Stochastic aggregation of reacting particles and their decay kinetics

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Stochastic aggregation of like particles, accompanied by generation, is considered in a stationary regime. The correlation function of the densities of the uncompensated charges of the electron-hole system is rigorously calculated in second order in the concentration in the one- and three-dimensional cases. It is shown that if the electron-hole pair creation radius exceeds its annihilation radius the concentration is determined by the effective-mass law subject to substantial corrections (of fluctuation origin), which become decisive in the diffusion-controlled limit, especially for few-dimensional systems. Relaxation from a stationary regime after turning off the generation is considered. An exact equation for the concentration is obtained in the three-dimensional case. It describes the fluctuation regime for long times, and contains the classical kinetics regime for intermediate ones. The long-time asymptote takes the form $c \propto t^{-3/4}$ for a finite pair-production radius, whereas for a large production radius the asymptotic form is $c \propto t^{-1/4}$. In the one-dimensional case and for a finite production radius the concentration decreases like $c \propto t^{-1/4}$.

I. INTRODUCTION

In Refs. 1–5 is reported a cycle of investigations of the influence of concentration fluctuations of reacting particles on the asymptotics of the approach of the density to equilibrium. Thus, for bimolecular recombination $A + B \to C$ with random (Poisson) initial distribution of the reagents, the following laws hold for long time intervals: $c \propto t^{-3/4}$ in place of t^{-1} if the initial component concentrations are equal, $c_A = c_B$ (Refs. 1 and 2), and

$$c_A \propto \exp(-\mathrm{const}\cdot t^{3/5})$$

in place of

$$c_A \propto \exp(-kc_B t),$$

if $c_A \ll c_B$ (Refs. 1 and 3). In the case of a reversible reaction $A + B \leftrightarrow C$ the equilibrium sets in accord with the law $\Delta c \propto t^{-3/2}$ rather in the exponential manner that results from classical kinetics.[4,5] Thus, in all cases, the reaction rate during the final stage is limited by a diffusive smoothing of the initial fluctuations of the reagent distribution.

Stochastic aggregate of particles generated by a stationary flux in an equal concentration was considered in Ref. 6. It was shown that although the initial particles are produced in space independently, the steady-state fluctuations do not have a Poisson spectrum—aggregation of like particles in space takes place. (Although the statement that like particles become aggregated was made in a number of papers,[7–10] the spectrum of their fluctuations was not obtained.) When the generation processes are turned off, the relaxation of the concentration of uncharged particles over long time intervals follows a $t^{-1/4}$ law.

The purpose of the present paper is a rigorous and more detailed solution of the problem of aggregation of uncharged particles, and an investigation of the kinetics of their decay after their generation is stopped.

We solve the problem by a method proposed in Refs. 11 and 5 and developed in Refs. 12 and 13 for an investigation of the kinetics of diffusion-controlled chemical reactions. According to Refs. 5 and 11, the diffusion equation with reactions between the particles can be reformulated in the second-quantization representation and, as shown in Ref. 5, this problem is similar to that of a quantum non-ideal Bose gas with condensate. The Bogolyubov method of separating the Bose condensate was used in Ref. 5 and it was shown that to obtain a result that is valid in the leading order in the concentration, at arbitrary reaction rates, it is necessary to sum perturbation-theory ladder diagrams. The corresponding calculations were made in Refs. 12 and 13 for the case of one-component chemical reaction with sources, using a diagram technique similar to that of Belyaev.[14,15]

2. TWO-COMPONENT REACTING SYSTEM: FUNDAMENTAL RELATIONS

Consider a system made up of electrons (e) and holes (h) that diffuse in a d-dimensional volume $V (V \to \infty)$ with respective diffusion coefficients D_e and D_h. We assume both components to have equal concentrations, $c_c = c_h$, so that the electroneutrality condition is met. We denote by $w_a(\mathbf{y} - \mathbf{x})$ the probability that an electron located at the point $\mathbf{x}$ will recombine with a hole at the point $\mathbf{y}$ in a unit time. The inverse process, due to thermal activation or photogeneration of pairs, is described by a probability $w_b(\mathbf{x} - \mathbf{y})$ that an electron and a hole will be correspondingly produced per unit time in the vicinities of the points $\mathbf{x}$ and $\mathbf{y}$. This, in contrast to Ref. 6, the particles of each pair are produced in space correlated, with a distribution function w_b. For simplicity, we disregard the potential interaction of the particles, and their concentration will be assumed small:

$$cr_a^d \ll 1, \tag{1}$$

where r_a (r_b) is the radius of the function $w_a(\mathbf{x})$ ($w_b(\mathbf{x})$).

The state of the considered multiparticle system containing m electrons making up a configuration $X^m = \{\mathbf{x}_1;...;\mathbf{x}_m\}$ and m holes $Y^m = \{\mathbf{y}_1;...;\mathbf{y}_m\}$ will be characterized by a distribution function $u_m(X^m,Y^m)$. The evolution of $u_m(X^m,Y^m)$ is described by corresponding diffusion-

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balance equations that can be rewritten, according to Refs. 5 and 11, in a form similar to a Schrödinger equation:

$$(\partial/\partial t)|F(t)\rangle=H|F(t)\rangle. \tag{2}$$

The "wave" function $|F(t)\rangle$ is defined here in terms of the field operators by the relation

$$|F(t)\rangle=\sum_{m=0}^{\infty}\int\frac{d\mathbf{x}_1\ldots d\mathbf{x}_m}{m!}\int\frac{d\mathbf{y}_1\ldots d\mathbf{y}_m}{m!}u_m(X^m,Y^m)\,|X^m,Y^m\rangle,$$

$$|X^m,Y^m\rangle=\psi_e^+(\mathbf{x}_1)\ldots\psi_e^+(\mathbf{x}_m)\psi_h^+(\mathbf{y}_1)\ldots\psi_h^+(\mathbf{y}_m)|0\rangle. \tag{3}$$

