

CORRELATION EFFECTS IN THE KINETICS OF BIMOLECULAR DIFFUSION-MEDIATED REACTIONS

Yu.B. GAIDIDEI, A.I. ONIPKO and I.V. ZOZULENKO

Institute for Theoretical Physics, Kiev-130, 252130, USSR

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Analytical and numerical methods are used to study the kinetics of a bimolecular reaction such as $A + B = 0$ when interparticle correlations are taken into account in the Kirkwood superposition approximation for a three-particle reagent distribution function. A detailed analysis is made of the dependence of the reagent concentration decay rate on the value of the initial concentration $c(0)$ and of the parameter k that characterises the reaction efficiency in reagent collision. It is shown that in the reaction depth range $0.5 \leq \eta \leq 5$ ($\eta = \log[c(0)/c(t)]$) the concentration decay is described by a dependence of the form $c(t) \sim t^{-\alpha}$ and the values of α are obtained as a function of the parameters $c(0)$ and k . At long time ($\eta > 5$) the dependence of the concentration decay goes to the "three-fourth" law, $c(t) \sim t^{-3/4}$.

1. Introduction

The past decade has witnessed an increased number of papers devoted to studying the kinetics of bimolecular reaction between particles that diffuse in condensed media. A revived interest in this classical problem discussed already by Smoluchovsky [1], and Waite [2] who determined its theoretical basis has been generated by a paper of Zeldovich and Ovchinnikov [3] that drew the physicists' attention to elucidating the role of reagent density fluctuations under the reaction. The above paper has shown that in the processes following the scheme $A + B = 0$ and involving diffusing particles (A does not react with A and B with B), the decay law $c(t) \sim t^{-1}$, with the same initial reagent density $c_A = c_B = c$, that appeared to be applicable for bimolecular reactions in three-dimensional system may be replaced by the law $c(t) \sim t^{-3/4}$, if we take into account the existence of reagent number density fluctuations in a system. The physical interpretation of the effect predicted in ref. [3] is as follows. Before the reaction starts the reagent distribution in space is supposed to be the same as the equilibrium one for a system of non-interacting particles. In this case thermal density fluctuations give rise to local macroscopic regions in which the density of non-interacting particles of the same type is higher than statistical average. After the reaction begins and lasts for a definite time t , basically only the particles that belong to fluctuation accumulations will survive (non react). The average volume V of the regions of unreacted particles $\sim I_D^3$ ($I_D = Dt$, D is the diffusion coefficient supposed to be the same for A and B particles). On the other hand, the equilibrium density fluctuations $\delta c \sim V^{-1/2}$, so that for the time $\geq t$ the further decrease in the reagent density number will be defined by the diffusive dispersion rates of fluctuation accumulations of identical particles, that is, $c(t) \sim I_D^{-3/2} \sim t^{-3/4}$.

The authors of many subsequent papers [4–10] that took into account the influence of fluctuations on the kinetics of bimolecular reactions in d -dimensional systems, and also of the reactions involving a greater number of particles in the act, for example, $A + B + C = 0$ employed the ideas of ref. [3] or equivalent scaling hypotheses. More specifically, the almost obvious generalization of the law $t^{-3/4}$ to the case of a smaller-dimensionality system gives $c(t) \sim t^{-d/4}$, $d = 1, 2, 3$ for one-, two-, and three-dimensional systems [5].

The above results effect significantly the conventional views on reaction kinetics law. Moreover, they were obtained largely by using quite physical, yet not strict enough assumptions. The limitations of the papers under consideration also include the artificial sorting out of particles belonging to fluctuation accumulations, among most others distributed on an equally probable basis over the entire volume of a system. As a result, it is very difficult to estimate the contributions of reagents, singled out in the above manner, to the experimentally determined decay rates of their average concentration. In ref. [3], some guiding estimates are given and it is stressed that the $t^{-3/4}$ dependence defines an intermediate reaction stage, that is, it implies an intermediate asymptotics in the behaviour of a system of particles that react according to the scheme $A + B = 0$. At the same time the authors of refs. [5,9,10] and some other papers state that the $t^{-\alpha}$ law, $\alpha \neq 1$, governs the behaviour of such systems at $t \rightarrow \infty$. This concept is questioned by Antonov-Romanovsky [11] and Noyes and Gardiner [12] who concluded that diffuse reagent mixing under the reaction eventually eliminates the fluctuation effect, so that asymptotically the concentration drop caused by bimolecular reactions is described by the conventional law of formal chemical kinetics, $c(t) \sim t^{-1}$, $t \rightarrow \infty$. The question of the role of reagent density fluctuations in defining the observed characteristics of the processes that follow the scheme of bimolecular reactions is still questionable and must be elaborated.

A consistent approach to describe systems of reacting particles is known [13–17] to be based on employing a chain of coupled Bogoliubov–Born–Green–Kirkwood–Yvon equations for N -particle distribution functions that produce full information both on the microscopic picture of the process and on the character of its experimental manifestation. The availability of a small parameter-reagent concentration enables us to use effectively standard methods to find one- and two-particle distribution functions, thus fully realizing the possibilities to compare theory with experiment.

Using the superposition approximation for a three-particle function in a chain that reduces an infinite set of linear equations to a closed set of non-linear equations for 1,2-particle distribution functions Kotomin and Kuzovkov investigated the evolution of particle system reacting according to the scheme $A + B = 0$ [18–21]. We mention here only some results directly concerned with the present study. Estimating the asymptotics $c(t)$, $t \rightarrow \infty$ disregarding the fluctuations in the initial reagent distribution the authors of ref. [18] obtained a result formally coinciding with the predictions by Ovchinnikov and Zeldovich, with the only (fundamental) difference that the asymptotics in ref. [18] is absolute, but not intermediate. We stress that the effect discussed in ref. [3] is actually due to the macroscopic spatial inhomogeneity of a system in the initial state resulting from equilibrium fluctuations (we mean the instantaneous realization of a system in initial time), whereas the choice of initial conditions in ref. [18] excludes any inhomogeneity. The seemingly surprising coincidence of the index $\alpha = \frac{3}{4}$ in ref. [3] and ref. [18] has a deep physical basis. The mutual influence (correlation) of particles leads to their spatial redistribution in the course of the reaction that manifests itself, as shown in ref. [21], in the formation of accumulations of identical particles, that is, we have dynamic (non-equilibrium) density fluctuations. Obviously, there is thus a common physical nature of the reagent decay law for the process $A + B = 0$, predicted in refs. [3,18], and in both cases it is the result of identical-particle accumulations, although the mechanisms forming equilibrium and dynamical fluctuations are different.

The question naturally arises of whether it is possible to confirm experimentally the value of the index $\alpha = \frac{3}{4}$ (or of the others under appropriate realizations of a system of reacting particles). The answer seems to require a physical specification of the term “asymptotic dependence”, in other words, the definition of a time period after the process beginning when the concentration decay must theoretically be described by the dependence $t^{-\alpha}$ ($\alpha \neq 1$). The limitations of scaling theories [3–10], as well as of the possibilities of the method in ref. [18] to analyze the solutions of equations for 1,2-particle distribution functions do not enable us to obtain the necessary estimation. Besides, there are practically no data on the dependence of correlation effects leading to dynamic fluctuations upon the parameters of a system of reacting particles: the initial reagent concentration and the rate of reaction upon contact. The elucidation of the interrelation

observed is of fundamental importance for estimating the role of correlation (fluctuation) effects in reaction kinetics and, consequently, for predicting the possibilities of their experimental observation. The present study is devoted to solving these problems.

2. The model of a system of reacting particles and the basic equations of theory

In describing the reaction between diffusing particles (quasiparticles) it is convenient to employ the lattice model [13,15,16], regarding the reagent motion as a markovian process of random walks in which each particle of type A and type B moves by hopping between neighbouring lattice sites with unit time probability W^A and W^B , respectively. A lattice of dimensionality d is assumed for simplicity to be cubic with a lattice constant a . When only particles of different types draw together to a minimum distance a there occurs a reaction (recombination, annihilation) with a unit time probability ω . The choice of the reaction mechanism corresponds to the most popular model of a contact reaction that proceeds instantly when $\omega \rightarrow \infty$, or involves a partial repulsion of particles in collisions when ω is finite [1,2,16,22,23].

Because the elementary act of the process under consideration is of two-particle character, we can, by analogy with formal chemical kinetics laws, represent the change in the average reagent concentration on $c_{A(B)}(t)$ – the ratio between the total number of particles of type A (B) at time t and the total number of lattice sites N^d as

$$\frac{dc_{A(B)}(t)}{dt} = -\gamma(t)c_A(t)c_B(t), \quad (1)$$

where the apparent (experimentally observed) reaction rate, ARR, is defined by the pair distribution function for particles of different types at minimum distance between them [16]

$$\gamma(t) = 2 d\omega g_a^{AB}(t). \quad (2)$$

$g_n^{AB}(t)$ is the probability with which the pair AB can be observed at lattice sites separated by a vector n . So, when the motion of particles in a system is non-correlated, $g_n^{AB}(t) = 1$ for any n and t .

