Fluctuation kinetics in systems with reversible recombination

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The authors investigate the kinetics and the spectrum of the density correlators for reversible and irreversible bimolecular processes with the participation of neutral and charged particles in systems in which the reagents are generated in different ways. Explicit forms are obtained for the intermediate asymptotic forms (mean-field solutions) and long-time asymptotic forms due to fluctuation effects.

There has recently been a sharp increase in interest in many-particle aspects of the theory of diffusion-controlled reactions. This is explained, on the one hand, by the growing number of applications in physics, chemical physics, and biology,[1,2] and, on the other hand, by the fact that this has now taken its place among related problems in statistical physics in which the fluctuation behavior of the systems is important.[3,4] One should also mention the large number of investigations of fractal systems with developed fluctuation structure,[5,6] in which the kinetics of the diffusion-controled reactions[7] both determines the rate of growth and the geometrical characteristics of the systems being formed and also provides a specific way of investigating their topological properties.

Until the appearance of Refs. 8–11 it was assumed that after a time $\tau = L^2/D$, where L is the characteristic length scale of the spatial nonuniformity of the distribution of the reagents and D is the diffusion coefficient, a steady-state regime is established in which the kinetics of the bimolecular reaction does not depend on the initial conditions. In this approximation (the mean-field approximation, which ignores density fluctuations) the kinetics of a bimolecular irreversible reaction $A + B \rightarrow C$ in the final stage (at times $t > t_A$, where $t_A = [k_s n(0)]^{-1}$, k_s being the effective rate constant of the reaction) is determined for a nonstoichiometric initial mixture of reagents by an exponential dependence of the density $n(t)$ of the reacting particles on the time, and in the stoichiometric case by a power law

$$n(t)=\left[\int_0^t k_s(\tau)\,d\tau\right]^{-1}.$$

For a reversible reaction the mean-field approximation predicts exponential relaxation of the mean density to the equilibrium value.

The influence of Poisson density fluctuations on the long-time kinetics of a reaction involving destruction at stationary traps (the reaction $A + B \rightarrow B$, in which the mean density of the stationary traps B is much greater than the mean density of A) was investigated for the first time in Refs. 8 and 10. It was shown that in the final stage of the reaction the density of particles of A is determined by the regions with an anomalously low density of the traps B.

For a bimolecular two-component irreversible reaction $A + B \rightarrow C$ in which A and B are uncharged particles diffusing in the volume, in the case when the densities of A and B are equal on the average $(n_A(t) = n_B(t))$, the presence of thermodynamic fluctuations of the density also leads to slowing down of the reaction rate in comparison with that predicted by mean-field approximations and at large t the mean density is determined by the dependence $n(t) \propto t^{-d/4}$, where d is the dimensionality of space. This result was obtained first in Refs. 9 and 10, and also in Ref. 11, and has been reproduced subsequently in a number of papers.[12–15] In the case of a one-component bimolecular irreversible reaction $A + A \rightarrow B$ (Refs. 16,17) and two-component irreversible recombination of charged particles,[9,18,19] fluctuation effects are found to be suppressed and the long-time kinetics of the reactions is determined by the mean-field dependence. For a reversible one-component reaction $A + A \leftrightarrow B$ (Ref. 20) and a reversible two-component reaction $A + B \leftrightarrow C$ (Ref. 21), small spatial density fluctuations, which can be assumed to be Gaussian, determine the long-time relaxation to the equilibrium value, and $\delta n(t) \propto t^{-d/2}$, in contrast to the exponential dependence obtained in the mean-field approximation.

Depending on the way in which the reagents are generated, the reaction system is characterized by different initial spectra of the density fluctuations. For instantaneous generation, when the generation time satisfies $t_g \ll t_A$, the long-wavelength part of the fluctuation spectrum is flat, i.e., the initial density fluctuations are δ-correlated. The results in Refs. 9–15 were obtained for precisely such systems. Fluctuation effects are substantially enhanced in a system prepared by a steady-state external source.[12,18] If the particles of A and B are generated randomly and independently of each other, with a constant mean rate I, in the reaction volume, the process of the irreversible reaction leads to the appearance of correlations in the distributions of the reagents. The long-wavelength asymptotic form of the fluctuation spectrum changes,[12,13,18,22] and this leads to a change of the long-time kinetics of the irreversible two-component reaction after the source is switched off: $n(t) \propto t^{-1/4}$ for $d = 3$ (Refs. 12,18). For one-dimensional and two-dimensional systems the presence of a nonintegrable singularity in the fluctuation spectrum signals the separation of the reaction volume into macroscopic regions containing only one of the reagents.[18,12,13,23] This effect has been observed in a numerical experiment for $d = 1,2$ (Refs. 24,25) and for fractal systems in Ref. 26.

In the present paper, using the method (analogous to that proposed in Ref. 11) of decoupling of fourth-order correlation functions into a product of pair correlators of the density, we investigate the fluctuation kinetics and the spectrum of the density correlators for reversible two-component and one-component reactions with the participation of neutral and charged reagents in systems in which the particles are generated in different ways.

In Ref. 27 it was shown that in problems related to those investigated in the present paper (systems with a bimolecular reaction of particles present with equal mean densities, for which the long-time asymptotic form of the time dependence of the mean density is determined by small Gaussian fluctuations) the method of Ref. 11 leads to results that are asymptotically exact at large times. Here, in the long-time dependence $n(t) = bt^{-\nu}$ the exponent ν is determined exactly, while the coefficient b is determined to within a constant numerical factor of order unity. In the present paper it is shown that allowance for the singular part of the third-order correlators, which is due to the spatial coincidence of two particles of the same kind in three-particle interactions, leads to a renormalization of the rate constants of the forward and backward reactions in the equation determining the evolution of the mean density. The method of Ref. 11, improved in this manner, reproduces for moderate values of t the intermediate asymptotic forms of the Smoluchowski type[28] (or of the Debye type,[29] for charged particles) in systems of any dimensionality. These asymptotic forms can be obtained in mean-field approximations (effective-medium theory, summation of no-loop diagrams, perturbation-theory series, single-site t-matrix theory, and other equivalent approxmations).[28–32]

In this paper we obtain a number of new results on the fluctuational long-time asymptotic behavior for reversible reactions of neutral particles in systems with a stationary source and for reversible reactions involving charged particles, and also find dependences describing the rates of reactions occurring on fractal structures in parallel with the generation of particles of the reagents.

1. EVOLUTION EQUATIONS FOR THE MEAN DENSITIES AND DENSITY CORRELATORS: NEUTRAL REAGENTS

We shall consider the influence of density fluctuations on the kinetics of the bimolecular reversible recombination of classical uncharged particles undergoing diffusion. When particles of the reagents come within a distance a of each other (the reaction radius, equal to the sum of the radii of the reacting particles) they can recombine, with a nonzero probability that determines the "true" rate constant k of the forward reaction. The rate of the reverse process (the dissociation of the reaction product C into a pair of reagents A and B, produced at a distance a from each other) is determined by the rate constant k_- of the backward reaction.