Our task is to calculate the correlation function that describes the spatial distribution of the uncompensated charges

$$\langle\Delta c(0)\Delta c(\mathbf{x})\rangle=\langle[c_e(0)-c_h(0)][c_e(\mathbf{x})-c_h(\mathbf{x})]\rangle, \tag{4}$$

and is expressed in terms of the particle-number density operator

$$c_e(\mathbf{x})=\psi_e^+(\mathbf{x})\psi_e(\mathbf{x}). \tag{5}$$

The "Hamiltonian" (2) has in **k**-space the form

$$H=H_0+H_{int}, \tag{6}$$

where H_0 corresponds to free diffusion

$$H_0=-D_e\sum k^2\alpha_\mathbf{k}^+\alpha_\mathbf{k}-D_h\sum k^2\beta_\mathbf{k}^+\beta_\mathbf{k}, \tag{7}$$

and H_{int} includes terms with the reaction

$$H_{int}=\sum w_b(\mathbf{k})\alpha_\mathbf{k}^+\beta_{-\mathbf{k}}^+ +\sum w_a(k)\alpha_\mathbf{k}\beta_{-\mathbf{k}}-Vw_b(0)$$
$$-V^{-1}\sum w_a(\mathbf{k}-\mathbf{k}_1)\alpha_\mathbf{k}^+\alpha_{\mathbf{k}_1}\beta_{\mathbf{k}_2}^+\beta_{\mathbf{k}_3}\Delta(\mathbf{k}+\mathbf{k}_2-\mathbf{k}_1-\mathbf{k}_3). \tag{8}$$

Here $\Delta(\mathbf{k})=\delta_{k_1,0},\ldots,\delta_{k_d,0}$ is the Kronecker symbol. Averaging the operator of the total number of particles, we obtain an expression for the concentration in terms of the condensate operators $\alpha_0,\beta_0,\ (\alpha_0=\beta_0)$ (Ref. 5):

$$c=V^{-1/2}\langle\alpha_0\rangle. \tag{9}$$

Writing next in the Heisenberg representation the equations of motion for the condensate operators and replacing them with c-numbers in accordance with the procedure[5,13]

$$\alpha_0^+,\ \beta_0^+\to V^{1/2},\quad \alpha_0,\ \beta_0\to cV^{1/2}, \tag{10}$$

we obtain an equation for the concentration

$$(d/dt)c(t)=w_b(0)-w_a(0)c^2(t)-V^{-1}\sum{}' w_a(\mathbf{k})\langle\alpha_\mathbf{k}\beta_{-\mathbf{k}}\rangle, \tag{11}$$

where the prime on the summation sign means that the summation index is not zero. The condensation operators are separated also in the Hamiltonian and in the calculated correlator.

Finally, we arrive at the interaction representation and introduce an S matrix in standard fashion,[13,14] so that the wave function is given by

$$|F(t)\rangle=S(t;-\infty)|F(t=-\infty)\rangle, \tag{12}$$

where $|F(t=-\infty)\rangle$ corresponds to randomly distributed particles of concentration c, and the interaction is assumed to be turned on adiabatically.

The expression for the correlation function of interest to us becomes

$$\langle\Delta c(0)\Delta c(\mathbf{x})\rangle=2c\delta(\mathbf{x})-2V^{-1}\sum{}'\cos\mathbf{kx}\langle\alpha_\mathbf{k}\beta_{-\mathbf{k}}\rangle$$
$$+V^{-1}\sum{}'\exp(i\mathbf{kx})[\langle\alpha_\mathbf{k}\alpha_{-\mathbf{k}}\rangle+\langle\beta_\mathbf{k}\beta_{-\mathbf{k}}\rangle]. \tag{13}$$

To calculate the correlator $\Gamma_\mathbf{k}=\langle\alpha_\mathbf{k}\beta_{-\mathbf{k}}\rangle$ in the lowest (second) order in the concentration, it is necessary to sum ladder diagrams which contain a minimum number of condensate lines that yield a factor c, and of vertices with small interaction w_b. They are made up of the following terms in the Hamiltonian

$$H_{int}=\sum{}' w_b(\mathbf{k})\alpha_\mathbf{k}^+\beta_{-\mathbf{k}}^+-c^2\sum{}' w_a(\mathbf{k})\alpha_\mathbf{k}^+\beta_{-\mathbf{k}}^+$$
$$-V^{-1}\sum{}' w_a(\mathbf{k}-\mathbf{k}_1)\alpha_\mathbf{k}^+\alpha_{\mathbf{k}_1}\beta_{\mathbf{k}_2}^+\beta_{\mathbf{k}_3}\Delta(\mathbf{k}+\mathbf{k}_2-\mathbf{k}_1-\mathbf{k}_3)-\ldots. \tag{14}$$

It is easy to verify that the correlators $\langle\alpha_\mathbf{k}\alpha_{-\mathbf{k}}\rangle\langle\beta_\mathbf{k}\beta_{-\mathbf{k}}\rangle$ are proportional to c^3 and should be discarded.

The free Green's function (GF), as can be easily seen from the Heisenberg equations of motion, is defined as

$$G_\mathbf{k}^\alpha(t)=\exp[-D_ek^2t]\theta(t). \tag{15}$$

It is important that $G_\mathbf{k}(t)\equiv0$ at $t<0$.