In the case of a homogeneous reagent mixture, $g_n^{AB}(t)$ is defined by solving a non-linear system of equations including (1), (2) and

$$\begin{aligned} \frac{dg_n^{AB}(t)}{dt} = & -\frac{1}{2d}\gamma(t)\delta_{n,a} + \sum'_{\Delta} (W^A + W^B) [g_{|n+\Delta|}^{AB}(t) - g_n^{AB}(t)] \\ & - \gamma(t)g_n^{AB}(t) \frac{1}{2d} \sum'_{\Delta} \{ c_A(t) [\bar{g}_{|n+\Delta|}^{AA}(t) - 1] + c_B(t) [\bar{g}_{|n+\Delta|}^{BB}(t) - 1] \}, \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{d\bar{g}_n^{AA(BB)}(t)}{dt} = & 2W^{A(B)} \sum'_{\Delta} [\bar{g}_{|n+\Delta|}^{AA(BB)}(t) - \bar{g}_n^{AA(BB)}(t)] \\ & - 2\gamma(t)c_{A(B)}(t)\bar{g}_n^{AA(BB)} \left(\frac{1}{2d} \sum'_{\Delta} g_{|n+\Delta|}^{AB}(t) - 1 \right), \end{aligned} \quad (4)$$

where $\bar{g}_n^{AA(BB)}(t)$ is the pair distribution function for identical particles A (B), that has a meaning similar to $g_n^{AB}(t)$; the summation over Δ is bounded by the values of a lattice vector that connects neighboring lattices; the primes on the summations indicate that the condition $g_0^{AB}(t) = \bar{g}_0^{AA(BB)}(t) = 0$ is satisfied, which corresponds to taking into account a kinematic particle repulsion, in other words, the solution of (3), (4) at $\omega = \gamma(t) = 0$ describes a system of particles elastically reflected from one another while approaching

to a minimum distance a . The set (1)–(4) is obtained within the conventional scheme of cutting off an infinite chain of coupled equations for N -particle distribution functions by representing a three-particle function in the Kirkwood superposition approximation [15–18]. The use of this approximation to take into account three-particle, and thus interparticle correlations of higher orders, is justified under the condition of small particle concentration $c_A(t)$, $c_B(t) \ll 1$, which is valid for many energy- and charge-transport processes that follow the scheme $A + B = 0$.

In what follows we restrict ourselves to investigating the above system of equations in the particular case $c_A(t) = c_B(t) = c(t)$, $W^A = W^B = W$, so that the indices A, B and those for pair distribution function may be omitted. To carry out intermediate calculations, we go over to a dimensionless time $\tau = 2Wt$ and a dimensionless ARR $\lambda(\tau) = \gamma(t)/W$, but all the final results will be given in dimensional form. Besides, in non-linear term of the equations we neglect the insignificant change in the distribution functions with distance a . Using the above simplifications, (3), (4) take the form

$$\frac{dg_n(\tau)}{d\tau} = -\frac{1}{4d}\lambda(\tau)\delta_{n,a} + \sum'_\Delta [g_{|n+\Delta|}(\tau) - g_n(\tau)] - c(\tau)\lambda(\tau)g_n(\tau)[\bar{g}_n(\tau) - 1], \quad (5)$$

$$\frac{d\bar{g}_n(\tau)}{d\tau} = \sum'_\Delta [\bar{g}_{|n+\Delta|}(\tau) - \bar{g}_n(\tau)] - c(\tau)\lambda(\tau)\bar{g}_n(\tau)[g_n(\tau) - 1]. \quad (6)$$

If the distribution functions are smooth, the expansions $g_{|n+\Delta|}(t)$ and $\bar{g}_{|n+\Delta|}(t)$ in Δ can be used to reduce (5), (6) to a set of non-linear diffusion equations employed in refs. [18–21] (see section 4). The boundary conditions necessary to solve such a system follow in a natural manner from (5), (6) [22], but are not chosen from a priori consideration, as in diffusive theory of bimolecular reactions. We also note that under certain conditions the present lattice model describes adequately the triplet–triplet annihilation of incoherent excitons.

The set (5), (6) can be reduced to an equation that involves only a distribution function of particles of different types. For this purpose we introduce a new unknown $X_n(\tau) = \bar{g}_n(\tau) - g_n(\tau)$, the equation for which is non-linear

$$\frac{dX_n(\tau)}{d\tau} = \frac{1}{4d}\lambda(\tau)\delta_{n,a} + \sum'_\Delta [X_{|n+\Delta|}(\tau) - X_n(\tau)] - c(\tau)\lambda(\tau)X_n(\tau), \quad (7)$$

but formally admits an exact solution.

Considering (1), we use in (7) the replacement

$$X_n(\tau) = x_n(\tau) \exp\left(\int_0^\tau dt \lambda(t)c(t)\right) = \frac{c^2(0)}{c^2(\tau)}x_n(\tau), \quad (8)$$

where $x_n(\tau)$ satisfies the equation

$$\frac{dx_n(\tau)}{d\tau} = \frac{1}{4d}\lambda(\tau)\frac{c^2(\tau)}{c^2(0)}\delta_{n,a} + \sum'_\Delta [x_{|n+\Delta|}(\tau) - x_n(\tau)]. \quad (9)$$

Denoting

$$\Pi(\tau) = \lambda(\tau)c^2(\tau)/c^2(0) \quad (10)$$

we go over to the Laplace image space in (9),

$$s\tilde{x}_n(s) = X_n(0) + \frac{1}{4d}\tilde{\Pi}(s)\delta_{n,a} + \sum'_\Delta [\tilde{x}_{|n+\Delta|}(s) - \tilde{x}_n(s)]. \quad (11)$$

Here and in the remainder of the paper the tildes denote the correspondence $\tilde{A}(s) = \int_0^\infty dt e^{-st} A(t)$. The solution (11) taking into account kinematic particle repulsion has the form

$$\begin{aligned} \tilde{x}_n(s) = & \sum_m G_{|n-m|}(s) X_m(0) + \frac{sG_n(s) - \delta_{n,0}}{1 - sG_1(s)} \left[\left(1 + \frac{s}{2d}\right) \sum_m G_m(s) X_m(0) - \frac{1}{2d} X_0(0) \right] \\ & + \frac{\tilde{\Pi}(s)}{2} \left(-\frac{1}{2d} \delta_{n,0} + \frac{1 + (2d)^{-1}s}{1 - sG_1(s)} G_n(s) (1 - \delta_{n,0}) \right), \end{aligned} \quad (12)$$

where the summation is over all the lattice site coordinates, and

$$\begin{aligned} G_n(s) = & \frac{1}{N^d} \sum_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{n}) / \left(s + 2d - 2 \sum_{i=1}^d \cos(k_i a_i) \right), \\ \mathbf{k} = & (k_1, \dots, k_d), \quad k_i = \pi l / Na, \quad l = 0, \pm 1, \dots, \pm N, \end{aligned} \quad (13)$$

is the Green function that satisfies the equation

$$(s + 2d)G_{|n-n'|} - \sum_{\Delta} G_{|n-n'-\Delta|} = \delta_{n,n'}. \quad (14)$$

It is easily seen that (12) with $X_0(0) = 0$ gives 0 for $\tilde{x}_0(s)$. The spatially uniform distribution of reagents at an initial time corresponds to the conditions

$$g_n(0) = \bar{g}_n(0) = 1 - \delta_{n,0}, \quad X_n(0) = 0. \quad (15)$$

The expression (12) is in this case simplified to

$$\tilde{x}_n(s) = \frac{\tilde{\Pi}(s)}{2} \frac{G_n(s)}{1 - sG_0(s)}, \quad n \neq 0. \quad (16)$$

Reverting it to the original and substituting it into (8), we obtain

$$X_n(\tau) = \frac{c^2(0)}{2c^2(\tau)} \int_0^\tau K_n(\tau - t) \Pi(t) dt = \frac{1}{2c^2(\tau)} \int_0^\tau dt K_n(\tau - t) \lambda(t) c^2(t), \quad (17)$$

where

$$K_n(\tau) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} ds e^{s\tau} \frac{G_n(s)}{1 - sG_0(s)}. \quad (18)$$

The solution obtained enables us to exclude the unknown $\bar{g}_n(\tau)$ from (5), and we thus have

$$\frac{dg_n(\tau)}{d\tau} = -\frac{1}{4d} \lambda(\tau) \delta_{n,a} + \sum_{\Delta} [g_{|n+\Delta|}(\tau) - g_n(\tau)] (\delta_{n,a} - 2d\delta_{n,0}) g_a(\tau) - \nu_n(\tau), \quad (19)$$

where

$$\nu_n(\tau) = \lambda(\tau) c(\tau) \{ X_n(\tau) - [1 - g_n(\tau)] [X_n(\tau) + g_n(\tau)] \} \quad (20)$$

and the terms that take into account a kinematic reagent repulsion are explicitly written out.

