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## Adiabatic kinetics in the theory of diffusion-limited recombination: II

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**Abstract.** Deterministic evolution that corresponds to the adiabatic Liouvillean for recombination  $A+B \rightarrow 0$  derived in the preceding paper I, is found. It is expressed by a set of linear kinetics equations for occupation numbers,  $n_{\sigma i}(t)$ ,  $\sigma = a, b$  and describes flows of particles inside domains to time-independent interfaces between  $A$  and  $B$  phases, where the particles annihilate. The interface locations are defined by a static 'potential'. Averaging of  $n_{\sigma i}(t)$  has been carried out both over random distribution of locations of interfaces and a Gaussian distribution of initial density profile. For an arbitrary fraction of initial species and comparable diffusion coefficients, the expectation value of density decays as  $t^{-d/2}$ , while standard variance,  $\langle(\delta c_{\sigma i})^2\rangle^{1/2}$ , decreases more slowly at  $t \rightarrow \infty$ , i.e. as  $t^{-d/4}$  for the  $d$ -dimensional case, pointing to the importance of initial fluctuations for the deterministic kinetics.

### 1. Introduction

In a recent paper [1] referred to here as I, we have constructed an effective Liouvillean  $L_{\text{eff}}$  for many-body systems with instantaneous local recombination  $A+B \rightarrow 0$ . This research was motivated by interest in the effect of the slowing of diffusion-limited recombination (DLR). This phenomenon, which was first proposed theoretically [2], was later observed in computer simulations [3] and is being extensively discussed [4-9]. The purpose of our work is to investigate an extreme case with large rate of local recombination  $U$

$$U \gg D = \max\{D_{\sigma}\} \quad \text{explicitly } U \rightarrow \infty \quad (1)$$

where  $D_{\sigma}$  are diffusion jump rates, with  $\sigma = a, b$  referring to species. Stratification of species occurs in this case from the very beginning of the reaction. A many-body effective Liouvillean for this system obeying (1) has been derived in I. To obtain average density and its variance, however, further simplification is necessary, requiring application of deterministic approximation to the analysis of evolution described by  $L_{\text{eff}}$ . This can be justified by recalling the main argument of fluctuation theory [2], i.e. relaxation of initially created fluctuations can be studied assuming all temporary molecular fluctuations are suppressed, since they decay quickly and have amplitude small compared to deterministic ones. This assumption is valid due to the stability of reaction  $A+B \rightarrow 0$ . As a result, only initial fluctuations are important. Formally, the deterministic approximation means that the evolution obeys a deterministic equation

without stochastic terms in rates, given an initial average density and a variance in the density fluctuations.

We outline in section 2.1 two possible ways to use  $L_{\text{eff}}$  for our purposes. In section 2.2 we introduce a kinetics equation for a probability distribution function (PDF) that follows from  $L_{\text{eff}}$ . In section 2.3 deterministic kinetics equations for occupation numbers  $n_{\sigma i}$  (density number) are derived. Deterministic transition is correct if each cell on the lattice contains many particles of an arbitrary sort

$$\langle n_{\sigma i} \rangle \gg 1. \quad (2)$$

In the opposite case, when  $\langle n_{\sigma i} \rangle \approx 1$ , local temporary fluctuations,  $\langle (\delta n_{\sigma i})^2 \rangle^{1/2}$ , are comparable with  $\langle n_{\sigma i} \rangle$ . For  $n \gg 1$  to be realized, on the one hand, the dimension of a cell,  $l$  (chosen in this paper as unity) must be large enough, and on the other hand, it must be small in order to provide a uniform distribution of the particles within the cells. On large time-scale, a non-equilibrium system is supposed to behave as diffusion-like, and in the continuum limit a variance in the  $l$  affects only a renormalization of transport coefficients, but no change in the temporary behaviour of the system [10]. As stressed in I, the existence of two large parameters (relations (1) and (2)) are vital for our analysis. Solution of the kinetics equations is shown to correspond to domain structure of the mixture. Characteristic configurations are described. We argue that topological conservation law holds for deterministic approximation. Correspondence of the results to known lattice models of diffusive transport is established. Analogy with unimolecular decay is discussed. Quasilinearity of the operator  $L_{\text{eff}}$  introduced in I is proved in this section. In section 3 an approximate solution of the kinetics equations is presented. As a result, desirable time dependence of the average density and of the particle number variance is calculated by averaging over different initial configurations. The conclusions are summarized in section 4. We use the same notations as in I.

## 2. Deterministic kinetics of the DLR

### 2.1. Introduction

Since kinetic processes in classical statistical mechanics may be formulated with the help of two different languages, i.e. in terms of fields  $\{a_i, b_i\}$  [11] and in terms of physical configurations of particles  $\{n_{\sigma i}\}$  [10, 12], the dilemma arises which method is more appropriate for the calculation of fluctuations and average density. Quite a number of techniques, including perturbation theory in powers of  $\langle n_{\sigma i} \rangle$  in the weak coupling limit [11, 13], the analogy with the Bose condensation [14], path integral formulation [15], and decoupling schemes with self-consistent closure [5, 6], are worked out in 'field' chemical kinetics. The effect of stratification, however, has not been explained in terms of these approaches.

For the calculation of observable values, some sort of contracted description of many-body state  $|F\rangle$  is needed. Usually, it is provided by projection,  $\mathcal{P}$ , on pair state  $\mathcal{P}|F\rangle$  [16], i.e.

$$\partial_t \mathcal{P}|F\rangle = \mathcal{P}L_{\text{eff}}|F\rangle \quad (3)$$

where  $\mathcal{P} = a_k^+ b_{-k}^+ |0\rangle \langle 0| a_k b_{-k}$  is the projector operator in the Fourier basis. Operator  $\mathcal{P}$  now performs a second reduction of the many-body system alongside the projector  $R$ . Approximate equation for  $\mathcal{P}|F\rangle$  can be obtained from (3) by selecting all diagrams

that are linear in powers of  $\langle n_{\sigma i} \rangle$  and including all powers of  $D_{\sigma}$ . The recombination of particle clouds is believed to be taken into account in this way. However, resulting perturbation theory for the effective diffusion coefficient gives no slowing of the reaction, though small  $\langle n_{\sigma i} \rangle$  is just the case where asymptotic stochastic kinetics are applied. The effect of clusterization, being more difficult for calculation, is likely to be involved in higher orders of the perturbation theory. We shall not discuss this further.