The change of the local density of the reagents as a consequence of the forward and backward reactions, and also as a consequence of diffusion, is determined by the equation

$$\dot{n}_i(\mathbf{r},t)=-k\gamma_d(a)\int d\mathbf{r}_1\delta(|\mathbf{r}-\mathbf{r}_1|-a)\,n_A(\mathbf{r},t)\,n_B(\mathbf{r}_1,t)+D_i\Delta n_i(\mathbf{r},t)+k_-n_C(\mathbf{r},t)+L_i(\mathbf{r},t), \tag{1}$$

where $\gamma_3=(4\pi a^2)^{-1}$, $\gamma_2=(2\pi a)^{-1}$, $\gamma_1=1$, the index i takes the values A and B, and $L_i(\mathbf{r},t)$ is a term describing the fluctuations of the diffusion current.[2] The change of the local density of the products C of the forward reaction obeys the condition of conservation of the total number of reacting particles in an elementary reaction event:

$$2n_C(\mathbf{r},t)+n_A(\mathbf{r},t)+n_B(\mathbf{r},t)=\text{const}.$$

Henceforth we shall consider only the case of equal diffusion coefficients $D_A=D_B=D_C=D/2$.

We write the densities of the reacting particles in the form of a sum

$$n_i(\mathbf{r},t)=n(t)+\sigma_i(\mathbf{r},t),\quad n_C(\mathbf{r},t)=n_C(t)+\sigma_C(\mathbf{r},t),$$

where $n(t)$ and $n_C(t)$ are averages over the volume and the σ_i are random deviations from the average. Averaging Eq. (1) over the volume, for $n(t)$ we obtain

$$\dot{n}(t)=-k\Big[n^2(t)+\gamma_d(a)V^{-1}\iint d\mathbf{r}\,d\mathbf{r}_1\delta(|\mathbf{r}-\mathbf{r}_1|-a)\times\sigma_A(\mathbf{r},t)\sigma_B(\mathbf{r}_1,t)\Big]+k_-n_C(t),\quad \dot{n}(t)+\dot{n}_C(t)=0, \tag{2}$$

where V is the volume of the system. Correspondingly, the equations for the change with time of the random deviations have the following appearance:

$$\dot{\sigma}_i(\mathbf{r},t)={}^1\!/_2D\Delta\sigma_i(\mathbf{r},t)-k\gamma_d(a)\int d\mathbf{r}_1\delta(|\mathbf{r}-\mathbf{r}_1|-a)\times\Big\{n(t)[\sigma_A(\mathbf{r},t)+\sigma_B(\mathbf{r}_1,t)]+\sigma_A(\mathbf{r},t)\sigma_B(\mathbf{r}_1,t)-V^{-1}\times\int d\mathbf{r}\sigma_A(\mathbf{r},t)\sigma_B(\mathbf{r}_1,t)\Big\}+L_i(\mathbf{r},t)-V^{-1}\int d\mathbf{r}\,L_i(\mathbf{r},t). \tag{3}$$

We define the pair correlation functions:

$$G_{ij}(\lambda,t)=V^{-1}\iint d\mathbf{r}\,d\mathbf{r}_1\,\delta(\mathbf{r}-\mathbf{r}_1-\lambda)\,\sigma_i(\mathbf{r},t)\sigma_j(\mathbf{r}_1,t),$$

where λ is a d-dimensional correlation parameter. The following system of equations is valid for $G_{ij}(\lambda,t)$:

$$\dot{G}_{ij}=-kn(t)[G_{Ai}+G_{Bi}+G_{Aj}+G_{Bj}]+D\Delta G_{ij}+k_-[G_{iC}+G_{jC}]-\delta_{ij}Dn(t)\Delta\delta(\lambda)-k[T_{ABj}+T_{ABi}];\quad i,\ j\neq C, \tag{4a}$$

$$\dot{G}_{jC}=kn(t)[G_{Aj}+G_{Bj}-G_{AC}-G_{BC}]+k_-[G_{CC}-G_{jC}]+D\Delta G_{jC}-k[T_{ABC}-T_{ABj}],\quad j\neq C, \tag{4b}$$

$$\dot{G}_{CC}=2kn(t)[G_{AC}+G_{BC}]-2k_-G_{CC}+D\Delta G_{CC}-Dn_C(t)\Delta\delta(\lambda)+2kT_{ABC}, \tag{4c}$$

where δ_{ij} is the Kronecker symbol and the T_{ijk} are third-order correlators. In Appendix II the third-order correlators are represented in the form of the sum of a fluctuation part τ_{ijk} and a regular part $\widetilde{T}_{ijk}$ Under certain assumptions about the structure of the fourth-order correlation functions (see Appendix II) the fluctuation part of the third-order correlators is identically equal to zero. The regular part arises when the discreteness of the density distributions of the reagents is taken into account. Allowance for the discreteness leads to the appearance of short-wavelength pair correlations, which, in their turn, lead to renormalization of the rate constants of the forward and backward reactions in the equation (2) for the evolution of $n(t)$:

$$\dot{n}(t)=-k_s[n^2(t)+g_{AB}(a,t)]+k_-^{s}n_C(t),$$

$$k_s=\frac{kk_d}{k+k_d},\quad k_-^{s}=\frac{k_-k_d}{k+k_d}, \tag{5}$$

where $k_3=4\pi Da$, $k_2=4\pi D/\ln(Dt/a^2)$, $k_1=(D/\pi t)^{1/2}$, and $g_{AB}(a,t)$ is the fluctuation part of the pair correlator $G_{AB}(a,t)$.

The regular and the fluctuation parts have a different origin and a different physical meaning. The former take into account the decrease of the density of one of the reagents near each of the particles of the other reagent. The fluctuation parts of the pair correlators take into account the depletion of particles of A (B) near parts of the system (large in comparison with the average spacing between the particles) in which the continuum local density of B (A) is larger than the average.

The fluctuational long-time asymptotic forms that are investigated in the present paper are connected with the long-wavelength singularities of the spectrum of the fluctuation parts of the correlators that determine the behavior of the mean density (5). The short-wavelength region of the spectrum of $g_{AB}(a,t)$, generally speaking, should be cut off at length scales l that exceed the mean interparticle spacing $\bar{l} \sim n^{-1/d}$, which depends parametrically on the time if the density is changing with time. In the systems under consideration it is always possible to choose l so that $(Dt)^{1/2} \gg l \gg \bar{l}$. The results are then practically independent of l; the corrections containing l are small in the gas parameter and, simultaneously, in the ratio $\bar{l}/l$. Below, such corrections are not given, and the cutoff of the short-wavelength part of the spectrum is not stipulated. We note that the renormalized rate constants of the forward and the backward reaction—the so-called "observable" constants—also do not appear in any long-time asymptotic dependence.