To avoid divergences that occur in few-dimensional systems as a result of the singularity of the free GF $G_\mathbf{k}(\omega)$ as $\mathbf{k}\to0$ and $\omega\to0$, we construct ladder diagrams made up of "dressed" GF:

$$G_\mathbf{k}^\alpha(\omega)=[D_ek^2-i\omega-\Sigma_\mathbf{k}^{\alpha\alpha}(\omega)]^{-1}, \tag{16}$$

where the mass operator $\Sigma_\mathbf{k}(\omega)$ is also calculated in the ladder approximation. Since it is small in terms of concentration [see (19)], $\Sigma_\mathbf{k}(\omega)$ in (16) can be replaced by its values Σ_0 at $\mathbf{k}=0$ and $\omega=0$, when the free GF (15) has a singularity.[15,13]

3. STOCHASTIC AGGREGATION OF PARTICLES IN A STATIONARY REGIME

We denote by $\Gamma_\mathbf{k}^{(1)}$ the sum of ladder diagrams that start with the first term of the interaction Hamiltonian (14), and by $\Gamma_\mathbf{k}^{(2)}=\Gamma_\mathbf{k}-\Gamma_\mathbf{k}^{(1)}$ those starting respectively with the second term. For $\Gamma_\mathbf{k}^{(1)}$ and $\Gamma_\mathbf{k}^{(2)}$ we have the integral equations

$$\Gamma_\mathbf{k}^{(1)}=[Dk^2+2|\Sigma_0|]^{-1}\left\{w_b(\mathbf{k})-V^{-1}\sum{}' w_a(\mathbf{k}-\mathbf{k}_1)\Gamma_{\mathbf{k}_1}^{(1)}\right\}, \tag{17}$$

$$\Gamma_\mathbf{k}^{(2)}=-[Dk^2+2|\Sigma_0|]^{-1}\left\{c^2w_a(\mathbf{k})+V^{-1}\sum{}' w_a(\mathbf{k}-\mathbf{k}_1)\Gamma_{\mathbf{k}_1}^{(2)}\right\}, \tag{18}$$

where D denotes the total diffusion coefficient $D=D_e+D_h$.

The mass operator Σ_0 calculated in the ladder approximation is easily seen to be expressed in terms of $\Gamma_\mathbf{k}^{(2)}$ as follows:

$$|\Sigma_0|=cw_a(0)+(cV)^{-1}\sum{}' w_a(\mathbf{k})\Gamma_\mathbf{k}^{(2)}. \tag{19}$$

In view of the presence of an incoming condensate line

$\alpha_0(\beta_0)$ the mass operator Σ_0 is small in terms of the concentration.

Relations (11) and (17)–(19) for the stationary regime form a closed system, the solution of which determines the particle concentration and the correlation function of the densities of the excess charges (13). This problem is easily solved if the probabilities $w_a(\mathbf{x})$ and $w_b(\mathbf{x})$ are taken in a δ-function form corresponding to creation and annihilation of pairs at fixed distances. We consider a three-dimensional case, when

$$w_b(\mathbf{x})=k_b(4\pi r_b^2)^{-1}\delta(|\mathbf{x}|-r_b), \tag{20}$$

and a one-dimensional one

$$w_b(x)={}^1/_2k_b[\delta(x-r_b)+\delta(x+r_b)], \tag{21}$$

while the recombination probabilities $w_a(\mathbf{x})$ are obtained from (20) and (21) by interchange $b\to a$ of all the indices. (In the two-dimensional case are encountered additional mathematical difficulties, and we shall not consider it here.) Here k_b is the pair-production rate constant, i.e., the probability of pair production per unit time and per unit volume, and k_a is the annihilation rate constant. The classical effective-mass law, which is valid for thermodynamic systems, i.e., when the detailed balance equation is met in local form ($r_a=r_b$ in our case), connects the particle concentration with the constants k_a and k_b:

$$c^2=k_b/k_a. \tag{22}$$

The dimensionalities of k_a and k_b are respectively time^{-1} $\cdot$volume and time$^{-1}\cdot$volume^{-1}. Note that in the case when the local detailed balance condition is not met, for example for carrier photogeneration, the effective-mass law (22) requires, generally speaking, substantial corrections [see (30) and (42) below].

We consider thus first a three-dimensional case. The mass operator Σ_0 can be set here equal to zero, i.e., we can construct ladder diagrams of free GF; no divergences occur.

Adding (17) and (18) and taking (11) into account, we obtain the system

$$\Gamma_{\mathbf{k}}=(Dk^2)^{-1}\left\{w_b(\mathbf{k})-c^2w_a(\mathbf{k})-(2\pi)^{-d}\int d\mathbf{k}_1\, w_a(\mathbf{k}-\mathbf{k}_1)\Gamma_{\mathbf{k}_1}\right\}, \tag{23}$$

$$c^2w_a(0)=w_b(0)-(2\pi)^{-d}\int d\mathbf{k}\, w_a(\mathbf{k})\Gamma_{\mathbf{k}}, \tag{24}$$

in terms of the solution of which the correlator of the excess-charge densities is expressed as follows:

$$\langle\Delta c(0)\Delta c(\mathbf{x})\rangle=2c\delta(\mathbf{x})-\pi^{-2}x^{-1}\int dk\,\Gamma_k k\sin kx. \tag{25}$$

After calculating the three-dimensional integrals in the equations of the system and substituting (24) in (23), the integral term in the equation for $\Gamma_{\mathbf{k}}$ drops out and we get

$$\Gamma_k=\frac{k_b}{Dk^2}\left[\frac{\sin kr_b}{kr_b}-\frac{\sin kr_a}{kr_a}\right]. \tag{26}$$