Instead, we shall return to the description in terms of occupation numbers,  $n_{\sigma i}$ , our aim being to establish typical configurations,  $\{n_{\sigma i}\}$ , that are determined by initial conditions and  $L_{\text{eff}}$ . The method enables us to describe separation of heterogeneous medium.

It is reasonable to start by asking why did we begin with the field formulation in the Fock space of states, and now are returning to the system of equations for many-body PDF  $F(\{n_{\sigma i}\}; t)$ . We can say, briefly, that the DLK kinetics is quasilinear (it is proved in section 2.3) and is governed by the Liouvillean  $L_{\text{eff}}$  stated in I. The Fock space formalism has allowed us to analyse transitions of individual particles, and to prove that a bimolecular elementary rate constant for these transitions is replaced with a unimolecular one in the limit  $U \rightarrow \infty$ . This point will be discussed in detail in section 2.3. Previously that property was not evident in the 'first quantization formalism' with finite rate  $U$ .

## 2.2. Balance equation in adiabatic conditions

It is not known which component is in an arbitrary cell, so a pair of occupation numbers  $\{m_{ai}, m_{bi}\}$  attributed to it to describe its state. The evolution of the total state vector

$$|F(t)\rangle = \sum_{\{m_{\sigma i}\}} F(\{m_{\sigma i}\}; t) \prod_i (a_i^+)^{m_{ai}} (b_i^+)^{m_{bi}} |0\rangle \quad (4)$$

is now calculated in the effective space of states for the scenario determined with the Liouvillean  $L_{\text{eff}}$ . It was previously obtained that  $L_{\text{eff}}$  causes four types of transitions, each having its own rate. In particular, the expression for the rate of the transitions (I.36 $\beta$ ) can be calculated by acting with the second term of the operator (I.35) on vector (4)

$$\begin{aligned} (\partial_t)_\beta |F(t)\rangle &= D_b \sum_{\{m_{\sigma i}\}} F(\{m_{\sigma i}\}; t) \sum_{i,e} m_{bi} \theta(m_{ai+e}) [1 - a_{i+e}^+ b_i^+] \\ &\quad \times (a_{i+e}^+)^{m_{ai+e}-1} (b_i^+)^{m_{bi}-1} \prod_{\substack{x \neq i \\ x \neq i+e}} (a_x^+)^{m_{ax}} (b_x^+)^{m_{bx}} |0\rangle. \end{aligned} \quad (5)$$

The rate of change of PDF by transitions (I.36 $\beta$ ) for the configuration  $\{n_{\sigma i}\}$  is found by projecting vector (5) on vector

$$\langle \{n_{\sigma i}\} | = \langle 0 | \prod_x (a_x)^{n_{ax}} (b_x)^{n_{bx}} (n_{ax}! n_{bx}!)^{-1}. \quad (6)$$

Carrying out the necessary calculations, we find

$$\begin{aligned} (\partial_t)_\beta F(\{n_{\sigma i}\}, t) &= D_b \sum_{i,e} \{ (n_{bi} + 1) \theta(n_{ai+e} + 1) F(\dots, n_{ai+e} + 1, \dots, n_{bi} + 1, \dots; t) \\ &\quad - n_{bi} \theta(n_{ai+e}) F(\dots, n_{ai+e}, \dots, n_{bi}, \dots; t) \} \end{aligned} \quad (7a)$$

where leaders indicate remaining configurations that do not participate in the transition (I.36 $\beta$ ). The contribution of (I.36 $\gamma$ ) transitions to the rate of  $F(\{n_{\sigma i}\}, t)$  is calculated analogously

$$\begin{aligned}
 (\partial_t)_\gamma F(\{n_{\sigma i}\}; t) &= D_b \sum_{i,e} \{ (n_{b_i} + 1) F(\dots, n_{b_i+e} - 1, \dots, n_{b_i} + 1, \dots; t) \\
 &\quad - n_{b_i} F(\dots, n_{a_i+e}, \dots, n_{b_i}, \dots; t) \} \delta(n_{a_i+e}). \quad (7b)
 \end{aligned}$$

The rate of change of the state  $\{n_{\sigma i}\}$  due to transitions (I.36 $\alpha$ ) and (I.36 $\delta$ ) are obtained from equations (7) by permutating indices  $a$  and  $b$ . The combined effect of all types of transitions is contained in a total balance equation for  $F$

$$\partial_t F = ((\partial_t)_\alpha + (\partial_t)_\beta + (\partial_t)_\gamma + (\partial_t)_\delta) F. \quad (8)$$

Equation (8) corresponds to slow kinetics of a many-body state in local equilibrium.

### 2.3. Deterministic regime

To write out kinetics equations for local density, the Kramers-Moyal expansion in (8) should be carried out to present it in the form of a continuity equation for  $F$  in the configuration space  $\{n_{\sigma i}\}$  under the drift approximation

$$\partial_t F(\{n_{\sigma i}\}, t) = - \sum_{i,\sigma} (\partial / \partial n_{\sigma i}) (w_{\sigma i}(\{n_{\sigma i}\}) F(\{n_{\sigma i}\}; t)). \quad (9)$$

Required kinetics equations can be found [10, 12] as characteristics of (9)

$$\partial_t n_{\sigma i} = w_{\sigma i}. \quad (10)$$

The expansion in (8) must be taken with care to fulfil the balance conditions in the kinetics equation (10). To this end, the functions  $\theta(n_{\sigma i})$  should be considered as a limit of sequence of smoother functions of corresponding arguments.