The fluctuation parts of the pair correlators of the density obey the following system of equations, which, together with (5), completely determines the kinetics of the reaction under consideration:

$$\dot{g}_{AA} = -2kn(t)(g_{AA}+g_{AB}) + 2k_- g_{AC} + D\Delta g_{AA} - Dn(t)\Delta\delta(\lambda), \tag{6a}$$

$$\dot{g}_{AB} = -2kn(t)(g_{AA}+g_{AB}) + 2k_- g_{AC} + D\Delta g_{AB}, \tag{6b}$$

$$\dot{g}_{AC} = kn(t)(g_{AA}+g_{AB}-2g_{AC}) + k_-(g_{CC}-g_{AC}) + D\Delta g_{AC}, \tag{6c}$$

$$\dot{g}_{CC} = 4kn(t)g_{AC} - 2k_- g_{CC} + D\Delta g_{CC} - Dn_C(t)\Delta\delta(\lambda). \tag{6d}$$

2. KINETICS OF BIMOLECULAR REVERSIBLE REACTIONS $A+B \leftrightarrow C$ and $A+A \leftrightarrow B$ WITH INSTANTANEOUS GENERATION OF THE REAGENTS

We shall consider a few types of initial conditions for the system of equations (6). In the case of instantaneous generation of uncorrelated reagents, when particles of A and B (C) are injected rapidly into the system with a constant mean density $n(0)$ ($n_C(0)$) and with statistically independent fluctuations, the initial distribution of the reagents can be assumed to be Gaussian δ-correlated:

$$g_{ij}(\lambda, 0) = n_i(0)\delta_{ij}\delta(\lambda); \quad i, j = A, B, C.$$

In the case of instantaneous generation of the reagents A and B in correlated pairs, when A and B are created at a fixed distance λ_g from each other, the initial fluctuations of the densities of A and B are not statistically independent and the fluctuation parts of the pair correlators are equal to

$$g_{AB}(\lambda, 0) = n(0)\gamma_d(\lambda_g)\delta(|\lambda|-\lambda_g), \quad g_{ii}(\lambda, 0) = n_i(0)\delta(\lambda),$$

$$g_{iC}(\lambda, 0) = 0.$$

This case is especially important, since, as a rule, this is precisely the way in which defects and vacancies, electrons and holes, and radical pairs are generated.

For instantaneous generation of statistically independent particles we obtain from (6) the following expression for the Fourier transform of the pair correlator $g_{AB}(\lambda,t)$ (we give only the long-time leading terms, and omit the terms that decrease exponentially with time):

$$g_{AB}(p, t) = g_{AB}(p) - {}^1\!/_2\Delta n(1+\bar{k}_-^2 t_{AB}^2)\exp(-Dtp^2), \tag{7}$$

where $\Delta n = n(0) - n_A$, $t_{AB} = (2kn_A + k_-)^{-1}$, n_A is the steady-state solution of Eq. (5), and

$$g_{AB}(p) = -\frac{2kn_A^2 t_{AB}}{2+Dt_{AB}p^2} + 2k_- t_{AB}^2(k_- n_C - kn_A^2)$$
$$\times[(1+Dt_{AB}p^2)^{-1} - (2+Dt_{AB}p^2)^{-1}]. \tag{8}$$

The expression (8) determines the fluctuation corrections (calculated previously in Ref. 18) to the mean-field equilibrium constant.

Correspondingly, it follows from Eq. (5) that in the final stage of the reaction ($t \to \infty$) the relaxation of the density of the reagents A and B to the equilibrium value n_A is determined by fluctuation effects

$$\delta n(t) = -kt_{AB}\delta g_{AB}(a, t)$$

and is described by the power dependence

$$\delta n(t) = \frac{kt_{AB}}{2}(1+k_-^2 t_{AB}^2)\Delta n(Dt)^{-d/2},$$

whereas the mean-field approximation (Eq. (5) with $g_{AB} \equiv 0$) predicts a more rapid dependence:

$$\delta\bar{n}(t) = \Delta n \exp\left\{-\int_0^t d\tau[2n_A k_s(\tau) + k_-^s(\tau)]\right\}.$$

For instantaneous generation of correlated pairs of particles the long-time relaxation of the mean density to the equilibrium value is determined by the following expression:

$$\delta n(t) = -\frac{kt_{AB}}{2}(1+k_-^2 t_{AB}^2)(n_A - n(0)\lambda_g^2/Dt)(Dt)^{-d/2}.$$

We note that, depending on the relationship between the initial value of the mean density of the reagent A and the equilibrium constant k_p ($k_p = k_-/k$), the density $n(t)$ can be a nonmonotonic function of the time, since for $t \to \infty$ we have $\delta n(t) < 0$ independently of the value $n(0)$.

For an irreversible reaction $A + B \to C$ it follows from the above expressions for $g_{AB}(p,t)$ and Eq. (5) (for $k_- = 0$) that in the case of instantaneous generation of uncorrelated reagents[9–11,14,15]

$$n(t) = (n(0)/2)^{1/2}(Dt)^{-d/4},$$

while in the case of generation as correlated pairs

$$g_{AB}(a, t) \sim -t^{-(d+2)/4},$$

i.e., the density correlator falls off more rapidly than the square of the mean-field dependence (the solution of Eq. (5) with $g_{AB} \equiv 0$ and $k_- = 0$ has the form $\bar{n}_1(t) \sim t^{-1/2}$, $\bar{n}_2(t) \sim (\ln t)/t$, $\bar{n}_3(t) \sim 1/t$). Accordingly, the fluctuation effects in this case are found to be suppressed, and the long-time kinetics of the irreversible reaction is described by the mean-field approximations.

For the one-component reversible reaction

$$\mathrm{A}+\mathrm{A}\leftrightarrow\mathrm{B} \tag{9}$$

the change of the local density of reagent A is determined by the equation

$$\begin{gathered}\dot n_A(\mathbf{r},t)=-k\gamma_d(a)\int d\mathbf{r}_1\delta(|\mathbf{r}-\mathbf{r}_1|-a)\,n_A(\mathbf{r},t)\,n_A(\mathbf{r}_1,t)\\ +D_A\Delta n_A(\mathbf{r},t)+k_-n_B(\mathbf{r},t)+L_A(\mathbf{r},t),\\ n_A(\mathbf{r},t)+2n_B(\mathbf{r},t)=\mathrm{const.}\end{gathered}$$

For the fluctuation part of the pair correlators and the mean density we obtain the following system of equations:

$$\dot g_{AA}=-4kn(t)g_{AA}+2k_-g_{AB}+D\Delta g_{AA}-Dn(t)\Delta\delta(\lambda), \tag{10a}$$

$$\dot g_{AB}=kn(t)(g_{AA}-2g_{AB})+k_-(g_{BB}-{}^1/{}_2g_{AB})+D\Delta g_{AB}, \tag{10b}$$

$$\dot g_{BB}=2kn(t)g_{AB}-k_-g_{BB}+D\Delta g_{BB}-Dn_B(t)\Delta\delta(\lambda), \tag{10c}$$

$$\dot n(t)=-k_s[n^2(t)+g_{AA}(a,\ t)]+k_-^sn_B(t),\quad \dot n(t)+2\dot n_B(t)=0, \tag{11}$$

where k_s and k^s_- are the same as for the two-component reversible reaction.

