

## Influence of the force interaction on accumulation of macroscopic correlations in elementary reaction $A + B \rightarrow C$

Alexander A. Kipriyanov · Alexander A. Kadetov · Alexey A. Kipriyanov · Alexander B. Doktorov

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**Abstract** The applicability of the Encounter Theory (ET) (the prototype of the Collision Theory) concepts for widely occurring diffusion assisted irreversible bulk reaction  $A + B \rightarrow C$  (for example, radical reaction) in dilute solutions taking account of initial microscopic correlations and force interactions between reactants has been treated theoretically with modern many-particle method for the derivation of non-Markovian binary kinetic equations. The method shows that taking into consideration initial correlations and force interactions leads to the redefinition of the Markovian rate constant only in the expressions derived earlier. Thus, just as in the reaction  $A + A \rightarrow C$  and the reaction  $A + B \rightarrow C$  neglecting force and initial correlations, the Modified Encounter Theory (MET), when reduced to equations of a Regular Form, both extends the time applicability range of ET homogeneous rate equation, and yields the inhomogeneous equation of the Generalized Encounter Theory (GET). It reveals macroscopic correlations induced by the encounters in the reservoir of free walks in full agreement with physical considerations. Time accumulation of macroscopic correlations obeys the same time law as in the previously considered case neglecting force interactions. Just the rate of the process will change, according to traditional redefinition of the steady-state constant of the reaction.

**Keywords** Kinetic equation · Irreversible bulk reaction · Non-Markovian theory · Encounter Theory · Modified Encounter Theory · Correlations

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A. A. Kipriyanov (✉) · A. A. Kadetov · A. A. Kipriyanov · A. B. Doktorov  
Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russia  
e-mail: alexander.kipriyanov@yandex.com

A. A. Kipriyanov · A. B. Doktorov  
Physics Department, Novosibirsk State University, 630090 Novosibirsk, Russia

## 1 Introduction

Development of diffusion controlled reactions is related to the Smoluchowski works on coagulation theory in colloid chemistry [1]. Extension of these works to the theory of chemical reactions in liquid solutions has led to the so-called Smoluchowski approach. In the frame of this approach the kinetic equations have the form of differential ones (rate equations) similar to formal chemical kinetics equations with the only difference that the reaction rate constant is time dependent. Later on, traditional approaches to the derivation of kinetic equations in the theories of reactions in solutions [2–9] based on the concepts of independent reactant pairs (“free pairs” [10, 11]) confirmed the results of the Smoluchowski approach. The exact many-particle (with respect to reactants) substantiation of these theories was performed for the simplest irreversible reaction using the so-called “target model” [8, 9], and at small concentrations—by Waite using superposition decoupling in hierarchies for Reduced Distribution Functions [10–13]. However, these approaches turned out to be inapplicable in the investigation of dynamic processes (determined by the Hamiltonians) and reversible chemical reactions.

Therefore the Encounter Theory (ET) [14–16] was proposed. It is the prototype of the Collision Theory (CT) in gases [17–19] adapted for the consideration of physicochemical processes in dilute liquid solutions (solutions with small value of density parameter). The Encounter Theory based on somewhat different, more general physical concepts, is more universal from the standpoint of the description of reacting systems evolution than the Smoluchowski approach. In particular, ET takes account of non-contact nature of the reaction, it can be applied to reversible and multi-stage reactions, makes it possible to allow for the Hamiltonian, internal structure, nonsphericity of reactants, etc. In the specific case of the Smoluchowski problem statement, ET reproduces its result. The advantage of ET is that the concepts it is based on allows one to obtain clear physical interpretation of the results.

The applicability of the Collision Theory concepts to reactions in liquid solutions is based on the fact that in traditional consideration of a solvent dilute solutions resemble a “gas” of reactants dissolved in a homogeneous chemically inert solvent (not in solution) treated as a continual medium (from the standpoint of molecular dynamics this corresponds to the limiting case of “over damped” Langevin dynamics, or to the Langevin dynamics without inertia, i.e., corresponds to the Brownian dynamics methods). Note that along with such a treatment of a solvent, there exist the approaches allowing for its molecular structure [20–22]. However, unlike the Collision Theory, ET allows for the interaction with the medium affecting both the course of the elementary event, and the character of reactants mobility (the kinematics of “collision”) that is transformed to random walks [23].

In the framework of ET the reactants are for the most part in the process of “free” random walks (in the reservoir of free random walks), and the reaction takes place upon their pair (binary) encounters the duration of which is much less than the mean time between them. Under such conditions, pair encounters were considered to be independent and three and more particles encounters are neglected (just as for collisions in gases). It means that the effects of the encounters occurring at different moments of time are uncorrelated, and, therefore, additive. These concepts, as in gases, lead to

differential kinetic equations (rate equations) differing from formal chemical kinetics equations based on the kinetic law of mass action only in the time dependence of the rate constant.

However, the conception of independent pair encounters of reactants in solution needs consistent substantiation that may be performed only on the basis of many-particle consideration of the reacting systems. Different many-particle techniques were proposed in the literature [24–26] but we use the method most closely related to the Encounter Theory notions. Such a method based on the adaptation of non-stationary quantum scattering theory techniques and non-equilibrium statistical mechanics methods to chemically reacting systems now has become possible [27–34].

This method consists of several steps beginning from the many-particle statement of the problem to the final derivation of binary kinetic equations. The detailed microscopic many-particle description of the reacting system and passing to the thermodynamic limit make it possible to write hierarchies for Reduced Distribution Functions. Further derivation of the equations relies on the idea to treat the evolution of the reacting system as the evolution of space-time correlations in spatial location of reactants. The obtained hierarchies of equations for correlation patterns require closing on some level. The simplest method of such a closure is taking into consideration just two-particle correlations between reactants neglecting all three-particle ones. This approximation corresponds to the development of the so-called Integral Encounter Theory (IET) [35, 36] and leads to integro-differential kinetic equations. The kernel of this equation calculated using the reacting pair parameters is the basic kinetic coefficient of the theory that completely describes the encounter. However, the kinetic equations themselves can be employed in a narrow time interval [36–38]. To expand their applicability in the range of binary description, it is necessary to allow for correlation patterns of higher order than two-particle ones. Closing of a hierarchy of equations on the level of three-particle correlation patterns is implemented by extracting binary channels in the evolution of three-particle correlation patterns; this corresponds to the next step in the many-particle derivation and the development of the Effective Pair Approximation (EPA) [28, 39]. On the basis of this approximation, we derive more general integro-differential binary equations of the Modified Encounter Theory (MET) [39] valid over the entire time range of binary description. However, the demerit of this theory is the dependence of the kinetic coefficient (the kernel) on initial concentrations of reactants that contradict the principles of kinetic theory. Within the accuracy of binary approximation the kinetic equations of irreversible reactions admit further reduction to the form of the rate equation (Regular form) that allows direct comparison with the Encounter Theory. The aim of the present contribution is the application of the developed method for the derivation of the kinetic equation for the reaction  $A + B \rightarrow C$  with allowance for the force interaction between reactants.

## 2 Statement of the problem

For the irreversible reaction under discussion  $A + B \rightarrow C$  (in this particular case) the non-Markovian (with time dependent reaction rate constant) binary kinetic equation

is of the same form both in ET, and in Waite-Smoluchowski theories

$$\frac{d[A]_t}{dt} = \frac{d[B]_t}{dt} = -\frac{d[C]_t}{dt} = -K(t)[A]_t[B]_t, \quad (2.1)$$

where  $[A]_t$ ,  $[B]_t$  and  $[C]_t$  are concentrations of reactants.  $K(t)$  is the non-Markovian rate constant attaining its steady-state value (the Markovian rate constant or the steady-state constant)

$$k = \lim_{t \rightarrow \infty} K(t). \quad (2.2)$$

In this Markovian version of the theory Eq. (2.1) is transformed into the equation of formal chemical kinetics corresponding to the kinetic law of mass action (corresponding concentrations are marked by the upper index  $m$ )

$$\frac{d[A]_t^m}{dt} = \frac{d[B]_t^m}{dt} = -\frac{d[C]_t^m}{dt} = -k[A]_t^m[B]_t^m, \quad (2.3)$$

to give the familiar kinetics of the bimolecular reaction at hand

$$[A]_t^m = \frac{\Delta n \cdot [A]_0 \exp(-k \Delta n t)}{[B]_0 - [A]_0 \exp(-k \Delta n t)}; [B]_t^m = \frac{\Delta n \cdot [B]_0}{[B]_0 - [A]_0 \exp(-k \Delta n t)}, \quad (2.4)$$

where  $\Delta n = [B]_t - [A]_t = [B]_t^m - [A]_t^m = [B]_0 - [A]_0$ , and  $[A]_0$  and  $[B]_0$  are the initial concentrations of reactants. For definiteness, hereinafter we take that  $[B]_0 \geq [A]_0$  ( $\Delta n \geq 0$ ).

In the framework of ET Eqs. (2.1) and (2.3) have a clear physical meaning. The product of concentrations in the right-hand sides of the equations corresponds to the approach of uncorrelated particles which are in the process of free random walk in the bulk, while the kinetic coefficients (rate constants) specify the efficiency of the encounter of reactants brought close together. Note that the independence of pair encounters also means the independence of “reservoirs” of free random walks and the encounters.

In the paper in Ref. [40] we used the described above many-particle method for the derivation of kinetic equations to analyze the notions of the independence of pair encounters for the reaction  $A + B \rightarrow C$ . But this investigation was made without regard to force interaction between reagents (reactants were assumed to be point particles). This allowed us to concentrate on the study of correlations determined by the reaction. It has been established that the final kinetic equation written in the Regular form (as the rate equation) involves an extra term  $J(t)$  determined by accumulation of macroscopic correlations in a free walk “reservoir”

$$\frac{d[A]_t}{dt} = \frac{d[B]_t}{dt} = -\frac{d[C]_t}{dt} = -K(t)[A]_t[B]_t + J(t). \quad (2.5)$$

The appearance of extra inhomogeneous term in the kinetic equation is traditionally associated with the presence of initial correlations in the system that vanish with time,

in accordance with the general principles of non-equilibrium statistical mechanics [11, 41–43]. However, the time dependence of the obtained term  $J(t)$  in Eq. (2.5) is different: at the initial moment of  $J(t = 0) = 0$ . With time,  $J(t)$  reaches its maximum value, and then decreases to zero. To interpret the obtained source in the concepts of the Encounter Theory, the kinetic equation (2.5) can be conveniently rewritten as

$$\frac{d[A]_t}{dt} = \frac{d[B]_t}{dt} = -\frac{d[C]_t}{dt} = -K(t)\{[A]_t[B]_t + \Pi^{macro}(t)\}. \quad (2.6)$$

The presence of the correlator  $\Pi^{macro}(t)$  means that chemical correlations arising on the encounters of reactants are transferred to the “reservoir” of free random walks, and in the general case pair encounters of reactants in solution are dependent. Accumulation of the above correlations occurs at the times of the order of time between the encounters, and this corresponds to macroscopic time scales of chemical reaction course. That is why such correlations should be treated as macroscopic. The above mentioned phenomenon (absent in gas reactions) is determined by the fact that, unlike collisions in gases, the encounter of reactants in solution consists of re-contacts (cage effect) between which the reactants can move apart for macroscopic distances and interact with reactants in the bulk. Taking account of such dependence pair encounters leads to the Generalized Encounter Theory (GET) [40, 44].

Inclusion in the consideration the force interactions between reactants (and reaction products) makes it necessary to consider the appearance of additional force correlations on the encounters of particles in solution. Manifestation of such interactions in the framework of ET (dealing solely with independent pair encounters of reactants) is evident, and corresponds to the familiar recipe for its inclusion in the description of the motion of reactants in the encountering reacting pair [1, 11] which leads to the change in the rate constant  $K(t)$  in Eqs. (2.1)–(2.6). However, as for inhomogeneous sources in GET kinetic equations (2.5)–(2.6), they are intimately connected with the presence of three-particle correlations in the reaction system under discussion, thus investigation of the force interaction influence of reactants (both between each other and with the products in the bulk) is a separate problem the solution of which is the subject of the present contribution. It is essential that in calculating inhomogeneous sources one should take into account only the effects that provide corrections to the kinetics, of the order of contributions from binary encounters of reactants in solution allowed for in ET.

Consistent consideration of the force interaction requires allowing for initial correlations of the Boltzmann type [45]. However, here we shall consider the presence of arbitrary initial correlations, since no radical change in the many-particle approach is needed for this purpose [44]. Note that taking into account the force interaction (and arbitrary initial correlations) in the context of the Encounter Theory based on the conception of independent pair encounters is evident. To this end, it should be allowed for just in the reacting pair of the encountering particles  $A$  and  $B$ . The influence of the interaction of the reacting pair  $AB$  with other particles (including products  $C$ ) is insignificant, since taking it into consideration is beyond the limits of making allowance for two-particles only. Of course, as the density parameter increases (in this case ET is inapplicable) such a consideration becomes essential, and this is confirmed

by numerical calculations available in the literature [20,46–48]. However, even at small density parameters, ignoring the above force interactions in the more general GET theory that considers the dependence of pair encounters of reactants in solution determined by the contribution of three-particle correlations into the kinetics is not so apparent. In this case the interaction of reactants with the product can affect the accumulation of macroscopic correlations. Investigation of the role of this effects is the main subject of the present contribution.

In the third section we give the many-particle description of the considered reacting system  $A + B \rightarrow C$ . Section 4 presents the Integral Encounter Theory (IET) that is the first step in the derivation of kinetic equations. In the fifth section the Effective Pair Approximation (EPA) equations are derived, and the matrix kinetic equation necessary for the development of the binary theory is formed. The non-Markovian binary Modified Encounter Theory (MET) and the reduction of non-Markovian MET equations to their Regular Form (RF) corresponding to the Generalized Encounter Theory (GET) are constructed in Sect. 6. Section 7 deals with the time behaviour of the correlations between reactant encounters and reaction kinetics. The results are summarized in Conclusion. The intermediate calculations are given in Appendices.

### 3 Many-particle description of the reacting system

#### 3.1 Many-particle model

For many-particle description of the reacting system, first it is necessary to determine its microscopic parameters. As in [40,44], free motion of non-interacting (point) reactants in continual medium is described by the Markovian process of random walks defined by the motion operator (in the general case by the integral operator)  $\hat{L}_\alpha$ , where  $\alpha$  denotes the reactants. The force interaction between two reactants is determined by the corresponding potential energy of the pair interaction of reactants, and is specified by the operators of the force interaction  $\hat{L}'_{\alpha\beta}$  between  $\alpha$  and  $\beta$  reactants that satisfy the condition of the preservation of the number of particles

$$\int d\alpha \hat{L}_\alpha = 0 ; \int d\alpha d\beta \hat{L}'_{\alpha\beta} = 0. \quad (3.1)$$

Here  $\alpha$  and  $\beta$  denote space coordinates  $\mathbf{r}_\alpha$  and  $\mathbf{r}_\beta$  of  $\alpha$  and  $\beta$  reactants.

For example, for continual diffusion of reactants these operators are of the form

$$\hat{L}_\alpha = D_\alpha \Delta_\alpha ; \hat{L}'_{\alpha\beta} = \frac{D_\alpha}{k_B T} \nabla_\alpha (\nabla_\alpha U_{\alpha\beta}) + \frac{D_\beta}{k_B T} \nabla_\beta (\nabla_\beta U_{\alpha\beta}), \quad (3.2)$$

where  $D_\alpha$  is the diffusion coefficient of the reactant under consideration,  $\Delta_\alpha$  is the Laplacian,  $\nabla_\alpha$  is the nabla-operator of  $\alpha$  reactant,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature.

The elementary rate of the reaction is described by three-center rate  $R(C_k | A_i, B_j)$  depending on the coordinates of the initial reactants  $A_i, B_j$  and the final product  $C_k$ .

Since the solution is assumed to be spatially homogeneous, the elementary rate has a shift symmetry, i.e., for arbitrary vector  $\mathbf{r}$  the equality holds

$$R(C_k|A_i, B_j) = R(C_k + \mathbf{r}|A_i + \mathbf{r}, B_j + \mathbf{r}). \quad (3.3)$$

Along with the rate  $R(C_k|A_i, B_j)$ , we introduce the elementary event rate

$$w(A_i - B_j) = \int dC_k R(C_k|A_i, B_j), \quad (3.4)$$

that defines the complete vanishing rate of the initial reactants  $A$  and  $B$  no matter where the product  $C$  is formed.

In further mathematical description (as in Refs. [40,44]), we shall use the extended time interval  $-\infty < t < \infty$ . At  $t < 0$  the values of all functions are taken equal to zero, and at  $t > 0$  these values coincide with corresponding physical quantities. Thus the functions at extended time interval are obtained by multiplication of original functions (defined on the ordinary time interval  $0 < t < \infty$ ) by the stepwise Heaviside function  $\theta(t)$ . So differential equations for such functions do not require that the initial conditions be stated. They are taken into account by introducing  $\delta$ -functional source in the right-hand side of appropriate differential equation. This makes it possible to consider space and time variables on equal terms which is necessary for the introduction of integral operators acting on space-time variables that simplify essentially the intermediate calculations. For simplicity, we denote the time derivative on the extended time interval as  $\partial_t$ . If the kernel of some integral operator is time invariant, then time dependence is introduced by multiplication of this value by the  $\delta(t)$  function.

Thus the elementary event of chemical conversion may be described by the integral operator  $\hat{R}^{(k|i,j)}$  defined by the kernel

$$R^{(k|i,j)}(C_k, t|A_i, B_j, t_0) = R(C_k|A_i, B_j)\delta(t - t_0). \quad (3.5)$$

The integral operator  $\hat{V}^{(i,j)}$  describing chemical interaction of reactants is defined by the kernel

$$V^{(i,j)}(A_i, B_j, t|A_{0i}, B_{0j}, t_0) = -w(A_i - B_j)\delta(A_i - A_{0i})\delta(B_j - B_{0j})\delta(t - t_0). \quad (3.6)$$

The introduced quantities enable one to perform a many-particle description of the reacting system  $A + B \rightarrow C$ . For this purpose, let the total number of  $A$  and  $C$  reactants be equal to  $N$ , and the difference in the number of  $A$  and  $B$  reactants be  $M$ . In the course of the reaction the numbers  $M$  and  $N$  remain time constant. At the instant of time  $t$  the reacting system is described by a set of distribution functions depending on the number  $L$  of  $A$  reactants

$$\left\{ \Phi^{(0)}(B^M, C^N, t); \dots; \Phi^{(L)}(A^L, B^{M+L}, C^{N-L}, t); \dots; \Phi^{(N)}(A^N, B^{M+N}, t) \right\}. \quad (3.7)$$

Each function  $\Phi^{(L)}(A^L, B^{M+L}, C^{N-L}, t)$  is the density of the probability that by the moment of time  $t$   $L$  identical  $A$  particles,  $M + L$  identical  $B$  particles, and  $N - L$  identical  $C$  particles will be found at the points  $A^L \equiv \{A_1, A_2, \dots, A_L\}$ ,  $B^{M+L} \equiv \{B_1, B_2, \dots, B_{M+L}\}$ , and  $C^{N-L} \equiv \{C_1, C_2, \dots, C_{N-L}\}$  of the macroscopic volume  $V$ , respectively (vectors with such components form the so-called Fock space [49]).