For our further discussion it is instrumental to distinguish in the ARR equation the contributions from terms linear and non-linear in $g_n(\tau)$. To achieve this, we use the Green function (13) to transform the Laplace image of the equation (19) to

$$\begin{aligned} \tilde{g}_n(s) = & \frac{1}{s} - \frac{d\omega}{sWq(s)} \left(1 + \frac{s}{2d}\right) \frac{G_n(s)}{G_1(s)} \\ & - \sum_{m \neq 0} \left[G_{|n-m|}(s) - \left(1 + \frac{s}{2d}\right) [q(s) - G_1^{-1}(s)] \frac{G_n(s)G_m(s)}{q(s)G_1(s)} \right] \tilde{v}_m(s), \quad n \neq 0, \end{aligned} \quad (21)$$

where $q(s) = G_1^{-1}(s) - s + (d\omega/W)(1 + s/2d)$. Substituting (21) into the definition of the ARR Laplace image

$$\tilde{\lambda}(s) = 2d(\omega/W)\tilde{g}_a(s)$$

and taking the relation (14) into account, we obtain

$$\tilde{\lambda}(s) = \frac{2d\omega}{Wq(s)} \left[[sG_1(s)]^{-1} - 1 - \left(1 + \frac{s}{2d}\right) \sum_{n \neq 0} \frac{G_n(s)}{G_1(s)} \tilde{v}_n(s) \right]. \quad (22)$$

The original (22) has the form

$$\gamma(t) = \gamma^{(0)}(t) - 2W \int_0^{2Wt} d\tau \sum_{n \neq 0} Q_n(2Wt - \tau) v_n(\tau), \quad (23)$$

where

$$Q_n(\tau) = \frac{d\omega}{W} \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} ds e^{s\tau} \frac{1 + (2d)^{-1}s}{q(s)G_1(s)} G_n(s) \quad (24)$$

and $\gamma^{(0)}(t)$ corresponds to the ARR definition in the two-particle approximation (when non-linear terms in the equation for $g_n(t)$ are neglected)

$$\gamma^{(0)}(t) = W\lambda^{(0)}(2Wt) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} ds e^{2Wst} \lambda^{(0)}(s), \quad (25)$$

$$\lambda^{(0)}(s) = (2d\omega/W) [1 - sG_1(s)] / sq(s)G_1(s). \quad (26)$$

The set of equations (21), (23) is an exact analog of (2), (5), (6) at $d = 1, 2, 3$. The specific form of the Green function that defines, finally, the ARR behaviour at large times is rather sensitive to the system dimensionality. Below we investigate the influence of correlation effects on the reagent concentration decay rate at various reaction stages, using (23) and restricting ourselves to the case of a three-dimensional system.

3. Limit estimates of the correlation effects in $(A + B = 0)$ -reaction kinetics

A characteristic feature of the initial set of equations (5), (6) is the existence of a "positive feedback" through non-linear terms that take into account interparticle correlation in the superposition approximation. The decrease in $g_n(\tau)$ caused by the presence of a drain at $n = a$ leads to $\bar{g}_n(\tau)$ (and $X_n(\tau)$) increasing with time. In the two-particle approximation that neglects third and higher-order correlations this effect is disregarded.

Under the initial condition (15) $X_n(\tau) \geq 1 - g_n(\tau) \geq 0$, the function $\nu_n(\tau)$ is positively definite at any time, so that taking into account higher-order correlations (in addition to two-particle ones) results in $\gamma(\tau)$ decreased as compared to $\gamma^{(0)}(\tau)$.

We note that in the case of identical-particle reactions $A + A = 0$ (a corresponding equation for $\gamma(\tau)$ follows from (23) at $X_n(\tau) = 0$) the effect is opposite and is small at sufficiently small initial reagent concentration (see appendix B for more details).

We now estimate the upper limit of the possible decrease in ARR in the reaction $A + B = 0$ for the case $\omega \rightarrow \infty$, when the correlation effects are most pronounced. Since the condition $\nu_n(\tau) < c(\tau)\gamma(\tau)X_n(\tau)$ is valid at $\tau > 0$, we can use the right-hand side of the inequality as a majorant $\nu_n(\tau)$ to obtain the above estimate by replacing the exact equation (22) with an approximate one

$$\tilde{\lambda}(s) = \tilde{\lambda}^{(0)}(s) - \frac{2}{G_1(s)} \sum_{n \neq 0,1} G_n(s) \int_0^\infty dt e^{-st} \lambda(t) c(t) X_n(t) \quad (27)$$

which involves no term with $n = 1$, because $\tilde{g}_1(s) = 0$. The replacement simplifies the problem of studying the equations (1), (21) that define $g_n(\tau)$ and $c(\tau)$, but it still requires solving the set of non-linear equations (1), (27) for the unknown $\gamma(\tau)$, $c(\tau)$. An additional simplification can be achieved by excluding $c(\tau)$ from (27) with the help of the formal solution (1)

$$c(\tau) = c(0) \left(1 + \frac{c(0)}{2} \int_0^\tau dt \lambda(t) \right)^{-1}. \quad (28)$$

Substituting (28) into (27) yields

$$\tilde{\lambda}(s) = \tilde{\lambda}^{(0)}(s) - \frac{c(0)}{G_1(s)} \sum_{n \neq 1,0} G_n(s) \int_0^\infty dt e^{-st} \lambda(t) \left(1 + \frac{c(0)}{2} \int_0^t d\tau \lambda(\tau) \right) x_n(t), \quad (29)$$

$$x_n(\tau) = \int_0^\tau dt K_n(\tau - t) \lambda(t) \left(1 + \frac{c(0)}{2} \int_0^t d\tau' \lambda(\tau') \right)^{-2}. \quad (30)$$

Under sufficiently small initial reagent concentration there appears to be a time interval from the reaction beginning τ_0 , for which the following conditions hold:

$$\tau_0 \gg 1, \quad c(\tau_0) \approx c(0). \quad (31)$$

This implies that an appreciable change in the reagent concentration at $c(0) \ll 1$ is observed only after a sufficiently large number of hops performed by each of the particles. As is seen from (29), (30), the contribution of the non-linear term to (29) for $\tau \leq \tau_0$ is proportional to $c(0)$ and it can be neglected. With $\tau > \tau_0$, however, the above proportionality no longer holds, and to compare the contributions from the first and the second terms in (29) we must have their explicit forms.

At $\omega \rightarrow \infty$, we have from (26)

$$\tilde{\lambda}^{(0)}(s) = 2[1 - sG_1(s)]/s(1 + \frac{1}{6}s)G_1(s) \quad (32)$$

and taking the dependence $G_1(s)$ at $s \rightarrow 0$ into account (see appendix A), we finally get

$$\gamma^{(0)}(t) = W\lambda^{(0)}(\infty) \left[1 + O((Wt)^{-1/2}) \right], \quad Wt \gg 1, \quad (33)$$

where

$$\lambda^{(0)}(\infty) = \lim_{s \rightarrow 0} s\tilde{\lambda}^{(0)}(s) = 2/G_1(0). \quad (34)$$

We now derive the expression $\gamma(t)$ for long times in first-order perturbation theory, regarding the second term in (29) as a perturbation. Substituting (33) into (29), (30) and using the above definition of τ_0 , we find

$$\begin{aligned} \tilde{\lambda}^{(1)}(s) = & s^{-1}\lambda^{(0)}(\infty) - \frac{c(0)}{G_1(s)} \sum_{n \neq 0,1} G_n(s) \left(\int_0^{\tau_0} dt e^{-st} [\lambda^{(0)}(t) - \lambda^{(0)}(\infty)] x_n^{(0)}(t) \right. \\ & \left. + \lambda^{(0)}(\infty) [\tilde{x}_n^{(0)}(s) - \frac{1}{2}\lambda^{(0)}(\infty)c(0)\partial\tilde{x}_n^{(0)}(s)/\partial s] \right), \quad s \ll 1, \end{aligned} \quad (35)$$

where the index (0) at $x_n(\tau)$ (and in the other functionals that follow) denotes the replacement of $\gamma(\tau)$ with $\gamma^{(0)}(\tau)$ in the functional (30). Using the definition of $x_n^{(0)}(\tau)$, (32), (33), it is easy to show that the term with the integral in (35) gives a negligibly small contribution to $\tilde{\lambda}^{(1)}(s)$ at $s \rightarrow 0$, so that (35) with (16) taken into account can be rewritten as

$$\begin{aligned} \tilde{\lambda}^{(1)}(s) = & s^{-1}\lambda^{(0)}(\infty) - \frac{c(0)\lambda^{(0)}(\infty)}{G_1(s)} \left(\frac{\Pi^{(0)}(s)}{1-sG_0(s)} - \frac{c(0)}{2}\lambda^{(0)}(\infty) \frac{\partial}{\partial s} \frac{\Pi^{(0)}(s)}{1-sG_0(s)} \right. \\ & \left. - \frac{c(0)}{4}\lambda^{(0)}(\infty) \frac{\Pi^{(0)}(s)}{1-sG_0(s)} \frac{\partial}{\partial s} \right) \sum_{n \neq 0,1} G_n^2(s). \end{aligned} \quad (36)$$