By (7), not more than a single molecule is involved in the elementary event in each cell of the lattice. Now we are interested in the stage when occupation numbers are large and we may treat them as continuous variables that are varying by a small amount  $\varepsilon$  in elementary acts. Then [10, 12], equations (7) are equivalent to equations containing shift operators  $E_{\sigma i} = \exp(\varepsilon \partial / \partial n_{\sigma i})$  with  $\varepsilon = 1$ :

$$(\partial_t)_\beta F(\{n_{\sigma i}\}; t) = D_b \sum_{i,e} \{ E_{b_i} E_{a_i+e} - 1 \} n_{b_i} \theta(n_{a_i+e}) F(\{n_{\sigma i}\}; t) \quad (11a)$$

$$(\partial_t)_\gamma F(\{n_{\sigma i}\}; t) = D_b \sum_{i,e} \{ E_{b_i} E_{b_i+e}^{-1} - 1 \} n_{b_i} \delta(n_{a_i+e}) F(\{n_{\sigma i}\}; t). \quad (11b)$$

Missing equations for the processes (I.36 $\delta$ ) and (I.36 $\beta$ ) are obtained from equations (11) by relabelling the indices  $a \leftrightarrow b$ . Truncating the Kramers-Moyal expansion in equations (11) at linear terms in powers of  $\varepsilon$  and putting  $\varepsilon = 1$  at the end of the calculations, one gets the kinetic equation in the drift approximation

$$\begin{aligned}
 \partial_t F(\{n_{\sigma i}\}; t) &= \left( \sum_{i,e} D_a \{ \partial_{a_i} + \partial_{b_i+e} \} n_{a_i} \theta(n_{b_i+e}) + D_b \{ \partial_{b_i} + \partial_{a_i+e} \} n_{b_i} \theta(n_{a_i+e}) \right. \\
 &\quad \left. + D_b \{ \partial_{b_i} - \partial_{b_i+e} \} n_{b_i} \theta(n_{a_i+e}) + D_a \{ \partial_{a_i} - \partial_{a_i+e} \} n_{a_i} \theta(n_{b_i+e}) \right) F(\{n_{\sigma i}\}; t) \quad (12)
 \end{aligned}$$

with  $\partial_{\sigma i} \equiv \partial/\partial n_{\sigma i}$ . Finally, transforming the derivatives  $\partial/\partial n_{\sigma i}$  in all terms in (12) so that they contain only one index of summation, we obtain characteristic equations. Equations of the deterministic kinetics for recombinative processes (I.36 $\alpha$ ) and (I.36 $\beta$ ) are derived from the first and second terms in (12)

$$(\partial_t)_{\alpha+\beta} n_{bi} = -D_b n_{bi} \sum_e \theta_{ai+e} - D_a \theta_{bi} \sum_e n_{ai+e} \tag{13}$$

and from the third term follows the kinetic equation due to the diffusive process (I.36 $\gamma$ )

$$(\partial_t)_\gamma n_{bi} = -D_b n_{bi} \sum_e \delta_{ai+e} + D_b \delta_{ai} \sum_e n_{bi+e}. \tag{14}$$

Here the abbreviations are introduced

$$\theta_{ai} = \theta(n_{ai}) \quad \delta_{ai} = \delta(n_{ai}).$$

The total balance for *B* particles encompasses transitions (I.36 $\alpha$ ), (I.36 $\beta$ ), (I.36 $\gamma$ )

$$\partial_t n_{bi} = (\partial_t)_{\alpha+\beta} n_{bi} + (\partial_t)_\gamma n_{bi}. \tag{15}$$

It is useful to study the meaning of each transition in (15). According to the scheme (I.36 $\gamma$ ), equation (14) represents Lorentz's model of correlated Brownian motion of *B* particles in gas of *A* scatterers, with no annihilation of particles. It can be seen from (14) that the only allowed transitions for *B* particles are to cells containing no *A* particles with  $n_{aj} = 0$ ,  $\delta_{aj} = 1$ . Transitions to cells containing *A* particles with  $n_{aj} \geq 1$  and  $\delta_{aj} = 0$  are forbidden. Collisions of *A* and *B* particles are permitted in the channels (I.36 $\alpha$ ) and (I.36 $\beta$ ) which are opened when the adjacent cells are occupied by *A* particles to make possible the recombination process, i.e. equation (13).

Now we want to show that the kinetics described by equations (13) and (14) guarantees that interfaces are motionless. According to the results of section I.2.5, after the first stage of the reaction, the lattice is separated into homogeneous domains. The interfaces of these regions are random to the extent of irregularity of the initial distribution, so empty places, i.e. gaps without particles *A* or *B*, are not excluded, in principle. In the deterministic approximation, each cell, however, contains a large number of particles either of *A* or *B* kind, so the splits are forbidden. To understand what happens on the lattice when the kinetics (15) turns on, the motion of *B* particles should be considered. The (I.36 $\gamma$ ) transitions for which jumps in the *A* regions are forbidden, apparently, do not mix the two types of particles in cells. Recombination channels (I.36 $\alpha$ ) and (I.36 $\beta$ ) cannot do this, since the resulting rate for  $n_{bi}$  in (12) is always negative. In what follows, in cell *i* the *B* particles never appear if they were initially absent there. Thus the unified action of diffusion and recombination channels conserves initial contours of particle distribution, with the redistribution of the concentration profile proceeding within domains. This picture may be visualized as follows: if the particles were coloured, all parts would be pale but not deform with time.