Each distribution function is normalized to the probability  $p^{(L)}(t)$  to find the system in the state  $(L)$

$$\int \frac{dA^L}{L!} \frac{dB^{M+L}}{(M+L)!} \frac{dC^{N-L}}{(N-L)!} \Phi^{(L)}(A^L, B^{M+L}, C^{N-L}, t) = p^{(L)}(t). \quad (3.8)$$

The set of this probabilities is normalized to unity

$$\sum_{L=0}^N p^{(L)}(t) = 1. \quad (3.9)$$

The distribution function  $\Phi^{(L)}$  obeys the Liouville equation which is the balance equation in the Fock space. This equation is a basis for consistent many-particle description. Further it will serve to derive equations for Reduced Distribution Functions and Correlation Patterns. So the Liouville equation on the extended time interval  $-\infty < t < \infty$  takes the form

$$\begin{aligned} & \left( \partial_t - \sum_{i=1}^L \hat{L}_{A_i} - \sum_{j=1}^{M+L} \hat{L}_{B_j} - \sum_{k=1}^{N-L} \hat{L}_{C_k} - \sum_{i,k=1}^{L,N-L} \hat{L}'_{A_i C_k} - \sum_{i,j=1}^{L,M+L} \hat{L}'_{A_i B_j} - \sum_{j,k=1}^{M+L,N-L} \hat{L}'_{B_j C_k} \right. \\ & \left. - \frac{1}{2} \sum_{\substack{i,i'=1 \\ i \neq i'}}^L \hat{L}'_{A_i A_{i'}} - \frac{1}{2} \sum_{\substack{j,j'=1 \\ j \neq j'}}^{M+L} \hat{L}'_{B_j B_{j'}} - \frac{1}{2} \sum_{\substack{k,k'=1 \\ k \neq k'}}^{N-L} \hat{L}'_{C_k C_{k'}} \right) \Phi^{(L)}(A^L, B^{M+L}, C^{N-L}, t) \\ & = \delta(t) \Phi_0^{(L)}(A^L, B^{M+L}, C^{N-L}) + \sum_{\substack{i,j=1 \\ i \neq j}}^{L,M+L} \hat{V}^{(i,j)} \Phi^{(L)}(A^L, B^{M+L}, C^{N-L}, t) \\ & + \sum_{k=1}^{N-L} \hat{R}^{(k|L+1, M+L+1)} \Phi^{(L+1)}(A^{L+1}, B^{M+L+1}, C^{N-L}/C_k, t), \end{aligned} \quad (3.10)$$

where  $C^{N-L}/C_k$  denotes the set of coordinates  $C^{N-L}$  except the coordinate  $C_k$ . The left-hand side of this equation describes random motion of reactants in the medium with allowance for their force interaction. The first term in the right-hand side proportional to  $\delta(t)$  takes into consideration the initial condition. The second term after the equality sign describes the escape from the state  $(L)$  due to the reaction, and the third term—coming from the state  $(L + 1)$ .

### 3.2 Reduced Distribution Functions and correlation patterns

Reduced Distribution Functions (RDF) are defined by the relation [42, 43]



$$\begin{aligned} & \varphi_{p,q,r}(A^p, B^q, C^r, t) \\ &= T - \lim \sum_{L=0}^{\infty} \int \frac{dA_{p+1} \dots dA_L dB_{q+1} \dots dB_{M+L} dC_{r+1} \dots dC_{N-L}}{(L-p)!(M+L-q)!(N-L-r)!} \Phi^{(L)}(A^L, B^{M+L}, C^{N-L}, t). \end{aligned} \tag{3.11}$$

where  $T - \lim$  denotes the thermodynamic limit. For instance, local concentrations of reactants coincide with RDF of the first order

$$n_A(A, t) = \varphi_{1,0,0}(A, t), \quad n_B(B, t) = \varphi_{0,1,0}(B, t), \quad n_C(C, t) = \varphi_{0,0,1}(C, t). \tag{3.12}$$

The mean concentration of  $A$  reactants in solution is expressed in terms of local concentration in the familiar fashion

$$[A]_t = \lim_{v \rightarrow \infty} \int_v \frac{dA}{v} n_A(A, t). \tag{3.13}$$

Here the symbol  $v$  under the integral means that integration is performed over the volume  $v$ .

With definition (3.11) and properties (3.1), Eq. (3.10) gives the infinite hierarchies (since in the thermodynamic limit the system contains the infinite number of reactants) wherein the RDF evolution of the lower order is related to RDF evolution of the higher order. Thus integration procedure (3.11) of Eq. (3.10), in view of property (3.1), yields

$$\begin{aligned} & \left( \partial_t - \sum_{i=1}^p \hat{L}_{A_i} - \sum_{j=1}^q \hat{L}_{B_j} - \sum_{k=1}^r \hat{L}_{C_k} - \sum_{i,k=1}^{p,r} \hat{L}'_{A_i C_k} - \sum_{i,j=1}^{p,q} \hat{L}'_{A_i B_j} - \sum_{j,k=1}^{q,r} \hat{L}'_{B_j C_k} \right. \\ & - \frac{1}{2} \sum_{\substack{i,i'=1 \\ i \neq i'}}^p \hat{L}'_{A_i A_{i'}} - \frac{1}{2} \sum_{\substack{j,j'=1 \\ j \neq j'}}^q \hat{L}'_{B_j B_{j'}} - \frac{1}{2} \sum_{\substack{k,k'=1 \\ k \neq k'}}^r \hat{L}'_{C_k C_{k'}} \Big) \varphi_{p,q,r}(A^p, B^q, C^r, t) \\ & - \int dA_{p+1} \left( \sum_{i=1}^p \hat{L}'_{A_i A_{p+1}} + \sum_{j=1}^q \hat{L}'_{A_{p+1} B_j} + \sum_{k=1}^r \hat{L}'_{A_{p+1} C_k} \right) \varphi_{p+1,q,r}(A^{p+1}, B^q, C^r, t) \\ & - \int dB_{q+1} \left( \sum_{i=1}^p \hat{L}'_{A_i B_{q+1}} + \sum_{j=1}^q \hat{L}'_{B_j B_{q+1}} + \sum_{k=1}^r \hat{L}'_{B_{q+1} C_k} \right) \varphi_{p,q+1,r}(A^p, B^{q+1}, C^r, t) \\ & - \int dC_{r+1} \left( \sum_{i=1}^p \hat{L}'_{A_i C_{r+1}} + \sum_{j=1}^q \hat{L}'_{B_j C_{r+1}} + \sum_{k=1}^r \hat{L}'_{C_k C_{r+1}} \right) \varphi_{p,q,r+1}(A^p, B^q, C^{r+1}, t) \\ & = \delta(t) \varphi_{p,q,r}^0(A^p, B^q, C^r) + \sum_{\substack{i,j=1 \\ i \neq j}}^{p,q} \hat{V}^{(i,j)} \varphi_{p,q,r}(A^p, B^q, C^r, t) \\ & + \sum_{i=1}^p \int dB_{q+1} \hat{V}^{(i,q+1)} \varphi_{p,q+1,r}(A^p, B^{q+1}, C^r, t) \end{aligned}$$

$$\begin{aligned}
& + \sum_{j=1}^q \int dA_{p+1} \hat{V}^{(p+1,j)} \varphi_{p+1,q,r}(A^{p+1}, B^q, C^r, t) \\
& + \sum_{k=1}^r \hat{R}^{(k)p+1,r+1} \varphi_{p+1,q+1,r-1}(A^{p+1}, B^{q+1}, C^r/C_k, t). \quad (3.14)
\end{aligned}$$

Here  $\varphi_{p,q,r}^0(A^p, B^q, C^r) = \varphi_{p,q,r}(A^p, B^q, C^r, t=0)$ .

As an example consider the equation for the lower order RDF

$$\begin{aligned}
(\partial_t - \hat{L}_{A_1}) \varphi_{1,0,0}(A_1, t) &= \delta(t) \varphi_{1,0,0}^0(A_1) + \int dB_1 \left( \hat{V}^{(1,1)} + \hat{L}'_{A_1 B_1} \right) \varphi_{1,1,0}(A_1, B_1, t) \\
&+ \int dC_1 \hat{L}'_{A_1 C_1} \varphi_{1,0,1}(A_1, C_1, t) + \int dA_2 \hat{L}'_{A_1 A_2} \varphi_{2,0,0}(A_1, A_2, t). \quad (3.15)
\end{aligned}$$

Accumulation of  $C$  product and the decay of  $B$  reactant are obviously related to  $A$  reactant decay by balance relation of the number of particles. Thus further we shall confine the discussion to the kinetics of  $A$  reactant.

The next step is to invoke Prigogine's idea to treat the evolution of RDFs infinite hierarchy as correlation dynamics [50]. Correlation Patterns (CP) are introduced as the terms of the well-known group expansion of Reduced Distribution Functions [28,42,43,50,51]. For example, for some lower order RDFs this expansion is

$$\begin{aligned}
\varphi_{1,0,0}(A_1, t) &= \pi_{1,0,0}(A_1, t), \\
\varphi_{0,1,0}(B_1, t) &= \pi_{0,1,0}(B_1, t), \\
\varphi_{0,0,1}(C_1, t) &= \pi_{0,0,1}(C_1, t), \\
\varphi_{2,0,0}(A_1, A_2, t) &= \pi_{2,0,0}(A_1 \setminus A_2, t) + \pi_{2,0,0}(A_1, A_2, t). \quad (3.16)
\end{aligned}$$

Each CP involving the division of reactants coordinates into several groups by back slash “\” is uncorrelated with respect to these groups, and may be factorized. For example,

$$\begin{aligned}
\pi_{2,0,0}(A_1 \setminus A_2, t) &= \pi_{1,0,0}(A_1, t) \pi_{1,0,0}(A_2, t), \\
\pi_{1,1,1}(A_1, B_1 \setminus C_1, t) &= \pi_{1,1,0}(A_1, B_1, t) \pi_{0,0,1}(C_1, t). \quad (3.17)
\end{aligned}$$

So in view of Eqs. (3.12), (3.15) gives the relation between local concentration and two-particle CPs

$$\begin{aligned}
(\partial_t - \hat{L}_{A_1}) n_A(A_1, t) &= \delta(t) n_A^0(A_1) \\
&+ \int dB_1 \left( \hat{V}^{(1,1)} + \hat{L}'_{A_1 B_1} \right) [\pi_{1,1,0}(A_1, B_1, t) + n_A(A_1, t) n_B(B_1, t)] \\
&+ \int dC_1 \hat{L}'_{A_1 C_1} [\pi_{1,0,1}(A_1, C_1, t) + n_A(A_1, t) n_C(C_1, t)] \\
&+ \int dA_2 \hat{L}'_{A_1 A_2} [\pi_{2,0,0}(A_1, A_2, t) + n_A(A_1, t) n_A(A_2, t)]. \quad (3.18)
\end{aligned}$$

Note that the presence of the force interaction between reactants result in additional terms in Eq. (3.18) absent in paper [40]. In particular, the interaction of initial reactants with the reaction product is observed.

As is seen, to close Eq. (3.18) and thus to derive the desired kinetic equation, we need to know two-particle correlation patterns  $\pi_{1,1,0}(A_1, B_1, t)$ ,  $\pi_{1,0,1}(A_1, C_1, t)$ , and  $\pi_{2,0,0}(A_1, A_2, t)$ . Equations for them are derived in the same manner, and are given in “Appendix A”. These equations may be solved using some approximations that make it possible to break an infinite hierarchy of equations for correlation patterns on a definite level.

### 4 The Integral Encounter Theory

#### 4.1 General description

The simplest way to close CPs hierarchy which gives the Integral Encounter Theory (IET) kinetic equation is to neglect the contributions of any three-particle CPs into the evolution of two-particle CPs [28, 29, 40, 44]. Note that in this case equations for CPs  $\pi_{1,1,0}(A_1, B_1, t)$ ,  $\pi_{1,0,1}(A_1, C_1, t)$ , and  $\pi_{2,0,0}(A_1, A_2, t)$  (see Eqs. (A.1), (A.2), and (A.3) in “Appendix A” neglecting all three-particle CPs) are closed, and the reaction is determined just by the evolution of  $\pi_{1,1,0}(A_1, B_1, t)$

$$\begin{aligned} & \left( \partial_t - \hat{L}_{A_1} - \hat{L}_{B_1} - \left( \hat{L}'_{A_1 B_1} + \hat{V}^{(1,1)} \right) \right) \pi_{1,1,0}(A_1, B_1, t) \\ & = \delta(t) \pi_{1,1,0}^0(A_1, B_1) + \left( \hat{L}'_{A_1 B_1} + \hat{V}^{(1,1)} \right) n_A(A_1, t) n_B(B_1, t). \end{aligned} \tag{4.1}$$

The difference between the above equation and similar equation from paper [40] is that it involves the terms responsible for initial correlations and the force interaction between reactants, as it was in the case of the reaction  $A + A \rightarrow C$  [44]. Note that chemical and force interactions appear in Eq. (4.1) in an additive way, thus force and chemical interactions can be considered on equal terms. The solution of Eq. (4.1) has the form

$$\pi_{1,1,0}(A_1, B_1, t) \hat{G}_{A_1 B_1} \left[ \left( \hat{V}^{(1,1)} + \hat{L}'_{A_1 B_1} \right) n_A(A_1, t) n_B(B_1, t) + \delta(t) \pi_{1,1,0}^0(A_1, B_1) \right], \tag{4.2}$$

and is of the same form for  $\pi_{1,0,1}(A_1, C_1, t)$  and  $\pi_{2,0,0}(A_1, A_2, t)$  appearing in Eq. (3.18)

$$\begin{aligned} \pi_{1,0,1}(A_1, C_1, t) & = \hat{G}_{A_1 C_1}^0 \left[ \delta(t) \pi_{1,0,1}^0(A_1, C_1) + \hat{L}'_{A_1 C_1} n_A(A_1, t) n_C(C_1, t) \right], \\ \pi_{2,0,0}(A_1, A_2, t) & = \hat{G}_{A_1 A_2}^0 \left[ \delta(t) \pi_{2,0,0}^0(A_1, A_2) + \hat{L}'_{A_1 A_2} n_A(A_1, t) n_A(A_2, t) \right], \end{aligned} \tag{4.3}$$

where the propagator kernels of AB, AC, and AA pairs satisfy the equations

$$\left( \partial_t - \hat{L}_{A_1} - \hat{L}_{B_1} - \left( \hat{L}'_{A_1 B_1} + \hat{V}^{(1,1)} \right) \right) G_{A_1 B_1}(A_1, B_1, t | A_{01}, B_{01}, t_0)$$

$$\begin{aligned}
&= \delta(A_1 - A_{01})\delta(B_1 - B_{01})\delta(t - t_0), \\
&\left(\partial_t - \hat{L}_{A_1} - \hat{L}_{C_1} - \hat{L}'_{A_1C_1}\right) G_{A_1C_1}^0(A_1, C_1, t|A_{01}, C_{01}, t_0) \\
&= \delta(A_1 - A_{01})\delta(C_1 - C_{01})\delta(t - t_0), \\
&\left(\partial_t - \hat{L}_{A_1} - \hat{L}_{A_2} - \hat{L}'_{A_2A_2}\right) G_{A_1A_2}^0(A_1, A_2, t|A_{01}, A_{02}, t_0) \\
&= \delta(A_1 - A_{01})\delta(A_2 - A_{02})\delta(t - t_0).
\end{aligned} \tag{4.4}$$

The upper index “0” denotes the propagator of the pair in which chemical interaction is absent.

To develop the theory by analogy with papers [40,44], we introduce two-particle  $T$ -operators  $\hat{T}_{A_iB_j}$ ,  $\hat{T}_{A_iC_k}^0$ , and  $\hat{T}_{A_iA_j}^0$  of the pairs  $AB$ ,  $AC$ , and  $AA$ , respectively, that are defined by the equalities

$$\begin{aligned}
\hat{T}_{A_iB_j} &= \left(\hat{V}^{(i,j)} + \hat{L}'_{A_iB_j}\right) + \left(\hat{V}^{(i,j)} + \hat{L}'_{A_iB_j}\right) \hat{G}_{A_iB_j} \left(\hat{V}^{(i,j)} + \hat{L}'_{A_iB_j}\right), \\
\hat{T}_{A_iC_k}^0 &= \hat{L}'_{A_iC_k} + \hat{L}'_{A_iC_k} \hat{G}_{A_iC_k}^0 \hat{L}'_{A_iC_k}, \\
\hat{T}_{A_iA_j}^0 &= \hat{L}'_{A_iA_j} + \hat{L}'_{A_iA_j} \hat{G}_{A_iA_j}^0 \hat{L}'_{A_iA_j},
\end{aligned} \tag{4.5}$$

and similar to that in quantum scattering theory [52]. We call the  $T$ -operator  $\hat{T}_{AB}$  of the pair  $AB$  expressed in terms of the sum of force and reaction interactions the ultimate  $T$ -operator. Other  $T$ -operators defined solely in terms of force interactions will be called force  $T$ -operators, they are marked off by the upper index “0”.  $T$ -operators are important characteristics of the pairs of reactants and completely describe their evolution.

