Chemical Physics 152 (1991) 13–21
North-Holland

Kinetics of chemical short-range ordering in liquids and diffusion-controlled reactions

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Received 25 July 1990

We study the kinetics of chemical short-range ordering in liquids within the framework of diffusion-controlled reaction theory. We present the long-time dependence caused by the essentially many-particle behavior of reaction–diffusion systems, and the intermediate asymptotic similar to Smoluchowski's results.

1. Introduction

The theoretical description of chemical short-range ordering kinetics in liquid and solid solutions is one of the fundamental unsolved problems of statistical physics of solutions [1–4]. The major difficulty is in its essentially many-particle nature.

Let us consider a triple system containing diffusive substances A and B and solvent S. Substances A and B interact with each other by means of a potential $U_{AB}(r)$, which is attractive for $r>r_0$ and repulsive for $r<r_0$. Besides, $U_{AB}(r)$ tends to infinity as r goes to zero and $U_{AB}(r)\rightarrow -0$ for $r\rightarrow\infty$. We assume that potential interactions defined by $U_{AB}(r)$ dominate interactions of substances with solvent.

In disordered random mixtures of noninteracting particles A and B the concentration n_C of pairs A and B being in contact is defined completely by the product $n_A n_B$ of their mean concentrations and geometry of the first coordination sphere. The mutual attraction of unlike particles leads to the increase of n_C, i.e. increases the probability to find a particle A in the vicinity of particle B. In the initially disordered systems of attractive substances the short-range order parameter $n_C(t)$ grows with t and approaches the steady-state value $n_C(\infty)$ as $t\rightarrow\infty$.

Each, even homogeneous in average, solution contains large (as compared to the mean distance between particles) randomly distributed regions enriched (or depleted) by particles of one type, say A. In the ordering process the concentration of particles B in such regions grows (or vanishes). This phenomenon is followed by the complicated redistribution of diffusive fluxes of particles B. One can assume that in systems with low concentrations of A and B such many-particle (or, in other words, fluctuation-induced) effects can be neglected. However, as we will show below, these effects support the long-time relaxation of $n_C(t)$ and the decrease of pair correlation functions.

Diffusion-controlled reactions (DCR) kinetics is characterized by the analogous processes. The course of contact reactions leads to the alteration of the probability to find a particle of one of the reagents in the vicinity of a particle of the other reagent as compared to this value in disordered systems without reactions. Diffusive motion of particles smooths the spatial inhomogeneities appearing in the reactive systems. The alteration of statistic properties of the solution leads to the alteration of the reaction rates.

In this paper we describe the evolution of the chemical short-range order parameter $n_C(t)$ by means of an analogy between the kinetics of short-range ordering and the diffusion-controlled reaction $A+B\rightleftharpoons C$ kinetics, i.e. within the context of quasichemical approximation [5] kinetic version. This analogy enables us to estimate the relaxation rates at intermediate times and to evaluate the universal fluctuation-induced long-time dependences.

Despite the fact that kinetics of DCR is an essentially many-particle process, considerable progress has been gained. The field of diffusion-controlled processes was first stimulated by the work of Smoluchowski [6] concerning the kinetics of irreversible coagulation of colloid particles $A+A\to 2A$. According to Smoluchowski's approach one has to put the origin to the center of the labelled particle A and to solve the homogeneous diffusion equation with doubled diffusion constant and deterministic spatially homogeneous initial distribution. The reaction is accounted for by introducing the absorbing boundary condition on the surface of the reaction sphere $r=2R_A$, where R_A is particle's radius. Within the context of this approach the reaction rate of particles being in contact is assumed to be infinitely large, and all many-particle effects are neglected. The reaction rate equals the composition of particles. A concentration and diffusive flux through the reaction sphere. This leads to the following mean-field type equation,

$$\dot{n}_A(t)=-K_{\mathrm{eff}}n_A^2(t)\ , \tag{1a}$$

where in three-dimensional systems

$$K_{\mathrm{eff}}=4\pi Da[1+a/(\pi Dt)^{1/2}]\ ,\quad a=2R_A\ .$$

If the contact reaction between particles occurs with some finite probability, the reaction act is defined by the radiation boundary condition – the model of the "grey sphere" [7–13]. This boundary leads to the following renormalized effective rate constant

$$K_{\mathrm{eff}}=4\pi DaK/(4\pi Da+K)\ . \tag{1b}$$

The solution to eq. (1a) in 3D is simply $n_A(t)\propto 1/K_{\mathrm{eff}}t$ for $t\gg[K_{\mathrm{eff}}n_A(0)]^{-1}$. It can be easily shown that Smoluchowski's approach leads to the similar description of two-species reaction, $A+B\to C$. In this case the rate equation reads