The correlation function (25) takes ultimately the form

$$\langle\Delta c(0)\Delta c(\mathbf{x})\rangle=2c\delta(\mathbf{x})+k_bk_d^{-1}x^{-1}$$
$$\times\{x+r_a-|x-r_a|-r_ar_b^{-1}[x+r_b-|x-r_b|]\}, \tag{27}$$

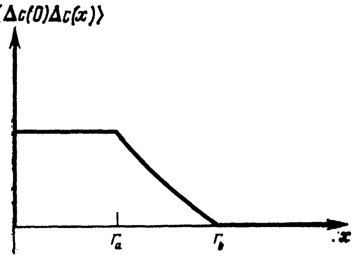

FIG. 1. Plot of correlation function of the densities of uncompensated charges at $r_b>r_a$. Three-dimensional system, stationary regime.

where the diffusion rate constant k_d is determined in the three-dimensional case by the usual relation

$$k_d=4\pi Dr_a. \tag{28}$$

A plot of the corresponding relation is shown in Fig. 1 for the case when the pair-production radius exceeds the annihilation radius. If $r_b>r_a$, the correlation function consists of a δ-function at zero and a positive constant equal to $2k_bk_d^{-1}(1-r_a/r_b)$; at $r_a<x<r_b$ it decrease hyperbolically to zero: $2k_bk_d^{-1}r_a(x^{-1}-r_b^{-1})$ and vanishes identically at $x>r_b$. The positive spatial correlation of the density of the uncompensated charges describes the phenomenon of stochastic aggregation of like particles in a reacting medium. It is easy to estimate the average number of uncompensated charges in such a cluster:

$$N\sim1+(4\pi/3)k_b^{1/2}k_d^{-1}r_a(r_b^2-r_a^2)[k_a^{-1}+k_d^{-1}(1-r_a/r_b)]^{-1/2}. \tag{29}$$

The excess charge is proportional to the square root of the low pair-production probability, but with the small total diffusion coefficient, which enters in the form of the factor $D^{-1/2}$, and with the large creation rate r_b ($N\sim r_b^2$), it may be not small at all.

According to this picture, radioactive irradiation of a dielectric should produce in it spontaneously regions that contain predominantly electrons (holes). This is naturally accompanied by the appearance of internal electric fields which are stronger the lower the carrier mobility and the higher the irradiation intensity. This effects was experimentally observed in Ref. 16, and the internal field reached breakdown values. Note that to describe this effect quantitatively account must be taken of the Coulomb interaction of the electrons and holes.[6]

At the inverse ratio of the creation and annihilation radii, r_b and r_a change places and the continuous component in the correlator becomes negative; this corresponds to "screening" of particles of one species by particles of the other.

It is also of interest to examine the expression obtained from (24) and (26) for the average concentration:

$$c^2=k_bk_a^{-1}+k_bk_d^{-1}(1-r_a/r_b)\theta(r_b-r_a). \tag{30}$$

The first term in the right-hand side of (30) corresponds to the classical law of effective masses (22), while the second is a correction to it. This correction was first obtained in Ref. 5 for the limiting case of low carrier density and low-efficiency annihilation compared with diffusion. It was found there to be small in the parameter $k_a/k_d\ll1$.

It can be seen from (30) that in a system under thermodynamic equilibrium, by virtue of the detailed-balancing condition $r_a = r_b$, the classical law of effective masses is exactly satisfied. If the carrier creation process is equilibrium (although the process may be stationary), we have generally speaking $r_a \neq r_b$. If, moreover, the electron-hole pair moves apart upon creation to a distance exceeding its annihilation radius (as, for example, in γ irradiation), the correction to the law of effective masses differs from zero, and in the case of slow diffusion and effective annihilation $k_d \ll k_a$ (the limit of the diffusion-controlled process) it is the correction which becomes decisive.

As shown above, in this regime there are produced in space clusters of like particles, the spreading of which is slow and by diffusion. Clearly, clustering of like particles increases the stationary value of the concentration (the sign of the correction is strictly positive): if particle clusters are uniformly mixed the annihilation processes become more effective and the equilibrium concentration decreases. Thus, the essense of the correction to the low of effective masses is that it consists of stationary fluctuation effects that manifest themselves at $r_b > r_a$.

We note that the large number of the like particles in a cluster having a characteristic dimension $r_b \gg r_a$ (29) does not contradict the low-concentration limit (1). At the same time, if the total diffusion coefficient D in (27) and (30) tends to zero, the fluctuation effects and the equilibrium concentrations increase without limit, so that at

$$k_d \ll k_b r_a^6 (1-r_a/r_b)$$

the conditions for the validity of the concentration expansion are violated.

We proceed now to the one-dimensional case. Equations (17) and (18) have degenerate kernels. Introducing the symbols

$$\Gamma_c(x) = \int dk\, \Gamma_k \cos kx, \quad \Gamma_s(x) = \int dk\, \Gamma_k \sin kx, \tag{31}$$

we obtain from (17) and (18) a system of algebraic equations for Γ_c and Γ_s, whose solution takes the form

$$\Gamma_s^{(1)}(x) = \Gamma_s^{(2)}(x) \equiv 0,$$

$$\Gamma_c^{(1)}(x) + \Gamma_c^{(2)}(x) = k_b[I_1(x, r_b) - I_1(x, r_a)], \tag{32}$$

$$\Gamma_c^{(2)}(r_a) = k_b I_1(r_a, r_b)[1 + (2\pi)^{-1} k_a I_1(r_a, r_a)]^{-1}, \tag{33}$$

where the quantity

$$I_1(x, r) = \pi(8|\Sigma_0|D)^{-1/2}\{\exp[-(2|\Sigma_0|/D)^{1/2}|x-r|] + \exp[-(2|\Sigma_0|/D)^{1/2}|x+r|]\} \tag{34}$$

depends on the mass operator Σ_0 which is self-consistently connected with $\Gamma_c^{(2)}$ by Eq. (19). The equilibrium concentration and the correlation function of the concentrations of the uncompensated charges are expressed in terms of I_1:

$$c^2 = k_b k_a^{-1} - (2\pi)^{-1} k_b [I_1(r_a; r_b) - I_1(r_a; r_a)], \tag{35}$$

$$\langle \Delta c(0) \Delta c(x) \rangle = 2c\delta(x) - \pi^{-1} k_b [I_1(x, r_b) - I_1(x, r_a)]. \tag{36}$$