For  $T$ -operators the useful relations are known [53,54]

$$\begin{aligned}
\left(\hat{V}^{(i,j)} + \hat{L}'_{A_iB_j}\right) \hat{G}_{A_iB_j} &= \hat{T}_{A_iB_j} \hat{G}_{A_iB_j}^{00}; \quad \hat{L}'_{A_iC_k} \hat{G}_{A_iC_k}^0 = \hat{T}_{A_iC_k}^0 \hat{G}_{A_iC_k}^{00}, \\
\hat{L}'_{A_iA_j} \hat{G}_{A_iA_j}^0 &= \hat{T}_{A_iA_j}^0 \hat{G}_{A_iA_j}^{00},
\end{aligned} \tag{4.6}$$

where  $\hat{G}_{A_iB_j}^{00}$ ,  $\hat{G}_{A_iC_k}^{00}$ , and  $\hat{G}_{A_iA_j}^{00}$  are the propagators of the pairs  $AB$ ,  $AC$ , and  $AA$ , respectively, in the absence of any interactions between reactants in the pairs (see Eq. (4.4) at  $\hat{L}'_{\alpha\beta} = \hat{V}^{(i,j)} = 0$ ). Thus the given propagators define the motion of point non-interacting reactants.

Substituting solutions (4.2) and (4.3) in Eq. (3.18) yields the desired kinetic equation of IET

$$\begin{aligned}
\left(\partial_t - \hat{L}_{A_1}\right) n_A(A_1, t) &= \delta(t) n_A^0 + \int dB_1 \hat{T}_{A_1B_1} n_A(A_1, t) n_B(B_1, t) \\
&+ \int dB_1 \hat{T}_{A_1B_1} \hat{G}_{A_1B_1}^{00} \delta(t) \pi_{1,1,0}^0(A_1, B_1) \\
&+ \int dC_1 \hat{T}_{A_1C_1}^0 n_A(A_1, t) n_C(C_1, t)
\end{aligned}$$

$$\begin{aligned}
& + \int dC_1 \hat{T}_{A_1 C_1}^0 \hat{G}_{A_1 C_1}^{00} \delta(t) \pi_{1,0,1}^0(A_1, C_1) \\
& + \int dA_2 \hat{T}_{A_1 A_2}^0 n_A(A_1, t) n_A(A_2, t) + \int dA_2 \hat{T}_{A_1 A_2}^0 \hat{G}_{A_1 A_2}^{00} \delta(t) \pi_{2,0,0}^0(A_1, A_2).
\end{aligned}
\tag{4.7}$$

The above hierarchy closure (the averaged  $t$ -matrix approximation) is widely employed to describe various bimolecular processes in the condensed phase. It is the analog of the non-equilibrium statistical mechanics approach to the derivation of binary equations which is based on the simplification of the mass operator of kinetic integro-differential equations by way of expansion into a series in concentrations of reactants and retention of the first non-vanishing term. This ensures taking into account just a part of the effect of binary encounters of reactants in solution. That is why IET is the simplest non-Markovian binary theory which, however, may only be applied in a narrow time interval (as compared to the binary description).

In full agreement with the general kinetic theory principles [42, 43], the obtained binary kinetic equation (4.7) is an inhomogeneous integro-differential equation. The terms in the right-hand side of the equation the integrands of which are proportional to the product of concentrations define the contributions into local concentration evolution from binary encounters of the corresponding reactants in solution. These terms are commonly called collision integrals. Note that in the context of IET consideration of the force interaction of reactants results in that the collision integral of the reaction pair (the second term in (4.7)) involves ultimate  $T$ -operator (4.5) instead of reaction  $T$ -operator [40]. Besides, In contrast to paper Ref. [40], taking account of the force interaction leads to the appearance of additional terms (the fourth and the sixth terms) determined by the encounters of chemically non-reacting reactants.

Inhomogeneous sources consisting of the third, the fifth, and the seventh terms describe the contributions into local concentration evolution made by initial correlations appearing in the system. Thus, unlike IET equation given in [40] (neglect of force interaction and initial correlations), Eq. (4.7) involves additional terms determined by the force interaction and initial correlations. So in the general case of inhomogeneous reacting systems the force interaction (including that between  $A$  reactant and the reaction product  $C$ ) affects the reaction kinetics even in the framework of IET.

#### 4.2 Spatially homogeneous systems

However, for spatially homogeneous systems the obtained kinetic equation (4.7) is simplified. All spatial functions depend solely on the relative position of reactants, and local concentrations of reactants (3.12) coincide with the mean concentration defined by relation (3.13) ( $n_A(A, t) = [A]_t$ ). So note that for spatially homogeneous systems one can change to relative coordinates  $\mathbf{r}$  in any pair of reactants. For instance, for the pair  $AB$  with the coordinates of reactants  $A_1$  and  $B_1$  the relative position vector is  $\mathbf{r} = A_1 - B_1$ . This is done by the introduction of the projection operator  $\hat{\Pi}$  into the space of relative coordinates using the identity

$$\int dA_1 dB_1 \dots = \int d\mathbf{r} \int dA_1 dB_1 \delta(\mathbf{r} - (A_1 - B_1)) \dots = \int d\mathbf{r} \hat{\Pi} \dots \quad (4.8)$$

The use of relative coordinates will be convenient in the next sections. At this stage we shall still employ the laboratory system of coordinates.

Since the  $T$ -operator is the renormalized interaction operator (see Eq. (4.5)), the terms in the right-hand side of kinetic equation (4.7), involving the force  $T$ -operators are equal to zero due to properties (3.1). So for spatial homogeneous systems IET kinetic equation reduces to

$$\begin{aligned} \partial_t [A]_t &= \delta(t) [A]_0 + \int dB_1 \hat{T}_{A_1 B_1} [A]_t [B]_t \\ &+ \int dB_1 \hat{T}_{A_1 B_1} \hat{G}_{A_1 B_1}^{00} \delta(t) \pi_{1,1,0}^0(A_1 - B_1), \end{aligned} \quad (4.9)$$

In kinetic equation (4.9) both the collision integral and the inhomogeneous source depend only on the evolution of the reaction pair  $AB$ . Thus for spatially homogeneous reacting systems in IET the evolution of concentration of reactants does not depend on the encounters of  $A$  with  $C$  and  $A$  with  $A$  (though in the general case such encounters can affect essentially the trajectories of reactants in solution due to the force interaction), and on the initial correlations that may take place between them.

To describe initial correlations, the following representation may be used [30]

$$\pi_{1,1,0}^0(A_1 - B_1) = [A]_0 [B]_0 (p^T(A_1 - B_1) - 1), \quad (4.10)$$

where  $p^T(A_1 - B_1)$  is the initial distribution in the reaction pair

$$p^T(A_1 - B_1) = \varphi(A_1 - B_1) \exp\left(-\frac{U(A_1 - B_1)}{kT}\right). \quad (4.11)$$

Here the function  $\varphi(A_1 - B_1)$  describes initial distribution of point reactants, while the factor  $\exp(-U(A_1 - B_1)/(kT))$  is responsible for their force interaction. In the present contribution we shall take that the scale of initial correlations  $\pi_{1,1,0}^0(A_1 - B_1)$  and that of the pair energy of force interaction  $U(A_1 - B_1)$  are microscopic quantities.

Separating out the explicit time dependence in kinetic equation (4.9), we have the kinetic equation in familiar form

$$\partial_t [A]_t = \delta(t) [A]_0 - \int_{-0}^t dt_0 \Sigma_0^e(t - t_0) [A]_{t_0} [B]_{t_0} + J_{init}^{IET}(t), \quad (4.12)$$

where the kernel of this equation (the memory function) is defined through the complete evolution of reaction pair including the force interaction. It is defined as the averaged  $T$ -operator

$$\Sigma_0^e(t - t_0) = - \int dB_1 T_{A_1 B_1}(A_1, B_1, t - t_0 | A_{01}, B_{01}, 0) dA_{01} dB_{01}. \quad (4.13)$$

As the  $T$ -operator is the time difference function, the memory function also exhibits this property.

The inhomogeneous source is of the form

$$J_{init}^{IET}(t) = \int dB_1 \hat{T}_{A_1 B_1} \hat{G}_{A_1 B_1}^{00} \delta(t) \pi_{1,1,0}^0(A_1 - B_1). \quad (4.14)$$

According to paper [44], the derived kinetic equation (4.12) may be reduced to a homogeneous equation consistent with the Encounter Theory concepts. Using expression (4.10) for initial correlations, rewrite the inhomogeneous term as

$$J_{init}^{IET}(t) = [A]_0[B]_0 (K_0(t) - K(t)). \quad (4.15)$$

The value  $K_0(t)$  is defined by the relation

$$\begin{aligned} K_0(t) &\equiv \int_{-0}^t d\tau \Sigma_0^e(\tau) \\ &= - \int_{-0}^t d\tau \int dB_1 dA_{01} dB_{01} T_{A_1 B_1}(A_1, B_1, \tau | A_{01}, B_{01}, 0) \\ &= - \int dB_1 \hat{T}_{A_1 B_1} \hat{G}_{A_1 B_1}^{00} \delta(t) 1(A_1 - B_1) \end{aligned} \quad (4.16)$$

The last equality in Eq. (4.16) is obtained in view of the fact that the unit function  $1(A_1 - B_1)$  is a static contour for the propagator  $\hat{G}_{A_1 B_1}^{00}$  (the equilibrium distribution for the system the evolution of which is described by this propagator), i.e.,

$$\hat{G}_{A_1 B_1}^{00} \delta(t) 1(A_1 - B_1) = \theta(t) 1(A_1 - B_1). \quad (4.17)$$

Just as the value  $K_0(t)$  (4.16), the value  $K(t)$  is defined by the relation

$$K(t) \equiv - \int dB_1 \hat{T}_{A_1 B_1} \hat{G}_{A_1 B_1}^{00} \delta(t) p^T(A_1 - B_1). \quad (4.18)$$

The introduced quantity differs from  $K_0(t)$  only in the function of initial spatial distribution of reactants in the pair  $AB$ . The difference of this function  $p^T(A_1 - B_1)$  in  $K(t)$  from unity  $1(A_1 - B_1)$  specifies the initial correlations in the pair  $AB$ . So it is easily seen that in the absence of initial correlations  $K(t) = K_0(t)$ , and inhomogeneous term (4.15) goes to zero.

Just as the identity in Eq. (4.16), the quantity  $K(t)$  may be represented as a time integral of the function  $\Sigma^e(t)$  defined by the equality

$$\Sigma^e(t) = \partial_t K(t). \quad (4.19)$$

With  $t \rightarrow \infty$  both functions  $K_0(t)$  and  $K(t)$  reach the same limit, thus, in full agreement with the familiar statement concerning the decrease of initial correlations on the encounters of reactants in solution, the inhomogeneous term goes to zero. This limit corresponding, as shown below, to the Markovian rate constant (2.2) is defined taking into account the force interaction in reacting pair as

$$k = - \int dB_1 dA_{01} dB_{01} T_{A_1 B_1}^s(A_1, B_1 | A_{01}, B_{01}), \quad (4.20)$$

where  $T_{A_1 B_1}^s(A_1, B_1 | A_{01}, B_{01})$  is the kernel of stationary  $T$ -operator

$$\hat{T}_{A_1 B_1}^s = \int_{-0}^{\infty} dt \hat{T}_{A_1 B_1}(t) = \lim_{s \rightarrow 0} \hat{T}_{A_1 B_1}^L(s). \quad (4.21)$$

Hereinafter the upper index  $L$  denotes the Laplace transform of the quantity depending on the Laplace variable  $s$ . The given limit for the quantity  $K(t)$  is obtained using the mixing principle [53]

$$\lim_{t \rightarrow \infty} \hat{G}_{A_1 B_1}^{00} \delta(t) \psi^T(A_1 - B_1) = \theta(t) 1(A_1 - B_1), \quad (4.22)$$

where  $\psi^T(A_1 - B_1)$  is an arbitrary spatial distribution function in the thermodynamic limit.

To get the desired values of the memory function and inhomogeneous term of integro-differential kinetic equations, we used, according to Eqs. (4.16) and (4.18), the ultimate  $T$ -operator (defined in Eq. (4.5)) involving both chemical and force interaction on equal terms. This shows that chemical reaction kinetics is affected by accumulation of chemical and force correlations of the system of interacting reactants in formally the same fashion. The ultimate  $T$ -operator formalism may be identically transformed into the reaction  $T$ -operator one more usual for the reader. The method is similar to that described in detail in paper [44]. As in [44], initial correlations in pairs may be treated as incomplete pair encounters of reactants, and taken into consideration in the redefinition of the memory function  $\Sigma^e(\tau)$  of the homogeneous integro-differential equation

$$\partial_t [A]_t = \delta(t) [A]_0 - \int_{-0}^t dt_0 \Sigma^e(t - t_0) [A]_{t_0} [B]_{t_0}. \quad (4.23)$$

As in [40] and [44], using the point encounter approximation [27, 36]

$$\Sigma_0^e(t) = \Sigma^e(t) = k \delta(t), \quad k = \int_{-0}^{\infty} dt \Sigma_0^e(t) = \int_{-0}^{\infty} dt \Sigma^e(t). \quad (4.24)$$



we easily show that in IET narrow time interval the non-Markovian kinetic equations (4.12) and (4.23) reduce to the Markovian kinetic equation (2.3) corresponding to the kinetic law of mass action of formal chemical kinetics. Thus the limiting value  $k$  of the quantities  $K_0(t)$  and  $K(t)$  introduced by expression (4.20) is the Markovian (steady-state) rate constant, and the quantities themselves are non-Markovian rate constants in appropriate differential binary kinetic equations of the Encounter Theory

$$\begin{aligned}\partial_t[A]_t &= \delta(t)[A]_0 - K_0(t)[A]_t[B]_t + J_{init}^{IET}(t), \\ \partial_t[A]_t &= \delta(t)[A]_0 - K(t)[A]_t[B]_t,\end{aligned}\quad (4.25)$$

where the inhomogeneous term is the same (see Eq. (4.15)) as in the corresponding integro-differential IET equation. So in IET making allowance for the force interaction between reactants (as well as for the initial correlations including those associated solely with the presence of the force interaction between  $A$  and  $B$  reactants ( $\varphi(A_1 - B_1) = 1$ )) reduces just to traditional redefinition of rate constants  $K(t)$  or  $K_0(t)$  (at  $p^T(A - B) = 1$ ). It is of interest that the presence of the force interaction between the initial reactants and the reaction product  $C$  does not show itself at all in IET kinetics of homogeneous systems.

## 5 The effective pair approximation

### 5.1 Equations for two-particle CP in EPA

Extending the time validity range of kinetic equations requires that hierarchies be closed on a higher level; this leads us to the evolution of effective pairs the examination of which forms the basis of some currently existing theories of reactions in solutions such as Self-Consistent Relaxation Time Approximation (SCRTA) [55]. It is able to describe both the binary kinetics of some types of reactions, and its fluctuation tails, though, generally speaking, this theory is not a binary one.

The Effective Pair Approximation (EPA) corresponds to extracting the contributions of binary channels (two-particle correlations) into the evolution of three-particle completely correlated patterns (see “Appendix B”). Thus, in contrast to IET, this approximation does not ignore three-particle correlations completely but decouples them to extract the evolution of two-particle and one-particle correlations, just as the well-known superposition decoupling [56]. However, close similarity of channel extraction and superposition decoupling takes place only for the simplest reaction  $A + B \rightarrow C + B$  in spatially homogeneous reacting systems. Any complication of the system makes the superposition approximation unsuitable [57, 58] and essentially different from EPA. For the reaction under study the above channel extraction gives the equation for two-particle correlation pattern  $\pi_{1,1,0}(A_1, B_1, t)$  (see “Appendix B”)

$$\begin{aligned}& \left( \partial_t - \hat{L}_{A_1} - \hat{L}_{B_1} - \hat{L}'_{A_1 B_1} - \hat{V}^{(1,1)} \right) \pi_{1,1,0}(A_1, B_1, t) \\ &= \delta(t) \pi_{1,1,0}^0(A_1, B_1) + \left( \hat{L}'_{A_1 B_1} + \hat{V}^{(1,1)} \right) \varphi_{1,0,0}(A_1, t) \varphi_{0,1,0}(B_1, t)\end{aligned}$$

$$\begin{aligned}
& + \int dA_2 \left[ \widehat{T_{A_2 B_1} G_{A_1}^0} \right] \left[ n_A(A_2, t) \pi_{1,1,0}(A_1, B_1, t) + n_B(B_1, t) \pi_{2,0,0}(A_1, A_2, t) \right] \\
& + \int dA_2 \left[ \widehat{T_{A_1 A_2}^0 G_{B_1}^0} \right] \left[ n_A(A_1, t) \pi_{1,1,0}(A_2, B_1, t) + n_A(A_2, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
& + \int dB_2 \left[ \widehat{T_{A_1 B_2} G_{B_1}^0} \right] \left[ n_A(A_1, t) \pi_{0,2,0}(B_1, B_2, t) + n_B(B_2, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
& + \int dB_2 \left[ \widehat{T_{B_1 B_2}^0 G_{A_1}^0} \right] \left[ n_B(B_1, t) \pi_{1,1,0}(A_1, B_2, t) + n_B(B_2, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
& + \int dC_1 \left[ \widehat{T_{A_1 C_1}^0 G_{B_1}^0} \right] \left[ n_A(A_1, t) \pi_{0,1,1}(B_1, C_1, t) + n_C(C_1, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
& + \int dC_1 \left[ \widehat{T_{B_1 C_1}^0 G_{A_1}^0} \right] \left[ n_B(B_1, t) \pi_{1,0,1}(A_1, C_1, t) + n_C(C_1, t) \pi_{1,1,0}(A_1, B_1, t) \right],
\end{aligned} \tag{5.1}$$

where  $G_\alpha^0$  is the kernel of one-particle free propagator of  $\alpha$  reactant that satisfies the equation

$$\left( \partial_t - \hat{L}_\alpha \right) G_\alpha^0(\alpha, t | \alpha_0, t_0) = \delta(\alpha - \alpha_0) \delta(t - t_0). \tag{5.2}$$

The force  $T$ -operators  $T_{B_1 C_1}^0$  and  $T_{B_1 B_2}^0$  are defined by analogy with  $T$ -operators  $T_{A_1 C_1}^0$  and  $T_{A_1 A_2}^0$  (see Eq. (4.5))

$$\begin{aligned}
\hat{T}_{B_i C_k}^0 &= \hat{L}'_{B_i C_k} + \hat{L}'_{B_i C_k} \hat{G}_{B_i C_k}^0 \hat{L}'_{B_i C_k}, \\
\hat{T}_{B_i B_j}^0 &= \hat{L}'_{B_i B_j} + \hat{L}'_{B_i B_j} \hat{G}_{B_i B_j}^0 \hat{L}'_{B_i B_j}.
\end{aligned} \tag{5.3}$$

The propagator kernels of the pairs  $B_i C_k$  and  $B_i B_j$  are defined by the equations

$$\begin{aligned}
\left( \partial_t - \hat{L}_{B_i} - \hat{L}_{C_k} - \hat{L}'_{B_i C_k} \right) G_{B_i C_k}^0(B_i, C_k, t | B_{0i}, C_{0k}, t_0) &= \delta(B_i - B_{0i}) \delta(C_k - C_{0k}) \delta(t - t_0), \\
\left( \partial_t - \hat{L}_{B_i} - \hat{L}_{B_j} - \hat{L}'_{B_i B_j} \right) G_{B_i B_j}^0(B_i, B_j, t | B_{0i}, B_{0j}, t_0) &= \delta(B_i - B_{0i}) \delta(B_j - B_{0j}) \delta(t - t_0).
\end{aligned} \tag{5.4}$$

Equations for other two-particle correlation patterns in EPA necessary for Eq. (5.1) closure may be derived in a similar way as it is shown in ‘‘Appendix B’’.