$$\dot{n}_A(t)=\dot{n}_B(t)=-K_{\mathrm{eff}}n_A(t)n_B(t)\ . \tag{2}$$

The solution to this equation gives an exponential decay of $n(t)$ for the minority component for $n_A(0)>n_B(0)$ and power-law decay $n_A(t)=n_B(t)\approx(K_{\mathrm{eff}}t)^{-1}$ with $a=R_A+R_B$ for equal initial concentrations. Finally, Smoluchowski's approach leads to the following definition of reversible reaction $A+B\rightleftharpoons C$ rates [14],

$$\dot{n}_A(t)=\dot{n}_B(t)=-K_{\mathrm{eff}}n_A(t)n_B(t)+K_{\mathrm{eff}}^{-}n_C(t)\ , \tag{3a}$$

where the effective backward reaction rate constant equals

$$K_{\mathrm{eff}}^{-}=4\pi DaK_{-}/(4\pi Da+K)\ ,\quad d=3\ . \tag{3b}$$

K_{-} is the intrinsic backward reaction constant. The solution to eq. (3a) predicts an exponential relaxation of mean concentrations to the equilibrium values.

The Smoluchowski approach was the basis of traditional (mean-field) methods of reaction+diffusion systems investigations. An interested reader can be addressed to the exhaustive reviews [10–13]. Prior to mid'70s it was generally accepted that DCR theory based on the Smoluchowski's approach leads to the exact description of the reaction kinetics for systems with low volume fraction of substances. However, it was recognized that perturbation theory corrections to the effective rate constant tend to infinity as $t\to\infty$ [7,11]. It was shown in refs. [15–17] that in some reaction+diffusion systems eqs. (1)–(3) are invalid at the $t\to\infty$ limit and the long-time behavior is governed by the evolution of the fluctuation spectrum. In particular, for irreversible bimolecular reaction of two diffusive substances A and B, which react at the first encounter, $A+B\to$inert, it was shown that mean A and B concentrations follow an anomalous long-time decay [15–24],

$$n_A(t)=n_B(t)\approx t^{-d/4}\ , \tag{4}$$

which displays a slower kinetic behavior as compared to the mean-field predictions. This decay law stems from the tendency for longer persistence of particles in spatial regions created by fluctuations in which either A or B substance dominates. For sufficiently large times the kinetic behavior if bimolecular reaction is controlled by diffusive smoothing of these spatial regions (depleted or enriched by particles of one type) what entails the decay of eq. (4).

We stress, however, that these long-lived fluctuation states govern the mean concentration decrease only in case of equal initial concentrations (EIC), $n_A(0) = n_B(0)$. If the initial mean concentrations are not equal to each other (NEIC) the fluctuation effects are suppressed at large times and the mean-field exponential decay is still valid. The mean-field description is also valid for the EIC bimolecular irreversible reaction of charged substances [15,25]. The spatial regions created by fluctuations of A and B induce the local electric fields which smooth the inhomogeneities faster than diffusion.

The fluctuation effects induce the universal long-time behavior of reversible conversions, associated with the conservation of summary concentrations of particles and products. It was shown that in systems with random initial distributions of substances a wide variety of reversible bimolecular reactions are defined by power-law approach to equilibrium at $t \to \infty$

$$n(t) - n(\infty) \approx (Dt)^{-d/2}, \tag{5}$$

instead of exponential mean-field decay. For instance, such kinetic behavior exhibit the reversible binary reaction: $A + A \rightleftharpoons B$ [22] and the more general coagulation/fragmentation reaction $A_n + A_m \rightleftharpoons A_{n+m}$ [26]. The power-law decay (5) defines the long-time kinetics of EIC reversible reaction $A + B \rightleftharpoons C$ of uncharged species [23,24] and even of charged substances [27,28].

Interestingly, in the latter case the decay of eq. (5) is supported by the special type of density fluctuations – the fluctuations of the same sign, i.e. the spatial regions where the deviations from the mean density have the same value and the same sign both for A and B. These electrically neutral fluctuations are smoothed only by the diffusive processes, what causes the power-law approach to equilibrium. However, one is unable to predict at once the type of dependence characterizing the long-time behavior of reversible NEIC reaction $A + B \rightleftharpoons C$, since the effect of NEIC can be decisive.