A transcendental equation is obtained to determine Σ_0 from (19) and (32)–(35). We consider its solution for three physical cases of interest.

Assume first that in (34)

$$|\Sigma_0| r_a^2 D^{-1} \ll 1, \quad |\Sigma_0| r_b^2 D^{-1} \ll 1. \tag{37}$$

Then

$$|\Sigma_0| = 4k_b k_a^{-1}[2D + k_a(r_b - r_a)\theta(r_b - r_a)] + \ldots \tag{38}$$

and from (35) and (34) we obtain an expression for the concentration:

$$c^2 = k_b k_a^{-1} + k_b(2D)^{-1}(r_b - r_a)\theta(r_b - r_a) - \ldots. \tag{39}$$

Comparing now (38) and (39), we see that the inequalities (37), which determine the region of applicability of the resultant expressions, are equivalent to

$$cr_a \ll 1, \quad cr_b \ll 1. \tag{40}$$

This case corresponds thus to finite values of the creation and annihilation radii $r_a \sim r_b$. The first inequality in (40) is equivalent to the condition for the applicability of the concentration expansion (1), while the second means that on the average the number of particles in a segment of length $r_b \sim r_a$ is small.

Just as in the three-dimensional case, the effective-mass law when particle aggregation takes place. The correlation function of the densities of the uncompenstated charges is obtained from (34), (36), and (38), and takes the following forms (Fig. 2a): at $x < r_a, r_b$ it is equal to the constant $k_b(r_b - r_a)D^{-1}$, at $\min\{r_a; r_b\} < x < \max\{r_a; r_b\}$ it decreases (increases) linearly to the small quantity $\varepsilon_1 = -(8k_a k_b/D)^{1/2}c^2$, and at $x > r_a, r_b$ it decreases exponentially in absolute value with a small coefficient in the exponent, $\sim \varepsilon_1 \exp[2\varepsilon_1 D x k_b^{-1}(r_b^2 - r_a^2)^{-1}]$.

The second limiting case corresponds to large creation radii $r_b \gg r_a$, so that the signs of the inequalities in (37) are replaced respectively by ⟨⟨ and ⟩⟩. Expressed in terms of the concentrations, the inequalities (37) take in this regime the form

$$cr_a \ll 1, \quad cr_b \gg 1, \tag{41}$$

i.e., in contrast to (40), the line segment r_b contains on the average many particles.

The expression for the concentration is found in this case to be quite similar to the law of effective masses (22);

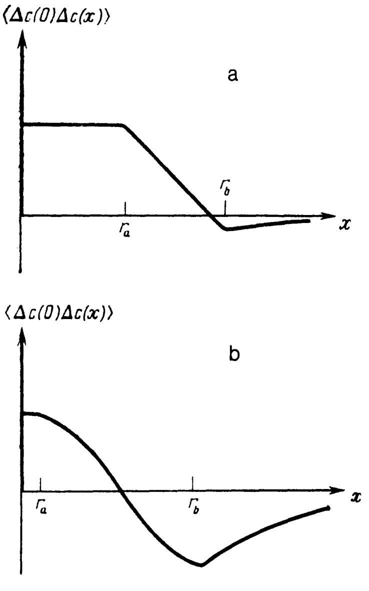

FIG. 2. Correlation function of excess-charge densities in a one-dimensional system (a) $r \gtrsim r_a$, (b) $r_b \gg r_a$.

$$c^2=\frac{k_b^{2/3}}{4D^{2/3}}+\frac{5k_b}{6k_a}-\frac{2k_b r_a}{3D}+\frac{k_a k_b^{1/3}}{24D^{4/3}}\exp\left[-\frac{2k_b^{1/3}r_b}{D^{1/3}}\right]+\dots\ . \tag{42}$$

In the principal term of (42), the dependence on the creation rate is very weak, $\propto k_b^{2/3}$ instead of linear. It does not depend at all on the annihilation rate, but on the other hand it contains a diffusion coefficient; this is evidence that the limiting stage in the recombination processes is diffusive wandering of the particles in large-scale fluctuations. The fluctuation effects play thus a very substantial role in this regime.

The correlation function of the densities of uncompensated charges (Fig. 2b) consists of a δ function at zero and a constant $\varepsilon_2=(k_b/D)^{2/3}/2$ at $x<r_a$ and $x<r_b$, decreases exponentially like $\sim\varepsilon_2\{\exp[-4\varepsilon_2^{1/2}x]-\exp[-4\varepsilon_2^{1/2}(r_b-x)]\}$ to $-\varepsilon_2$ at $r_a<x<r_b$, and decrease exponentially to zero with a small coefficient in the exponent, $\sim-\varepsilon_2\{\exp[-4\varepsilon_2^{1/2}(x-r_b)]$, at $x>r_b$. Thus, strong interparticle correlations extend over quite large distances $\gtrsim r_b$.