The appearance of integral terms in Eq. (5.1) makes the theory at hand different from IET, and extends the applicability of kinetic equations to the range of macroscopic time scales. That is why, unlike Eq. (4.7) of general IET, calculations of additional terms also containing  $T$ -operators must be done for rather large times.

Now we pass to spatially homogeneous systems. In this case all spatial functions depend solely on the relative position of reactants, and local concentrations of reactants (3.12) coincide with the mean concentration defined by relation (3.13) ( $n_A(A, t) \Rightarrow [A]_t$ ,  $n_B(B, t) \Rightarrow [B]_t$ ). This allows one to use the binary scaling procedure for the required calculations on extended space-time scales and simplifies the obtained

expressions [54, 59]. Scaling is made by introducing the scaling parameter  $\gamma$  ( $\gamma \gg 1$ ) the increase in the value of which corresponds to the examination of more and more dilute solutions. Obviously, taking into account the encounters of reactants in higher order solution becomes less essential, and in the limit of infinitely dilute system only pair encounters of reactants will take place. Thus in the binary theory  $\gamma \gg 1$ . Consideration of infinitely dilute reacting systems (scaling-systems) corresponds to the fact that spatial size of the reaction pair is equal to zero on the scales of distances between reactants. Realization of such an idea for reactants in solution allows one to develop the point encounter approximation [27, 36] that is the analog of impact approximation [16].

First consider the estimation scaling for  $T$ -operators. Note that the  $T$ -operator is the quantity well-defined in the scaling-system, and serves to develop the point encounter approximation. In the binary approximation it is determined by making allowance solely for the first two terms of the expansion in the scaling parameter  $\gamma \rightarrow \infty$  for  $T$ -operator. Such an account for the kernel of ultimate  $T$ -operator  $\hat{T}_{A_i B_j}$  gives [54, 59]

$$\tilde{T}_{A_i B_j}(A_i, B_j, t|A_{0i}, B_{0j}, t_0) \underset{\gamma \rightarrow \infty}{\sim} \tilde{T}_{A_i B_j}^P(A_i, B_j, t|A_{0i}, B_{0j}, t_0) + O(\gamma^{-13}). \quad (5.5)$$

Hereinafter the quantities describing the evolution of reactants in scaling-systems are denoted by tilde “ $\sim$ ”. The quantity  $T_{A_i B_j}^P(A_i, B_j, t|A_{0i}, B_{0j}, t_0)$  is the point approximation of ultimate  $T$ -operator, and has the following scaling estimate [54, 59]

$$\begin{aligned} \tilde{T}_{A_i B_j}^P(A_i, B_j, t|A_{0i}, B_{0j}, t_0) = & \gamma^{-11}(T_{A_i B_j}^{ps}(A_i, B_j, t|A_{0i}, B_{0j}, t_0) \\ & + \gamma^{-1}\chi(A_i, B_j, t|A_{0i}, B_{0j}, t_0)). \end{aligned} \quad (5.6)$$

The value  $T_{A_i B_j}^{ps}(A_i, B_j, t|A_{0i}, B_{0j}, t_0)$  is the kernel of the point stationary  $T$ -operator defined by equality

$$T_{A_i B_j}^{ps}(A_i, B_j, t|A_{0i}, B_{0j}, t_0) = -k\delta(A_i - B_j)\delta(A_i - A_{0i})\delta(B_j - B_{0j})\delta(t - t_0). \quad (5.7)$$

The  $\delta$ -shaped spatial variables singularity means that on the scales in question the encounter of  $A$  and  $B$  reactants occurs at one point. Such encounters are called point.  $\delta$ -shaped time dependence implies that in the first approximation such encounters proceed instantaneously, and are described by stationary (or Markovian) value of  $T$ -operator, and the finite duration of the encounters is allowed for by the term  $\chi(A_i, B_j, t|A_{0i}, B_{0j}, t_0)$  which is the next term (of the expansion  $\hat{T}_{A_i B_j}$  in the binary scaling parameter  $\gamma$ ). This term defines the non-Markovian effects in the binary approximation, and is a non-stationary part of the point  $T$ -operator. However, we omit its explicit form because it is of no use in further discussion. For force  $T$ -operators we have [54]

$$\begin{aligned}
\tilde{T}_{A_i A_j}^0(A_i, B_j, t | A_{0i}, B_{0j}, t_0) &\underset{\gamma \rightarrow \infty}{\sim} \tilde{T}_{A_i A_j}^{0ps}(A_i, B_j, t | A_{0i}, B_{0j}, t_0) \underset{\gamma \rightarrow \infty}{\sim} O(\gamma^{-13}), \\
\tilde{T}_{A_i C_k}^0(A_i, B_j, t | A_{0i}, B_{0j}, t_0) &\underset{\gamma \rightarrow \infty}{\sim} \tilde{T}_{A_i C_k}^{0ps}(A_i, B_j, t | A_{0i}, B_{0j}, t_0) \underset{\gamma \rightarrow \infty}{\sim} O(\gamma^{-13}), \\
\tilde{T}_{B_i B_j}^0(A_i, B_j, t | A_{0i}, B_{0j}, t_0) &\underset{\gamma \rightarrow \infty}{\sim} \tilde{T}_{B_i B_j}^{0ps}(A_i, B_j, t | A_{0i}, B_{0j}, t_0) \underset{\gamma \rightarrow \infty}{\sim} O(\gamma^{-13}), \\
\tilde{T}_{B_j C_k}^0(A_i, B_j, t | A_{0i}, B_{0j}, t_0) &\underset{\gamma \rightarrow \infty}{\sim} \tilde{T}_{B_j C_k}^{0ps}(A_i, B_j, t | A_{0i}, B_{0j}, t_0) \underset{\gamma \rightarrow \infty}{\sim} O(\gamma^{-13}).
\end{aligned}
\tag{5.8}$$

i.e., the leading term of the expansion of force  $T$ -operators is of the higher order in scaling parameter. This means that correlations arising in the pair  $AB$  directly from the force interaction of reactants are much weaker than correlations caused by chemical reaction (decay of reactants), and may be neglected in low concentration approximation.

Consideration of asymptotic estimates (5.5)–(5.8) in Eq. (5.1) and changing to relative coordinates in the pairs of reactants (according to Eq. (4.8)) yield the desired equation for two-particle correlation pattern  $\pi_{1,1,0}(\mathbf{r}, t)$  in Effective Pair Approximation. Equations for CPs  $\pi_{2,0,0}(\mathbf{r}, t)$  and  $\pi_{0,2,0}(\mathbf{r}, t)$  can be derived in a similar way discussed earlier to give the following set of equations of EPA

$$\left\{ \begin{array}{l}
\left( \partial_t - \hat{\mathcal{L}}_{AB} - (\hat{v} + \hat{\mathcal{L}}'_{AB}) + k([A]_t + [B]_t) \right) \pi_{1,1,0}(\mathbf{r}, t) = \delta(t) \pi_{1,1,0}^0(\mathbf{r}) + (\hat{v} + \hat{\mathcal{L}}'_{AB}) [A]_t [B]_t \\
\quad - k([A]_t \pi_{2,0,0}(\mathbf{r}, t) + [B]_t \pi_{0,2,0}(\mathbf{r}, t)) \\
\left( \partial_t - \hat{\mathcal{L}}_{AA} - \hat{\mathcal{L}}'_{AA} + 2k[B]_t \right) \pi_{2,0,0}(\mathbf{r}, t) = \delta(t) \pi_{2,0,0}^0(\mathbf{r}) + \hat{\mathcal{L}}'_{AA} [A]_t^2 - 2k[A]_t \pi_{1,1,0}(\mathbf{r}, t) \\
\left( \partial_t - \hat{\mathcal{L}}_{BB} - \hat{\mathcal{L}}'_{BB} + 2k[A]_t \right) \pi_{0,2,0}(\mathbf{r}, t) = \delta(t) \pi_{0,2,0}^0(\mathbf{r}) + \hat{\mathcal{L}}'_{BB} [B]_t^2 - 2k[B]_t \pi_{1,1,0}(\mathbf{r}, t)
\end{array} \right.
\tag{5.9}$$

The operators  $\hat{\mathcal{L}}_{AB}$ ,  $\hat{\mathcal{L}}_{AA}$ , and  $\hat{\mathcal{L}}_{BB}$  define the translational motion in the space of relative coordinates of the pairs  $AB$ ,  $AA$ , and  $BB$ , respectively. The operators  $\hat{\mathcal{L}}'_{AB}$ ,  $\hat{\mathcal{L}}'_{AA}$ , and  $\hat{\mathcal{L}}'_{BB}$  are the force interaction operators in appropriate pairs written in relative coordinates. The operator  $\hat{v}$  is the reaction operator in relative coordinates.

Equation (5.9) are a closed set of EPA equations for two-particle CPs for the reaction under study. To derive EPA kinetic equation, the above equations should be complemented by the first equation of correlation pattern hierarchy (3.15). For spatially homogeneous systems it has the form

$$\partial_t [A]_t = \delta(t) [A]_0 + \int d\mathbf{r} (\hat{v} + \hat{\mathcal{L}}'_{AB}) \pi_{1,1,0}(\mathbf{r}, t) + \int d\mathbf{r} (\hat{v} + \hat{\mathcal{L}}'_{AB}) [A]_t [B]_t.
\tag{5.10}$$

These equations form the basis of the Effective Pair Approximation (EPA). Similar equations were also proposed in the literature on the basis of heuristic approach [55]. The difference from paper [55] is that not only chemical interaction is the source of correlations but also the force interactions brought about by the encounters of originally uncorrelated  $A$  and  $B$  reactants (the second terms in the right-hand side of Eq. (5.9)). Further evolution of the above interrelated correlation patterns is affected by several factors: translational migration of reactants (the second and the third terms in

the left-hand side of Eq. (5.9)), chemical and force interactions in a correlated pair (the fourth terms in the left-hand side of Eq. (5.9)), the reaction between reactants of the pair and those in solution (the fifth terms in the left-hand side of Eq. (5.9)), and transformations of correlation patterns of different kinds into each other (the last terms in the right-hand side of Eq. (5.9)). Generally speaking, such a transformation of CP may occur both at the immediate approach of reactants (at the times of binary encounters), and at rather large times when reactants are separated by meso- and macro-distances but correlation between them is preserved. Thus accumulation of macroscopic correlations of both reacting and non-reacting particles takes place, and this inevitably affects the evolution of the correlation pattern  $\pi_{1,1,0}(\mathbf{r}, t)$  defining, according to Eq. (5.10), chemical conversion rate.

As in paper [40], set (5.9) of EPA equations is conveniently represented in a matrix form. By definition, we introduce the quantities

$$\begin{aligned} \boldsymbol{\pi}(\mathbf{r}, t) &= \begin{pmatrix} \pi_{1,1,0}(\mathbf{r}, t) \\ \pi_{2,0,0}(\mathbf{r}, t) \\ \pi_{0,2,0}(\mathbf{r}, t) \end{pmatrix}, \quad \boldsymbol{\pi}^0(\mathbf{r}) = \begin{pmatrix} \pi_{1,1,0}^0(\mathbf{r}) \\ \pi_{2,0,0}^0(\mathbf{r}) \\ \pi_{0,2,0}^0(\mathbf{r}) \end{pmatrix}, \quad \hat{\mathcal{L}} = \begin{pmatrix} \hat{\mathcal{L}}_{AB} & 0 & 0 \\ 0 & \hat{\mathcal{L}}_{AA} & 0 \\ 0 & 0 & \hat{\mathcal{L}}_{BB} \end{pmatrix} \\ \hat{\mathcal{L}}' &= \begin{pmatrix} \hat{\mathcal{L}}'_{AB} & 0 & 0 \\ 0 & \hat{\mathcal{L}}'_{AA} & 0 \\ 0 & 0 & \hat{\mathcal{L}}'_{BB} \end{pmatrix}, \quad \hat{\mathbf{v}} = \hat{\mathbf{v}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \hat{\mathbf{v}}\boldsymbol{\Pi}. \end{aligned} \tag{5.11}$$

Note that the projection operator  $\boldsymbol{\Pi}$  may be represented as the product of vectors

$$\boldsymbol{\Pi} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} (1 \ 0 \ 0) \tag{5.12}$$

The operator  $\boldsymbol{\Pi}$  itself extracts one-dimensional space from the complete three-dimensional one.

In view of the above definitions, Eq. (5.10) takes the form

$$\begin{aligned} \partial_t[A]_t &= \delta(t)[A]_0 + \int d\mathbf{r} (1 \ 0 \ 0)(\hat{\mathbf{v}} + \hat{\mathcal{L}}')\boldsymbol{\pi}(\mathbf{r}, t) \\ &+ \int d\mathbf{r} (1 \ 0 \ 0)(\hat{\mathbf{v}} + \hat{\mathcal{L}}') \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} [A]_t[B]_t \end{aligned} \tag{5.13}$$

Correspondingly, the matrix form of EPA set (5.9) is

$$\begin{aligned} & \left( \partial_t - \hat{\mathcal{L}} - (\hat{\mathbf{v}} + \hat{\mathcal{L}}') + k \begin{pmatrix} [A]_t + [B]_t & [B]_t & [A]_t \\ 2[A]_t & 2[B]_t & 0 \\ 2[B]_t & 0 & 2[A]_t \end{pmatrix} \right) \boldsymbol{\pi}(\mathbf{r}, t) \\ & = \delta(t) \boldsymbol{\pi}^0(\mathbf{r}) + (\hat{\mathbf{v}} + \hat{\mathcal{L}}') \begin{pmatrix} [A]_t [B]_t \\ [A]_t^2 \\ [B]_t^2 \end{pmatrix}. \end{aligned} \quad (5.14)$$

Owing to the matrix form, the solution of EPA set in the Green function formalism is rather compact

$$\boldsymbol{\pi}(\mathbf{r}, t) = \hat{\mathbf{g}}_{eff} \left[ \delta(t) \boldsymbol{\pi}^0(\mathbf{r}) + (\hat{\mathbf{v}} + \hat{\mathcal{L}}') \begin{pmatrix} [A]_t [B]_t \\ [A]_t^2 \\ [B]_t^2 \end{pmatrix} \right], \quad (5.15)$$

where  $\hat{\mathbf{g}}_{eff}$  is the effective pair propagator the kernel of which obeys the equation

$$\begin{aligned} & \left( \partial_t - \hat{\mathcal{L}} - (\hat{\mathbf{v}} + \hat{\mathcal{L}}') + k \begin{pmatrix} [A]_t + [B]_t & [B]_t & [A]_t \\ 2[A]_t & 2[B]_t & 0 \\ 2[B]_t & 0 & 2[A]_t \end{pmatrix} \right) \mathbf{g}_{eff}(\mathbf{r}, t | \mathbf{r}_0, t_0) \\ & = \delta(\mathbf{r} - \mathbf{r}_0) \delta(t - t_0) \mathbf{E}_3 \end{aligned} \quad (5.16)$$

where  $\mathbf{E}_3$  is a unit matrix of dimensionality 3. Substituting solution (5.15) in Eq. (5.13) gives EPA kinetic equation

$$\partial_t [A]_t = \delta(t) [A]_0 + \int d\mathbf{r} (1 \ 0 \ 0) \hat{\mathbf{i}}^{eff} \begin{pmatrix} [A]_t [B]_t \\ [A]_t^2 \\ [B]_t^2 \end{pmatrix} + J_{init}^{EPA}(t) \quad (5.17)$$

Here the  $T$ -operator of the effective pair is introduced

$$\hat{\mathbf{i}}^{eff} = \hat{\mathbf{v}} + \hat{\mathcal{L}}' + (\hat{\mathbf{v}} + \hat{\mathcal{L}}') \hat{\mathbf{g}}_{eff} (\hat{\mathbf{v}} + \hat{\mathcal{L}}'). \quad (5.18)$$

It can be shown that this operator satisfies the closed equation

$$\hat{\mathbf{i}}^{eff} = \hat{\mathbf{v}} + \hat{\mathcal{L}}' + (\hat{\mathbf{v}} + \hat{\mathcal{L}}') \hat{\mathbf{g}}_{eff}^{00} \hat{\mathbf{i}}^{eff}, \quad (5.19)$$

and the relations

$$(\hat{\mathbf{v}} + \hat{\mathcal{L}}') \hat{\mathbf{g}}_{eff} = \hat{\mathbf{i}}^{eff} \hat{\mathbf{g}}_{eff}^{00}; \quad \hat{\mathbf{g}}_{eff} (\hat{\mathbf{v}} + \hat{\mathcal{L}}') = \hat{\mathbf{g}}_{eff}^{00} \hat{\mathbf{i}}^{eff}, \quad (5.20)$$

where  $\hat{\mathbf{g}}_{eff}^{00}$  is the effective pair free propagator with the kernel satisfying Eq. (7.13) in the absence of interaction between reactants ( $\hat{\mathbf{v}} = 0, \hat{\mathcal{L}}' = 0$ ).