In the case of instantaneous generation of A the $t\to\infty$ leading terms in the Fourier transform of $g_{AA}(\lambda,t)$ are equal to

$$g_{AA}(p,t)=g_{AA}(p)-\Delta nk_-^2t_{AA}^2\exp(-Dtp^2),$$

where $t_{AA}=(4kn_A+k_-)^{-1}$, n_A is the steady-state solution of (11), and

$$\begin{gathered}g_{AA}(p)=n_A-\frac{4kn_A^2t_{AA}}{1+Dt_{AA}p^2}+4k_-t_{AA}^2(k_-n_B-kn_A^2)\\ \times\left[\left(\frac{1}{2}+Dt_{AA}p^2\right)^{-1}-(1+Dt_{AA}p^2)^{-1}\right].\end{gathered} \tag{12}$$

Accordingly, the long-time relaxation of the mean density of reagent A to the steady-state value is determined by the dependence

$$\delta n(t)=kk_-^2t_{AA}^3\Delta n(Dt)^{-d/2}. \tag{13}$$

We note that in the expression for $g_{AA}(p,t)$ and the corresponding expression for $\delta n(t)$ passage to the limit $k_-\to0$ leads to an incorrect result, since in (13) we omitted terms containing the exponential factor $\exp(-4kn_At)$. In the case of the irreversible reaction A + A→B the course of the reaction leads to the suppression of fluctuation effects, and the long-time kinetics of the irreversible reaction is determined by the mean-field dependence. For one-dimensional systems an analogous result has been confirmed by an exact calculation.[17]

We shall consider the case of practical importance in which the particles A and B have charges q and $-q$, respectively. In this case, the equations for the local changes of the densities of A and B have the form

$$\begin{gathered}\dot n_A(\mathbf{r},t)=-k\gamma_d(a)\int d\mathbf{r}_1\delta(|\mathbf{r}-\mathbf{r}_1|-a)\,n_A(\mathbf{r},t)\,n_B(\mathbf{r}_1,t)\\ +D_A\Delta n_A(\mathbf{r},t)+k_-n_C(\mathbf{r},t)+L_A(\mathbf{r},t)-\frac{D_Aq}{T}\\ \times\operatorname{div}(n_A(\mathbf{r},t)\nabla\Phi(\mathbf{r},t)),\end{gathered} \tag{14a}$$

$$\begin{gathered}\dot n_B(\mathbf{r},t)=-k\gamma_d(a)\int d\mathbf{r}_1\delta(|\mathbf{r}-\mathbf{r}_1|-a)\,n_A(\mathbf{r},t)\,n_B(\mathbf{r}_1,t)\\ +D_B\Delta n_B(\mathbf{r},t)+k_-n_C(\mathbf{r},t)+L_B(\mathbf{r},t)+\frac{D_Bq}{T}\\ \times\operatorname{div}(n_B(\mathbf{r},t)\nabla\Phi(\mathbf{r},t));\end{gathered} \tag{14b}$$

in which the potential $\Phi(\mathbf{r},t)$ obeys the Poisson equation

$$\Delta\Phi(\mathbf{r},t)=-\frac{4\pi q}{\varepsilon}[n_B(\mathbf{r},t)-n_A(\mathbf{r},t)],$$

where ε is the dielectric permittivity of the medium.

It is easy to see that in systems with small deviations from the mean density, in the absence of an external field, the quantity $\nabla\Phi\cdot\nabla n(\mathbf{r},t)$ is, on the average, small in comparison with $n(\mathbf{r},t)\Delta\Phi(\mathbf{r},t)$, since the former is quadratic in $\sigma(\mathbf{r},t)$ while the latter is linear.[33] For the system considered in this paper, at large t the relative deviations from the mean cease to be small, and, it would appear, there are no grounds for neglecting terms quadratic in $\sigma(\mathbf{r},t)$ (which is precisely equivalent to neglecting the third-order correlation functions). However, the results obtained in Ref. 27 indicate that as $t\to\infty$ the correlation functions of order $l+1$ have the same time dependence as the correlation functions of order l, but are numerically small. Correspondingly, in the long-time asymptotic dependence $\delta n(t)=At^{-\nu}$ the exponent ν is determined exactly and A is determined to within a numerical factor of order unity.

For the fluctuation part of the pair correlators the following equations are valid:

$$\begin{gathered}\dot g_{AA}=-2n(t)(k-\chi)g_{AB}-2n(t)(k+\chi)g_{AA}\\ +2k_-g_{AC}+D\Delta g_{AA}-Dn(t)\Delta\delta(\lambda),\end{gathered} \tag{15a}$$

$$\begin{gathered}\dot g_{AB}=-2kn(t)(g_{AB}+g_{AA})+2\chi n(t)(g_{AA}-g_{AB})\\ +2k_-g_{AC}+D\Delta g_{AB},\end{gathered} \tag{15b}$$

where $\chi=4\pi D\lambda_0$, λ_0 being the Onsager radius. The equations determining the evolution of the correlators g_{AC} and g_{CC} coincide with Eqs. (6c) and (6d). The change of the mean density is described by the equation

$$\begin{gathered}\dot n(t)=-k_D[n^2(t)+g_{AB}(a,t)]+k_-^Dn_C(t),\\ k_D=\frac{k_Ck_{dq}}{k_C+k_{dq}},\quad k_-^D=\frac{k_-k_{dq}}{k_C+k_{dq}},\end{gathered} \tag{16}$$

where

$$\begin{gathered}k_C=k\exp\left\{\frac{4\pi q^2}{\varepsilon aT}\right\},\quad k_{3q}=2\pi D\lambda_0[1+\mathrm{cth}(\lambda_0/2a)],\\ k_{2q}=4\pi D/\ln(Dt/a^2),\quad k_{1q}=(D/\pi t)^{1/2}.\end{gathered}$$

The value of k_{3q} was obtained in Ref. 29.

For instantaneous generation of statistically independent particles, from (15) and (16) we obtain

$$g_{AB}(p,t)=g_{AB}(p,q)-{}^1/{}_2\Delta nk_-^2t_{AB}^2\exp(-Dtp^2),$$

where

$$\begin{gathered}g_{AB}(p,q)=\frac{2\chi n_A^2}{Dp^2+4\chi n_A}-\frac{2kn_A^2t_{AB}}{2+Dt_{AB}p^2}\\ +2k_-\frac{t_{AB}^2(k_-n_C-kn_A^2)}{(1+Dt_{AB}p^2)(2+Dt_{AB}p^2)}.\end{gathered} \tag{17}$$

The expression (17) determines the fluctuation corrections (i.e., the corrections due to the spatial nonuniformity of the distribution of reagents) to an equation of the Saha type

$$n_A^2/n_C = k_p(T) + \Delta k_p,$$

where $k_p(T) = k_-^D/k_D$ is the mean-field ionization-equilibrium constant, and

$$\Delta k_p \propto -n_C^{-1} \int d\bar{p}\, \exp(i\bar{p}\bar{\lambda})\, g_{AB}(pq)\, \big|_{|\lambda|=a}.$$

For instantaneous generation of correlated pairs of charged particles, for the $t \to \infty$ leading terms in $g_{AB}(p,t)$ we obtain

$$g_{AB}(p,t) = g_{AB}(pq) + {}^1/_2 (n_A - n(0)\lambda_g^2 p^2) k_-^2 t_{AB}^2 \exp(-Dtp^2).$$

Correspondingly, the long-time relaxation to the equilibrium value of the density is determined by the power dependence

$$\delta n(t) = \frac{\Delta n k_C k_-^2 t_{AB}^2}{2(2k_C n_A + k_-)} (Dt)^{-d/2}$$

for generation of independent particles, and by the power dependence

$$\delta n(t) = -\frac{k_C k_-^2 t_{AB}^2}{2(2k_C n_A + k_-)} (n_A - n(0)\lambda_g^2/Dt)(Dt)^{-d/2}$$

for generation as pairs.
We note that, as in the case of uncharged reagents, $\delta n(t) < 0$ for $t \to \infty$, irrespective of the value of $n(0)$, and $n(t)$ can be a nonmonotonic function of time.