This paper is outlined as follows: In section 2 we discuss the basic assumptions and present the equations which govern the evolution of local concentrations. In section 3 we derive the system of reaction + diffusion equations, which describe the temporal behavior of mean concentrations and correlation functions and evaluate its solutions in case of suppressed breakup of C. In section 4 we consider the kinetics of short-range ordering in the "reversible" case, when the breakup of C is possible. We show that in the first case the fluctuation effects are suppressed and in the latter one they are decisive and the long-time approach of mean concentrations and correlation functions follow an anomalous power-law dependence, instead of exponential mean-field predictions.,

2. Basic assumptions

Treatment of the short-range ordering process within the framework of contact reaction $A + B \rightleftharpoons C$ is equivalent to the approximation of the real potential $U_{AB}(r)$ by some model function f. This function defines the following interaction of particles A and B: an infinite repulsion for $r < a$, where a is the closest approach distance between the centers of A and B (e.g., the sum of A and B radii for hard-core particles); infinitely narrow and deep potential well with its center at $r \to a$; and $f = 0$ for $f > a$. It is easy to show that the behavior of $U_{AB}(r)$ for $r > a$ can be accounted by means of some standard methods (see, e.g., ref. [12]). This will result only in the replacement of the "reaction radius" a by the effective Debye radius [12].

Therefore, the formation of the stable pair AB is represented as a product C of direct reaction, which occurs at the encounter of A and B with some finite probability determining the direct rate constant K. The backward reaction, unimolecular breakup of C into a geminate pair of A and B, born at distance a, is defined by the intrinsic constant K_-. The rate constants phenomenologically account the potential interactions between A and B defined by $U_{AB}(r)$.

The analogy between the short-range ordering process and the kinetics of the diffusion-controlled reaction $A+B \rightleftharpoons C$ might be straightforward only for the saturated potentials $U_{AB}(r)$. For unsaturated potentials one should consider the set of reactions

$$A_kB_{n-1}+B \rightleftharpoons A_kB_n\,, \quad A_{k-1}B_n+A \rightleftharpoons A_kB_n\,,$$

where k, n are less than Z, Z is the coordination number in the first coordination sphere.

We stress, however, that all the results concerning the long-time asymptotics of $n_C(t)$ are valid for this case too and the major conclusions of the present work will not be changed.

Within the framework of our assumptions on the analogy between the chemical short-range ordering process (formation of the stable pairs AB) and the kinetics of diffusion-controlled reversible reactions, the rates of local concentrations evolution are governed by the following equations:

$$\dot{n}_A(r,t)=D\,\Delta n_A(r,t)+L_A(r,t)-K\gamma\int dr_1\,\delta(|r-r_1|-a)n_A(r,t)n_B(r_1,t)+K_-n_C(r,t)\,,$$

$$\gamma\int dr_1\,\delta(|r-r_1|-a)=1\,, \tag{6a}$$

$$\dot{n}_B(r,t)=D\,\Delta n_B(r,t)+L_B(r,t)-K\gamma\int dr_1\,\delta(|r-r_1|-a)n_A(r,t)n_B(r,t)+K_-n_C(r,t)\,, \tag{6b}$$

where $\delta(x)$ is the delta-function and Δ the d-dimensional Laplacian. The terms $L_j(r,t)$ define the fluctuations of diffusive fluxes [13]. The first term in eq. (6a) or (6b) represents the contribution of diffusion, the second term, proportional to the product of local concentrations, represents the contribution of the direct reaction between A and B, and the third is the gain of particles due to the unimolecular breakup of stable pairs. For simplicity we have assumed that the diffusion coefficients of A, B, and C are equal to each other. The initial mean concentrations of A and B are not equal, $\langle n_A(r,0)\rangle_r$ is larger than $\langle n_B(r,0)\rangle_r$, i.e. the substance A is presented in excess (NEIC). Systems of equations, similar to eqs (6), are the starting point for the studies of diffusion-controlled reactions kinetics [13]. For local concentrations they seem to be obvious. The main problem is to average its solutions over the realizations of random initial distributions of substances and, in general, over the realizations of random functions $L_j(r,t)$.

The initial fluctuation spectrum we assume to be Gaussian and δ-correlated, i.e. initially the correlation functions are equal to

$$G_{AB}(R,0)=\left\langle\int dr_1\,\delta(|r-r_1|-R)[n_A(r,0)-\langle n_A(r,0)\rangle_r][n_B(r_1,0)-\langle n_B(r_1,0)\rangle_r]\right\rangle_r=0\,,$$

$$C_{jj}(R,0)=\left\langle\int dr_1\,\delta(|r-r_1|-R)[n_j(r,0)-\langle n_j(r,0)\rangle][n_j(r_1,0)-\langle n_j(r_j,0)\rangle_r]\right\rangle_r=n_j\delta(R)\,,$$

$$j=A,B,C\,.$$

These conditions correspond to the random uncorrelated initial distributions of particles A and B.