The third and final case corresponds to the limit of small diffusion coefficients [the conditions (40) and (41) were violated as D tended to zero in (39) and (32)]. The inequality signs in (4) are then replaced by $\gg$, the principal term of the expression for the concentration agrees with (42) apart from a numerical factor, and the validity conditions take the form

$$cr_a\gg1,\quad cr_b\gg1,$$

which prevents the use of the concentration expansion. Obviously, in this regime the spreading out of the produced clusters is so slow that the average concentration, which is determined by their population, is no longer small.

We shall find useful in the analysis of nonstationary processes an explicit expression for the correlator Γ_k. It is easily obtained from (32):

$$\Gamma_k=k_b(\cos kr_b-\cos kr_a)[Dk^2+2|\Sigma_0|]^{-1}. \tag{43}$$

4. RELAXATION OF THE PARTICLE-DENSITY FLUCTUATIONS

We consider the relaxation of particle clusters produced in the stationary regime after the generation was turned off. We assume that starting with the instant $t=0$ the arrival term in the Hamiltonian, which are proportional to k_b, vanish identically. We are interested in finding the law that governs the decrease, with time, of the average particle concentration and of the correlation function of the density of the excess charges.

The correlator $\Gamma'_\mathbf{k}(t)=\langle\alpha_\mathbf{k}(t)\beta_{-\mathbf{k}}(t)\rangle$, which enters in the expression $\langle\Delta c(0)\Delta c(\mathbf{x})\rangle$ (13) consists of ladder diagrams of two types. We denote by $\Gamma_\mathbf{k}^{(1)\prime}(t)$ the sum of the ladder diagrams that stem from the fluctuation produced in the stationary regime prior to turning off the generation, and by $\Gamma_\mathbf{k}^{(2)\prime}(t)$ the one stemming from the fluctuation produced after generation was turned off as a result of annihilation of a pair of particles in a homogeneous condensate. The equation for

$$\Gamma_\mathbf{k}'(t)=\Gamma_\mathbf{k}^{(1)\prime}(t)+\Gamma_\mathbf{k}^{(2)\prime}(t)$$

is of the form

$$\Gamma_\mathbf{k}'(t)=G_\mathbf{k}^\alpha(t)G_{-\mathbf{k}}^\beta(t)\Gamma_k-w_a(k)\int_0^t dt_1\,c^2(t_1)G_\mathbf{k}^\alpha(t-t_1)G_{-\mathbf{k}}^\beta(t-t_1)-V^{-1}\sum{}'\,w_a(\mathbf{k}-\mathbf{k}_1)\int_0^t dt_1\,G_\mathbf{k}^\alpha(t-t_1)G_{-\mathbf{k}}^\beta(t-t_1)\Gamma_{\mathbf{k}_1}'(t_1), \tag{44}$$

where $\Gamma_\mathbf{k}$ is the stationary correlator obtained above. The expression $\langle\Delta c(0)\Delta c(\mathbf{x})\rangle$ (13) and the equation (11) for the concentration remain valid if the substitution $\Gamma_\mathbf{k}\to\Gamma_\mathbf{k}'(t)$ is made and if $w_b(\mathbf{k})\equiv0$, $t>0$.

We consider first the three-dimensional case. Just as before, the kernel of the integral equation (44) with respect to $\mathbf{k}$ is degenerate. Evaluating the three-dimensional integrals and substituting in (44) the expression that follows for $c^2(t_1)$ for the concentration (11)

$$k_a^{-1}(d/dt)c(t)=-c^2(t)-(2\pi^2r_a)^{-1}\Gamma_s'(r_a,t), \tag{45}$$

where

$$\Gamma_s'(x,t)=\int dk\,\Gamma_k'(t)k\sin kx, \tag{46}$$

we see that the integral terms with $\Gamma_s'(x,t)$ cancel out and we get

$$\Gamma_s'(x,t)=\frac{k_b}{D}\int dk\exp[-Dk^2t]\frac{\sin kx}{k}\left[\frac{\sin kr_b}{kr_b}-\frac{\sin kr_a}{kr_a}\right]+\frac{1}{r_a}\int dk\sin kx\sin kr_a\int_0^t dt_1\exp[-Dk^2(t-t_1)]\frac{dc(t_1)}{dt_1}, \tag{47}$$

where the expression (26) for the stationary correlator was used. Note that by virtue of the presence of the exponential factor $\exp[-Dk^2(t-t_1)]$ in the last term of (47), the main contribution to the integral with respect t_1 is made by large $t_1\approx t$. Expanding therefore the derivative dc/dt in a Taylor series at the point t and integrating, we get

$$\Gamma_s'(x,t)=\frac{k_b}{D}\left[\frac{I_2(x,r_b)}{r_b}-\frac{I_2(x,r_a)}{r_a}\right]+\frac{1}{Dr_a}\frac{dc(t)}{dt}\left[I_2(x,r_a)\big|_{t=0}+\frac{2\pi^2r_a}{\varkappa(x)}\right], \tag{48}$$

where

$$I_2(x,r)=\frac{1}{2}(\pi Dt)^{1/2}\left\{\exp\left[-\frac{(x+r)^2}{4Dt}\right]-\exp\left[-\frac{(x-r)^2}{4Dt}\right]\right\}+\frac{\pi}{4}\left\{|x+r|\operatorname{erf}\left[\frac{|x+r|}{2(Dt)^{1/2}}\right]-|x-r|\operatorname{erf}\left[\frac{|x-r|}{2(Dt)^{1/2}}\right]\right\}, \tag{49}$$

and $\varkappa(x)$ denotes the quantity

$$\varkappa^{-1}(x)=-\frac{I_2(x,r_a)}{2\pi^2Dr_a^2}+\frac{1}{8\pi^{3/2}D^{1/2}r_a^2}\sum_{n=2}^{\infty}\frac{(-1)^n}{n!}\frac{d^nc(t)}{dt^n}\times\left[\frac{dc(t)}{dt}\right]^{-1}\int_{t^{-1}}^{\infty}\frac{d\gamma}{\gamma^{n+3/2}}\left\{\exp\left[-\frac{(x-r_a)^2}{4D}\gamma\right]-\exp\left[-\frac{(x+r_a)^2}{4D}\gamma\right]\right\}. \tag{50}$$