For an irreversible reaction involving charged particles the fluctuation effects are found to be suppressed, and the long-time kinetics is determined by the mean-field dependences.[9,18,19] Fluctuations of opposite sign—regions depleted or enriched in particles of one kind—create electric fields that, together with diffusion, facilitate uniformization of the initial spatial nonuniformity. Fluctuations for which the deviations from the mean density for A and for B have the same magnitude and sign can only accelerate the relaxation of the mean density to zero in the case of irreversible recombination, but for a reversible reaction A + B↔C, for which the quantity $n_A(\mathbf{r},t) + n_B(\mathbf{r},t) + 2n_C(\mathbf{r},t)$ is conserved, or for a system with no reaction,[33] such fluctuations give rise to a power-law relaxation of $n(t)$ to its equilibrium value.

3. GENERATION OF PARTICLES OF THE REAGENTS BY AN EXTERNAL SOURCE

We shall consider a situation that arises in the study of chemical reactions by radiation methods. In a system in which a reversible reaction A + B↔C involving neutral or charged reagents occurs, an external source acts that decomposes the product of the forward reaction into a pair of reagents created at a distance λ_g from each other. For a two-component reversible reaction involving neutral particles and proceeding in parallel with the action of the external source, the system of equations determining the behavior of the fluctuation part of the pair correlators has the following form:

$$\begin{aligned}\dot{g}_{AA} = {} & -2kn(t)(g_{AA}+g_{AB}) + 2k_- g_{AC} + D\Delta g_{AA} \\ & - Dn(t)\Delta\delta(\lambda) + in_C(t)\delta(\lambda), \end{aligned} \qquad (18a)$$

$$\begin{aligned}\dot{g}_{AB} = {} & -2kn(t)(g_{AA}+g_{AB}) + 2k_- g_{AC} \\ & + D\Delta g_{AB} + in_C(t)\gamma_d(\lambda_g)\delta(|\lambda|-\lambda_g), \end{aligned} \qquad (18b)$$

$$\begin{aligned}\dot{g}_{AC} = {} & kn(t)(g_{AA}+g_{AB}-2g_{AC}) + k_-(g_{CC}-g_{AC}) \\ & + D\Delta g_{AC} - in_C(t)\delta(\lambda), \end{aligned} \qquad (18c)$$

$$\dot{g}_{CC} = 4kn(t)g_{AC} - 2k_- g_{CC} + D\Delta g_{CC} - Dn_C(t)\Delta\delta(\lambda) + in_C(t)\delta(\lambda), \qquad (18d)$$

$$\dot{n}(t) = -k_s[n^2(t) + g_{AB}(a,t)] + (k_-^s + i)n_C(t), \qquad (19)$$

where i is the mean intensity of the external radiation.

From (18) we obtain the steady-state value $g_{AB}(p,\lambda_g)$ with an external source acting:

$$g_{AB}(p,\lambda_g) = g_{AB}(p) - I(p,\lambda_g)\left[\frac{1+k_-^2 t_{AB}^2}{Dp^2} - \frac{k_-^2 t_{AB}^2}{2+Dt_{AB}p^2}\right], \qquad (20)$$

where $g_{AB}(p)$ is given by formula (8) and $I(p,\lambda_g)$ is the Fourier transform of the function

$$in_C(t)[\delta(\lambda) - \gamma_d(\lambda_g)\delta(|\lambda|-\lambda_g)].$$

For $\lambda_g \to \infty$ the expression (20) has a nonintegrable (in low-dimensional systems) singularity of the type p^{-2} as $p \to 0$, and this leads to the separation of systems with $d \leqslant 2$ into macroscopic domains of particles of the same kind; the mean density of the reacting particles increases without bound as the generation time increases. Such effects have been observed in a numerical experiment for the irreversible reaction A + B→C for $d = 1,2$ (Refs. 24,25), and for fractal systems in Ref. 26. After the external-generation processes have ceased, the relaxation of $g_{AB}(p,t)$ to the steady-state value (8) is determined by the dependence

$$\begin{aligned} g_{AB}(p,t) = g_{AB}(p) - \Big[& (1+k_-^2 t_{AB}^2)\frac{I(p,\lambda_g)}{2Dp^2} - t_{AB} k n_A^2 (1+k_- t_{AB}) \\ & + k_-^2 t_{AB}^2 n_C \Big] \exp(-Dtp^2). \end{aligned}$$

In the three-dimensional case, for $\delta n(t)$ as $\lambda_g \to \infty$ we obtain

$$\delta n(t) = kt_{AB}\frac{in_C}{4\pi Da}(1+k_-^2 t_{AB}^2)(a^2/Dt)^{-1/2},$$

while for finite values of λ_g Eq. (20) has a flat spectrum as $p \to 0$ and the long-time relaxation of the mean density to the equilibrium value is determined (for arbitrary d) by the dependence

$$\begin{aligned} \delta n(t) = kt_{AB}[& (1+k_-^2 t_{AB}^2) in_C \lambda_g^2/2D - t_{AB} k n_A^2 (1+k_- t_{AB}) \\ & + k_-^2 t_{AB}^2 n_C](Dt)^{-d/2}. \end{aligned}$$

In the case of charged reagents A and B the steady-state value $g_{AB}(p,\lambda_g)$ is equal to

$$\begin{aligned} g_{AB}(p,\lambda_g) = {} & g_{AB}(p,q) - \frac{I(p,\lambda_g)t_{AB}}{2} \\ & \times \left[\frac{k_-^2 t_{AB}}{Dp^2} + \frac{2n_A(k-\chi)+k_-}{Dp^2+4\chi n_A} - \frac{k_-^2 t_{AB}^2}{1+Dt_{AB}p^2}\right], \end{aligned}$$

where $g_{AB}(p,q)$ is determined by formula (17). After the external-generation processes are switched off, the relaxation of $g_{AB}(p,t)$ to the equilibrium value (17) is determined by the expression

$$\begin{aligned} g_{AB}(p,t) = g_{AB}(p,q) - \Big[& k_-^2 t_{AB}^2 \left(n_C + \frac{n_A}{2} + \frac{I(p,\lambda_g)}{Dp^2}\right) \\ & + \frac{k_- t_{AB}^2 n_A (k-\chi)}{Dp^2+4\chi n_A} I(p,\lambda_g)\Big] \exp(-Dtp^2). \end{aligned}$$