3. Kinetics of short-range ordering with suppressed breakup of C

The kinetics of short-range ordering within the framework of chemical reactions $A+B \rightleftharpoons C$ is governed by the system of eqs. (6).

We introduce the substances concentrations as follows

$$n_j(r,t)=n_j(t)+\sigma_j(r,t)\,,\quad \langle\sigma_j(r,t)\rangle=0\,,$$

where the angle brackets refer to volume averaging, index j extends over A, B, C. Averaging eqs. (6) we get the exact equation for the mean concentrations evolution

$$\begin{aligned}&\dot n_{\rm A}(t)=\dot n_{\rm B}(t)=-K[n_{\rm A}(t)n_{\rm B}(t)+G_{\rm AB}(|R|-a,t)]+K_-n_{\rm C}(t)\,,\\&\dot n_{\rm A}(t)+\dot n_{\rm C}(t)=0\,.\end{aligned}\qquad(7)$$

Combining eqs. (6), (7) and using the obvious equality

$$\dot G_{iji}=\left\langle\int \mathrm{d}r_1\;\delta(r-r_1-R)(\sigma_i\dot\sigma_j+\dot\sigma_i\sigma_j)\right\rangle,$$

one can derive the system of reaction + diffusion equations governing the temporal and spatial behavior of correlation functions

$$\begin{aligned}\dot G_{ij}=&-K[n_{\rm A}(t)\{G_{{\rm B}i}+G_{{\rm B}j})+n_{\rm B}(t)(G_{{\rm A}i}+G_{{\rm A}j})]+K_-(G_{i{\rm C}}+G_{j{\rm C}})+2D[\Delta_RG_{ij}-\delta_{ij}n_j(t)\;\Delta_R\delta(R)]-KT_{ij}\,,\\&i,j={\rm A,B}\,,\end{aligned}\qquad(8a)$$

$$\dot G_{i{\rm C}}=-K[n_{\rm A}(t)(G_{{\rm B}i}-G_{\rm BC})+n_{\rm B}(t)(G_{{\rm A}i}-G_{\rm AC})]+K_-(G_{\rm CC}-G_{i{\rm C}})+2D\;\Delta_RG_{i{\rm C}}-KT_{i{\rm C}}\,,\quad i={\rm A,B}\,,\qquad(8b)$$

$$\dot G_{\rm CC}=2K[n_{\rm A}(t)G_{\rm BC}+n_{\rm B}(t)G_{\rm AC}]-2K_-G_{\rm CC}+2D[\Delta_RG_{\rm CC}-n_{\rm C}(t)\;\Delta_R\delta(R)]-KT_{\rm CC}\,,\qquad(8c)$$

where δ_{ij} is the Kroneker delta, T_{ij} are the third-order correlation functions. Thus, we have to face the problem of solving an infinite hierarchy of coupled equations. One has obviously to resort to approximate methods to solve it. One of such methods, connected with the fourth-order correlation functions decoupling, was recently applied in refs. [17,26–28] to describe the fluctuation-induced behavior of bimolecular reversible and irreversible reactions. It was proved in ref. [29] that this approach leads to the definition of the upper bound on the expected densities. Moreover this bound differs from the exact result for irreversible reaction [29,30] only by a numerical multiplier, while the time dependence is the same. In this paper we extend the decoupling of fourth-order correlation functions on the case of reversible reactions in NEIC mixtures. This procedure enables us to present the enclosed description of the long-time kinetics of short-range ordering taking into account the spatial correlations between substances. Next, by extracting the short-wave correlations of high-orders (before decoupling) we define the intermediate times kinetics tantamount to the Smoluchowski's approach predictions.