The source responsible for the presence of initial correlations, in view of relations (5.20), has the form

$$J_{init}^{EPA}(t) = \int d\mathbf{r} (1\ 0\ 0) \hat{\mathbf{i}}^{eff} \hat{\mathbf{g}}_{eff}^{00} \delta(t) \boldsymbol{\pi}^0(\mathbf{r}) \tag{5.21}$$

Let us introduce the  $T$ -operator of the generalized reaction pair  $\hat{\mathbf{i}}$  (by the generalized reaction pair we mean a combination of pairs  $AB$ ,  $AA$ , and  $BB$ )

$$\hat{\mathbf{i}} = \hat{\mathbf{v}} + \hat{\mathcal{L}}' + (\hat{\mathbf{v}} + \hat{\mathcal{L}}') \hat{\mathbf{g}} (\hat{\mathbf{v}} + \hat{\mathcal{L}}'). \tag{5.22}$$

Here we use the generalized reaction pair propagator  $\hat{\mathbf{g}}$  with the kernel satisfying the equation

$$\left( \partial_t - \hat{\mathcal{L}} - (\hat{\mathbf{v}} + \hat{\mathcal{L}}') \right) \mathbf{g}(\mathbf{r}, t | \mathbf{r}_0, t_0) = \delta(\mathbf{r} - \mathbf{r}_0) \delta(t - t_0) \mathbf{E}_3 \tag{5.23}$$

The operators in the left-hand side being diagonal, the propagator  $\hat{\mathbf{g}}$  is also of diagonal form

$$\hat{\mathbf{g}} = \begin{pmatrix} \hat{g}_{AB} & 0 & 0 \\ 0 & \hat{g}_{AA}^0 & 0 \\ 0 & 0 & \hat{g}_{BB}^0 \end{pmatrix} \tag{5.24}$$

where the propagators  $\hat{g}_{AB}$ ,  $\hat{g}_{AA}$ , and  $\hat{g}_{BB}$  are the propagators of the pairs  $AB$ ,  $AA$ , and  $BB$  (see Eqs. (4.4) and (5.4)) in relative coordinates of the pair. The  $T$ -operator of the generalized reaction pair  $\hat{\mathbf{i}}$  (5.22) satisfies the familiar closed equation

$$\hat{\mathbf{i}} = \hat{\mathbf{v}} + \hat{\mathcal{L}}' + (\hat{\mathbf{v}} + \hat{\mathcal{L}}') \hat{\mathbf{g}}^{00} \hat{\mathbf{i}}, \tag{5.25}$$

where  $\hat{\mathbf{g}}^{00}$  is the free propagator of the generalized reaction pair which is obviously matrix in structure (5.24) with matrix elements equal to free propagators of the corresponding pairs. The equation for the kernel of this free propagator follows immediately from Eq. (5.23) at  $(\hat{\mathbf{v}} + \hat{\mathcal{L}}') = 0$ .

The above quantities serve to form convenient equivalent equations for the effective pair  $T$ -operator [40]

$$\hat{\mathbf{i}}^{eff} = \hat{\mathbf{i}} + \hat{\mathbf{i}} (\hat{\mathbf{g}}_{eff}^{00} - \hat{\mathbf{g}}^{00}) \hat{\mathbf{i}}^{eff}. \tag{5.26}$$

Thus the difference between the deduced relations from the relations derived neglecting force interactions between reactants and initial correlations [40] is in the replacement of the reaction operator  $\hat{\mathbf{v}}$  by the operator  $\hat{\mathbf{v}} + \hat{\mathcal{L}}'$  to take force interactions into account. The major distinction associated with such a consideration leads to the appearance of additional terms in Eq. (5.17) proportional to concentration products of chemically non-reacting particles. Making allowance for initial correlations gives

rise to the inhomogeneous term. However, all these quantities are expressed in terms of the corresponding matrix elements of the effective  $T$ -operator.

## 6 The Modified Encounter Theory and regular form of binary kinetic equations

The initial set of EPA equations is rather complicated. To solve it, it should be remembered that CP evolution  $\pi_{1,1,0}(\mathbf{r}, t)$  is not determined solely by the evolution of independent reacting pair  $AB$  (as it was in the situations discussed in the previous sections), i.e., EPA is not a binary theory.

For some reactions the above approximation is able to describe fluctuation tails of kinetic dependencies occurring beyond the limits of the binary theory validity [55]. So to obtain the desired solution, one should develop the method for the extraction of binary evolution from the evolution of three-particle correlation patterns in EPA so as to derive the non-Markovian binary kinetic equations of the Modified Encounter Theory (MET) and their subsequent transformation into the Generalized Encounter Theory (GET), just as it was done in paper [40] in the absence of initial correlations and force interaction between reactants. However, representation of the equations in the matrix form reduces the problem to finding the binary solution of Eq. (5.26) which, according to the reasoning given in [40], takes the form

$$\hat{t}^{eff} \simeq \hat{t}^{MET} = \hat{t} + \hat{t}^{ps} (\hat{g}_{eff}^{00D} - \hat{g}^{00D}) \hat{t}^{ps}. \quad (6.1)$$

Here  $\hat{t}^{ps}$  denotes the stationary value of the point  $T$ -operator (in relative coordinates) of the generalized reaction pair that has a diagonal form with the matrix elements  $(\hat{t}^{ps})_{11} = t_{AB}^{ps}$ , (see Eq. (5.7)),  $(\hat{t}^{ps})_{22} = t_{AA}^{ps}$ ,  $(\hat{t}^{ps})_{33} = t_{BB}^{ps}$  (see Eq. (5.8)). The free diffusion propagator of the generalized effective pair  $\hat{g}_{eff}^{00D}$  and diffusion propagator of the generalized reaction pair  $\hat{g}^{00D}$  appearing in Eq. (6.1) are the approximations of appropriate free propagators on macroscopic space-time scales, and correspond to principal order in the binary scaling parameter. Mathematically they are much more simple than free propagators (motion by stochastic jumps), and their kernels obey equations of diffusion type.

The kernel of the diffusion propagator of the effective pair satisfies the equation

$$\left( \partial_t - \Delta_{\mathbf{r}} \begin{pmatrix} \bar{D}_{AB} & 0 & 0 \\ 0 & \bar{D}_{AA} & 0 \\ 0 & 0 & \bar{D}_{BB} \end{pmatrix} + k \begin{pmatrix} [A]_t^m + [B]_t^m & [B]_t^m & [A]_t^m \\ 2[A]_t^m & 2[B]_t^m & 0 \\ 2[B]_t^m & 0 & 2[A]_t^m \end{pmatrix} \right) \times \mathbf{g}_{eff}^{00D}(\mathbf{r}, t | \mathbf{r}, t_0) = \delta(\mathbf{r} - \mathbf{r}_0) \delta(t - t_0) \mathbf{E}_3. \quad (6.2)$$

Here  $\bar{D}_{AB}$ ,  $\bar{D}_{AA}$  and  $\bar{D}_{BB}$  are the relative macrodiffusion coefficients, and the Markovian concentrations  $[A]_t^m$  and  $[B]_t^m$  are defined in Eq. (2.4). The equation for the diffusion propagator  $\hat{g}^{00D}$  is obtained from Eq. (6.2) by passing to the limit  $k \rightarrow 0$ .

The binary nature of the derived expression (6.1) results from the fact that all quantities in their right-hand sides depend only on the quantities defined solely in terms



of the mean characteristics of independent pairs  $AB$ ,  $AA$ , and  $BB$ . Thus the deduced non-Markovian binary kinetic equation is obtained from EPA kinetic equation (5.17) using binary approximation (6.1) for the  $T$ -operator of the effective pair. Denoting appropriate matrix elements by lower indices, and abandoning matrix terminology, we have from Eq. (5.17)

$$\partial_t[A]_t = \delta(t)[A]_0 + \int d\mathbf{r} \left( (\hat{t}^{MET})_{11}[A]_t[B]_t + (\hat{t}^{MET})_{12}[A]_t^2 + (\hat{t}^{MET})_{13}[B]_t^2 \right) + J_{init}^{MET}(t), \tag{6.3}$$

where

$$J_{init}^{MET}(t) = \int d\mathbf{r} \left( (\hat{t}^{MET})_{11}; (\hat{t}^{MET})_{12}; (\hat{t}^{MET})_{13} \right) \hat{\mathbf{g}}_{eff}^{00} \delta(t) \boldsymbol{\pi}^0(\mathbf{r}). \tag{6.4}$$

Expanding the matrix form  $\hat{t}^{MET}$ , we have from Eq. (6.1)

$$\begin{aligned} (\hat{t}^{MET})_{11} &= \hat{t}_{AB} + \hat{t}_{AB}^{ps} \left( (\hat{\mathbf{g}}_{eff}^{00D})_{11} - \hat{\mathbf{g}}_{AB}^{00D} \right) \hat{t}_{AB}^{ps}, \\ (\hat{t}^{MET})_{12} &= \hat{t}_{AB}^{ps} (\hat{\mathbf{g}}_{eff}^{00D})_{12} \hat{t}_{AA}^{0ps}, \\ (\hat{t}^{MET})_{13} &= \hat{t}_{AB}^{ps} (\hat{\mathbf{g}}_{eff}^{00D})_{13} \hat{t}_{BB}^{0ps}. \end{aligned} \tag{6.5}$$

The derived MET kinetic equation (6.3) depends formally both on the concentration product  $[A]_t[B]_t$ , and on the products  $[A]_t^2$  and  $[B]_t^2$ . Besides, inhomogeneous source (6.4) depends on the initial correlations not only in the pair  $AB$ , but also in the pairs  $AA$  and  $BB$ , and this is an essential distinction from IET result. The contribution of these dependences may be evaluated on two time scales: micro-scale (times of the order of the encounter time  $\tau_e$  of reactants) and macro-scale (times of the order of the time between the encounters  $\tau_f$  that is the analog of mean free time in gases). On microscopic time scales estimation is made by the perturbation theory, on macroscopic ones—by procedure of binary scaling.

First we estimate the obtained expressions on microscopic time scales where the effective propagator of the generalized pair coincides with the propagator of the generalized pair, i.e.,

$$\hat{\mathbf{g}}_{eff}^{00} \xrightarrow{t \sim \tau_e} \hat{\mathbf{g}}^{00} = \begin{pmatrix} \hat{g}_{AB}^{00} & 0 & 0 \\ 0 & \hat{g}_{AA}^{00} & 0 \\ 0 & 0 & \hat{g}_{BB}^{00} \end{pmatrix}. \tag{6.6}$$

So at the times of the order of the encounter time

$$\begin{aligned} (\hat{t}^{MET})_{11} &\underset{t \sim \tau_e}{\sim} \hat{t}_{AB}, \\ (\hat{t}^{MET})_{12} &\underset{t \sim \tau_e}{\sim} 0, \\ (\hat{t}^{MET})_{13} &\underset{t \sim \tau_e}{\sim} 0. \end{aligned} \tag{6.7}$$

From this it immediately follows that on microscopic times MET kinetic equation (6.3) coincides with IET kinetic Eq. (4.9), i.e., MET memory function can be introduced

$$\Sigma_0^{MET}(t|t_0) \underset{t \sim \tau_e}{\sim} \Sigma_0^e(t - t_0), \quad (6.8)$$

Under the assumption of a microscopic character of initial correlations in the pairs  $AB$ ,  $AA$ , and  $BB$ , the inhomogeneous source differs from zero only at small times. Thus, in view of estimates (6.6), (6.7), and definition (6.4), we conclude that the following estimate is valid for the source of MET initial correlations

$$J_{init}^{MET}(t) \underset{t \sim \tau_e}{\sim} J_{init}^{IET}(t). \quad (6.9)$$

On macroscopic time scales estimation of expressions (6.5) is made by binary scaling procedure to give (see “Appendix B”)

$$\begin{aligned} (\hat{\mathbf{t}}^{MET})_{11} &\underset{\gamma \rightarrow \infty}{\sim} \hat{\mathbf{t}}_{AB}^p + \gamma^{-9} \hat{\mathbf{t}}_{AB}^{ps} \left( (\hat{\mathbf{g}}_{eff}^{00D})_{11} - \hat{\mathbf{g}}_{AB}^{00D} \right) \hat{\mathbf{t}}_{AB}^{ps} + O(\gamma^{-10}), \\ (\hat{\mathbf{t}}^{MET})_{12} &\underset{\gamma \rightarrow \infty}{\sim} O(\gamma^{-10}), \\ (\hat{\mathbf{t}}^{MET})_{13} &\underset{\gamma \rightarrow \infty}{\sim} O(\gamma^{-10}), \end{aligned} \quad (6.10)$$

where by analogy with estimation (5.6) the scaling of the kernel of point  $T$ -operator  $\hat{\mathbf{t}}_{AB}^p$  is determined by the first two terms of the expansion of  $\hat{t}^{AB}$  in the binary scaling parameter  $\gamma$ . However, taking into consideration just the relative motion of reactants in the pair results in that scaling estimations of  $T$ -operators in relative coordinates of the pair and in laboratory system of coordinates (5.6) differ by the factor  $\gamma^3$  responsible for the pair center motion [59]

$$\tilde{t}_{AB}^p(\mathbf{r}, t|\mathbf{r}_0, t_0) = \gamma^{-8} \left( t_{AB}^{ps}(\mathbf{r}, t|\mathbf{r}_0, t_0) + \gamma^{-1} \chi'(\mathbf{r}, t|\mathbf{r}_0, t_0) \right). \quad (6.11)$$

Stationary part of  $T$ -operator  $\hat{t}_{AB}^{ps}$  by analogy with expression (5.7) has a  $\delta$ -shaped singularity in space-time variables

$$t_{AB}^{ps}(\mathbf{r}, t|\mathbf{r}_0, t_0) = -k\delta(\mathbf{r})\delta(\mathbf{r}_0)\delta(t - t_0). \quad (6.12)$$

The quantity  $\chi'(\mathbf{r}, t|\mathbf{r}_0, t_0)$  in (6.11) responsible for non-Markovian effects is a non-stationary part of point  $T$ -operator in relative coordinates of the pair of reactants, and does not coincide with the non-Markovian part of point  $T$ -operator in laboratory system of coordinates (5.6).

From Eqs. (6.10) and (6.11) it evidently follows that consideration of matrix elements  $(\hat{\mathbf{t}}^{MET})_{12}$  and  $(\hat{\mathbf{t}}^{MET})_{13}$  on macroscopic time scales falls beyond the limits of the binary description accuracy, and they should be neglected. The subsequent scaling of inhomogeneous source  $J_{init}^{MET}(t)$  (6.4) in view of microscopic character of initial

correlations  $\pi(\mathbf{r}, t)$  yields (see “Appendix B”)

$$\tilde{J}_{init}^{MET}(t) \underset{\gamma \rightarrow \infty}{\sim} O(\gamma^{-6}). \tag{6.13}$$

In the binary description MET kinetic equation (6.3) is valid with allowance for the first two leading terms of the expansion in binary scaling parameter  $\gamma$ . Such an expansion gives the terms proportional to  $\gamma^{-4}$  and  $\gamma^{-5}$  (see “Appendix B”). So taking into consideration the inhomogeneous source (6.13) responsible for the presence of initial microscopic correlations on macroscopic scales is beyond the limits of binary description.

Thus MET kinetic equation (6.3) takes the following form over the entire time range of binary description

$$\partial_t[A]_t = \delta(t)[A]_0 + \int d\mathbf{r} (\hat{\mathbf{t}}^{MET})_{11}[A]_t[B]_t + J_{init}^{MET}(t), \tag{6.14}$$

where MET source is defined by analogy with the expression for IET source (4.14)

$$J_{init}^{MET}(t) = \int d\mathbf{r} (\hat{\mathbf{t}}^{MET})_{11} \hat{g}_{AB}^{00} \delta(t) \pi_{1,1,0}^0(\mathbf{r}). \tag{6.15}$$

Integrating Eq. (6.14) over spatial coordinates and separating out the explicit time dependence in the kernel of this kinetic equation, we get

$$\partial_t[A]_t = \delta(t)[A]_0 - \int_{-0}^t dt_0 \Sigma_0^{MET}(t|t_0)[A]_{t_0}[B]_{t_0} + J_{init}^{MET}(t), \tag{6.16}$$

where the equation kernel (MET memory function) is the averaged MET  $T$ -operator

$$\Sigma_0^{MET}(t|t_0) = - \int d\mathbf{r} (\mathbf{t}^{MET})_{11}(\mathbf{r}, t|\mathbf{r}_0, t_0) d\mathbf{r}_0. \tag{6.17}$$

As in paper [44] or in the Integral Encounter Theory considered in Sect. 4, the inhomogeneous source determined by initial microscopic correlations in MET kinetic equation (6.16), in view of estimates (6.8) and (6.9), may be entered into the memory function taking account of the initial correlations in the pair. This easily gives the homogeneous integro-differential MET equation

$$\partial_t[A]_t = \delta(t)[A]_0 - \int_{-0}^t dt_0 \Sigma^{MET}(t|t_0)[A]_{t_0}[B]_{t_0}, \tag{6.18}$$

where

$$\Sigma^{MET}(t|t_0) = -\partial_t \int d\mathbf{r} (\hat{\mathbf{t}}^{MET})_{11} \hat{g}_{AB}^{00} \delta(t) p^T(\mathbf{r}). \tag{6.19}$$

So the difference between the deduced kinetic equation and the corresponding equation from paper [40] is just in the redefinition of the kernel of this integro-differential equation with allowance for force interaction and initial correlation in the reacting pair  $AB$ . In full agreement with these results [40] and results in Ref. [44], using the binary solution for  $T$ -operator (6.5) and definitions (4.18) and (4.19) we have from Eq. (6.19)

$$\Sigma^{MET}(t|t_0) = \Sigma^e(t|t_0) - k^2(g_{eff}^{00D}(0, t|0, t_0) - g_{AB}^{00D}(0, t|0, t_0)). \quad (6.20)$$

In the derivation of Eq. (6.20) we use the fact, that the information of microscopic correlations is lost on macro scales. Thus the substitution of the second term (responsible for macroscopic correlations) of  $(\hat{t}^{MET})_{11}$  (6.5) in Eq. (6.19) was performed using the approximation  $p^T(\mathbf{r}) \simeq 1(\mathbf{r})$ .