The summation over n enables us to express $\tilde{\lambda}^{(1)}(s)$ for small s only in terms of $\Pi^{(0)}(s)$ and the Watson integral whose behaviour at $s \rightarrow 0$ is well studied [24]. The analysis of the contributions from different terms to (36) is made in appendix A. Restricting ourselves in the expansion $\Delta\tilde{\lambda}^{(1)}(s) = \tilde{\lambda}^{(1)}(s) - \lambda^{(0)}(\infty)/s$ to the term $\sim \Pi^{(0)}(0)[(\partial/\partial s)\sum_{n \neq 0,1} G_n^2(s)]_{s \rightarrow 0}$ that defines the asymptotics (36) at $s \rightarrow 0$ and inverting the resultant Laplace-image expansion by Abel's theorem, we have

$$\gamma^{(1)}(t) = \gamma^{(0)}(\infty) \left\{ 1 - \sqrt{2/\pi} [qc(0)\lambda^{(0)}(\infty)/24G_1(0)]\sqrt{Wt} \right\}, \quad Wt \gg 1, \quad (37)$$

where $6G_1(0) = 6G_0(0) - 1 = I(1) - 1$; $I(1) = 1.516$, $q = 3/2\pi$ [24], and $\lambda^{(0)}(\infty)$ is defined in (34).

The approximate equality (37) is meaningful only at $4.5c(0)\sqrt{Wt} \ll 1$. The definition of ARR within the traditional two-particle approximation is valid over the above time interval. The continuity of the initial reaction stage for which $\gamma(t) \approx \gamma^{(0)}(t)$ is obviously dependent on $c(0)$ and can be quite considerable under small enough initial concentrations, such that the reaction depth $\eta = \log c(0)/c(t)$ will be about or much greater than unity. (The dependence on $c(0)$ of the values of η defined with the values of t for which the correction term in (37) is equal to 0.1 is represented in fig. 1.) But already at $c(0) \approx 10^{-2}$ the correction to $\gamma^{(0)}(t)$ is small only in the region $Wt \leq 10^2$, so that under such concentrations the application of the linear theory to define ARR is limited to a small time interval.

We now define the applicability limits for the perturbation theory used to derive (37). The derivation was based on the condition (31). Since $\gamma^{(0)}(\tau_0) \approx \gamma^{(0)}(\infty)$, we can put $\frac{1}{2}c(0)\int_0^{\tau_0}\lambda(t) dt \approx c(0)\gamma^{(0)}(\infty)t_0$, to estimate $c(t)$ by the formula (28) at $Wt_0 \gg 1$. Setting $t_0 = 10W^{-1}$, $\gamma^{(0)}(\infty) = 24W$, we obtain the upper limit for the initial concentration $c(0) = 10^{-4}-10^{-3}$, up to which the conditions used to derive (37) are satisfied.

The analysis of the initial reaction stage kinetics that was made for $\omega \rightarrow \infty$ using the majorant estimation of non-linear terms in the ARR definition (24) remains basically unchanged, if the reaction rate under reagent collisions is finite. The form of (37) is in this case the same, whereas $\lambda^{(0)}(\infty)$ is defined not by (34), but by the general formula resulting from (26)

$$\lambda^{(0)}(\infty) = \frac{6\omega/W}{1 + 3G_1(0)\omega/W} \approx \frac{6\omega/W}{1 + \omega/4W}. \quad (38)$$

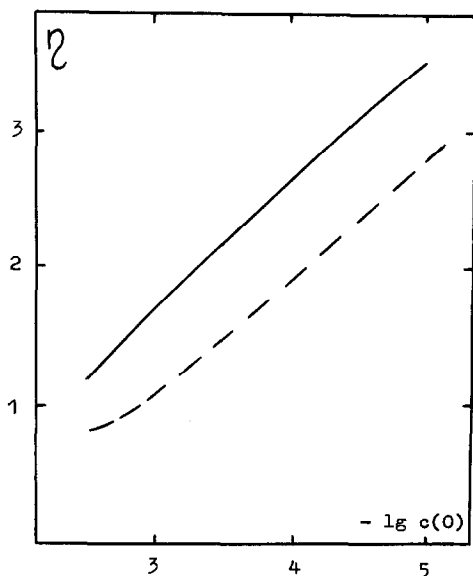


Fig. 1. The reaction depth $\eta = \log[c(0)/c(t)]$ for which $[\gamma^{(0)}(t) - \gamma(t)]/\gamma^{(0)}(t) = 0.1$, depending on the initial concentration value when $k \rightarrow \infty$; the dotted line corresponds to the calculations by formulas (1) and (39), the solid line to the results of a numerical solution to the set (1), (43), (44); $\gamma^{(0)}(t)$ is defined by the expression (B.2).

According to the formulas (37), (38) the time interval of the initial reaction stage will be greater (as compared to the case $\omega \rightarrow \infty$) with the ARR

$$\gamma(t) = \gamma^{(0)}(t)(1 - c(0)\chi\sqrt{Wt}), \tag{39}$$

where

$$Wt \ll [\chi c(0)]^{-2}, \quad \chi = \sqrt{2/\pi} q \lambda^{(0)}(\infty) / 24G_1(0) \approx 4.5, \tag{40}$$

as well as the estimate of the maximum initial concentration value for which the derivation of the approximate equality (39) is valid. The correlation effects that lead to an ARR decreasing with time are weakened with a decreasing parameter ω/W .

Let us turn to the initial equation (22). It is obvious (see (20)) that taking into account non-linear terms omitted in (27) will result in a partial compensation of the tendency for $\gamma(t)$ to decrease at times $Wt \geq [\chi c(0)]^{-2}$. As shown in appendix B, the time dependence (39) and the condition (40) remain unchanged qualitatively, if we use the exact equation (22) instead of (27), to define the ARR at the initial reaction stage. It then follows that the specific behaviour of $\gamma(t)$ at long times for the reaction $A + B = 0$ is due formally to the linear term taken into account in (27) and is primarily defined by a growth in time of the difference $\bar{g}_n(t) - g_n(t)$. Comparison with the results of the numerical solution of a set of non-linear equations confirms the above conclusion and the correctness of the estimating formulas (39), (40).

The long-time divergence (negativeness) of (39) is directly connected with the asymptotics $c^{(0)}(t) \sim t^{-1}$ used in (29). For clarity, we write out this equation at $t \rightarrow \infty$ (see appendix B)

$$[\gamma(t) - \gamma^{(0)}(\infty)]_{t \rightarrow \infty} = -WJ(t) = -\frac{W}{2\sqrt{\pi}} \int_0^t d\tau' \frac{\lambda(\tau')}{(\tau - \tau')^{3/2}} \left(\frac{c^2(\tau')}{c^2(\tau)} - 1 \right). \tag{41}$$

As seen from (41), the necessary conditions for $\gamma(t)$ being positively definite and bounded may be satisfied

only if the long-time concentration decay is described by a dependence slower than t^{-1} . The simplest approximation that satisfies this requirement is the following:

$$c(t) \sim t^{-\alpha}, \quad \gamma(t) \sim t^{-1+\alpha}, \quad t \rightarrow \infty, \quad 0 < \alpha < 1. \quad (42)$$

Employing the dependences (42) in (41) yields $J(t) \sim \tau^{2\alpha-3/2}$, so that we get $\alpha = \frac{3}{4}$ from the conditions for $J(t)$ to be convergent and monotonic. Substituting (42) into the definition of $X_n(t)$ also results in the value $\alpha = \frac{3}{4}$, if we require the time derivative of the function $X_n(t)$ at $t \rightarrow \infty$ being finite and having constant sign. We emphasize that the dependence in (42) indicates the character and the order of the values of the expected effects upon the reagent concentration decay deceleration and the ARR time fall, but are not intended to solve the system of non-linear equations (1), (21), (22).