First we consider the influence of density fluctuations on the kinetics of short-range ordering with the suppressed breakup. The time evolution of this process (from the viewpoint of our approximations) is governed by eqs. (7), (8) with $K_-=0$. The third-order correlation functions are equal to

$$T_{\rm AA}(R,t)=-\gamma\left\langle\int \mathrm{d}r_1\;\delta(r-r_1-R)\int \mathrm{d}r_2\;\sigma_{\rm A}(r,t)\sigma_{\rm B}(r_2,t)\sigma_{\rm A}(r_1,t)[\delta(|r_1-r_2|-a)+\delta(|r-r_2|-a)]\right\rangle\,,$$

$$\begin{aligned}T_{\rm AB}(R,t)=-\gamma\Big\langle\int \mathrm{d}r_1\;\delta(r-r_1-R)\int \mathrm{d}r_2\;\sigma_{\rm A}(r,t)\sigma_{\rm B}(r_1,t)\\\times[\sigma_{\rm A}(r_2,t)\delta(|r_1-r_2|-a)+\delta(|r-r_2|-a)\sigma_{\rm B}(r_2,t)]\Big\rangle,\end{aligned}$$

and $T_{\rm BB}$ is defined similar to $T_{\rm AA}$. Below we merely outline the decoupling procedure. To define the contribution of short-wavelength spectrum of correlations we represent substances densities as a sum of delta-functions [#1]

$$n_{\mathrm{A}}(r,t)=\sum_{n}\delta(r-R_n(t))\,,\quad n_{\mathrm{B}}(r,t)=\sum_{m}\delta(r-\rho_m(t))\,,$$

where R_n and ρ_m are the radius vectors of nth particle A and mth particle B respectively. The compositions $\sigma_{\mathrm{A}}\sigma_{\mathrm{A}}$ (or $\sigma_{\mathrm{B}}\sigma_{\mathrm{B}}$) in correlators T_{ij} can be written down as follows

$$\sigma_{\mathrm{A}}(r,t)\sigma_{\mathrm{A}}(r_1,t)=\sum_{n}\delta(r-R_n(t))\delta(r_1-R_n(t))$$
$$+\sum_{n}\sum_{n',n\neq n'}\delta(r-R_n(t))\delta(r_1-R_{n'}(t))-2n_{\mathrm{A}}(t)\sum\delta(r-R_n(t))+n_{\mathrm{A}}^2(t)\,,$$

i.e. we extract the summation over the coincident indexes n and n'. We denote the first on the right-hand side as a "regular" part of T_{ij} and all other terms as a "fluctuation" part of the third-order correlation functions. It is easy to calculate the "regular" part directly,

$$T^{*}_{\mathrm{AB}}(R,t)=K^{-1}\gamma\dot{n}_{\mathrm{A}}(t)\delta(|R|-a)\,,\quad T^{*}_{jj}(R,t)=K^{-1}\dot{n}_{\mathrm{A}}(t)\delta(R)\,.$$

Further on, we assume that the fourth-order correlation functions can be decoupled formally as a composition

$$H_{\mathrm{AB}ij}(R,t)=G_{\mathrm{AB}}(|R|=a,t)G_{ij}(R,t)\,.$$

Then, since $T_{ij}(t=0)=0$ this assumption actually leads to the absence of nontrivial solutions of equations determining the time evolution of the "fluctuation" part of T_{ij}. Thus, we get the enclosed system of equations determining the behavior of the pair correlation functions and mean concentrations.

It seems convenient to make the analogous extraction in the pair correlation functions. The "regular" part, G^{*}_{ij}, is connected with the short-wave correlations and is defined via the equations

$$\dot{G}^{*}_{ij}=-K[n_{\mathrm{A}}(t)(G^{*}_{\mathrm{B}i}+G^{*}_{\mathrm{B}j})+n_{\mathrm{B}}(t)\{G^{*}_{\mathrm{A}i}+G^{*}_{\mathrm{A}j}\}]+2D\,\Delta_R G^{*}_{ij}-KT^{*}_{ij}\,,$$

with $G^{*}(t=0)=0$. The quasi steady-state solution to these equations entails

$$G^{*}_{\mathrm{AB}}(R,t)=\frac{\dot{n}_{\mathrm{A}}(t)}{4\pi DR}\left[\exp\left(-\frac{R}{a}x\right)\left(\frac{\operatorname{sh}x}{x}-1\right)+\exp\left(-2^{1/2}\frac{R}{a}x\right)\right],$$

where the parameter $x=\pi a(2K\rho/D)^{1/2}$, $\rho=n_{\mathrm{A}}(0)-n_{\mathrm{B}}(0)$. A more detailed analysis, however, shows that the parameter x must be renormalized due to the contribution of the higher short-wave correlations as $X=\pi a[8\pi pDaK\rho/(4\pi Da+K)]^{1/2}$ (i.e. the "chemical" constant is in a usual fashion replaced by the effective Smoluchowski-type constant). Substituting