For $\lambda_g \to \infty$ we obtain

$$g_{AB}(p,t)=g_{AB}(p,q)-(k_-^2 t_{AB}^2 i n_C/Dp^2)\exp(-Dtp^2),$$

and, correspondingly,

$$\delta n(t)=\frac{k_C t_{AB}^2 k_-^2 i n_C}{4\pi Da(2k_C n_A+k_-)}(a^2/Dt)^{1/2}. \qquad (21)$$

For finite values of λ_g the expression (21) is the intermediate asymptotic dependence, and for $t \to \infty$ the relaxation of $n(t)$ to its equilibrium value is determined by the dependence

$$\delta n(t)=\frac{k_-^2 k_C t_{AB}^2}{2k_C n_A+k_-}\left(n_C+\frac{n_A}{2}+i n_C \lambda_g^2/D\right)(Dt)^{-d/2}.$$

For the reversible reaction (9), proceeding in parallel with the action of external radiation, the fluctuation part of the pair correlators of the density satisfies the following system of equations:

$$\begin{aligned}
\dot{g}_{AA}&=-4kn(t)g_{AA}+2k_-g_{AB}+D\Delta g_{AA}-Dn(t)\Delta\delta(\lambda)\\
&\quad+2in_B(t)[\delta(\lambda)+\gamma_d(\lambda_g)\delta(|\lambda|-\lambda_g)],\\
\dot{g}_{BB}&=2kn(t)g_{AB}-k_-g_{BB}+D\Delta g_{BB}-Dn_B(t)\Delta\delta(\lambda)+in_B(t)\delta(\lambda),\\
\dot{g}_{AB}&=kn(t)(g_{AA}-2g_{AB})+k_-(g_{BB}-{}^1/_2 g_{AB})\\
&\quad+D\Delta g_{AB}-2in_B(t)\delta(\lambda), \qquad (22)\\
\dot{n}(t)&=-k_s[n^2(t)+g_{AA}(a,t)]+(k_-^s+i)n_B(t);\\
\dot{n}_A(t)&+2\dot{n}_B(t)=0.
\end{aligned}$$

For the steady-state value of the Fourier transform of the correlator g_{AA} we obtain

$$g_{AA}(p,\lambda_g)=g_{AA}(p)-t_{AA}I(p,\lambda_g)\left[\frac{1}{1+Dt_{AA}p^2}+\frac{2k_-t_{AA}}{1+2Dt_{AA}p^2}+\frac{k_-^2t_{AA}}{Dp^2}\right]+\frac{4in_Bt_{AA}}{1+Dt_{AA}p^2},$$

where g_{AA} is determined by the expression (12) and n_B is the steady-state solution of Eq. (22). After the generation processes are switched off, the relaxation of $g_{AA}(p,t)$ to its equilibrium value (12) is determined by the dependence

$$g_{AA}(p,t)=g_{AA}(p)-k_-^2t_{AA}^2\left(n-n_A+\frac{I(p,\lambda_g)}{Dp^2}\right)\exp(-Dtp^2),$$

where n_A and n are the steady-state solutions of Eqs. (11) and (22). For the one-component reversible reaction (9), as for the two-component one, the equilibrium spectrum of the fluctuations has a nonintegrable singularity for $d \leqslant 2$ and $\lambda_g \to \infty$. This implies that the diffusion processes do not succeed in smoothing out the fluctuations generated by the external radiation; correspondingly, the complete spectrum of the fluctuations in low-dimensional systems diverges. In the three-dimensional case, for $\lambda_g \to \infty$,

$$\delta n(t)=(kk_-^2t_{AA}^3 i n_B/2\pi Da)(a^2/Dt)^{1/2},$$

while for finite values of λ_g we obtain for $\delta n(t)$ from (11)

$$\delta n(t)=kk_-^2t_{AA}^3(n-n_A+in_B\lambda_g^2/D)(Dt)^{-d/2}.$$

4. CONCLUSION

We have investigated the fluctuation kinetics of reversible bimolecular reactions occurring in systems in which charged and neutral particles are generated in various ways. To describe the kinetics of the reactions in such systems we propose a method similar to that of Ref. 11, based on the decoupling of fourth-order correlators into a product of pair correlators. As a result of such decoupling, the third-order correlators, after subtraction of the singular part, turn out to be identically equal to zero. Allowance for the singular part of the correlators leads to renormalization of the rate constants of the forward and backward reactions in the equation determining the evolution of the mean density of the reacting particles. The solution of the resulting diffusion-kinetic equations leads to the following results.

In the early stages of the reactions the intermediate asymptotic behavior obtained by Smoluchowski (or by Debye, for charged particles) in systems of any dimensionality is reproduced.

For reversible reactions of (neutral) particles of the same kind or of different kinds the results of Refs. 20 and 21 are reproduced. For instantaneous generation of the reagents as correlated pairs the long-time kinetics of a reversible two-component reaction involving neutral reagents is also determined by a power law, but, depending on the relationship between the initial density of the reagents A and B and the equilibrium constant,the relaxation of the density to the equilibrium value be a nonmonotonic function of time.

For reversible two-component reactions involving charged particles the Coulomb interaction leads to effective neutralization of the charge, i.e., in the limit $t \to \infty$ the fluctuations of the densities of A and B become strongly correlated (the regions of depletion in particles of A and the regions of enrichment in particles of B, or vice versa, coincide, in contrast to the case of systems of neutral particles). The relaxation of the density to its equilibrium value at large values of t, as for systems with neutral reagents, is determined by an algebraic dependence on the time, and, in the case of instantaneous generation of correlated pairs of A and B, can be a nonmonotonic function of the time.

We have investigated the kinetics of reversible reactions proceeding in parallel with the action of an external source that decomposes the product of the forward reaction into a pair of reagents that are produced at a distance λ_g from each other. For $\lambda_g \to \infty$ the fluctuation spectrum has a singularity of the form p^{-2} as $p \to 0$, and this leads to separation of low-dimensional systems into macroscopic domains containing only one kind of particle. In three-dimensional systems the long-time relaxation of the density after the external source is switched off is determined by the dependence $\delta n(t) \propto t^{-1/2}$. We have investigated the corresponding laws for the case of charged reagents.

The results obtained make it possible to make a number of generalizations. The fluctuation singularities of the kinetics and the structures of the equilibrium state in the reactions investigated are due to the presence of linear combinations of local densities of reagents that do not change during the course of the reaction, such as, e.g., the sum of the local densities of the reagents and products of the reaction, or the total density of clusters containing various numbers of particles in processes of the reversible-coagulation type. Since the law of conservation of matter is valid for any set of consecutive and parallel reactions, at least one such combination exists for all reversible transformations; consequently the long-time asymptotic behavior of the relaxation to equilibrium for all reversible reactions with diffusion is diffusion-controlled and is described by power laws (in contrast to the exponential laws that are obtained in approximations of the mean-field type). The exponent is determined by the fluctuation spectrum of the initial or the equilibrium distribution of the reagents.

In low-dimensional systems, in which the external source decomposes the products of any reactions into uncorrelated pairs of reagents, diffusion processes do not succeed in smoothing out the fluctuations generated by the source. In such systems, despite the fact that the equation for the mean density has an equilibrium solution, fluctuation effects become strong and the equilibrium is destroyed.