Values  $g_{eff}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0)$  and  $g_{AB}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0)$  appearing in Eq. (6.20) are by definitions

$$\begin{aligned} g_{eff}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0) &\equiv (g_{eff}^{00D})_{11}(\mathbf{r}, t|\mathbf{r}_0, t_0); \\ g_{AB}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0) &\equiv (g^{00D})_{11}(\mathbf{r}, t|\mathbf{r}_0, t_0). \end{aligned} \quad (6.21)$$

So, as follows from Eq. (6.20), to find the memory function of MET Eq. (6.18), it is sufficient to know the memory function  $\Sigma^e(t|t_0)$  obtained in the development of IET (see Sect. 4), the matrix element of the free propagator of the effective pair that satisfies Eq. (6.2), and free diffusion propagator of the reaction pair  $AB$ . The expression for the latter is available in the literature

$$g_{AB}^{00D}(0, t|0, t_0) = \frac{\theta(t - t_0)}{(4\pi \bar{D}_{AB}(t - t_0))^{3/2}}. \quad (6.22)$$

Further, to bring MET kinetic equation (6.18) to the differential form, rewrite its kernel (6.20) in an identical form

$$\Sigma^{MET}(t|t_0) \equiv \Sigma^e(t|t_0) \exp\left(-k \int_{t_0}^t d\tau ([A]_{\tau}^m + [B]_{\tau}^m)\right) + \Lambda(t|t_0). \quad (6.23)$$

Here we introduce the function  $\Lambda(t|t_0)$  which is responsible for macroscopic correlations between reactants encounters. This function can be simplified using point approximation for IET memory function  $\Sigma^e(t|t_0)$  [39]

$$\Sigma^e(t|t_0) \simeq k(t - t_0) + \frac{k^2}{4(\pi \bar{D}_{AB})^{3/2}} \partial_{t-t_0} \frac{\theta(t - t_0)}{\sqrt{t - t_0}}. \quad (6.24)$$

Thus, in view of Eqs. (6.20), (6.22), (6.23), and (6.24), the expression for  $\Lambda(t|t_0)$  is

$$\Lambda(t|t_0) = -k^2 \left( g_{eff}^{00D}(0, t|0, t_0) - \frac{\theta(t - t_0)}{(4\pi \bar{D}_{AB}(t - t_0))^{3/2}} \exp \left( -k \int_{t_0}^t d\tau ([A]_{\tau}^m + [B]_{\tau}^m) \right) \right). \tag{6.25}$$

It formally coincides with the form of similar function  $\Lambda(t|t_0)$  derived in paper Ref. [40], where the force interaction between reactants was ignored. Making allowance for the force interaction led just to redefinition of the Markovian rate constant  $k$  in accordance with Eq. (4.20). Such a modification of the obtained expression reducing only to redefinition of macroscopic parameters of the pair and preserving diffusion motion of reactants in the point approximation confirms a macroscopic nature of the function  $\Lambda(t|t_0)$ .

Using the time shift rule [40,44]

$$[A]_t \Rightarrow \exp \left( -k \int_{t_0}^t d\tau [B]_{\tau}^m \right) [A]_{t_0}; \quad [B]_t \Rightarrow \exp \left( -k \int_{t_0}^t d\tau [A]_{\tau}^m \right) [B]_{t_0} \tag{6.26}$$

we obtain a Regular Form of non-Markovian binary equations of the Generalized Encounter Theory (GET) from Eq. (6.18) in view of Eq. (6.23)

$$\partial_t [A]_t = \delta(t) [A]_0 - K(t) [A]_t [B]_t + J(t), \tag{6.27}$$

where the inhomogeneous source is of the form

$$J(t) = - \int_{-0}^t dt_0 \Lambda(t|t_0) [A]_{t_0}^m [B]_{t_0}^m. \tag{6.28}$$

GET kinetic equation (6.27) and kinetic coefficients ( $K(t)$  and  $J(t)$ ) appearing in it formally coincide with coefficients obtained neglecting the force interaction between reactants [40]. Modification of these equations reduces just to redefinition of rate constant with allowance for the force interaction in the reacting pair.

Written on ordinary time interval  $0 \leq t < \infty$  (not on the extended one) in the form

$$\frac{d[A]_t}{dt} = -K(t) \{ [A]_t [B]_t + \Pi^{macro}(t) \}, \tag{6.29}$$

with initial conditions  $[A]_{t=0} = [A]_0$  and  $[B]_{t=0} = [B]_0$ . Equation (6.29) shows the presence of macroscopic correlations of  $A$  and  $B$  reactants which are in the process of free random walks between the encounters, just as in the reaction  $A + B \rightarrow C$  ignoring force interactions and initial correlations between reactants [40], or in the reaction  $A + A \rightarrow C$  of identical reactants [44]. Such correlations are described by the correlation pattern

$$\Pi^{macro}(t) = -\frac{J(t)}{k}. \quad (6.30)$$

Note that when transforming the source in Eq. (6.27) into the correlation pattern in Eq. (6.29), we put  $K(t) \simeq k$  as in [40,44] which is possible in the limits of the required accuracy of the binary description.

Thus it is shown that in the general case taking consistent account of force interaction and initial microscopic correlations leads just to redefinition of the non-Markovian constant  $K(t)$  (defined only by the evolution of the reacting pair  $AB$ ) that serves to express all quantities appearing in the derived kinetic equations. So in the case described above the reaction kinetics investigation pursued in terms of rate constants is identical to that made in paper [40]. To make presentation more complete, let us calculate the time behaviour of correlations between the encounters of reactants and the reaction kinetics. We give brief survey of calculations from paper Ref. [40].

## 7 Time behaviour of the correlations between reactant encounters, and reaction kinetics

As follows from Eqs. (6.30), (6.28), and (6.25), to calculate the correlator between the encounters of reactants, it is necessary to calculate free diffusion propagator of the effective pair. Solving Eq. (6.2) it corresponds to, in the general case, will present difficulties. However, we restrict ourselves to the case of the equality of macrodiffusion coefficients of the relative motion of reactants in all pairs,  $\bar{D}_{AB} = \bar{D}_{AA} = \bar{D}_{BB} \equiv \bar{D}$ . Note that, generally speaking, we do not assume that the relative motion in the pairs on microscopic level is of the diffusion character. Under the assumptions made, the diffusion motion operator has the form

$$\hat{\mathcal{L}}_D = \bar{D}E_3\Delta_{\mathbf{r}}, \quad (7.1)$$

i.e., it is proportional to the unit matrix  $E_3$ . So it commutes with reactant concentration matrix in Eq. (6.2), and the free diffusion propagator kernel of the effective pair is

$$g_{eff}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0) = g_{AB}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0)\mathbf{H}(t|t_0), \quad (7.2)$$

where  $g_{AB}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0) = g_{AA}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0) = g_{BB}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0)$  is the diffusion approximation of the propagator kernel of the relative free motion in any of the pairs (6.22). The matrix  $\mathbf{H}(t|t_0)$  appearing in Eq. (7.2) is the solution of the equation

$$\left( \partial_t + k \begin{pmatrix} [A]_t^m + [B]_t^m & [B]_t^m & [A]_t^m \\ 2[A]_t^m & 2[B]_t^m & 0 \\ 2[B]_t^m & 0 & 2[A]_t^m \end{pmatrix} \right) \mathbf{H}(t|t_0) = \delta(t - t_0)\mathbf{E}_3. \quad (7.3)$$

Its solution is obtained in Ref. [40] by projection operator method. This solution and definitions in Eq. (6.21) give the expression for the effective pair diffusion propagator kernel

$$g_{eff}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0) = g_{AB}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0)(\mathbf{H})_{11}(t|t_0), \tag{7.4}$$

where the matrix element  $(\mathbf{H})_{11}(t|t_0)$  is [40]

$$(\mathbf{H})_{11}(t|t_0) = \frac{1}{2} + \frac{1}{2} e^{-2k \int_{t_0}^t d\tau ([A]_{\tau}^m + [B]_{\tau}^m)} - \frac{(\Delta n \cdot k)^2}{2} \left( \int_{t_0}^t dt_1 e^{-k \int_{t_1}^t d\tau ([A]_{\tau}^m + [B]_{\tau}^m)} \right)^2, \tag{7.5}$$

where  $\Delta n = [B]_t - [A]_t = [B]_0 - [A]_0$ . Thus, substituting expression (7.5) in Eq. (6.25) in view of Eqs. (6.22), (6.28) and (6.30) we have

$$\Pi^{macro}(t) = -\frac{k}{8(\pi \bar{D})^{3/2}} \int_{-0}^t \frac{dt_0}{(t-t_0)^{3/2}} \left\{ (\mathbf{H})_{11}(t|t_0) - e^{-k \int_{t_0}^t d\tau ([A]_{\tau}^m + [B]_{\tau}^m)} \right\} [A]_{t_0}^m [B]_{t_0}^m. \tag{7.6}$$

As is shown in Ref. [40], the correlator value is negative ( $J(t)$  is positive) at all times at  $t > 0$ . This means that taking account of binary encounter correlations in the reaction system under study results in the decrease in the reaction rate. Since  $A$  and  $B$  species of reactants participate in the reaction on equal terms, the greatest effect of such correlations is to be observed in the case where the initial concentrations of reactants coincide ( $\Delta n = 0$ ). Then Eq. (2.4) for the Markovian kinetics are simplified

$$[A]_t^m = [B]_t^m = \frac{[A]_0}{1 + tk[A]_0}. \tag{7.7}$$

So the integral in Eq. (7.6) is explicitly calculated, and the analytical expression may be obtained for the correlator

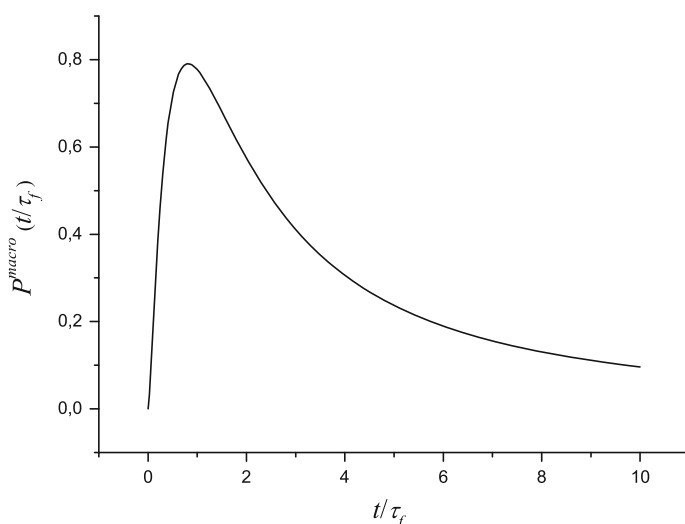
$$\Pi^{macro}(t) = -\frac{\varepsilon [A]_0^2}{12\sqrt{2}(1 + k[A]_0 t)^4} \left[ 9 \operatorname{arctanh} \left( \sqrt{\frac{k[A]_0 t}{1 + k[A]_0 t}} \right) (1 + k[A]_0 t)^{3/2} + 3(k[A]_0 t)^{5/2} - 4(k[A]_0 t)^{3/2} - 9\sqrt{k[A]_0 t} \right] \tag{7.8}$$

where a small parameter is introduced

$$\varepsilon = \frac{k^{3/2} \sqrt{[A]_0}}{(2\pi \bar{D})^{3/2}} \tag{7.9}$$

Its value is of the order of a square root of the density parameter.

It follows from the Markovian kinetics (7.7) that its characteristic decay time is  $\tau_f = (k[A]_0)^{-1}$ . This time can be identified with the mean time between sequential encounters of reactants (it is the analog of a free pass time in the gas phase reactions).



**Fig. 1** Time behavior of the dimensionless function  $P^{macro}(t/\tau_f)$

The times of the order of  $\tau_f$  have a macroscopic scale. The function  $P^{macro}(t) = J(t) * 12\sqrt{2}/(\varepsilon k[A]_0^2) = -\Pi^{macro}(t) * 12\sqrt{2}/(\varepsilon[A]_0^2)$  depends on dimensionless argument  $t/\tau_f$ . Its behavior is shown in Fig. 1. As is seen, accumulation of macroscopic correlations in the reservoir of free walks of reactants due to their encounters occurs at characteristic mesotimes:  $0.8\tau_f$ , while their subsequent decay because of the encounters takes place at characteristic macrotimes: several times  $\tau_f$ .

Now compare the kinetics obtained in the Encounter Theory (ET) and that derived in the Generalized Encounter Theory (GET) for the case of equal initial concentrations of reactants ( $\Delta n = 0$ ).

To solve the kinetic equation (2.1), we must know the non-Markovian rate constant  $K(t)$  which, generally speaking, depends on the form of initial microscopic correlations, the structure of reactants, and their mobility. Their specific features are most pronounced at the intermediate stage observed at the times of the order of the encounter time. At these times the Encounter Theory and the Generalized Encounter Theory describe the reaction in one and the same way. So consideration of the kinetics at these times is of no interest to us. We exclude the intermediate stage from the consideration using the point encounter approximation for the non-Markovian rate constant according to Eqs. (4.19) and (6.24)

$$K(t) = k + \frac{k^2}{4(\pi \bar{D})^{3/2}} \frac{1}{\sqrt{t}}. \quad (7.10)$$

The kinetic equation (2.1) may be solved by the perturbation theory method taking into account that the non-Markovian (the second) term in Eq. (7.10) is small as compared to the Markovian (the first) one. As a result, the non-Markovian kinetics in ET



is represented as a sum of two terms: Markovian and non-Markovian

$$[A]_t^{ET} = \frac{[A]_0}{1 + tk[A]_0} - \varepsilon \frac{[A]_0 \sqrt{2tk[A]_0}}{(1 + tk[A]_0)^2}. \tag{7.11}$$

The first (Markovian) term coincides with kinetics (7.7), and is the leading term in the scaling parameter. The second term describes the non-Markovian effect in the point encounter approximation. The obtained kinetics depends on a single dimensionless time parameter  $t/\tau_f$ , i.e., the encounter time is taken equal to zero.

Calculation of the kinetics in GET with due account of the encounter correlations is made on the basis of Eq. (6.27) by analogy with ET kinetics calculation. As a result, the non-Markovian kinetics of GET is

$$[A]_t^{GET} = \frac{[A]_0}{1 + tk[A]_0} - \varepsilon \frac{[A]_0 \sqrt{2tk[A]_0}}{(1 + tk[A]_0)^2} + \frac{1}{(1 + tk[A]_0)^2} \int_0^t dt_0 J(t_0) (1 + t_0 k[A]_0)^2. \tag{7.12}$$

The first two terms coincide with the Encounter Theory kinetics (7.11). The third term is non-Markovian, and is determined by taking into consideration the encounter correlation source. Its time dependence is quite similar to the behavior of the non-Markovian part of kinetics (7.11): it increases from zero with time, and decreases at large times with the characteristic time  $\tau_f$ .

Figure 2 shows the time behavior of the non-Markovian part of ET and GET kinetics in relative units (the relative deviation of the non-Markovian theory from the Markovian one) at the parameter  $\varepsilon = 0.1$  depending on dimensionless time  $\tau = t/\tau_f$

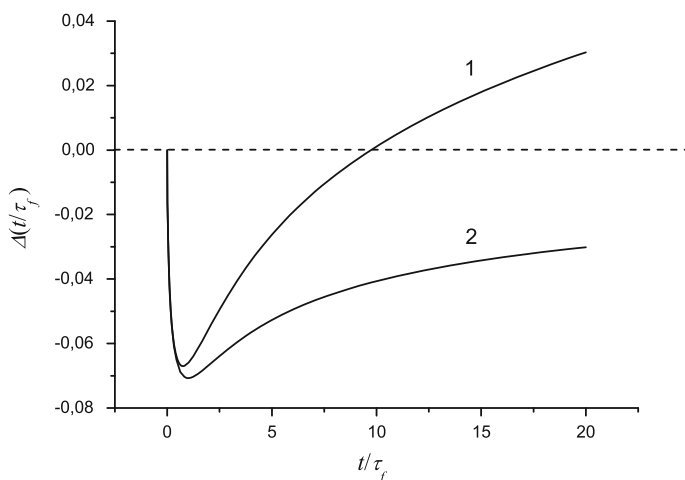
$$\Delta_{ET}(\tau) = \frac{[A]_t^{ET} - [A]_t^m}{[A]_t^m}; \quad \Delta_{GET}(\tau) = \frac{[A]_t^{GET} - [A]_t^m}{[A]_t^m}. \tag{7.13}$$

It is noteworthy that the non-Markovian part of the GET kinetics changes sign. As for ET kinetics, it does not exhibit this property.

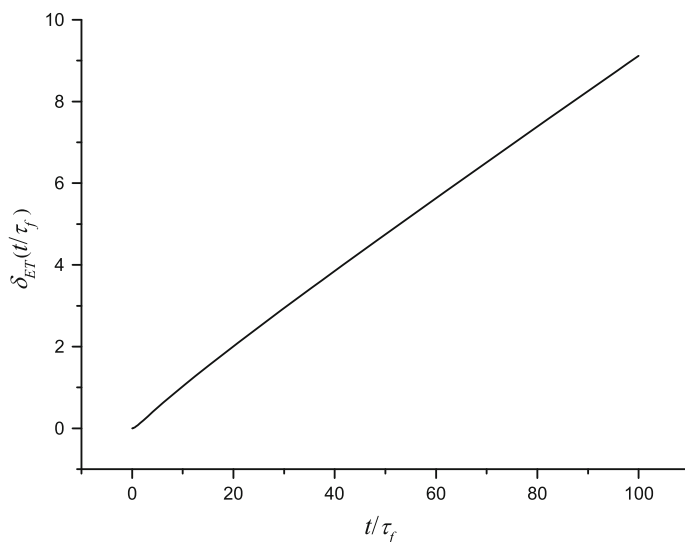
Figure 3 shows the deviation of the ratio between ET and GET kinetics non-Markovian parts from unity

$$\delta_{ET}(\tau) = 1 - \frac{[A]_t^{GET} - [A]_t^m}{[A]_t^{ET} - [A]_t^m}. \tag{7.14}$$

Inaccuracy of the Encounter Theory in calculations of the non-Markovian part of the kinetics increases almost linearly. Thus in the reaction in question the Encounter Theory cannot even qualitatively provide adequate description of complete non-Markovian kinetics.



**Fig. 2** Time behavior of relative deviation of the non-Markovian kinetics from the Markovian one at the parameter  $\varepsilon = 0.1$  depending on dimensionless time  $\tau = t/\tau_f$ :  $\Delta_{GET}(t/\tau_f)$  (curve 1) and  $\Delta_{ET}(t/\tau_f)$  (curve 2)



**Fig. 3** Time behavior of the deviation of the ratio between ET and GET non-Markovian parts from unity  $\delta_{ET}(t/\tau_f)$  at the parameter  $\varepsilon = 0.1$

## 8 Summary

The many-particle method for the derivation of non-Markovian binary kinetic equations available in the literature can be used to theoretically treat the applicability of the Encounter Theory conceptions in describing physicochemical processes in liquid dilute solutions. Such a consideration has been made by the authors in the previous

papers [40,44] for widely occurring diffusion assisted irreversible bulk reactions  $A + A \rightarrow C$  and  $A + B \rightarrow C$  (for example, radical reaction). It has been shown that in the general case pair encounters of reactants are dependent. This results in the inhomogeneous source responsible for the accumulation of macroscopic correlations between pair encounters, in non-Markovian binary kinetic equation written as a rate equation. However, in the examination of the reaction  $A + B \rightarrow C$  the force interaction of reactants and initial correlations between them were neglected. That is why the goal of the present contribution was to take consistent account of the force interaction and initial correlations in this reaction and to study their influence on accumulation of macroscopic correlations found earlier.