$$G_{\mathrm{AB}}(|R|=a,t)=\mathscr{G}_{\mathrm{AB}}(|R|=a,t)+G^{*}_{\mathrm{AB}}(|R|=a,t)\,,$$

where $\mathscr{G}_{\mathrm{AB}}$ is the "fluctuation" part of the correlation parameter, from eq. (7) we get the effective equation which accounts the short-wave and long-wave correlations in spatial distributions of substances:

$$\dot{n}_{\mathrm{A}}(t)=\dot{n}_{\mathrm{B}}(t)=-K_{\mathrm{eff}}[n_{\mathrm{A}}(t)n_{\mathrm{B}}(t)+\mathscr{G}_{\mathrm{AB}}(|R|=a,t)]+K^{-}_{\mathrm{eff}}n_{\mathrm{C}}(t)\,,\tag{9}$$

where the effective rate constants are equal to

$$K_{\mathrm{eff}}=\frac{4\pi DaK}{4\pi Da+K\{\exp(-X)[(\operatorname{sh}X)/X-1]+\exp(-2^{1/2}X)\}}\,,\quad K^{-}_{\mathrm{eff}}/K_{\mathrm{eff}}=K_{-}/K\,.$$

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

In the limit of small X (i.e. small volume fraction $\varepsilon = 4\pi a^3 \rho$) the terms in braces tends to unity and we recover the results of ref. [8]. Within the opposite limit $\varepsilon \approx 1$ the effective rate constants are reduced to $K_{\mathrm{eff}} = K$ and $K_{\mathrm{eff}}^{-} = K_{-}$, i.e. the diffusive transport can be neglected (perfect mixing).

For the "fluctuation" part of the correlation functions we get the following equations:

$$\dot{\mathscr{G}}_{ij} = -K[n_{\mathrm{A}}(t)(\mathscr{G}_{\mathrm{B}i} + \mathscr{G}_{\mathrm{B}j}) + n_{\mathrm{B}}(t)(\mathscr{G}_{\mathrm{A}i} + \mathscr{G}_{\mathrm{A}j})] + 2D[\Delta_R \mathscr{G}_{ij} - \delta_{ij} n_j(t)\,\Delta_R \delta(R)], \quad \mathscr{G}_{ij}(R, 0) = \delta_{ij} n_j(0) \delta(R). \tag{10}$$

One can show that eqs. (10) exhibit qualitatively different behavior for NEIC and EIC cases. For $\rho > 0$ in the $t \to \infty$ limit one gets

$$\mathscr{G}_{\mathrm{AB}}(a, t) = -\frac{n_{\mathrm{A}}(0)}{(Dt)^{-d/2}} \exp(-K\rho t)[1 - \exp(-K\rho t)],$$

i.e. $\mathscr{G}$ drops exponentially as time grows. Solving eqs. (10) for $\rho = 0$ we get that

$$\mathscr{G}_{\mathrm{AB}}(a, t) \approx -\frac{n_{\mathrm{A}}(0)}{(Dt)^{-d/2}},$$

i.e. a power-law decrease of the correlation functions. Consequently, we have quite different behavior of mean concentrations. Eq. (9), with $K_{-} = 0$, entails the mean-field exponential decay

$$n_{\mathrm{B}}(t) \approx n_{\mathrm{B}}(0) \exp(-K_{\mathrm{eff}} \rho t),$$

for $\rho > 0$, and for $\rho = 0$ the power-law decay [15–17]

$$n_{\mathrm{A}}(t) = n_{\mathrm{B}}(t) \approx [-\mathscr{G}_{\mathrm{AB}}(a, t)]^{1/2} \approx [n_{\mathrm{B}}^2(0)/2\pi Dt]^{d/4},$$

which is induced by the decrease of the correlation functions.

4. Kinetics of short-range ordering with breakup of C

Now we take into account the unimolecular breakup reaction. By means of the decoupling procedure presented in the previous section we derive the following system of reaction + diffusion equations which governs the temporal behavior of the correlation functions

$$\dot{G}_{ij} = -K[n_{\mathrm{A}}(t)(\mathscr{G}_{\mathrm{B}i} + \mathscr{G}_{\mathrm{B}j}) + n_{\mathrm{B}}(t)(\mathscr{G}_{\mathrm{A}i} + \mathscr{G}_{\mathrm{A}j})] + K_{-}(\mathscr{G}_{i\mathrm{C}} + \mathscr{G}_{j\mathrm{C}}) + 2D[\Delta_R \mathscr{G}_{ij} - \delta_{ij} n_j(t)\,\Delta_R \delta(R)],$$
$$i, j = \mathrm{A}, \mathrm{B}, \tag{11a}$$