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APPENDIX I

The kinetics of reactions on fractal structures

In Ref. 34 it was stated that the solution of the diffusion equation $\dot{S} = D\Delta S$ on fractal structures has the following form:

$$S(\lambda, t) = (Dt)^{-d_f/d_w} f(\lambda/(Dt)^{1/d_w}), \quad \lim_{t\to\infty} f = \text{const}, \qquad \text{(A1)}$$

where d_f is the fractal dimension of space and d_w is the random-walk dimension. This statement, taken together with the method given in this paper for describing the kinetics of bimolecular diffusion-controlled reactions, makes it possible to obtain, without any additional assumptions, a closed description of both the mean-field and the fluctuation kinetics of reactions occurring on fractal structures. Below we give the results of these calculations.

If the kinetics of the reaction under consideration in compact (with $d_f = d$) systems is determined at large times by fluctuation effects and at moderate times by a mean-field intermediate asymptotic dependence of the Smoluchowski type (as is the case, e.g., in a two-component irreversible reaction or in bimolecular reversible reactions), on a fractal structure fluctuation effects turn out to be significant from the very earliest stages of the reaction, and the intermediate asymptotic behavior is absent. If, however, in the corresponding system the fluctuation effects are small for any t, the kinetics of the reaction on the fractal structure is determined by the solution of an equation of the type (5), in which the diffusive reaction-rate constant calculated by the method of the present paper is equal to $k_d = (Dt)^{d_f/d_w} t^{-1}$.

In the case of a two-component irreversible reaction the fluctuation part of the pair correlator of the density has the following time dependence:

$$g_{AB}(a, t) \propto -t^{-d_f/d_w}, \qquad \text{(A2)}$$

and, accordingly, at large times the mean density decreases with time in accordance with the law $n(t) \propto t^{-d_f/2d_w}$, which is determined by fluctuation effects. For reversible reactions, both one-component and two-component, involving charged or uncharged particles, from the systems of equations (6), (10), and (15) we obtain for the fluctuation part of the pair correlator the result $\delta g_{AB} \propto at^{-d_f/d_w}$, and, thus, the mean density is determined by a power-law dependence on the time:

$$n(t) = n_A - kt_{AB}\alpha t^{-d_f/d_w}.$$

The coefficient α depends on the type of reaction and has been calculated in Secs. 2 and 3 of this paper.

If the fractal structure on which the reaction is proceeding is homogeneous[35,36] the ratio d_f/d_w is equal with good accuracy to $\frac{2}{3}$ (this is the so-called Alexander—Orbach hypothesis; the value $d_f/d_w = \frac{2}{3}$ is an exact result for "Cayley trees"). Correspondingly, for an irreversible two-component reaction we obtain $n(t) \propto t^{-1/3}$. This result was first obtained in Ref. 7 from dimensional arguments and was called by the authors a superuniversal law, since for $d > 1$ the power the power of the time does not depend on the dimensionality d of space. In the case of reversible reactions proceeding on homogeneous fractal structures we obtain $\delta n(t) \propto t^{-2/3}$.

In the case of a one-component irreversible reaction or a two-component irreversible reaction involving charged particles fluctuation effects turn out to be suppressed and the density is determined by the mean-field dependence $n(t) \propto t^{-2/3}$.

For regular fractal structures, e.g., "Serpinski gaskets", the fractal dimension is $d_f = \ln(d+1)/\ln 2$ and the random-walk dimension is $d_w = \ln(d+3)/\ln 2$ (Ref. 35). Accordingly, formal application of the methods of this paper leads to the following dependences. For a two-component irreversible reaction and for a one-component irreversible reaction the decreases of the density follow the laws

$$n(t) \propto t^{-\ln(d+1)/2\ln(d+3)} \quad \text{and} \quad n(t) \propto t^{-\ln(d+1)/\ln(d+3)}.$$

For reversible reactions the relaxation of the density to its equilibrium value is determined by fluctuation effects and is described by the following dependence:

$$\delta n(t) \propto t^{-\ln(d+1)/\ln(d+3)}.$$

For a reaction A + B → C proceeding on a fractal structure in parallel with the action of external radiation generating correlated pairs of particles of A and B, produced at a distance λ_g from each other, the steady-state spectrum of the correlator g_{AB}, unlike that in the previous cases of dense systems, is not flat at small values of the wave vector:

$$g_{AB}(p) = -\frac{I\lambda_g^2}{2D} p^{2-d_w} + \frac{I}{Dp^{d_w} + 4kn_A}, \quad I = in_C. \qquad \text{(A3)}$$

It is clear that this difference is due to the suppression of geminal recombination-particles created in a single pair can be found on different branches of the fractal structure, and, despite the fact that the pair radius is equal to λ_g, the "chemical" path between the particles of the pair will be considerably greater. The relaxation of the correlator $g_{AB}(p,t)$ to the steady-state value (A3) when an external source is acting occurs in accordance with the law (for $t \to \infty$)

$$g_{AB}(a, t) = g_{AB}(a)[1 - (a^{d_w}/Dt)^\nu], \quad \nu = \frac{d_f + 2 - d_w}{d_w}.$$

Accordingly, the kinetics of the approach to equilibrium is described by the dependence

$$n(t) = n_A + \frac{kg_{AB}(a)}{2k_s n_A + i}(a^{d_w}/Dt)^\nu.$$

After the generation processes have ceased the decrease of the density of the reacting particles occurs more slowly than by the law (A2):

$$n(t)=(I\lambda_g^2/2D)^{1/2}(Dt)^{-\nu/2}.$$

Similar behavior is found for reversible reactions:

$$\delta n(t)\propto t^{-\nu}.$$

If for a certain time t_g the external source is generating the particles of the reagents in a statistically independent manner, the growth of the mean density in the system occurs as follows:

$$n\sim t_g^{1-d_f/d_w}.$$

As $t_g\to\infty$ the fluctuation effects become strong, the equilibrium is destroyed, and the density increases without bound, as was proved in the numerical experiment of Ref. 26.

APPENDIX II

We shall represent the density of the reacting particles in the form of a sum[1)]

$$n_A(\mathbf{r},t)=\sum_n\delta(\mathbf{r}-\boldsymbol{\rho}_n(t)),\quad n_B(\mathbf{r},t)=\sum_m\delta(\mathbf{r}-\mathbf{R}_m(t)),$$

where $\boldsymbol{\rho}_n$ and $\mathbf{R}_m$ are the position vectors of the nth particle of type A and the mth particle of type B. Then the third-order correlators that appear in the system of equations (4), e.g., T_{AAB}, can be written as

$$\begin{aligned}T_{AAB}(\lambda,t)=&\gamma_d(a)V^{-1}\iiint d\mathbf{r}\,d\mathbf{r}_1\,d\mathbf{r}_2\delta(\mathbf{r}-\mathbf{r}_1-\lambda))\delta(|\mathbf{r}_1-\mathbf{r}_2|-a)\\&\times\Big[\sum_m\delta(\mathbf{r}_2-\mathbf{R}_m(t))-n(t)\Big]\Big\{\sum_n\delta(\mathbf{r}-\boldsymbol{\rho}_n(t))\delta(\mathbf{r}_1-\boldsymbol{\rho}_n(t))\\&+\sum_n\sum_{n',n'\neq n}\delta(\mathbf{r}-\boldsymbol{\rho}_n(t))\delta(\mathbf{r}_1-\boldsymbol{\rho}_{n'}(t))-2n(t)\\&\times\sum_n\delta(\mathbf{r}-\boldsymbol{\rho}_n(t))+n^2(t)\Big\}.\end{aligned}$$

We denote the first term in the curly brackets by $\tilde{T}_{AAB}$ and call it the regular part of the correlator T_{AAB}; the remaining terms will be called the fluctuation part of the third-order correlator.