To make the statement of motionless of interfaces more precise, it is useful to rewrite the balance equation for  $n_{bj}$  having in view equations (13) and (15)

$$\partial_t n_{bi} = -z D_b n_{bi} + D_b \delta_{ai} \sum_e n_{bi+e} - D_a \theta_{bi} \sum_e n_{ai+e}. \tag{16}$$

Here *z* is the coordination number of the lattice. Use was also made of the identities

$$n_{bi} \theta(n_{ai}) = 0 \tag{17a}$$

$$\theta(n_{ai}) + \theta(n_{bi}) = 1 \quad \delta(n_{ai}) = \theta(n_{bi}) \tag{17b}$$

where  $\theta(n_{\sigma j})$  ( $=0, 1$ ) are the Boolean variables. They represent that the cell  $j$  either contains  $A$  particles or is occupied by  $B$  only.

The distribution of  $A$  particles follows by symmetry. The evolution of 'local hybridization'  $\eta_i = n_{ai}n_{bi}$  is determined with the two kinetics equations

$$\partial_t \eta_i = -z(D_a + D_b)\eta_i - D_a n_{ai} \theta_{bi} \sum_e n_{ai+e} - D_b n_{bi} \theta_{ai} \sum_e n_{bi+e} \quad (18)$$

where the identity  $n_{\sigma i} \delta(n_{\sigma i}) = 0$  has been used. Initially, at  $t = +0$ , the configurations of  $A$  and  $B$  are non-intersecting, i.e.  $\eta_i = 0$ ,  $n_{ai} \theta(n_{bi}) = n_{bi} \theta(n_{ai}) = 0$ . It follows that for each  $i$ th cell  $\partial_t \eta_i(t = +0) = 0$ , and at time step  $dt$  later the configurations remain non-intersecting. Since (18) is of first order in time, then repeating iterates give  $\eta_i(t) = 0$  at following instants of time. Agreement of the result obtained with the conclusions of adiabatic analysis (see section I.2.1) shows that (16) reflects the natural properties of DLR kinetics.

However, the condition  $\eta_i(t) = 0$  does not mean that the interfaces are motionless, since a situation when one of the phases displaces another one also satisfies it. For the DLR, such a situation, nevertheless, is excluded. In order to displace a piece of interface, the cells at one side of the boundary have to become depleted with  $n_{\sigma i} \approx 0$ . In this case, fast particles jump into the hole resulting in replacement of one sort of molecule by another. The deterministic character of kinetics, however, is violated at earlier stages, and a fluctuation mechanism of redistribution of particles becomes more important.

Thus we arrive at the following scenario of the DLR. After the first instants of the recombination, the excess component (for instance of  $\sigma$ ) with density  $n_{\sigma i} \gg 1$  remains the only component in the  $i$ th cell. Cell clusters form homogeneous zones. The diffusion followed by mutual annihilation at interfaces cannot change positions of interfaces as time goes on. This law of conservation of topology may be termed the 'chemical arrest effect'

$$\theta_{\sigma i} = \theta(n_{\sigma i}(t)) = \theta(n_{\sigma i}(0)). \quad (19)$$

Within the framework of deterministic kinetics,  $\delta(n_{\alpha i}) = \theta(n_{\beta i})$  where  $\alpha$  and  $\beta$  are adjacent phases, i.e. gaps between zones are forbidden.

Formally, the time conservation of the 'colour' of each cell can be shown if we use equations (16) and (17)

$$\partial_t n_{bi} = D_b \sum_e (\theta_{bi} n_{bi+e} - n_{bi}) - D_a \theta_{bi} \Delta n_{ai}. \quad (20)$$

In view of the identity  $n_{bi} = \theta_{bi} n_{bi}$ , this equation is rewritten finally in terms of gradients of flows as a mass balance equation

$$\partial_t n_{bi} = \theta(n_{bi}) \Delta N_i \quad \text{where } N_i = D_b n_{bi} - D_a n_{ai}. \quad (21a)$$

The kinetics equation for the  $A$  species is obtained by permuting indices  $a$  and  $b$

$$\partial_t n_{ai} = -\theta(n_{ai}) \Delta N_i. \quad (21b)$$

This is the mass action equation for the density number for instantaneous recombination. As  $n_{\sigma i} \rightarrow 0$ , some smooth approximation of the function  $\theta(n_{\sigma i})$  tends to zero and makes density positively defined. However, by the time this nonlinear stage is reached, the deterministic kinetics breaks, leaving the stochastic one.

From equations (21) follows conservation of the total surplus of particles, i.e.  $\sum_i [n_{ai}(t) - n_{bi}(t)] = \text{constant}(t)$ , and the kinetics equation [2] for local surpluses of particles,  $z_i = n_{ai} - n_{bi}$ , in the case of equal diffusion coefficients is

$$\partial_t z_i = D \Delta z_i. \tag{22}$$

Due to (19), the static parameters  $\theta_{\sigma i}$  are determined by initial preparation and are responsible for the contours of the interfaces. From equations (21), it follows that in cells with  $\theta_{\sigma i} = 0$  the  $\sigma$  particles are always absent, therefore these equations correctly account for the effect of memory of the initial stratified state.

Linearity in equations (21) may be associated with the assumption that in the course of the analytical calculations displacement of an elementary amount of mass,  $\varepsilon$ , is taken into account, as if a statistical analogue of the linear stability analysis of kinetic schemes were carried out. In fact, this condition does not suffice for linearity. Derivation of the kinetics equation (3) with finite  $U$  also uses small  $\varepsilon$  but, due to interactions of particles within cells, results in nonlinear equations. Hence, the linearity suggests the importance of stratification formed under criterion (1). Due to fast recombination, domains are formed from the very beginning of the reaction, and the kinetics inside each of them is governed by linear transfer of particles in accordance with the values of the coefficients  $\theta_{\sigma i}$ , i.e. with information about neighbouring cells. The message of this consideration is that the kinetics under conditions (1) and (2) is of one-body character.