$$\dot{\mathscr{G}}_{i\mathrm{C}} = -K[n_{\mathrm{A}}(t)(\mathscr{G}_{\mathrm{B}i} - \mathscr{G}_{\mathrm{BC}}) + n_{\mathrm{B}}(t)(\mathscr{G}_{\mathrm{A}i} - \mathscr{G}_{\mathrm{AC}})] + K_{-}[\mathscr{G}_{\mathrm{CC}} - \mathscr{G}_{i\mathrm{C}}] + 2D\,\Delta_R \mathscr{G}_{i\mathrm{C}}, \quad i = \mathrm{A}, \mathrm{B}, \tag{11b}$$

$$\dot{\mathscr{G}}_{\mathrm{CC}} = 2K[n_{\mathrm{A}}(t)\mathscr{G}_{\mathrm{BC}} + n_{\mathrm{B}}(t)\mathscr{G}_{\mathrm{AC}}] - 2K_{-}\mathscr{G}_{\mathrm{CC}} + 2D[\Delta_R \mathscr{G}_{\mathrm{CC}} - n_{\mathrm{C}}(t)\,\Delta_R \delta(R)]. \tag{11c}$$

One can easily find the solutions to the latter equations in the large t limit,

$$\mathscr{G}_{\mathrm{AB}}(a, t) = \mathscr{G}_{\mathrm{AB}}(a) - n^* \frac{\Delta n_{\mathrm{A}}\, K K_{-}}{K_{-} + K[n_{\mathrm{A}}(\infty) + n_{\mathrm{B}}(\infty)]}\, 2(Dt)^{-d/2}$$
$$+ \exp\left(-\int_0^t \mathrm{d}\tau\, (K[n_{\mathrm{A}}(\tau) + n_{\mathrm{B}}(\tau)] + K_{-}]\right)[\ldots],$$

where $\Delta n_{\mathrm{A}} = n_{\mathrm{A}}(0) - n_{\mathrm{A}}(\infty) = \Delta n_{\mathrm{B}} = -\Delta n_{\mathrm{C}}$; $n_{\mathrm{A}}(0)$ and $n_{\mathrm{A}}(\infty)$ are the initial equilibrium values of substance A mean concentration, n^* is the conserved total concentration $n^* = n_{\mathrm{A}}(t) + n_{\mathrm{B}}(t) + 2n_{\mathrm{C}}(t)$. The terms in square brackets are omitted since they are multiplied by an exponentially vanishing function on time. Inserting the leading term in $\mathscr{G}_{AB}(a, t)$ into eq. (9) we notice that the asymptotical behavior of $\delta n_j(t)$, where δn_j are the small deviations from the steady-state values $n_j(\infty)$, is defined by the decrease of the correlation functions, i.e. the long-time solution of the eq. (9) is defined by

$$\delta n_C(t) = K_{\mathrm{eff}} \frac{\mathscr{G}_{AB}(a, t) - \mathscr{G}_{AB}(a)}{K_{\mathrm{eff}} + K_{\mathrm{eff}}^{-}[n_A(\infty) + n_B(\infty)]} = \frac{K_- K^2 n^* \Delta n_A}{K_- + K[n_A(\infty) + n_B(\infty)]} (Dt)^{-d/2}, \tag{12}$$

while the mean-field Smoluchowski approach predicts an exponential decrease of $\delta n_A(t)$,

$$\delta n_C(t) \approx \exp\{-(K_{\mathrm{eff}}[n_A(\infty) + n_B(\infty)] + K_{\mathrm{eff}}^{-})t\}. \tag{13}$$

However, the power law decay of eq. (12) is valid for sufficiently large times. For the intermediate times, when the correlation functions are small and does not contribute to decay, the mean-field exponential dependence (13) is valid. One can estimate the crossover time from eqs. (13)–(12),

$$t_{\mathrm{cr}} \approx \{K_{\mathrm{eff}}[n_A(\infty) + n_B(\infty)] + K_{-}^{\mathrm{eff}}\}^{-1} \ln\left(\frac{(1+\beta)(n+K_{\mathrm{eq}})}{\beta(n^* a)^{2/3}}\right) = \ln(\alpha) t_{\mathrm{cr}},$$

where $K_{\mathrm{eq}} = K_-/K$, $n = n_A(\infty) + n_B(\infty)$, $\beta = K/4\pi Da$, and the reaction depth $\delta n_C(t_{\mathrm{cr}})$ is the fraction of particles A which react via the asymptotic (12), $\delta n_C(t_{\mathrm{cr}}) \approx \alpha$.