In the context of the Encounter Theory based on the conception of independent pair encounters the force interaction is considered by including it solely in the reacting pair. The effects related to the force interaction of reactants of this pair with other particles are not important, because they are determined by three-particle interaction not taken into account in the theory. From this standpoint, the given effect could influence the reaction rate in the framework of the many-particle approach (MET and GET) that allowed for three-particle correlations. As is shown, the effect in question is actually taken into account by our theory (in Effective Pair Approximation). However, binary scaling has shown that it is beyond the limits of binary description accuracy, and thus is insignificant at small density parameter. Such an effect is to manifest itself with increasing concentration, as is shown by numerical calculations [20,46–48]. Making allowance for initial correlations in full agreement with general kinetic theory gave rise to the inhomogeneous source in the kinetic equation vanishing with time.

Such a consideration is demonstrated that in the presence of the forth interactions in the reaction system considered it is necessary just to refine usual kinetic characteristics (kinetic equations kernels, reaction rate constants) and the parameters in the inhomogeneous source of macroscopic correlations between successive encounters, with general kinetics of accumulation of macroscopic correlations being preserved, and therefore the reaction kinetics, considered in [40].

### Appendix A: Missing equations for two- and three-particle cps

Equations for the main two-particle patterns  $\pi_{1,1,0}(A_1, B_1, t)$ ,  $\pi_{2,0,0}(A_1, A_2, t)$ , and  $\pi_{1,0,1}(A_1, C_1, t)$  in Eq. (3.18) are as follows

$$\begin{aligned}
 & \left( \partial_t - \hat{L}_{A_1} - \hat{L}_{B_1} - \hat{L}'_{A_1 B_1} - \hat{V}^{(1,1)} \right) \pi_{1,1,0}(A_1, B_1, t) \\
 &= \delta(t) \pi_{1,1,0}^0(A_1, B_1) + \left( \hat{L}'_{A_1 B_1} + \hat{V}^{(1,1)} \right) n_A(A_1, t) n_B(B_1, t) \\
 &+ \int dA_2 \left( \hat{L}'_{A_2 B_1} + \hat{V}^{(2,1)} \right) \left[ \pi_{2,1,0}(A_1, A_2, B_1, t) + n_A(A_2, t) \pi_{1,1,0}(A_1, B_1, t) + n_B(B_1, t) \pi_{2,0,0}(A_1, A_2, t) \right] \\
 &+ \int dA_2 \hat{L}'_{A_1 A_2} \left[ \pi_{2,1,0}(A_1, A_2, B_1, t) + n_A(A_1, t) \pi_{1,1,0}(A_2, B_1, t) + n_A(A_2, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
 &+ \int dB_2 \left( \hat{L}'_{A_1 B_2} + \hat{V}^{(1,2)} \right) \left[ \pi_{1,2,0}(A_1, B_1, B_2, t) + n_A(A_1, t) \pi_{0,2,0}(B_1, B_2, t) + n_B(B_2, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
 &+ \int dB_2 \hat{L}'_{B_1 B_2} \left[ \pi_{1,2,0}(A_1, B_1, B_2, t) + n_B(B_1, t) \pi_{1,1,0}(A_1, B_2, t) + n_B(B_2, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
 &+ \int dC_1 \hat{L}'_{A_1 C_1} \left[ \pi_{1,1,1}(A_1, B_1, C_1, t) + n_A(A_1, t) \pi_{0,1,1}(B_1, C_1, t) + n_C(C_1, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
 &+ \int dC_1 \hat{L}'_{B_1 C_1} \left[ \pi_{1,1,1}(A_1, B_1, C_1, t) + n_B(B_1, t) \pi_{1,0,1}(A_1, C_1, t) + n_C(C_1, t) \pi_{1,1,0}(A_1, B_1, t) \right],
 \end{aligned}
 \tag{A.1}$$

and

$$\begin{aligned}
 & (\partial_t - \hat{L}_{A_1} - \hat{L}_{A_2} - \hat{L}'_{A_1 A_2}) \pi_{2,0,0}(A_1, A_2, t) \\
 &= \delta(t) \pi_{2,0,0}^0(A_1, A_2) + \hat{L}'_{A_1 A_2} n_A(A_1, t) n_A(A_2, t) \\
 &+ \int d B_1 \left( \hat{L}'_{A_1 B_1} + \hat{V}^{(1,1)} \right) \left[ \pi_{2,1,0}(A_1, A_2, B_1, t) + n_B(B_1, t) \pi_{2,0,0}(A_1, A_2, t) + n_A(A_1, t) \pi_{1,1,0}(A_2, B_1, t) \right] \\
 &+ \int d B_1 \left( \hat{L}'_{A_2 B_1} + \hat{V}^{(2,1)} \right) \left[ \pi_{2,1,0}(A_1, A_2, B_1, t) + n_B(B_1, t) \pi_{2,0,0}(A_1, A_2, t) + n_A(A_2, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
 &+ \int d A_3 \hat{L}'_{A_1 A_3} \left[ \pi_{3,0,0}(A_1, A_2, A_3, t) + n_A(A_1, t) \pi_{2,0,0}(A_2, A_3, t) + n_A(A_3, t) \pi_{2,0,0}(A_1, A_2, t) \right] \\
 &+ \int d A_3 \hat{L}'_{A_2 A_3} \left[ \pi_{3,0,0}(A_1, A_2, A_3, t) + n_A(A_2, t) \pi_{2,0,0}(A_1, A_3, t) + n_A(A_3, t) \pi_{2,0,0}(A_1, A_2, t) \right] \\
 &+ \int d C_1 \hat{L}'_{A_1 C_1} \left[ \pi_{2,0,1}(A_1, A_2, C_1, t) + n_A(A_1, t) \pi_{1,0,1}(A_2, C_1, t) + n_C(C_1, t) \pi_{2,0,0}(A_1, A_2, t) \right] \\
 &+ \int d C_1 \hat{L}'_{A_2 C_1} \left[ \pi_{2,0,1}(A_1, A_2, C_1, t) + n_A(A_2, t) \pi_{1,0,1}(A_2, C_1, t) + n_C(C_1, t) \pi_{2,0,0}(A_1, A_2, t) \right], \quad (\text{A.2})
 \end{aligned}$$

and

$$\begin{aligned}
 & (\partial_t - \hat{L}_{A_1} - \hat{L}_{C_1} - \hat{L}'_{A_1 C_1}) \pi_{1,0,1}(A_1, C_1, t) \\
 &= \delta(t) \pi_{1,0,1}^0(A_1, C_1) + \hat{L}'_{A_1 C_1} n_A(A_1, t) n_C(C_1, t) \\
 &+ \int d B_1 \left( \hat{L}'_{A_1 B_1} + \hat{V}^{(1,1)} \right) \left[ \pi_{1,1,1}(A_1, B_1, C_1, t) + n_A(A_1, t) \pi_{0,1,1}(B_1, C_1, t) + n_B(B_1, t) \pi_{1,0,1}(A_1, C_1, t) \right] \\
 &+ \int d B_1 \hat{L}'_{B_1 C_1} \left[ \pi_{1,1,1}(A_1, B_1, C_1, t) + n_B(B_1, t) \pi_{1,0,1}(A_1, C_1, t) + n_C(C_1, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
 &+ \int d A_2 \hat{L}'_{A_2 C_1} \left[ \pi_{2,0,1}(A_1, A_2, C_1, t) + n_A(A_2, t) \pi_{1,0,1}(A_1, C_1, t) + n_C(C_1, t) \pi_{2,0,0}(A_1, A_2, t) \right] \\
 &+ \int d A_2 \hat{L}'_{A_1 A_2} \left[ \pi_{2,0,1}(A_1, A_2, C_1, t) + n_A(A_1, t) \pi_{1,0,1}(A_2, C_1, t) + n_A(A_2, t) \pi_{1,0,1}(A_1, C_1, t) \right] \\
 &+ \int d C_2 \hat{L}'_{A_1 C_2} \left[ \pi_{1,0,2}(A_1, C_1, C_2, t) + n_A(A_1, t) \pi_{0,0,2}(C_1, C_2, t) + n_C(C_2, t) \pi_{1,0,1}(A_1, C_1, t) \right] \\
 &+ \int d C_2 \hat{L}'_{C_1 C_2} \left[ \pi_{1,0,2}(A_1, C_1, C_2, t) + n_C(C_1, t) \pi_{1,0,1}(A_1, C_2, t) + n_C(C_2, t) \pi_{1,0,1}(A_1, C_1, t) \right] \\
 &+ \hat{R}^{(12,1)} \left[ \pi_{2,1,0}(A_1, A_2, B_1, t) + n_A(A_2, t) \pi_{1,1,0}(A_1, B_1, t) + n_B(B_1, t) \pi_{2,0,0}(A_1, A_2, t) \right]. \quad (\text{A.3})
 \end{aligned}$$

The equations for the patterns  $\pi_{0,2,0}(B_1, B_2, t)$  and  $\pi_{0,1,1}(B_1, C_1, t)$  that are in Eq. (A.1) may be derived from Eqs. (A.2) and (A.3) by symmetric substitution of  $A$  for  $B$ , and, vice versa,

$$\begin{aligned}
 & (\partial_t - \hat{L}_{B_1} - \hat{L}_{B_2} - \hat{L}'_{B_1 B_2}) \pi_{0,2,0}(B_1, B_2, t) \\
 &= \delta(t) \pi_{0,2,0}^0(B_1, B_2) + \hat{L}'_{B_1 B_2} n_B(B_1, t) n_B(B_2, t) \\
 &+ \int d A_1 \left( \hat{L}'_{A_1 B_1} + \hat{V}^{(1,1)} \right) \left[ \pi_{1,2,0}(A_1, B_1, B_2, t) + n_B(B_1, t) \pi_{0,2,0}(B_1, B_2, t) + n_B(B_1, t) \pi_{1,1,0}(A_1, B_2, t) \right] \\
 &+ \int d A_1 \left( \hat{L}'_{A_1 B_2} + \hat{V}^{(1,2)} \right) \left[ \pi_{1,2,0}(A_1, B_1, B_2, t) + n_B(B_1, t) \pi_{0,2,0}(B_1, B_2, t) + n_B(B_2, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
 &+ \int d B_3 \hat{L}'_{B_1 B_3} \left[ \pi_{0,3,0}(B_1, B_2, B_3, t) + n_B(B_1, t) \pi_{0,2,0}(B_2, B_3, t) + n_B(B_3, t) \pi_{0,2,0}(B_1, B_2, t) \right] \\
 &+ \int d B_3 \hat{L}'_{B_2 B_3} \left[ \pi_{0,3,0}(B_1, B_2, B_3, t) + n_B(B_2, t) \pi_{0,2,0}(B_1, B_3, t) + n_B(B_3, t) \pi_{0,2,0}(B_1, B_2, t) \right] \\
 &+ \int d C_1 \hat{L}'_{B_1 C_1} \left[ \pi_{0,2,1}(B_1, B_2, C_1, t) + n_B(B_1, t) \pi_{0,1,1}(B_2, C_1, t) + n_C(C_1, t) \pi_{0,2,0}(B_1, B_2, t) \right] \\
 &+ \int d C_1 \hat{L}'_{B_2 C_1} \left[ \pi_{0,2,1}(B_1, B_2, C_1, t) + n_B(B_2, t) \pi_{0,1,1}(B_1, C_1, t) + n_C(C_1, t) \pi_{0,2,0}(B_1, B_2, t) \right]. \quad (\text{A.4})
 \end{aligned}$$

$$\begin{aligned}
 & (\partial_t - \hat{L}_{B_1} - \hat{L}_{C_1} - \hat{L}'_{B_1 C_1}) \pi_{0,1,1}(B_1, C_1, t) \\
 &= \delta(t) \pi_{0,1,1}^0(B_1, C_1) + \hat{L}'_{B_1 C_1} n_B(B_1, t) n_C(C_1, t) \\
 &+ \int d A_1 \left( \hat{L}'_{A_1 B_1} + \hat{V}^{(1,1)} \right) \left[ \pi_{1,1,1}(A_1, B_1, C_1, t) + n_B(B_1, t) \pi_{1,0,1}(A_1, C_1, t) + n_A(A_1, t) \pi_{0,1,1}(B_1, C_1, t) \right] \\
 &+ \int d A_1 \hat{L}'_{A_1 C_1} \left[ \pi_{1,1,1}(A_1, B_1, C_1, t) + n_A(A_1, t) \pi_{0,1,1}(B_1, C_1, t) + n_C(C_1, t) \pi_{1,1,0}(A_1, B_1, t) \right] \\
 &+ \int d B_2 \hat{L}'_{B_2 C_1} \left[ \pi_{0,2,1}(B_1, B_2, C_1, t) + n_B(B_2, t) \pi_{0,1,1}(B_1, C_1, t) + n_C(C_1, t) \pi_{0,2,0}(B_1, B_2, t) \right] \\
 &+ \int d B_2 \hat{L}'_{B_1 B_2} \left[ \pi_{0,2,1}(B_1, B_2, C_1, t) + n_B(B_1, t) \pi_{0,1,1}(B_2, C_1, t) + n_B(B_2, t) \pi_{0,1,1}(B_1, C_1, t) \right] \\
 &+ \int d C_2 \hat{L}'_{B_1 C_2} \left[ \pi_{0,1,2}(B_1, C_1, C_2, t) + n_B(B_1, t) \pi_{0,0,2}(C_1, C_2, t) + n_C(C_2, t) \pi_{0,1,1}(B_1, C_1, t) \right] \\
 &+ \int d C_2 \hat{L}'_{C_1 C_2} \left[ \pi_{0,1,2}(B_1, C_1, C_2, t) + n_C(C_1, t) \pi_{0,1,1}(B_1, C_2, t) + n_C(C_2, t) \pi_{0,1,1}(B_1, C_1, t) \right] \\
 &+ \hat{R}^{(12,1)} \left[ \pi_{1,2,0}(A_1, B_1, B_2, t) + n_B(B_2, t) \pi_{1,1,0}(A_1, B_1, t) + n_A(A_1, t) \pi_{0,2,0}(B_1, B_2, t) \right]. \quad (\text{A.5})
 \end{aligned}$$

Equation for  $\pi_{0,0,2}(C_1, C_2, t)$  is as follows

$$\begin{aligned}
 & \left( \partial_t - \hat{L}_{C_1} - \hat{L}_{C_2} - \hat{L}'_{C_1 C_2} \right) \pi_{0,0,2}(C_1, C_2, t) \\
 &= \delta(t) \pi_{0,0,2}^0(C_1, C_2) + \hat{L}'_{C_1 C_2} n_C(C_1, t) n_C(C_2, t) \\
 &+ \int d B_1 \hat{L}'_{B_1 C_1} \left[ \pi_{0,1,2}(B_1, C_1, C_2, t) + n_B(B_1, t) \pi_{0,0,2}(C_1, C_2, t) + n_C(C_1, t) \pi_{0,1,1}(B_1, C_2, t) \right] \\
 &+ \int d B_1 \hat{L}'_{B_1 C_2} \left[ \pi_{0,1,2}(B_1, C_1, C_2, t) + n_B(B_1, t) \pi_{0,0,2}(C_1, C_2, t) + n_C(C_2, t) \pi_{0,1,1}(B_1, C_1, t) \right] \\
 &+ \int d C_3 \hat{L}'_{C_2 C_3} \left[ \pi_{0,0,3}(C_1, C_2, C_3, t) + n_C(C_3, t) \pi_{0,0,2}(C_1, C_2, t) + n_C(C_2, t) \pi_{0,0,2}(C_1, C_3, t) \right] \\
 &+ \int d C_3 \hat{L}'_{C_1 C_3} \left[ \pi_{0,0,3}(C_1, C_2, C_3, t) + n_C(C_3, t) \pi_{0,0,2}(C_1, C_2, t) + n_C(C_1, t) \pi_{0,0,2}(C_2, C_3, t) \right] \\
 &+ \int d A_1 \hat{L}'_{A_1 C_1} \left[ \pi_{1,0,2}(A_1, C_1, C_2, t) + n_A(A_1, t) \pi_{0,0,2}(C_1, C_2, t) + n_C(C_1, t) \pi_{1,0,1}(A_1, C_2, t) \right] \\
 &+ \int d A_1 \hat{L}'_{A_1 C_2} \left[ \pi_{1,0,2}(A_1, C_1, C_2, t) + n_A(A_1, t) \pi_{0,0,2}(C_1, C_2, t) + n_C(C_2, t) \pi_{1,0,1}(A_1, C_1, t) \right] \\
 &+ \hat{R}^{(1|1,1)} \left[ \pi_{1,1,1}(A_1, B_1, C_1, t) + n_A(A_1, t) \pi_{0,1,1}(B_1, C_1, t) + n_B(B_1, t) \pi_{1,0,1}(A_1, C_1, t) \right] \\
 &+ \hat{R}^{(2|1,1)} \left[ \pi_{1,1,1}(A_1, B_1, C_2, t) + n_A(A_1, t) \pi_{0,1,1}(B_1, C_2, t) + n_B(B_1, t) \pi_{1,0,1}(A_1, C_2, t) \right]. \tag{A.6}
 \end{aligned}$$