#### 2.4. Analogy with unimolecular absorption

Kinetics of unimolecular absorption of moving  $B$  particles by motionless  $A$  traps involves two elementary diffusion transitions



which determine the Liouvillean of the problem expressed in terms of the correlation operators

$$L_{\text{eff}} = D_b \sum_{i,e} ((b_{i+e}^+ - b_i^+) b_i \delta(\hat{n}_{ai+e}) + (1 - b_i^+) b_i \theta(\hat{n}_{ai+e})).$$

It corresponds to the following kinetics equation for PDF

$$\begin{aligned} \partial_t F(\{n_{\sigma i}\}, t) &= D_b \sum_{i,e} \{(n_{bi} + 1) F(\dots, n_{bi} + 1, \dots; t) - n_{bi} F(\dots, n_{bi}, \dots; t)\} \theta(n_{ai+e}) \\ &+ D_b \sum_{i,e} \{(n_{bi} + 1) F(\dots, n_{bi+e} - 1, \dots, n_{bi} + 1, \dots; t) \\ &- n_{bi} F(\dots, n_{bi+e}, \dots, n_{bi}, \dots; t)\} \delta(n_{ai+e}). \end{aligned}$$

Derivation of a deterministic equation is performed with the help of the Kramers-Moyal expansion keeping only the linear terms in powers of  $\varepsilon$  supplemented with the identities (17)

$$\partial_t n_{bi} = D_b \delta_{ai} \sum_e n_{bi+e} - z D_b n_{bi} \equiv D_b \theta(n_{bi}) \Delta n_{bi}. \tag{23}$$

This equation describes the motion of  $B$  particles in the medium with  $A$  traps [17]. Solution of (23) satisfies the requirement that configurations for the two types of



particles do not intersect. If the traps are initially present in the cell  $i$ , i.e.  $n_{ai} \geq 1$ ,  $\delta(n_{ai}) = 0$ ,  $\theta(n_{bi}(+0)) = 0$ , then  $B$  particles do not appear there. The traps of  $A$  may be also interpreted as sinks of  $B$  particles giving the familiar model of unimolecular kinetics [17, 18]

$$\partial_t n_{bi} = D_b \Delta n_{bi} - V_{ai} n_{bi} \quad (24)$$

where  $V_{ai} = V\theta(n_{ai})$  is the static 'potential' caused by the  $A$  component;  $V_{ai} = \infty$  in cells occupied by the  $A$  traps and  $V_{ai} = 0$  in free cells. Equivalence of both formulations of unimolecular recombination follows from a coincidence of spatial-temporal solutions determined by equations (23) and (24). Indeed, in regions occupied by the  $A$  traps, the 'potential'  $V \gg D^b$  and the kinetics is chiefly governed by absorption. Particles of the  $B$  kind rapidly disappear in these regions with characteristic times of the order of  $V^{-1}$  resulting in flows of  $B$  particles down their density gradients.

A glance at (21) shows that it can be transformed into an expression with sink terms just like (23) has. Then, the system of kinetics equations written in matrix notation with symmetric operator in space representation

$$\partial_t \mathbf{n}_i = \begin{pmatrix} D^a & -D^b \\ -D^a & D^b \end{pmatrix} \Delta \mathbf{n}_i - \begin{pmatrix} V_{bi} & 0 \\ 0 & V_{ai} \end{pmatrix} \mathbf{n}_i \quad (25)$$

where  $\mathbf{n} = \text{col}(n_{ai}, n_{bi})$ , describes diffusion of the  $A(B)$  component in the absorbing medium  $B(A)$ . The static potential  $V_{\sigma i} = V\theta(n_{\sigma i})$ , where  $V \rightarrow \infty$ , plays the role of the potential of a substitutional alloy, with coefficients  $\theta(n_{\sigma i})$  coupled by relations (17). Analysing the motion of  $A$  particles, we can conclude that in  $B$  regions the particles experience instantaneous absorption, and outside  $B$  regions they freely diffuse. Hence, only the term  $D^a \Delta n_{ai}$  contributes to the equation for  $A$  particles inside  $A$  regions, while the second term,  $-D^b \Delta n_{bi}$ , is important at the interfaces.

An interesting feature of (25) is that it can be obtained from variational principles (vp) by minimization of the Liapunov functional, with density of the 'kinetic part' being  $\frac{1}{2}(\nabla N_x)^2$ , where  $N_x$  is defined in (21a), and the density of the 'potential part' being  $(V_{bi} n_{ai}^2 + V_{ai} n_{bi}^2)$ . Existence of vp was not evident from the very beginning, since, owing to the non-Hermitian form of  $L_{\text{eff}}$ , it is absent both for the problem with finite  $U$ , i.e. for (I.3), and in the many-body formulation with  $U \rightarrow \infty$ .

Thus, the bimolecular reaction can be decomposed into two independent unimolecular ones. Change of density at interfaces is caused by two simultaneous and independent processes: by jumps of  $A$  to  $B$  and by jumps of  $B$  to  $A$ . In this form, the bimolecular character of the reaction reveals itself as a process in which the two types of particles are equally participating. It will be shown in section 3 that the case with strongly differing  $D_\sigma$  corresponds to unimolecular kinetics (when one component is practically fixed), and the case with comparable coefficients is associated with bimolecular kinetics.

### 3. Averaging over the initial density fluctuations

#### 3.1. Effective kinetics of redistribution of density

In this section time dependence of the average density  $\langle n_{\sigma i} \rangle$  and variance  $\langle (\delta n_{\sigma i})^2 \rangle$  are evaluated assuming the initial distribution of configurations to be random.