Substituting finally (48) in (45) we arrive at an exact closed equation for the concentration $c(t)$:

$$\frac{dc(t)}{dt}=-[k_{eff}^{-1}+\varkappa^{-1}(r_a)]^{-1}\Big\{c^2(t)+\frac{2k_b}{\pi k_d}\Big[\frac{I_2(r_b,r_a)}{r_b}-\frac{I_2(r_a,r_a)}{r_a}\Big]\Big\}. \quad (51)$$

At large t, when $\varkappa^{-1}(r_a)$ can be neglected, this equation has a perfectly clear meaning. The second term in the curly brackets describes the relaxation of the fluctuations that serve as the initial condition for the nonstationary problem, while the first term gives the Smoluchowski equation with an effective rate constant that coincides, naturally, with the classical expression

$$k_{eff}^{-1}=k_a^{-1}+k_d^{-1}. \quad (52)$$

Equation (51) with large t contains thus both a fluctuation regime and a classical-kinetics regime.

Note that the integral equation (47) can be reduced exactly also to the partial differential equation

$$\frac{\partial\Gamma_s'(x,t)}{\partial t}=D\frac{\partial^2\Gamma_s'(x,t)}{\partial x^2}+\frac{\pi}{2r_a}\delta(x-r_a)\frac{dc(t)}{dt}, \quad (53)$$

which makes up with (45) a closed system. Equation (51), however, is more convenient for the investigation of the regions of long and short times.

Let us analyze the behavior of $c(t)$ in various regimes. Let the creation an annihilation radii be finite quantities of like order, $r_b\sim r_a$ and let the time t be long enough, so that

$$(r_b+r_a)^2(Dt)^{-1}\ll 1. \quad (54)$$

In this regime we obtain from (50)

$$\varkappa^{-1}(r_a)=-\text{const}\cdot D^{-3/4}t^{-1/4}+\ldots\ll k_{eff}^{-1}. \quad (55)$$

The second term in the curly brackets of (51), which describes the relaxation of the initial fluctuation, decreases as a power-law:

$$-at^{-3/2}+O(t^{-5/2}), \quad (56)$$

where

$$a=k_b(r_b^2-r_a^2)/48\pi^{3/2}D^{5/2}. \quad (57)$$

With allowance for (55) and (56), the solution of (51), neglecting the torms $O(t^{-9/4})$, is expressed in terms of modified Bessel functions:

$$c(t)=a^{1/2}I_1(4k_{eff}a^{1/2}t^{1/4})/t^{3/4}I_2(4k_{eff}a^{1/2}t^{1/4}). \quad (58)$$

The following expansion terms are exact and describe both the fluctuation and the transient regimes:

$$c(t)=a^{1/2}/t^{3/4}+3/8k_{eff}t+15/2^7k_{eff}a^{1/2}t^{5/4}+\ldots. \quad (59)$$

The first term leads to a slower power-law decrease of the density, $\propto t^{-3/4}$, than the classical kinetics ($\propto t^{-1}$) in which the fluctuations of the reagent distribution are not taken into account. Note that a similar time-dependent asymptote was obtained in a less rigorous manner for relaxation of Poisson fluctuations.[1,2] The second term of (59) is similar to the solution of the Smoluchowski equation, but differs by a numerical factor 3/8.

If the creation radius r_b exceeds considerably the annihilation radius r_a an the time t is not too long, viz.,

$$r_a^2(Dt)^{-1}\ll 1,\ r_b^2(Dt)^{-1}\gg 1, \quad (60)$$

we have an intermediate asymptotic form

$$c(t)=k_b^{1/2}/2\pi^{1/4}D^{3/4}t^{1/4}+\ldots, \quad (61)$$

that describes the rather slow power-law decrease, $\propto t^{-1/4}$, of the concentration. In the region of short times, the region where (61) is valid is bounded by the inequality

$$k_{eff}^2D^{-3}t^{-1}\ll 1, \quad (62)$$

thereby justifying the neglect of the term $\varkappa^{-1}(r_a)$. The fluctuation result (61) was obtained in Ref. 6, apart from a coefficient, by a less rigorous method.

Finally, at short times Eq. (51) takes the form

$$\Big[k_a^{-1}+\frac{t^{1/2}}{4\pi^{3/2}D^{1/2}r_a^2}+\ldots\Big]\frac{dc(t)}{dt}=-c^2(t)+\frac{k_b}{k_dr_b}\Big[(r_b-r_a)\theta(r_b-r_a)-\Big(\frac{Dt}{\pi}\Big)^{1/2}\frac{r_b}{r_a}+\ldots\Big] \quad (63)$$

and yields at zero the regular expansion

$$c(t)=c(t=0)-k_bt+k_bk_ac(t=0)t^2-\ldots, \quad (64)$$

where $c(t=0)$ is determined by the stationary value (30).