The above analysis shows that the non-linear terms in the ARR equation for the reaction $A + B = 0$ cannot, in general, be omitted at great times under arbitrarily small reagent concentrations (macroscopically viewed) and their consideration defines the qualitatively new time behaviour of the observed characteristics of a system of reacting particles at $Wt \geq [\chi c(0)]^{-2}$, more specifically, the ARR time decrease and, as a consequence, the concentration decay deceleration as compared to formal kinetics. The estimate (39) and the fact that the non-linear terms in (23), close in their values, have different signs enable us to make the qualitative conclusion that the expected deviation of $c(t)$ from $c^{(0)}(t)$ observed, according to (40), at times inversely proportional to the initial reagent concentration is "slow".

The details of the behaviour of $\gamma(t)$ and $c(t)$ are studied in the next section using numerical simulation.

4. Numerical results

In the concentration range considered the correlation effects that result in a decelerated reaction can be pronounced only at times $Wt \gg 1$, when the descriptions of the process in the framework of lattice and continuous (diffusion) models are basically the same. To solve the equations which define the pair distribution functions, we can therefore restrict ourselves to a continual approximation which reduces (5), (6) to a set of non-linear diffusion equations. The passage to a continual approximation is formally justified when the distribution functions change smoothly at distances in the order of the lattice constant. Under the initial conditions (15) this requirement should be satisfied already at times $Wt \geq 1$.

Following the passage procedure presented in ref. [22], we have, instead of (5), (6) at $d = 3$

$$\partial g(r, \tau) / \partial \tau = \nabla_r^2 g(r, \tau) - c(\tau) \lambda(\tau) g(r, \tau) [\bar{g}(r, \tau) - 1], \quad (43)$$

$$\partial \bar{g}(r, \tau) / \partial \tau = \nabla_r^2 \bar{g}(r, \tau) - c(\tau) \lambda(\tau) \bar{g}(r, \tau) [g(r, \tau) - 1], \quad (44)$$

where $g(r, \tau)$, $\bar{g}(r, \tau)$ are the analogues of the pair distribution functions, $g_n(\tau)$ (for particles of different type) and $\bar{g}_n(\tau)$ (for particles of the same type), r ($r > 1$) are the continuous variables which define the relative coordinates of particle pairs in lattice constant units. At $r = 1$, we have from (5), (6) [22]

$$\begin{aligned} \partial g(1, \tau) / \partial \tau &= \frac{2}{3} \pi \partial g(r, \tau) / \partial r |_{r=1} - (\omega/2W) g(1, \tau) - c(\tau) \lambda(\tau) g(1, \tau) [\bar{g}(1, \tau) - 1], \\ \partial \bar{g}(1, \tau) / \partial \tau &= \frac{2}{3} \pi \partial \bar{g}(r, \tau) / \partial r |_{r=1} - c(\tau) \lambda(\tau) \bar{g}(1, \tau) [g(1, \tau) - 1]. \end{aligned} \quad (45)$$

The second pair of boundary conditions corresponds to the principle of correlation weakening at infinity,

$$g(\infty, \tau) = \bar{g}(\infty, \tau) = 1, \quad (46)$$

which appears to be satisfied by the lattice model equations.

The boundary conditions (45) are different from those traditionally used in the theory of bimolecular reactions of diffusing particles (see, for example, ref. [23])

$$\partial g(r, \tau) / \partial r |_{r=1} = kg(1, \tau), \quad \partial \bar{g}(r, \tau) / \partial r |_{r=1} = 0. \tag{47}$$

If in (45) we neglect the time derivative and the non-linear terms that take into account three-particle correlations, we get $k = \frac{3}{4}\omega/W$ for the phenomenological parameter k which defines the reaction efficiency under reagent collisions.

It is easy to see that the definition of ARR (2) is in this case the same as the conventional one,

$$\gamma(t) = 8\pi W \partial g(r, t) / \partial r |_{r=1}. \tag{48}$$

The calculations made over a wide range of the parameters $c(0)$, k show that the difference between (45) and (47) is not fundamental. While the calculation results for $c(\tau)$, $\gamma(\tau)$ are qualitatively the same, their quantitative difference does not exceed 10% in the case $c(0) = 0.1$, and is less than 1% at $c(0) = 10^{-3}$. To facilitate a comparison with the predictions of the conventional theory of bimolecular reactions of diffusing particles [2,23], the results given below correspond to the numerical investigation of the set of non-linear equations (1), (43), (44), (48) under the boundary conditions (46), (47). We note that in the particular case $k \rightarrow \infty$ ($g(1, \tau) = 0$) these equations have been investigated by analytical and numerical methods in refs. [18–21].

The idea of the microscopic picture of the process $A + B = 0$ is given by the evolution of pair distribution functions of particles of the same and different types, represented in fig. 2. In the course of the reaction the deviation of $g(r, \tau)$ and $\bar{g}(r, \tau)$ from the initial (uniform) distribution rises with the time, and the rates are proportional to the initial reagent concentration. In the two-particle approximation, that is, when the non-linear terms in the equations (43), (44) are neglected, $\bar{g}(r, \infty) = 1$, and the dependence

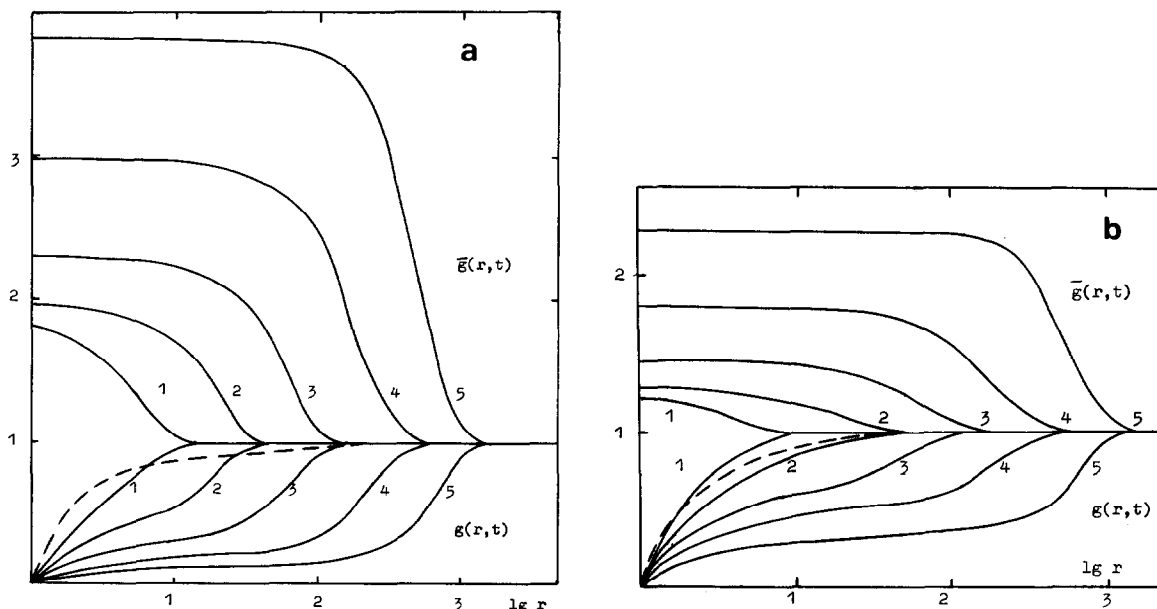


Fig. 2. The distribution function profiles of identical $g(r, t)$ and different $\bar{g}(r, t)$ particles ($k \rightarrow \infty$) at times $2Wt = 10, 10^2, 10^3, 10^4, 10^5$ for curves (1)–(5), respectively; (a) $c(0) = 0.1$, (b) $c(0) = 0.01$. The dashed line correspond to the values of $g^{(0)}(r, \infty)$, calculated in the two-particle approximation (Smoluchowski–Waite theory).

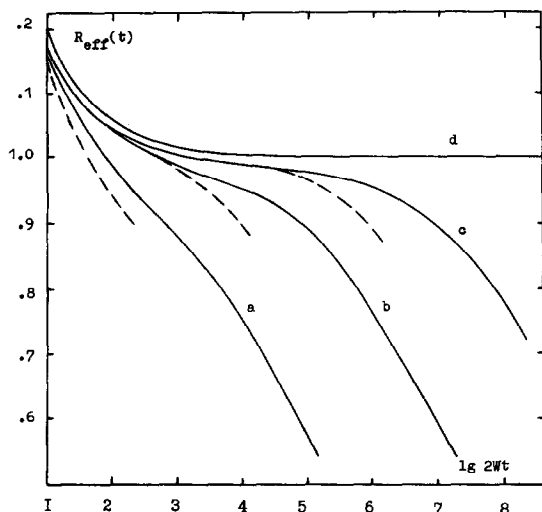


Fig. 3. The time dependence of $R_{\text{eff}} = \gamma(t)/8\pi W$ at different values of the initial concentration $c(0)$: $\log[c(0)] =$ (a) -2.6 , (b) -3.6 , (c) -4.6 ; $k \rightarrow \infty$. The dashed lines denote the values of $R_{\text{eff}} = R_{\text{eff}}^{(0)}[1 - 4.5c(0)\sqrt{2Wt}]$ where $R_{\text{eff}}^{(0)}$ is defined by the expression $R_{\text{eff}}^{(0)} = 1 + (2\pi Wt)^{-1/2}$ (curve (d)).