First, the closed equation for the kinetics of *A* particles can be found from linear system (21). We seek a solution of the form

$$n_{\sigma i}(t) = \theta(n_{\sigma i}) p_{\sigma i}(t) \tag{26}$$

where  $\theta(n_{\sigma i})$  is the static field. Making the Laplace transform over time in every equation of the system and substituting the formal solution to (21*a*), i.e.

$$\tilde{n}_{bi} = (\omega - \theta_{bi} D_b \Delta)^{-1} n_{bi}^0 - \theta_{bi} D_a \Delta \tilde{n}_{ai}$$

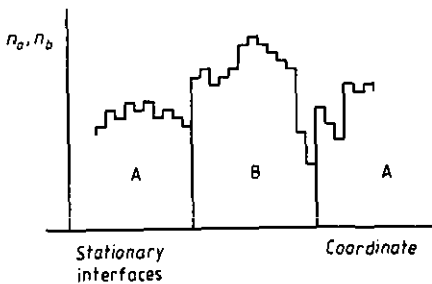
in (21*b*), we get immediately the equation for  $p_{ai}$

$$\omega \tilde{p}_{ai} - \Delta(\psi_i \tilde{p}_{ai}) = Y_i \equiv p_{ai}^0 - (D_b/\omega)\Delta(\theta_{bi} p_{bi}^0) \tag{27}$$

where  $\psi_i = D_a \theta_{ai} + D_b \theta_{bi}$  and  $p_i^0 = p_{ai}^0 + p_{bi}^0$  are random fields,  $p_{\sigma i}^0 = p_{\sigma i}(t=0)$ , with Laplacian,  $\Delta$ , on a lattice acts according to the rule:  $\Delta \phi_i = \sum_e (\phi_{i+e} - \phi_i)$  for any function  $\phi_i$ .

Equation (27) contains two independent fields. Configuration  $\theta_{\sigma i}$  determines contours of domains, and distribution  $p_{\sigma i}^0$  determines initial density profile within the domains. We see that Brownian *A* particles are moving in two-component medium with heterogeneous transition rates  $\psi_i$ . The field  $\{Y_i\}$  gives the initial condition, evolution of which should be determined. Although motion of *A* particles proceeds in the *A* phase, the formal structure of (27), after elimination of *B* phase, is such as if the *A* particle moved from time to time in the *B* phase with diffusion coefficient  $D_b$ .

Denote an effective Brownian particle obeying (27) as  $A^*$ . Two situations may be distinguished:  $D_b = 0$  and  $D_b \neq 0$ . Imagine a bounded *A* region within a larger *B* region. In the first case, when  $D_b = 0$ , those *B* cells which do not border the interface do not 'feel' the changing *A* profile. For this reason, every compact region of *A* is isolated from all other *A* regions, so destruction of particles within interfaces occurs independently of neighbouring regions (figure 1). It is known [19] that when the volume fraction of ill-conducting *B* regions exceeds a critical value,  $\Omega_b^*$ , localization of  $A^*$  takes place within conducting domains, the particles of  $A^*$  being destroyed at interfaces through unimolecular reaction [20]. Although for smaller fractions  $\Omega_b$ ,  $\Omega_b \leq \Omega_b^*$ , an effective diffusion on the whole lattice occurs, the asymptotic kinetics remains the same, i.e. the unimolecular one [20], and it is limited by motions in the bounded *A* regions [21].



**Figure 1.** The occupation numbers distribution of mixture on a lattice in the DLR process. On the deterministic stage, each cell represents a well-stirred reservoir with a large number of particles. In particular, at motionless interfaces, occupation numbers are not equal to zero. For  $D_b = 0$ , numbers of *A* particles in different *A* domains decrease independently. All regions are interconnected for  $D_a, D_b \neq 0$ .

In the second case when the coefficients are comparable,  $D_b \neq 0$ , perturbations of density occurring in some  $A$  region transfer through the moving  $B$  medium to the neighbourhood  $A$  regions, and in turn, the next  $B$ , and so on. As a result of such large-scale diffusive actions, all  $A$  regions which are far from one another and are separated by  $B$  domains, are involved in full kinetics. Destruction of particles obeys, in this case, laws different to those for fixed  $B$ .

### 3.2. Averaging for $D_b \neq 0$

It is hopeless to expect an explicit solution to (27) because of non-uniform field  $\psi_i$ . An approximation we are going to use is that the rate of density relaxation within some  $\sigma$  domain is mainly determined by intrinsic rate  $D_\sigma$

$$\tilde{p}_{ai} = [\omega - D_a \Delta]^{-1} p_{ai}^0 - [\omega - D_b \Delta]^{-1} (D_b / \omega) \Delta (\theta_{bi} p_{bi}^0). \quad (28)$$

The idea we use to simplify the problem is based on the fact that for equal diffusion coefficients,  $D = D_a = D_b$ , motion of particles occurs in uniform and inert medium with  $\psi_i = D$ . Hence, a transition from (27) to (28) is carried out exactly. In this case, fields  $p_{\sigma i}$  play the same role in the DLR kinetics as the field  $z_i$  in the kinetics with finite rate  $U$  [2]. According to (26), calculation of  $A$  particle numbers requires 'cutting out' regions with  $A$  phase from the field  $p_{ai}$ . The remaining profile  $p_{ai}$  does not contribute to the calculation of  $n_{ai}$ , since the  $B$  phase has its own equation for  $p_{bi}$  which is analogous to (27). As a result, the total number of particles of the sort  $\sigma$  determined by (26) changes in time, although the value  $p_{\sigma i}$ , being integrated over the whole lattice, is conserved.

Thus, choosing (28) as an approximate solution to (27), the problem is reduced to averaging of the right-hand side in (28). It should be noticed that although coefficients  $\theta_{\sigma i}$  are presented both in function  $\psi_i$  and in  $Y_i$ , we suppose that the function  $Y(\theta_{\sigma i})$  is more important for the kinetics than  $\psi(\theta_{\sigma i})$ .