We proceed to consider the correlation function of the densities of the uncompensated charges. The expression for this function, with allowance for (48), takes the form

$$\langle\Delta c(0)\Delta c(x)\rangle=2c(t)\delta(x)-\frac{k_b}{\pi^2Dx}\Big\{\frac{I_2(x,r_b)}{r_b}-\frac{I_2(x,r_a)}{r_a}\Big\}+\frac{4}{\pi k_dx}\frac{dc(t)}{dt}\Big\{I_2(x,r_a)\big|_{t=0}+\frac{2\pi^2r_a}{\varkappa(x)}\Big\}. \quad (65)$$

At distances on the order of the creation and annihilation radii and for long times

$$x\sim r_a\sim r_b,\ x^2(Dt)^{-1}\ll 1 \quad (66)$$

we have

$$\varkappa^{-1}(x)=\text{const}\cdot xD^{-3/4}r_a^{-1}t^{-1/4}+\ldots \quad (67)$$

and (65) yields the following dependences:

$$\langle\Delta c(0)\Delta c(x)\rangle=2c(t)\delta(x)+\frac{A}{t^{3/2}}+\frac{B\theta(x-r_a)}{xt^{7/4}}-\frac{Cx^2}{t^{5/2}} \quad (68)$$

where

$$A=k_b(r_b^2-r_a^2)/24\pi^{3/2}D^{5/2}-\ldots,\ B=3^{1/2}A^{1/2}/4\pi D,\ C=A/4D.$$

The particle clusters are thus spread out in this regime by diffusion, and in proportion to $t^{-3/2}$.

Similarly, in the intermediate asymptotic regime (6), the coordinate dependence of the correlation function $\langle\Delta c(0)\Delta c(x)\rangle$ remains unchanged over distances $x\propto r_a\ll r_b$ on the order of the annihilation radius, but has in this case a different time dependence:

$$\langle\Delta c(0)\Delta c(x)\rangle=2c(t)\delta(\mathrm{x})+\frac{A'}{t^{1/2}}+\frac{B'\theta(x-r_a)}{xt^{5/4}}-\frac{C'x^2}{t^{3/2}}. \quad (69)$$

It can be seen that in this case the spreading of the central part of an extended bunch is slower, $\propto t^{-1/2}$.

We consider now one-dimensional systems. Repeating the operations that led to relations (48)–(50), we get

$$\Gamma_c'(x,t)=\frac{k_b}{D}[I_3(x,r_b)-I_3(x,r_a)]+\left(\frac{\pi}{4D}\right)^{1/2}\sum_{n=0}^{\infty}\frac{d^{n+1}c(t)}{dt^{n+1}}\frac{(-1)^n}{n!}\times\int_{t^{-1}}^{\infty}\frac{d\gamma}{\gamma^{n+3/2}}\left\{\exp\left[-\frac{(x-r_a)^2}{4D}\gamma\right]+\exp\left[-\frac{(x+r_a)^2}{4D}\gamma\right]\right\},\tag{70}$$

where

$$I_3(x,r)=-(\pi Dt)^{1/2}\left\{\exp\left[-\frac{(x-r)^2}{4Dt}\right]+\exp\left[-\frac{(x+r)^2}{4Dt}\right]\right\}-\frac{\pi}{2}\left\{|x-r|\operatorname{erf}\frac{|x-r|}{2(Dt)^{1/2}}+|x+r|\operatorname{erf}\frac{|x+r|}{2(Dt)^{1/2}}\right\}.\tag{71}$$

Relations (70) and (71) and Eq. (11) for the concentration at large t

$$r_a^2(Dt)^{-1}\ll 1,\ r_b^2(Dt)^{-1}\ll 1\tag{72}$$

lead, in contrast to the three-dimensional case, to an equation that is not similar to that of Smoluchowski

$$\left(\frac{t}{\pi D}\right)^{1/2}\left[\frac{dc(t)}{dt}-\frac{t}{3}\frac{d^2c(t)}{dt^2}+\frac{t^2}{5}\frac{d^3c(t)}{dt^3}-\dots\right]=-c^2(t)+\frac{k_b(r_b^2-r_a^2)}{4\pi^{1/2}D^{3/2}t^{1/2}}+O(t^{-3/2}).\tag{73}$$

The two principal terms in the expansion of its solution are

$$c(t)=\frac{[k_b(r_b^2-r_a^2)]^{1/2}}{2\pi^{1/4}D^{3/4}t^{1/4}}+\frac{\text{const}}{4(\pi Dt)^{1/2}}-\dots.\tag{74}$$

The principal fluctuation term of (74), proportional to $t^{-1/4}$, can be determined, just as in the three-dimensional case, by equating to zero the right-hand side of (73), and the second term, in contrast to (51), is determined by the derivatives of all orders. To find the next terms of the expansion it is necessary to solve the corresponding integral equation for all t.

For short times ($r^2_{a,b}/Dt \gg 1$) the concentration decreases in regular fashion, just as in the three-dimensional case:

$$c(t)=c(t=0)-k_bt+\dots,\tag{75}$$

where $c(t=0)$ is determined by the stationary value (39) and (42).

The correlation function of the densities of the uncompensated charges, for distances of the order of the creation and annihilation radii, is obtained in the limit (72) from (13) and (70):

$$\langle\Delta c(0)\Delta c(x)\rangle=2c(t)\delta(x)+\frac{k_b(r_b^2-r_a^2)}{2\pi^{1/2}D^{3/2}t^{1/2}}+\frac{[k_b(r_b^2-r_a^2)]^{1/2}}{4\pi^{3/4}D^{5/4}t^{3/4}}\text{const}-\dots.\tag{76}$$

It can be seen from (76) that at $x\sim r_a\sim r_b$ the spreading of the particle bunches is mainly by diffusion and in proportion to $t^{-1/2}$.

Obviously, the kinetics of reaction processes in fractal systems of dimensionality $d<2$ is similar to that considered above for the one-dimensional case.

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