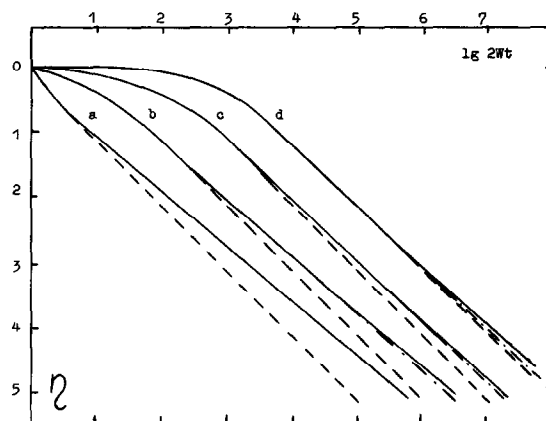


Fig. 4. The time dependence of the reaction depth $\eta = \log[c(0)/c(t)]$ for various values of the initial concentration $c(0) =$ (a) 10^{-1} , (b) 10^{-2} , (c) 10^{-3} , (d) 10^{-4} (solid lines); $k \rightarrow \infty$. The dot-dashed lines determine the incline $t^{-\alpha}$: $\alpha =$ (a) 0.82 , (b) 0.88 , (c) 0.93 , (d) 0.97 . The dotted lines correspond to the values of $c^{(0)}(t)$ obtained in the framework of the two-particle approximation.

$g(r, \infty)$ is marked by the dotted line. As shown in appendix B, this approximation is quite satisfactory for the reactions $A + A = 0$, but cannot be applied to describe the process $A + B = 0$. The separation of particles of different kind is important for the latter process, and this is manifest in the behaviour of pair distribution functions and is not taken into account in the conventional Smoluchowski–Waite theory of bimolecular reactions. The character of the increasing $\bar{g}(r, \tau)$ shows that identical particles primarily survive at small distances, that is, accumulations of identical particles form under the reaction. The regions with closely placed particles of different kind become depleted. The fraction of the reagents in the accumulations increases with the time. The formation and the increase of accumulations may account for the decrease in ARR (see below). We wish to emphasize that there is an analogy in the reaction deceleration by accumulations of identical particles (dynamical fluctuations) and by fluctuations in the initial reagent distribution.

We now consider the time dependence of the reagent concentration and ARR. We first of all appraise the correctness of the analytical approximation of the ARR (38) which describes the initial reaction stage. Fig. 3 compares the values of the effective reaction radius (expressed in units a : $R_{\text{eff}}(t) = \gamma(t)/8\pi W$) that were obtained by numerical calculations and by the formula (39) at $k \rightarrow \infty$. The difference in the corresponding values of $R_{\text{eff}}(t)$ does not exceed 5% over the time interval $Wt \ll [\chi c(0)]^{-2}$. The same coincidence is typical of the finite values of the parameter k . The functional dependence on t of the correction term in (39) fairly roughly reflects the behaviour of $R_{\text{eff}}(t)$ because of the approximations used in deriving it, and yet this dependence is quite acceptable for qualitative estimates over the time interval considered.

The dependences $c(t)$ at $Wt \geq [\chi c(0)]^{-2}$, when the perturbation theory developed in section 3 is inapplicable, are represented in figs. 4, 5. As the calculations show, the reagent concentration decay in the reaction depth range $0.5 \leq \eta \leq 5$ may be described by the dependence (42), where the index α is a function of the initial concentration $c(0)$ and k . The time interval over which the dependence is realized is defined by the value of $c(0)$ at fixed k . For example, at $k \rightarrow \infty$, $c(0) = 0.1$ the lower bound of the above interval is at $Wt \approx 5$, the upper bound at $Wt \approx 10^6$; for $c(0) = 10^{-4}$, $10^3 \leq Wt \leq 10^8$. To determine the dependence

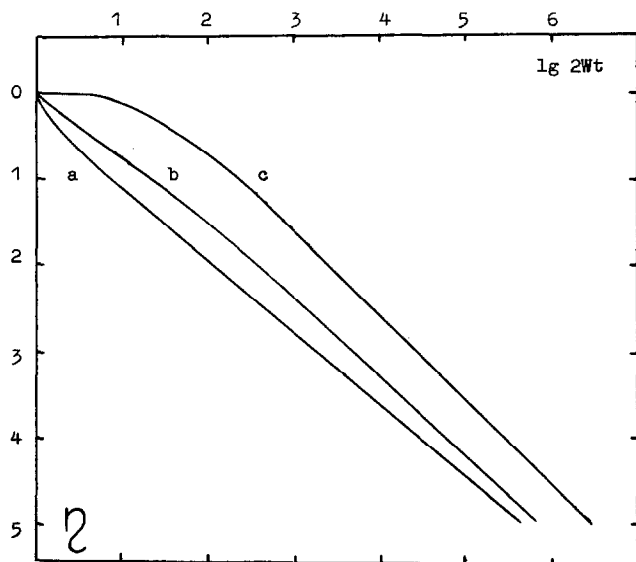


Fig. 5. The time dependence of the reaction depth η for various values of the parameter $k = 3\omega/4W$ (solid lines); $c(0) = 0.1$. The dot-dashed lines determine the incline $t^{-\alpha}$: (a) $\log k = 1.5$, $\alpha = 0.82$, (b) $\log k = -0.5$, $\alpha = 0.93$, (c) $\log k = -1.5$, $\alpha = 0.98$.

$\alpha = \alpha(c(0), k)$, numerical calculations were made over a wide range of the parameters $c(0)$ and k . The corresponding results are given in figs. 6, 7. We emphasize the fast decrease in the deviation of α from unity when both $c(0)$ and k decrease. For example, in the case $k \rightarrow \infty$, $\alpha = 0.82, 0.86, 0.97$ at $c(0) = 10^{-1}, 10^{-2}, 10^{-4}$, respectively.

As the calculated results show (fig. 8), the lesser the value of the parameter k , the weaker the decrease in ARR is displayed and the larger are its decay times. Such a dependence was to be expected, because the ARR time drop effect is due to interparticle correlations whose contribution is proportional to the reagent interaction intensity (ω). Also, the diffusion in the system (W) leads to a dissipation of dynamical fluctuations that form under the reaction and are a direct consequence of interparticle correlations. (The rise and dissipation of fluctuations are pronounced in the evolution of the pair distribution function of identical particles, see fig. 2.) The result of the competition between the two opposite tendencies is thus dependent on the ratio ω/W , defining the value of α for a given initial reagent concentration. In

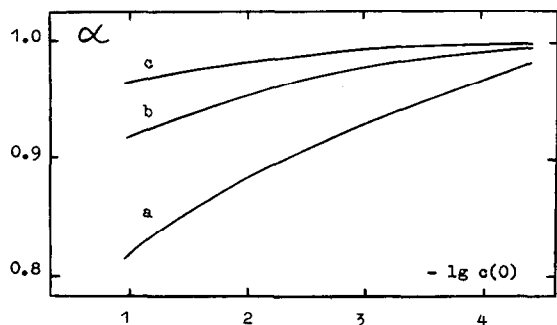


Fig. 6. The dependence of the index α on the initial concentration $c(0)$ for various values of the parameter k ; $k =$ (a) ∞ , (b) 0.4, (c) 0.1.

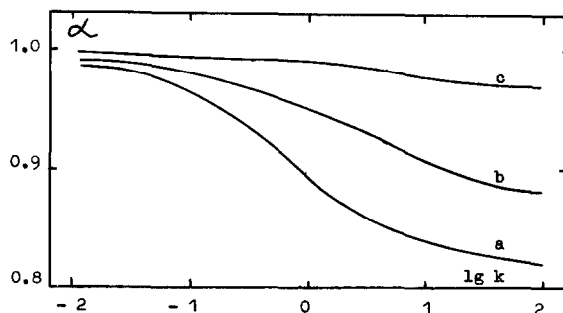


Fig. 7. The dependence of the index α on the parameter k for various values of the initial concentration $c(0)$; $c(0) =$ (a) 10^{-1} , (b) 10^{-2} , (c) 10^{-4} .