The Green function (GF) for a diffusive motion on a homogeneous three-dimensional lattice has the form [17]:

$$\mathcal{G}_r^{(\sigma)}(t) = \prod_{\nu=1}^3 \{ \exp(-2D_\sigma t) I_{r_\nu}(2D_\sigma t) \} \quad (29)$$

where  $I_{r_\nu}$  is the modified Bessel function of order  $r_\nu$ , and  $r = \{r_1, r_2, r_3\}$  is the displacement vector. In the coordinate representation,  $p_{ai}(t)$  in (28) is given by

$$p_{ax}(t) = \sum_x \{ \mathcal{G}_{ix}^{(a)} p_{ax}^0 - \mathcal{G}_{ix}^{(b)} p_{bx}^0 \} \quad (30)$$

where  $p_{\sigma i}^0 = \theta_{\sigma i} m_{\sigma i}$ . When deriving (30) the identity

$$[\omega - D_b \Delta]^{-1} (D_b / \omega) \Delta = [\omega - D_b \Delta]^{-1} - \omega^{-1}$$

was used. For random numbers  $p_{\sigma x}^0$ , the value  $p_{ax}(t)$  is also random. The fields  $\theta_{\sigma i}$  and  $m_{\sigma i}$  are supposed to be statistically independent, with correlation functions

$$\begin{aligned} \langle \theta_{\sigma i} \rangle &= \Omega_\sigma & \langle \theta_{ai} \theta_{bj} \rangle &= \langle \theta_{ai} \rangle \langle \theta_{bj} \rangle & \text{where } i \neq j \\ \langle \theta_{\sigma i}^2 \rangle &= \Omega_\sigma & \langle m_{\sigma i} \rangle &= \rho_\sigma & \langle m_{\sigma i}^2 \rangle &= \rho_\sigma^2 + x_\sigma. \end{aligned} \quad (31)$$

Here the following notation is introduced:  $\Omega_\sigma$  is the part of the volume occupied by  $\sigma$  component so that  $1 = \Omega_a + \Omega_b$ ,  $\rho_\sigma$  is average number density of  $\sigma$  particles in some

cell, and  $x_\sigma$  measures fluctuations in number density (for the Gaussian model  $x_\sigma = \rho_\sigma$ ). For these conditions, averaging yields

$$\langle n_{aj}(t) \rangle = \Omega_a \{ k_a + \Omega_b (\rho_a \mathcal{G}_0^{(a)}(t) + \rho_b \mathcal{G}_0^{(b)}(t)) \} \tag{32}$$

where  $k_a = (\rho_a \Omega_a - \rho_b \Omega_b)$  is a constant. Actually, we have calculated the average density of  $A$  particles,  $\langle c_a(t) \rangle$ , weighted by the fraction  $\Omega_a$  of the volume of  $A$  species, i.e.  $\langle n_{aj}(t) \rangle = \Omega_a \langle c_a(t) \rangle$ . In the absence of  $B$  phase when  $\Omega_b = 0$ ,  $\Omega_a = 1$ , we have  $\langle n_{aj}(t) \rangle = \rho_a$ . When  $r = 0$  and  $t = 0$ , the lattice GF equals unity,  $\mathcal{G}_0^{(\sigma)}(0) = 1$ , so  $\langle n_{aj}(0) \rangle = \rho_a \Omega_a$ . At large times, GF  $\mathcal{G}_0^{(\sigma)}(t)$  decreases at  $t^{-3/2}$ , and if  $k_a < 0$ , then after some time the density  $\langle n_{aj}(t) \rangle$  becomes negative. This result is not surprising since at low concentrations of the particles in cells the deterministic kinetics breaks, leaving a stochastic one. In the case  $k_a < 0$ , the density of  $B$ ,  $\langle c_b(t) \rangle$ , has positive coefficient  $k_b = \Omega_b (\rho_b \Omega_b - \rho_a \Omega_a) = -k_a > 0$ , i.e.  $B$  particles are in excess and the condition of deterministic approximation (2) is approximately applicable for them. For the  $d$ -dimensional case, the same procedure yields  $\langle n_{aj}(t) \rangle \approx t^{-d/2}$  for  $t \rightarrow \infty$ .

To calculate the number fluctuations, we should first find the second moment

$$\begin{aligned} \langle n_{aj}^2(t) \rangle = & \sum_x \sum_y \{ \mathcal{G}_{j-x}^{(a)} \mathcal{G}_{j-y}^{(a)} \langle \theta_{aj} n_{ax}^0 n_{ay}^0 \rangle + \mathcal{G}_{j-x}^{(b)} \mathcal{G}_{j-y}^{(b)} \langle \theta_{aj} n_{bx}^0 n_{by}^0 \rangle \\ & - 2 \mathcal{G}_{j-x}^{(a)} \mathcal{G}_{j-y}^{(b)} \langle \theta_{aj} n_{ax}^0 n_{by}^0 \rangle \}. \end{aligned} \tag{33}$$

The result may be expressed in the form  $\langle n_{aj}^2(t) \rangle = \Omega_a \langle c_a^2(t) \rangle$  that is merely a definition for  $\langle c_a^2(t) \rangle$ . Using correlation functions (31), we determine the expressions for correlations  $\langle \theta_{aj} n_{ax}^0 n_{by}^0 \rangle$ , where  $\alpha, \beta = a, b$ , depending on whether the cells  $x$  and  $y$  coincide with each other and with the cell  $j$ . After summation, we find that the variance  $\langle (\delta c_{aj})^2 \rangle = \langle c_{aj}^2 \rangle - \langle c_{aj} \rangle^2$  equals explicitly

$$\begin{aligned} \langle (\delta c_{aj})^2 \rangle = & \Omega_b [x_a (\mathcal{G}_0^{(a)})^2 - x_b (\mathcal{G}_0^{(b)})^2] + [G^{(a)} x_a \Omega_a + G^{(b)} x_b \Omega_b] - \Omega_a \Omega_b (\rho_a \mathcal{G}_0^{(a)} + \rho_b \mathcal{G}_0^{(b)})^2 \\ & + \Omega_a \Omega_b (\rho_a^2 G^{(a)} + \rho_b^2 G^{(b)} + 2\rho_a \rho_b \sum_x \mathcal{G}_x^{(a)} \mathcal{G}_x^{(b)}). \end{aligned} \tag{34}$$