To summarize, we have studied the kinetics of short-range ordering within the framework of chemical reactions of diffusive species in systems with inequal initial concentrations. We have shown that in the case of a suppressed breakup of C the fluctuation effects are suppressed and the mean-field approximation is valid over the entire time domain. Application of our results to systems with a high concentration of one of the reagents ($\varepsilon \approx 1$) shows that the rate constants are not renormalized due to the diffusive transport of reagents to each other, i.e. in such systems the reaction becomes kinetically controlled.

We have shown that kinetics of short-range ordering exhibits qualitatively different behaviour, i.e. is not sensitive to the difference of initial particles' mean concentrations, if the breaking up of C is not suppressed. In this case the long-time approach of short-order parameter to the equilibrium value is governed by slow power-law dependence. This supports our recent conjecture [26–28] that all reversible reactions are diffusion-controlled over a long period of time and are characterized by fluctuation-induced power-law kinetic dependences.

References

[1] J.M. Ziman, Models of Disorder (Cambridge Univ. Press, Cambridge, 1979).
[2] J.M. Gunton and M. Droz, Introduction to the Theory of Metastable and Unstable States (Springer, Berlin, 1983).
[3] D. Gazzilo, G. Pastore and S. Enzo, J. Phys. Condensed Matter 1 (1989) 3469;
O. Schneeweiss, J. Phys. Condensed Matter 1 (1989) 4749.
[4] B.V. Bondarev, Physica A 155 (1989) 123.
[5] E.A. Guggenheim, Proc. Roy. Soc. A 148 (1935) 304.
[6] M. von Smoluchowsky, Phys. Z. B 16 (1915) 321.
[7] J. Keizer, J. Phys. Chem. 86 (1982) 5052.
[8] F.C. Collins and G.E. Kimball, J. Colloid Sci. 4 (1949) 425.
[9] T.R. Waite, Phys. Rev. 107 (1957) 463.
[10] G.H. Weiss, J. Stat. Phys. 42 (1986) 3.
[11] D. Calef and J.M. Deutch, Ann. Rev. Phys. Chem. 34 (1983) 493;
G.H. Weiss and R.J. Rubin, Advan. Chem. Phys. 52 (1982) 363.
[12] A.A. Ovchinnikov, S.F. Timashev and A.A. Belyy, Kinetics of Diffusion-Controlled Chemical Processes (Nova, New York, 1989).
[13] C.W. Gardiner, Handbook of Stochastic Methods (Springer, Berlin, 1983).
[14] S.F. Burlatsky, P.P. Levin, I.V. Khudyakov, V.A. Kuzmin and A.A. Ovchinnikov, Chem. Phys. Letters 66 (1979) 565.
[15] Ya.B. Zeldovich, Elektrochimia 13 (1977) 677.
[16] A.A. Ovchinnikov and Ya.B. Zeldovich, Chem. Phys. 28 (1978) 215.

[17] S.F. Burlatsky, Teor. Exp. Chem. 14 (1978) 483.
[18] D. Toussaint and F. Wilczek, J. Chem. Phys. 78 (1983) 2642.
[19] K. Kang and S. Redner, Phys. Rev. Letters 52 (1984) 955.
[20] P. Meakin and H.E. Stanley, J. Phys. A 18 (1985) 923.
[21] R.F. Kayser and J.B. Hubbard, Phys. Rev. Letters 51 (1983) 79.
[22] Ya.B. Zeldovich and A.A. Ovchinnikov, Soviet Phys. JETP 47 (1978) 82.
[23] Ya.B. Zeldovich and A.A. Ovchinnikov, JETP Letters 26 (1977) 440.
[24] K. Kang and S. Redner, Phys. Rev. A 32 (1985) 437.
[25] T. Ohtsuki, Phys. Letters A 106 (1986) 224.
[26] G.S. Oshanin and S.F. Burlatsky, J. Phys. A 22 (1989) 947.
[27] G.S. Oshanin, A.A. Ovchinnikov and S.F. Burlatsky, J. Phys. A 22 (1989) 977.
[28] S.F. Burlatsky, G.S. Oshanin and A.A. Ovchinnikov, Soviet Phys. JETP 68 (1989) 1153.
[29] S.F. Burlatsky and A.A. Ovchinnikov, Soviet Phys. JETP 65 (1987) 1153.
[30] M. Bramson and J. Lebowitz, Phys. Rev. Letters 61 (1988) 2397.