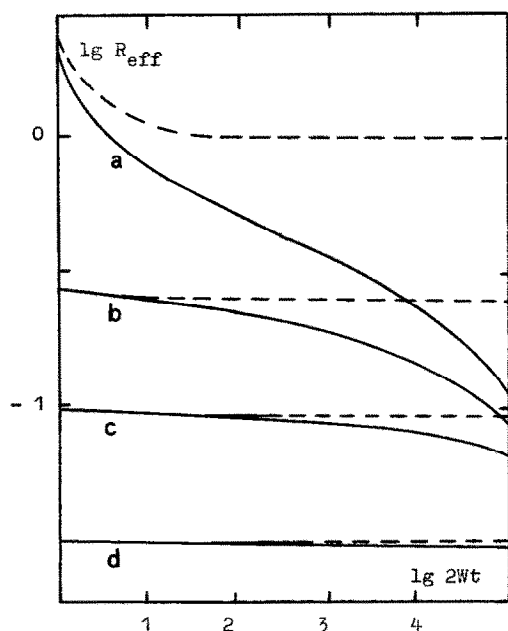


Fig. 8. The time dependence of the effective reaction radius $R_{\text{eff}}(t)$ for various values of the parameter k ; $c(0) = 0.1$; $\log k =$ (a) 1.5, (b) -0.5 , (c) -1 , (d) -1.5 . The dashed lines correspond to the values of $R_{\text{eff}}^{(0)}(t)$, obtained in the two-particle approximation.

particular, at $c(0) = 0.1$, $\alpha = 0.92$ at $k = 0.4$; $\alpha = 0.98$ at $k = 0.1$. The first of the values of k corresponds to $\omega = 2W$, that is, to an equal probability for a pair of reagents that come into contact to react and go away at a large distance (see the lattice model definition, section 2).

The influence of density fluctuations on the reagent concentration drop rate is maximum for the case of diffusion-controlled reactions and is fastly weakened with decreasing ratio between the rates of reaction and diffusion. This conclusion appears to us to be independent of a specific mechanism generating density fluctuations. We note that the relationship between the manifestation of the fluctuations in reaction kinetics and the value of the parameter ω/W has not been investigated.

The calculation of the kinetics of more distant reaction stages indicates a slow deviation of the dependence $c(t)$ from $t^{-\alpha}$ towards concentration fall deceleration (decreased ARR), figs. 4, 5. This trend may be regarded as evidence of the existence of a limit dependence $c(t) \sim t^{-3/4}$, $t \rightarrow \infty$ in the reactions $A + B = 0$ ($c_A = c_B = c$) for any values of the parameters $c(0)$ and ω/W . The possibility to experimentally confirm such a dependence is quite problematic, because it is very difficult to achieve and measure the necessary reaction depth $\eta > (\gg) 5$.

5. Conclusion

The present analytic and numerical investigation of the solutions to the equations which define one- and two-particle distribution functions (with higher-order correlations taken into account) in a system of reacting particles enables us to outline the basic features of the microscopic picture of the process $A + B = 0$ involving diffusing particles and to conjecture its experimental behaviour.

In the case of a uniform initial reagent distribution in space when the reagent concentrations are the same (small) the Smoluchovsky–Waite theory has been confirmed to be able to define the kinetics of the process at an initial stage, the duration of which depends on the initial concentration and the ratio between the rates of reaction when the reagents are in contact, ω and their diffusion, W . At this reaction stage

accumulations of identical particles are formed as a result of a depletion of pairs of different particles and the preservation of pairs of identical particles with a probability inversely proportional to the distance between particles in a pair. The higher the concentration and the larger the ratio ω/W , the more pronounced is the accumulation generation effect. The generation of accumulations of identical particles under the reaction $A + B = 0$ results in a monotonic (very slow) decrease in ARR with the time. With the reaction depth $0.5 \leq \eta \leq 5$, the ARR time dependence is *approximately* described by the dependence $\gamma(t) \sim t^{1-\alpha}$, $\frac{3}{4} < \alpha(c(0), \omega/W) < 1$.

The correlation effects that lead to the formation of accumulations of identical particles in the reactions $A + B = 0$ (dynamic fluctuations) can be detected experimentally by the deviation of the dependences $c(t)$, $\gamma(t)$ from the predictions of the two-particle approximation. The dependence $\alpha(c(0), \omega/W)$ obtained in this paper indicates the range of the parameters in which we can expect an experimental manifestation of the correlation effects under study that are negligibly small if $\alpha \approx 1$. In particular, at $c(0) = 10^{-4}$, $\omega \rightarrow \infty$, $\alpha = 0.97$.

The dependence of α on the initial reagent concentration and on the ratio between the rates of the reaction and of diffusion over the experimentally most important time interval distinguishes clearly the manifestations of dynamical density fluctuations in reaction kinetics from the effect due to fluctuations of the initial reagent distribution. This effect must, according to ref. [3], lead to a decay law $c(t) \sim t^{-3/4}$ independent of the values of the parameters $c(0)$ and ω/W .

Appendix A

The sums in (36) are easily calculated

$$- \sum_{n \neq 0,1} G_n^2(s) = \partial G_0(s)/\partial s + \left[1 + 6\left(1 + \frac{1}{6}s\right)^2\right] G_0^2(s) - 2\left(1 + \frac{1}{6}s\right) G_0(s) + \frac{1}{6}, \quad (\text{A.1})$$

$$- \frac{\partial}{\partial s} \sum_{n \neq 0,1} G_n^2(s) = \partial^2 G_0(s)/\partial s^2 + 2\left[1 + 6\left(1 + \frac{1}{6}s\right)^2\right] G_0(s) \partial G_0/\partial s + 2\left(1 + \frac{1}{6}s\right) G_0^2(s) - 2\left(1 + \frac{1}{6}s\right) \partial G_0(s)/\partial s - \frac{1}{3} G_0(s), \quad (\text{A.2})$$

$$6G_0(s) = I(\mu) = \frac{1}{\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi \frac{dx dy dz}{\mu^{-1} - \frac{1}{3}(\cos x + \cos y + \cos z)}, \quad \mu^{-1} = 1 + \frac{1}{6}s. \quad (\text{A.3})$$

Substituting into (A.1), (A.2) the expression for a Watson integral at small s ($\mu \rightarrow 1-0$) [24],

$$I(\mu) = I(1) - qs^{1/2} + \tilde{q}s^{3/2} \quad (\text{A.4})$$

(q and \tilde{q} are constants), we get

$$\begin{aligned} \sum_{n \neq 0,1} G_n^2(s) &= \frac{1}{12}qs^{-1/2} + O(1) \\ \sum_{n \neq 0,1} \frac{\partial G_n^2(s)}{\partial s} &= \frac{q}{24}s^{-3/2} + \frac{1}{4} \left(q \frac{6 - 7I(1)}{9} + \frac{\tilde{q}}{2} \right) s^{-1/2} + O(1), \quad s \rightarrow 0. \end{aligned} \quad (\text{A.5})$$

We now consider the behaviour of the function $[1 - sG_0(s)]^{-1}\Pi^{(0)}(s)$ and its derivative for $s \rightarrow 0$. The equalities (A.4) and

$$\Pi^{(0)}(s) = \int_0^{\tau_0} dt e^{-st} \lambda^{(0)}(t) + \lambda^{(0)}(\infty) \int_{\tau_0}^{\infty} \frac{e^{-st} dt}{\left[1 + \frac{1}{2}\lambda^{(0)}(\infty)c(0)t\right]^2} \quad (\text{A.6})$$

that takes into account the condition (31) yield directly

$$\lim_{s \rightarrow 0} \Pi^{(0)}(s) / [1 - sG_0(s)] = 2/c(0). \quad (\text{A.7})$$

The above equation makes it possible to note that as seen from (26) and (13), (21), $\tilde{\lambda}^{(0)}(s)$ for $s \rightarrow \infty$ is independent of s , that is, $\lambda^{(0)}(+0) = \text{const}$. As is known [2,16,23], in the diffusion approximation $\lambda^{(0)}(\tau) \sim \tau^{-1/2}$ as $\tau \rightarrow 0$, but in this case, too, the equality (A.7) remains valid.

Using (A.6), we have for the derivative of the function considered

$$\frac{\partial}{\partial s} \frac{\Pi^{(0)}(s)}{1 - sG_0(s)} = \frac{4}{\lambda^{(0)}(\infty)c^2(0)} \ln s + O(1). \quad (\text{A.8})$$

Substituting (A.5), (A.7) and (A.8), we get

$$\tilde{\lambda}^{(1)}(s) = \frac{\lambda^{(0)}(\infty)}{s} \left(1 - \frac{qc(0)\lambda^{(0)}(\infty)}{48G_1(s)} s^{-1/2} \right) + O(s^{-1/2} \ln s). \quad (\text{A.9})$$

The behaviour of $\gamma^{(1)}(t)$ defined by (A.9) is described by the function (37) presented in the main text.

