing in a system with mobile traps is formally exactly expressed in terms of a path integral. It is shown that the two-particle Smoluchowski approximation yields the lower bound of $\rho(t)$. An asymptotically exact expression was obtained for the survival probability of a particle that diffuses in an absorbing medium in which the absorption probability obeys the diffusion equation and has initially a Gaussian δ-correlated distribution. In systems in which the average rates of multiplication and annihilation on mobile traps are equal, and in which $k_m = 4\pi a(D_A + B_B)n$ and $D_A > D_B$, the solution obtained predicts a slow growth of the average density in accordance with the relation

$$\ln\rho(t) \approx (2 - 2^{1/2})\left(\frac{D_A + D_B}{D_B}\right)^{1/2}\left(\frac{\alpha\tau}{\pi}\right)^{1/2},$$

whereas the Smoluchowski two-particle approximation predicts a decrease like $\ln\rho(t) = -2(\alpha\tau/\pi)^{1/2}$. For systems with moving traps, the induction period needed to reach the fluctuation regime is equal to $T_2 = [4\pi a(D_A + D_B)n\alpha]^{-1}$.

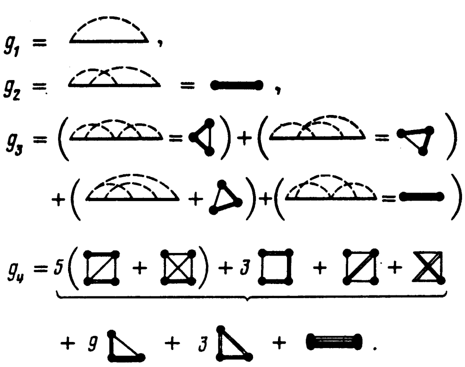

FIG. 4. Graphs corresponding to first corrections to the mass operator.

APPENDIX

Figure 4 shows several irreducible graphs that make a contribution $g(\lambda)$ to the mass operator in Eq. (14). The contribution of the first graph is

$$g_1 = Z - (\alpha\lambda')^{1/2},$$

where

$$\lambda' = \lambda/4\pi n D a, \quad (\alpha\lambda)^{1/2} = \varkappa a, \quad Z = \{\alpha[\lambda' + \exp(\alpha\lambda')]\}^{1/2}.$$

The second term in the expression for g_1 is cancelled by the corresponding term that appears when $e^{\varkappa a}$ is expanded in the expression for x; this lead to Eq. (15a) for the first approximation in $\rho(\lambda)$.

The contribution of the second irreducible diagram diverges logarithmically for small r. Allowance for effects of the excluded-volume type, in which the particle A was initially unable to be present in a volume occupied by traps, as well as in the fact that the traps do not overlap in space, lead to cutoff at small r, which yields

$$g_2 = \alpha\,\mathrm{Ei}(-3Z)\exp[(\alpha\lambda^{1/2})],$$

where Ei is the integral exponential function.

With the excluded volume taken into account we have

$$g_3 = -Z^{-1}\alpha^2\exp[2(\alpha\lambda')^{1/2}]\int d^3k\,\mathrm{arctg}^2\left[\frac{k}{2(k_2+1)}\right] + \alpha\exp[(\alpha\lambda')^{1/2}][\exp(-4Z) + Z\,\mathrm{Ei}(Z)].$$

The leading terms of g_4 as $Z \to 0$ are equal to

$$g_4 = \text{const}\, Z^{-2}\{\alpha\exp[(\alpha\lambda')]\}^3.$$

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