The regular part of T_{ijk} arises when account is taken of the fact that the distribution $n(\mathbf{r},t)$ possesses discreteness arising from spatial coincidence in the positions of two particles of the same kind in three-particle interactions. Direct calculation shows that, to within the small gas parameter the regular part of T_{AAB} is equal to the number of AB pairs, multiplied by a delta function:

$$\tilde{T}_{AAB}=k^{-1}\gamma_d(a)\dot{n}(t)\delta(|\lambda|-a)=\tilde{T}_{ABB},$$

while the regular part of the correlator T_{ABC} is equal to zero.

Using (3), for the fluctuation part τ_{ijk} of T_{ijk} we obtain the following system of equations:

$$\begin{aligned}\dot{\tau}_{ABi}=&-kn(t)[\tau_{AAB}+\tau_{ABB}+2\tau_{ABi}+\tau_{AAi}+\tau_{BBi}]\\&+k_-[\tau_{BCC}+\tau_{ACC}-\tau_{ABC}]\\&-k[H_{ABAB}+H_{ABAi}+H_{ABBi}-G_{AB}(a,t)\\&\times(G_{AB}(\lambda,t)+G_{Ai}(\lambda,t)+G_{Bi}(\lambda,t))],\qquad i\neq C,\\\dot{\tau}_{CCi}=&-kn(t)[\tau_{ACC}+\tau_{BCC}-2\tau_{AiC}-2\tau_{BiC}]+k_-[\tau_{CCC}-\tau_{CCi}]\\&-k[H_{ABCC}-2H_{ABiC}-G_{AB}(a,t)(G_{CC}(\lambda,t)-2G_{iC}(\lambda,t))],\\\dot{\tau}_{ijC}=&-kn(t)[\tau_{AjC}+\tau_{BjC}+\tau_{AiC}+\tau_{BiC}-\tau_{Aij}-\tau_{Bij}]\\&+k_-[\tau_{jCC}+\tau_{iCC}-\tau_{ijC}]\\&-k[H_{ABjC}+H_{ABiC}-H_{ABij}-G_{AB}(a,t)\\&\times(G_{jC}(\lambda,t)+G_{iC}(\lambda,t)-G_{ij}(\lambda,t))],\\\dot{\tau}_{CCC}=&3kn(t)[\tau_{ACC}+\tau_{BCC}]-3k_-\tau_{CCC}\\&+3k[H_{ABCC}-G_{AB}(a,t)G_{CC}(\lambda,t)],\end{aligned}$$

where the H_{ABkl} are fourth-order correlators.

We represent H_{ABkl} in the form

$$H_{ABkl}=G_{AB}(a,t)G_{kl}(\lambda,t).$$

Then, by virtue of the fact that $\tau_{ijk}|_{t=0}\equiv 0$ independently of the way in which the reagents are generated, the system of equations determining the evolution of the fluctuation part of the third-order correlation functions will have no nontrivial solutions. We shall write G_{ij} in the form of a sum

$$G_{ij}=g_{ij}+\tilde{G}_{ij},$$

where g_{ij} is the fluctuation part of the pair correlators and $\tilde{G}_{ij}$ is the regular part. Using (4) and (6) in the first approximation in the gas parameter α we obtain quasistationary solutions for $\tilde{G}_{AB}(a,t)$, for $d=1,2,3$, respectively:

$$\tilde{G}_{AB}(a,t)={}^1/_4\dot{n}(t)(\pi t/D)^{1/2},$$

$$\tilde{G}_{AB}(a,t)=(4\pi D)^{-1}\dot{n}(t)\ln(Dt/a^2),$$

$$\tilde{G}_{AB}(a,t)=(4\pi Da)^{-1}\dot{n}(t).$$

Because of the presence of terms of the type $kn(t)\tilde{G}_{ij}$ in Eqs. (4) and (6), the regular parts of $G_{AB}(\lambda,t)$ decrease exponentially with distance for values of λ much greater than the mean spacing between the particles. The physical cause of this behavior of the regular part of the correlators is the effective screening of a given particle by other particles of the same reagent. However, in the above values of $\tilde{G}_{AB}(a,t)$ the exponential factors are omitted because of the small value of the gas parameter.

Substituting the values obtained for $\tilde{G}_{AB}(a,t)$ into Eq. (2), we obtain the desired equation (5) determining the evolution of the mean density. It can be seen by comparing Eqs. (2) and (5) that allowance for $\tilde{T}$ and $\tilde{G}$, i.e., allowance for the discreteness of the density distribution of the reagents, leads to a decrease of the true rate constant of the reaction and to its replacement by an effective rate constant, which, for various systems, has been calculated previously in Refs. 28–32 by means of methods that ignore fluctuation effects. We note that the value obtained for the effective rate constant of the reaction does not appear in the expressions for the fluctuational long-time asymptotic forms.

The decoupling of the fourth-order correlators does not guarantee the correctness of results pertaining to the long-time asymptotic forms. However, in Ref. 27 it was shown that in a number of systems analogous to those investigated in the present paper (a bimolecular irreversible reaction A + B → C in which the initial distribution of the reagents is perturbed by small thermodynamic fluctuations) the long-time kinetics of the reaction is determined by Gaussian equilibrium fluctuations of the density and the approximations obtained by means of such decoupling are asymptotically exact.

We note also that the study of such systems with the aid of quantum-field methods[10,12,21,37] leads to the same results as this decoupling. Calculation of higher-order correlators leads to the conclusion that their time dependence is not more singular than that for pair correlators, in contrast to systems with second-order phase transitions near a critical point. It is obvious that this difference is due to the fact that the structures determining the long-time kinetics of diffusion-controlled reactions (macroscopic regions containing only one of the reagents[10]) are not fractal, unlike the structures that arise near a critical point.

The indicated decoupling leads to incorrect results in the description of systems whose fluctuation kinetics is concentrated in the nonequilibrium deviations from the mean that occur, e.g., in the reaction $A + B \rightarrow B$, where B are stationary traps and A are particles diffusing in the volume. In this case the long-time asymptotic form of the survival probability is determined by the presence of the improbable fluctuational zones that are free of traps of type B.

1) Formally, the diffusion equation is not valid for unsmoothed functions $n(\mathbf{r},t)$. All the conclusions of the paper pertain to average densities or correlators obtained by averaging over the initial distribution $n(\mathbf{r},0)$ or over the volume of the system. Despite this, the discreteness of the distribution exerts an important influence on the short-wavelength region of the spectrum of the correlators.

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