Appendix B

As shown in section 3, in the case of sufficiently small concentrations an appreciable deviation from the usual kinetics of bimolecular reactions $A + B = 0$, described in the two-particle approximation (without non-linear terms in (23)), is observed only at $Wt \gg 1$. Taking into account the smoothness of the function in (23), we can therefore represent the solution to this equation in first-order perturbation theory as

$$\begin{aligned} \gamma^{(1)}(\tau) = & \gamma^{(0)}(\tau) - 8\pi \int_1^\infty dr r^2 \int_0^\tau Q(r, \tau - t) \gamma^{(0)}(t) c^{(0)}(t) \\ & \times \{ X^{(0)}(r, t) - [1 - g^{(0)}(r, t)] [g^{(0)}(r, t) + X^{(0)}(r, t)] \} dt, \end{aligned} \quad (\text{B.1})$$

where the summation over discrete coordinates is replaced by the integration over continuous coordinates r , and to obtain the functions

$$\gamma^{(0)}(\tau) = 8\pi W [1 + (\pi\tau)^{-1/2}], \quad (\text{B.2})$$

$$Q(r, \tau) = [(r-1)/2r\pi^{1/2}\tau^{3/2}] \exp[-(r-1)^2/4\tau], \quad (\text{B.3})$$

$$X^{(0)}(r, \tau) = \frac{r-1}{16r\pi^{3/2}[c^{(0)}(t)]^2} \int_0^\tau dt \frac{\gamma^{(0)}(t)[c^{(0)}(t)]^2}{(\tau-t)^{3/2}} \exp\left(-\frac{(r-1)^2}{4(\tau-t)}\right), \quad (\text{B.4})$$

$$g^{(0)}(r, \tau) = 1 - \int_0^\tau dt Q(r, t), \quad (\text{B.5})$$

use was made of the expansion of the Green function (13) with an accuracy up to the term $s^{1/2}$. Eqs. (B.2)–(B.5) correspond to the instantaneous reaction model $\omega \rightarrow \infty$ and are obviously generalized to the case of arbitrary ω .

We first confine ourselves to taking into account only the first term in the curly brackets, and this corresponds to the majorant estimate of correlation effects performed in section 3. Substituting (B.3), (B.4) into (B.1) and integrating over r , we get

$$\gamma^{(1)}(\tau) - \gamma^{(0)}(\tau) \equiv \Delta\gamma^{(1)}(\tau) = -\frac{W}{2\sqrt{\pi}} \int_0^\tau dt \frac{\gamma^{(0)}(t)}{c^{(0)}(t)} \int_0^t dt_1 \frac{\gamma^{(0)}(t_1)[c^{(0)}(t_1)]^2}{(\tau-t_1)^{3/2}}, \quad (\text{B.6})$$

or, on integrating by parts,

$$\Delta\gamma^{(1)}(\tau) = -\frac{W}{2\sqrt{\pi}} \int_0^\tau dt \frac{\gamma^{(0)}(t)}{(\tau-t)^{3/2}} \left[\left(\frac{c^{(0)}(t)}{c^{(0)}(\tau)} \right)^2 - 1 \right]. \tag{B.7}$$

For large times, $\gamma^{(0)}(\infty)c(0)t \gg 1$, the dominant contribution to (B.7) is given by the integration in the range of small t ($\leq \tau_0 \ll \tau$), so that the resulting integral is easily calculated

$$\Delta\gamma^{(1)} = -\frac{c(0)\lambda^{(0)}(\infty)\gamma^{(0)}(\infty)}{2\sqrt{2\pi}} \sqrt{Wt}. \tag{B.8}$$

The estimate (B.8) is seen to agree well with (37). The small difference in numerical coefficients is due to the diffusion approximation used in (B.2)–(B.5).

We now consider the second of the integrals in (B.1) that contain $X^{(0)}(r, t)$

$$J_1(\tau) = 8\pi W \int_1^\infty dr r^2 \int_0^\tau Q(r, \tau-t) \gamma^{(0)}(t) c^{(0)}(t) [1 - g^{(0)}(r, t)] X^{(0)}(r, t) dt.$$

Noting that

$$J_1(\tau) < \frac{W}{8\pi^{3/2}} \int_1^\infty dr r^2 \int_0^\tau dt \frac{\gamma^{(0)}(t) \exp[-(r-1)^2/4(\tau-t)]}{c^{(0)}(t)(\tau-t)^{3/2}} \\ \times \int_0^t dt_1 t_1^{-3/2} \exp\left(-\frac{(r-1)^2}{4t_1}\right) \int_0^{t_1} dt_2 \frac{\gamma^{(0)}(t_2) [c^{(0)}(t_2)]^2}{(t-t_2)^{3/2}} \exp\left(-\frac{(r-1)^2}{4(t-t_2)}\right)$$

we perform the integration over the variables r and t_1 . As a result, we get

$$J_1(\tau) < \frac{W}{2\sqrt{\pi}} \int_0^\tau dt \frac{\gamma^{(0)}(t)}{c^{(0)}(t)} \int_0^t dt_1 \frac{\gamma^{(0)}(t_1) [c^{(0)}(t_1)]^2}{(t-t_1)^{3/2}} \phi(\tau, t, t_1), \tag{B.9}$$

where

$$\phi(\tau, t, t_1) = \frac{2}{\pi} \left[\arctan\left(\frac{t^{1/2}(\tau-t_1)^{1/2}}{(\tau-t)^{1/2}(t-t_1)^{1/2}}\right) - \frac{[t(\tau-t)(t-t_1)(\tau-t_1)]^{1/2}}{t(\tau-t) + \tau(t-t_1)} \right].$$

The condition $0 < \phi \leq 1$ is satisfied for the function ϕ at any values of the variables $\tau \geq t \geq t_1 \geq 0$, and at $\phi = 1$, (B.9) is the same as (B.6). It then follows that the estimate of $\Delta\gamma^{(1)}(t)$ by the formula (B.8) remains basically the same also with the integral $J_1(\tau)$ taken into account in (B.1).

The integral in (B.1) that contains no function $X^{(0)}(r, t)$ is represented as

$$8\pi W \int_1^\infty dr r^2 \int_0^\tau dt \gamma^{(0)}(t) c^{(0)}(t) Q(r, \tau-t) g^{(0)}(r, t) [1 - g^{(0)}(r, t)] \\ = 2W \int_0^\infty dr r^2 \int_0^\tau dt \gamma^{(0)}(t) c^{(0)}(t) \frac{\exp[-r^2/4(\tau-t)]}{(\tau-t)^{3/2}} \\ \times \int_0^t dt_1 \frac{\exp(-r^2/4t_1)}{t_1^{3/2}} \left(1 - \frac{r}{2(r+1)\sqrt{\pi}} \int_0^t dt_1 \frac{\exp(-r^2/4t_1)}{t_1^{3/2}} \right) = J_2 - J_3. \tag{B.10}$$

Note that at $X^{(0)}(r, t) = 0$ the equality (B.1) corresponds to the ARR definition for identical reagents in the first order of perturbation theory.

On integration over r and t_1 in $J_2(\tau)$, we get

$$J_2(\tau) = 8\pi^{1/2}W \int_0^\tau dt \gamma^{(0)}(t)c^{(0)}(t)(1/\sqrt{\tau-t} - 1/\sqrt{\tau}).$$

At $\tau \gg \tau_0$ we thus have finally

$$J_2(t) \approx \gamma^{(0)}(\infty)(Wt)^{-1/2}. \quad (\text{B.11})$$

It is easy to show that $J_3(t) < J_2(t)$, so the maximum contribution from (B.10) into the ARR definition for large times can be estimated by the formula (B.11) and is negligibly small compared to (B.8).

The effect of triple and higher interparticle correlations in the reactions $A + A = 0$ is thus insignificant under small reagent concentrations, but can result in appreciable decrease in ARR for large times in the reaction $A + B = 0$.

The present estimate of the integral term in (B.1) immediately generalizes to the case of a finite reaction rate under collisions, ω , and reduces to the replacements in (B.8), (B.11), of the expression for $\gamma^{(0)}(\infty)$ at $\omega \rightarrow \infty$ (see (B.2)) by the general expression for $\gamma^{(0)}(\infty)$ in the diffusion approximation

$$\gamma^{(0)}(\infty) = 8\pi Wk/(1+k), \quad k = (3/4\pi)\omega/W.$$

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