Here the function

$$G^{(\sigma)}(t) = \sum_x \{ \mathcal{G}_x^{(\sigma)}(t) \}^2$$

is linked with GF for returning random walk due to the Chapman-Kolmogorov equation [10, 12], i.e.  $G^{(\sigma)}(t) = \mathcal{G}_0^{(\sigma)}(2t)$ . Using expression for GF, (29), and the theorem of summation of Bessel functions [22], the sum

$$\sum_x \mathcal{G}_x^{(a)} \mathcal{G}_x^{(b)} = \mathcal{G}_0^{(*)}(2t)$$

is related to GF with diffusion coefficient  $D_* = \frac{1}{2}(D_a + D_b)$ . At time  $t = 0$ , (34) gives  $\langle (\delta c_{aj})^2 \rangle = x_a$  that is in agreement with (31). Asymptotic behaviour of  $\langle (\delta c_{aj})^2 \rangle$  is determined by asymptotes of the functions  $\mathcal{G}_0^{(\sigma)}(2t)$  and  $\mathcal{G}_0^{(*)}(2t)$  that decrease as  $t^{-3/2}$  for  $t \rightarrow \infty$ . This gives time dependence of the standard deviation in the density

$$\langle (\delta c_{aj})^2 \rangle^{1/2} \approx t^{-3/4}.$$

We see so that not only  $\langle (\delta c_{aj})^2 \rangle^{1/2}$  decreases as  $t^{-3/4}$ , but also the typical local fluctuations in number density,  $\langle (\delta c_{aj})^2 \rangle^{1/2}$ , do the same. For the  $d$ -dimensional case,  $\langle (\delta c_{aj})^2 \rangle^{1/2} \approx t^{-d/4}$  for  $t \rightarrow \infty$ .

Contributions of higher moments to the asymptotic behaviour of  $\{\langle c_{\sigma i}^k \rangle\}^{1/k}$  that are certainly to be proportional to

$$\left\{ \sum_x \{ \mathcal{G}_x^{(\sigma)}(t) \}^k \right\}^{1/k} \approx t^{-\nu} \quad \text{where } \nu = 3(k-1)/2k$$

are small compared to the  $k=2$  term.

#### 4. Summary and discussion

Although computer simulations [3] revealing slowing of DLR kinetics are quoted as confirming the theory [2], in fact, they concern a different physical situation. Using statistical simulations, one has to deal with dilute gas particles for which temporary fluctuations in density are essential. In contrast, the analytical results [2] concern a high density stage with small fluctuations. To understand the numerical simulations, analysis of temporary fluctuations on stochastic stage, when  $\langle n_{\sigma i} \rangle \ll 1$  and large domains survive, is required. At the deterministic level, it is hardly possible to confirm the numerical results with the desired accuracy or to make any conclusions about the asymptotic behaviour.

The stochastic equation is more difficult to derive as it involves motion of randomly distributed interfaces. The authors [2] attributed the decrease of  $\langle |z_i(t)| \rangle$  (the value is expressed through even moments of  $z_i = n_{ai} - n_{bi}$ ) to decrease of the average density  $\langle n_{\sigma i} \rangle$ , assuming that  $\langle n_{\sigma i}^2 \rangle = \langle n_{\sigma i} \rangle^2$ , which implies that  $\langle (\delta n_{\sigma i})^2 \rangle = 0$ . Meanwhile, if the solution of the kinetics equations (21) is used, the first and the second moments are determined independently, and has been shown (see equations (32) and (34)), that while criteria (1) and (2) are fulfilled (adiabaticity + determinism), the formula  $t^{-3/4}$  describes the standard deviation,  $\langle (\delta c_{\sigma i})^2 \rangle^{1/2}$ , while the average density decreases faster, as  $t^{-3/2}$ , with relation  $\langle c_{aj}^2 \rangle = \langle (\delta c_{aj})^2 \rangle + \langle c_{aj} \rangle^2$  holding. In general, for dimension  $d$ , it can be obtained that  $\langle (\delta c_{\sigma i})^2 \rangle^{1/2} \approx t^{-d/4}$  and  $\langle c_{\sigma i} \rangle \approx t^{-d/2}$ . The result contradicts that of [2] and the common point of view [5-9]. So, the question is relevant here: why does the intermediate asymptote of  $\langle c_{\sigma i}^2 \rangle^{1/2}$  (on transient deterministic stage) correspond to calculations of  $\langle c_{\sigma i} \rangle$  in exactly the asymptotic stage [3]?

Consider now the recombination operator in a two-species system. It has been shown in I that bosonization technique, applied to operator  $RL_D$  that is expressed originally in terms of Hubbard operators, gives correlation operators  $\theta(\hat{n}_{\sigma i})$  and  $\delta(\hat{n}_{\sigma i})$ . The trigger role of this operator consists in choosing the way of changing the current state. It may go along either a diffusive (jump) or recombinative (jump + annihilation) pathway. Equation of deterministic kinetics corresponding to this form of  $L_{\text{eff}}$  is strongly nonlinear due to functions  $\theta(n_{\sigma i})$ . The latter are responsible for the positions of interfaces. For  $n_{\sigma i} > 1$ , these functions hold in time. Because of this, in the deterministic picture, the particles of each kind are confined to regions with fixed interfaces determined by initial preparation of the system ('chemical arrest effect') and recombine at interfaces. The kinetics of redistribution of particles within interfaces is linear and formulated in terms of density of every component, not merely in terms of excess density as in [2].

The motion of interfaces occurs when the deterministic character of recombination breaks down.

The possibility to linearize the nonlinear DLR problem is an important property of the Bose models with fast recombination. We hope that this property, that is valid

exclusively in the deterministic approximation, may be used to investigate effective transport-limited reaction by reducing the piecewise-linear problem for random heterogeneous medium to a globally linear one in the spirit of the effective medium theory.

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