Equations for three-particle CPs are presented using the notation  $\hat{L}_{\alpha\beta\gamma} = \hat{L}_\alpha + \hat{L}_\beta + \hat{L}_\gamma + \hat{L}'_{\alpha\beta} + \hat{L}'_{\alpha\gamma} + \hat{L}'_{\beta\gamma}$ , where  $\alpha, \beta$ , and  $\gamma$  denote the reactant

$$\begin{aligned}
 & \left( \partial_t - \hat{L}_{A_1 B_1 C_1} - \hat{V}^{(1,1)} \right) \pi_{1,1,1}(A_1, B_1, C_1, t) \\
 &= \delta(t) \pi_{1,1,1}^0(A_1, B_1, C_1) + \left( \hat{L}'_{A_1 B_1} + \hat{L}'_{A_1 C_1} + \hat{V}^{(1,1)} \right) n_A(A_1, t) \pi_{0,1,1}(B_1, C_1, t) \\
 &+ \left( \hat{L}'_{A_1 B_1} + \hat{L}'_{B_1 C_1} + \hat{V}^{(1,1)} \right) n_B(B_1, t) \pi_{1,0,1}(A_1, C_1, t) \\
 &+ \left( \hat{L}'_{A_1 C_1} + \hat{L}'_{B_1 C_1} \right) n_C(C_1, t) \pi_{1,1,0}(A_1, B_1, t), \tag{A.7}
 \end{aligned}$$

$$\begin{aligned}
 & \left( \partial_t - \hat{L}_{A_1 A_2 B_1} - \hat{V}^{(1,1)} - \hat{V}^{(2,1)} \right) \pi_{2,1,0}(A_1, A_2, B_1, t) \\
 &= \delta(t) \pi_{2,1,0}^0(A_1, A_2, B_1) + \left( \hat{L}'_{A_1 B_1} + \hat{L}'_{A_1 A_2} + \hat{V}^{(1,1)} \right) n_A(A_1, t) \pi_{1,1,0}(A_2, B_1, t) \\
 &+ \left( \hat{L}'_{A_1 B_1} + \hat{L}'_{A_2 B_1} + \hat{V}^{(1,1)} + \hat{V}^{(2,1)} \right) n_B(B_1, t) \pi_{2,0,0}(A_1, A_2, t) \\
 &+ \left( \hat{L}'_{A_2 B_1} + \hat{L}'_{A_1 A_2} + \hat{V}^{(2,1)} \right) n_A(A_2, t) \pi_{1,1,0}(A_1, B_1, t), \tag{A.8}
 \end{aligned}$$

$$\begin{aligned}
 & \left( \partial_t - \hat{L}_{A_1 B_1 B_2} - \hat{V}^{(1,1)} - \hat{V}^{(1,2)} \right) \pi_{1,2,0}(A_1, B_1, B_2, t) \\
 &= \delta(t) \pi_{1,2,0}^0(A_1, B_1, B_2) \\
 &+ \left( \hat{L}'_{A_1 B_1} + \hat{L}'_{A_1 B_2} + \hat{V}^{(1,1)} + \hat{V}^{(1,2)} \right) n_A(A_1, t) \pi_{0,2,0}(B_1, B_2, t) \\
 &+ \left( \hat{L}'_{A_1 B_1} + \hat{L}'_{B_1 B_2} + \hat{V}^{(1,1)} \right) n_B(B_1, t) \pi_{1,1,0}(A_1, B_2, t) \\
 &+ \left( \hat{L}'_{A_1 B_1} + \hat{L}'_{B_1 B_2} + \hat{V}^{(1,2)} \right) n_B(B_2, t) \pi_{1,1,0}(A_1, B_1, t), \tag{A.9}
 \end{aligned}$$

$$\begin{aligned}
 & \left( \partial_t - \hat{L}_{A_1 C_1 C_2} \right) \pi_{1,0,2}(A_1, C_1, C_2, t) \\
 &= \delta(t) \pi_{1,0,2}^0(A_1, C_1, C_2) + \left( \hat{L}'_{A_1 C_1} + \hat{L}'_{A_1 C_2} \right) n_A(A_1, t) \pi_{0,0,2}(C_1, C_2, t) \\
 &+ \left( \hat{L}'_{A_1 C_1} + \hat{L}'_{C_1 C_2} \right) n_C(C_1, t) \pi_{1,0,1}(A_1, C_2, t) \\
 &+ \left( \hat{L}'_{A_1 C_2} + \hat{L}'_{C_1 C_2} \right) n_C(C_2, t) \pi_{1,0,1}(A_1, C_1, t), \tag{A.10}
 \end{aligned}$$

$$\begin{aligned}
& (\partial_t - \hat{L}_{A_1 A_2 C_1}) \pi_{2,0,1}(A_1, A_2, C_1, t) \\
&= \delta(t) \pi_{2,0,1}^0(A_1, A_2, C_1) + \left( \hat{L}'_{A_1 C_1} + \hat{L}'_{A_1 A_2} \right) n_A(A_1, t) \pi_{1,0,1}(A_2, C_1, t) \\
&+ \left( \hat{L}'_{A_1 C_1} + \hat{L}'_{A_2 C_1} \right) n_C(C_1, t) \pi_{2,0,0}(A_1, A_2, t) \\
&+ \left( \hat{L}'_{A_2 C_1} + \hat{L}'_{A_1 A_2} \right) n_A(A_2, t) \pi_{1,0,1}(A_1, C_1, t), \tag{A.11}
\end{aligned}$$

$$\begin{aligned}
& (\partial_t - \hat{L}_{B_1 C_1 C_2}) \pi_{0,1,2}(B_1, C_1, C_2, t) \\
&= \delta(t) \pi_{0,1,2}^0(B_1, C_1, C_2) + \left( \hat{L}'_{B_1 C_1} + \hat{L}'_{B_1 C_2} \right) n_B(B_1, t) \pi_{0,0,2}(C_1, C_2, t) \\
&+ \left( \hat{L}'_{B_1 C_1} + \hat{L}'_{C_1 C_2} \right) n_C(C_1, t) \pi_{0,1,1}(B_1, C_2, t) \\
&+ \left( \hat{L}'_{B_1 C_2} + \hat{L}'_{C_1 C_2} \right) n_C(C_2, t) \pi_{0,1,1}(B_1, C_1, t), \tag{A.12}
\end{aligned}$$

$$\begin{aligned}
& (\partial_t - \hat{L}_{B_1 B_2 C_1}) \pi_{0,2,1}(B_1, B_2, C_1, t) \\
&= \delta(t) \pi_{0,2,1}^0(B_1, B_2, C_1) + \left( \hat{L}'_{B_1 C_1} + \hat{L}'_{B_1 B_2} \right) n_B(B_1, t) \pi_{0,1,1}(B_2, C_1, t) \\
&+ \left( \hat{L}'_{B_1 C_1} + \hat{L}'_{B_2 C_1} \right) n_C(C_1, t) \pi_{0,2,0}(B_1, B_2, t) \\
&+ \left( \hat{L}'_{B_2 C_1} + \hat{L}'_{B_1 B_2} \right) n_B(B_2, t) \pi_{0,1,1}(B_1, C_1, t), \tag{A.13}
\end{aligned}$$

$$\begin{aligned}
& (\partial_t - \hat{L}_{A_1 A_2 A_3}) \pi_{3,0,0}(A_1, A_2, A_3, t) \\
&= \delta(t) \pi_{3,0,0}^0(A_1, A_2, A_3) + \left( \hat{L}'_{A_1 A_2} + \hat{L}'_{A_1 A_3} \right) n_A(A_1, t) \pi_{2,0,0}(A_2, A_3, t) \\
&+ \left( \hat{L}'_{A_1 A_2} + \hat{L}'_{A_2 A_3} \right) n_A(A_2, t) \pi_{2,0,0}(A_1, A_3, t) \\
&+ \left( \hat{L}'_{A_1 A_3} + \hat{L}'_{A_2 A_3} \right) n_A(A_3, t) \pi_{2,0,0}(A_1, A_2, t), \tag{A.14}
\end{aligned}$$

$$\begin{aligned}
& (\partial_t - \hat{L}_{B_1 B_2 B_3}) \pi_{0,3,0}(B_1, B_2, B_3, t) \\
&= \delta(t) \pi_{0,3,0}^0(B_1, B_2, B_3) + \left( \hat{L}'_{B_1 B_2} + \hat{L}'_{B_1 B_3} \right) n_B(B_1, t) \pi_{0,2,0}(B_2, B_3, t) \\
&+ \left( \hat{L}'_{B_1 B_2} + \hat{L}'_{B_2 B_3} \right) n_B(B_2, t) \pi_{0,2,0}(B_1, B_3, t) \\
&+ \left( \hat{L}'_{B_1 B_3} + \hat{L}'_{B_2 B_3} \right) n_B(B_3, t) \pi_{0,2,0}(B_1, B_2, t), \tag{A.15}
\end{aligned}$$

$$\begin{aligned}
& (\partial_t - \hat{L}_{C_1 C_2 C_3}) \pi_{0,0,3}(C_1, C_2, C_3, t) \\
&= \delta(t) \pi_{0,0,3}^0(C_1, C_2, C_3) + \left( \hat{L}'_{C_1 C_2} + \hat{L}'_{C_1 C_3} \right) n_C(C_1, t) \pi_{0,0,2}(C_2, C_3, t) \\
&+ \left( \hat{L}'_{C_1 C_2} + \hat{L}'_{C_2 C_3} \right) n_C(C_2, t) \pi_{0,0,2}(C_1, C_3, t) \\
&+ \left( \hat{L}'_{C_1 C_3} + \hat{L}'_{C_2 C_3} \right) n_C(C_3, t) \pi_{0,0,2}(C_1, C_2, t). \tag{A.16}
\end{aligned}$$

## Appendix B: Equations for CPs in IET approximation and epa

Derivation of closed equations for correlation patterns evolution calls for the use of correlation termination procedure. The simplest technique is including only pair correlations into consideration neglecting all three-particle patterns. Such a hierarchy termination is typical of many-particle collision theory in gases, and corresponds to making allowance solely for pair diagrams in the derivation of the collision theory mass operator. In this approximation Eq. (A.1) for the two-particle CP  $\pi_{1,1,0}(A_1, B_1, t)$  is simplified to IET Eq. (4.1). Equations for other main two-particle patterns  $\pi_{2,0,0}(A_1, A_2, t)$  and  $\pi_{1,0,1}(A_1, C_1, t)$  in IET approximation are easily derived from Eqs. (A.2) and (A.3) neglecting all three-particle patterns. They are as follows

$$\begin{aligned} & \left( \partial_t - \hat{L}_{A_1} - \hat{L}_{A_2} - \hat{L}'_{A_1 A_2} \right) \pi_{2,0,0}(A_1, A_2, t) \\ & = \delta(t) \pi_{2,0,0}^0(A_1, A_2) + \hat{L}'_{A_1 A_2} n_A(A_1, t) n_A(A_2, t), \end{aligned} \quad (\text{B.1})$$

and

$$\begin{aligned} & \left( \partial_t - \hat{L}_{A_1} - \hat{L}_{C_1} - \hat{L}'_{A_1 C_1} \right) \pi_{1,0,1}(A_1, C_1, t) \\ & = \delta(t) \pi_{1,0,1}^0(A_1, C_1) + \hat{L}'_{A_1 C_1} n_A(A_1, t) n_C(C_1, t). \end{aligned} \quad (\text{B.2})$$

Another method of hierarchy closure that enables one to include into consideration all binary terms when dealing with small concentrations of reactants employs termination of correlations on the level of three-particle ones. In solving the corresponding Eqs. (A.1), (A.2), and (A.3) the method of extracting pair channels in the analysis of the evolution of three spatially correlated particles is used [28] which is similar to the Faddeev method applied in quantum three-body theory [60]. The essence of the method is that in studying the evolution of three particles account is taken solely of the situation where only two reactants interact with one another (force interaction or reaction one), while the third reactant moves freely.

Thus in the approximation (of pair channel account), it is necessary to determine the contributions from three-particle completely correlated patterns  $\pi_{2,1,0}(A_1, A_2, B_1, t)$ ,  $\pi_{1,2,0}(A_1, B_1, B_2, t)$ , and  $\pi_{1,1,1}(A_1, B_1, C_1, t)$  to the collision integral in the calculation of  $\pi_{1,1,0}(A_1, B_1, t)$  evolution in Eq. (A.1). For example, consider the pattern  $\pi_{2,1,0}(A_1, A_2, B_1)$  and the value  $(\hat{V}^{(2,1)} + \hat{L}'_{A_2 B_1}) \pi_{2,1,0}(A_1, A_2, B_1, t)$  appearing in Eq. (A.1). First of all use the solution of Eq. (A.8) that can be obtained in a common way by Green function formalism neglecting the influence of initial three-particle correlations  $\pi_{2,1,0}^0(A_1, A_2, B_1)$  [28]

$$\begin{aligned} \pi_{2,1,0}(A_1, A_2, B_1, t) = & \hat{G}_{A_1 A_2 B_1} \left[ \left( \hat{L}'_{A_1 B_1} + \hat{L}'_{A_1 A_2} + \hat{V}^{(1,1)} \right) n_A(A_1, t) \pi_{1,1,0}(A_2, B_1, t) \right. \\ & + \left( \hat{L}'_{A_1 B_1} + \hat{L}'_{A_2 B_1} + \hat{V}^{(1,1)} + \hat{V}^{(2,1)} \right) n_B(B_1, t) \pi_{2,0,0}(A_1, A_2, t) \\ & \left. + \left( \hat{L}'_{A_2 B_1} + \hat{L}'_{A_1 A_2} + \hat{V}^{(2,1)} \right) n_A(A_2, t) \pi_{1,1,0}(A_1, B_1, t) \right]. \end{aligned} \quad (\text{B.3})$$

Here  $\hat{G}_{A_1A_2B_1}$  is the three-particle propagator the kernel of which satisfies the equation

$$\begin{aligned} & (\partial_t - \hat{L}_{A_1A_2B_1} - \hat{V}^{(1,1)} - \hat{V}^{(2,1)}) G_{A_1A_2B_1}(A_1, A_2, B_1, t | A_{01}, A_{02}, B_{01}, t) \\ & = \delta(A_1 - A_{01})\delta(A_2 - A_{02})\delta(B_1 - B_{01})\delta(t - t_0). \end{aligned} \quad (\text{B.4})$$

Accordingly to the mentioned idea of binary channel extracting we should consider the situation when two particles interact, and the third one just moves freely. If we consider the pattern  $\pi_{2,1,0}(A_1, A_2, B_1)$  and the interaction of particles  $A_2$  and  $B_1$  (which is described by the operators  $\hat{V}^{(2,1)}$  and  $\hat{L}'_{A_2B_1}$ ), only the terms describing the interaction of just this pair of particles should be retained in the right-hand of Eq. (B.3). Moreover, the propagator of three particles  $\hat{G}_{A_1A_2B_1}$  is also simplified. Its kernel can be represented as the product of the propagator kernel of the interacting pair  $\hat{G}_{A_2B_1}$  and the free propagator of the third particle  $\hat{G}_{A_1}^0$ . Such approximation allows us to calculate the value  $(\hat{V}^{(2,1)} + \hat{L}'_{A_2B_1})\pi_{2,1,0}(A_1, A_2, B_1, t)$  appearing in Eq. (A.1). Multiplying the Eq. (B.3) on the left by  $(\hat{V}^{(2,1)} + \hat{L}'_{A_2B_1})$  we have

$$\begin{aligned} & (\hat{V}^{(2,1)} + \hat{L}'_{A_2B_1})\pi_{2,1,0}(A_1, A_2, B_1, t) \\ & \simeq (\hat{V}^{(2,1)} + \hat{L}'_{A_2B_1})[\widehat{G_{A_2B_1}G_{A_1}^0}](\hat{V}^{(2,1)} + \hat{L}'_{A_2B_1}) \\ & \quad (n_A(A_2, t)\pi_{1,1,0}(A_1, B_1, t) + n_B(B_1, t)\pi_{2,0,0}(A_1, A_2, t)). \end{aligned} \quad (\text{B.5})$$

The kernel of the propagator  $\hat{G}_{A_2B_1}$  of the pair  $AB$  and that of the free motion propagator  $\hat{G}_{A_1}^0$  of the particle  $A$  are defined by relations (4.4) and (5.2), respectively. Similar procedure for the quantity  $\hat{L}'_{A_1A_2}\pi_{2,1,0}(A_1, A_2, B_1, t)$  gives the representation for the three-particle pattern  $\pi_{2,1,0}(A_1, A_2, B_1, t)$

$$\begin{aligned} & \hat{L}'_{A_1A_2}\pi_{2,1,0}(A_1, A_2, B_1, t) \\ & \simeq \hat{L}'_{A_1A_2}[\widehat{G_{A_1A_2}G_{B_1}^0}]\hat{L}'_{A_1A_2}(n_A(A_1, t)\pi_{1,1,0}(A_2, B_1, t) + n_A(A_2, t)\pi_{1,1,0}(A_1, B_1, t)). \end{aligned} \quad (\text{B.6})$$

The propagators  $\hat{G}_{A_1A_2}^0$  and  $\hat{G}_{B_1}^0$  are defined by relations (4.4) and (5.2) respectively. Representation for other three-particle evolutions in binary channel approximation appearing in Eq. (A.1) are derived by analogy. As a result, we have from Eq. (A.1) the equation for the two-particle pattern  $\pi_{1,1,0}(A_1, B_1, t)$  (5.1).

### Appendix C: Scaling

Transformation of any function  $\Phi(\mathbf{r}^A, \mathbf{r}^B, t)$  defining the pair in the initial system into the function  $\tilde{\Phi}(\mathbf{r}^A, \mathbf{r}^B, t)$ , describing the same pair but in the scaling-system has the form

$$\tilde{\Phi}(\mathbf{r}_A, \mathbf{r}_B, t) \equiv \Phi(\gamma\mathbf{r}_A, \gamma\mathbf{r}_B, \gamma^2t). \quad (\text{C.1})$$



This makes it possible to easily scale any expression, and analyze its different contributions on macroscopic space-time scales in powers of the scaling parameter  $\gamma$ .

Before scaling the required matrix elements of the effective pair  $T$ -operator (6.5), note that scaling parameter estimates  $\gamma$  for  $T$ -operators (5.5), (5.6), and (5.8) are given in the laboratory system of coordinates. Estimates for  $T$ -operators in relative coordinates differ from them by the factor  $\gamma^3$  taking account of the pair center motion. In particular, scaling of the kernels of force  $T$ -operators necessary for further calculation is as follows

$$\begin{aligned} \tilde{t}_{AA}^0(\mathbf{r}, t|\mathbf{r}_0, t_0) &\underset{\gamma \rightarrow \infty}{\sim} \tilde{t}_{AA}^{0ps}(\mathbf{r}, t|\mathbf{r}_0, t_0) \underset{\gamma \rightarrow \infty}{\sim} O(\gamma^{-10}), \\ \tilde{t}_{BB}^0(\mathbf{r}, t|\mathbf{r}_0, t_0) &\underset{\gamma \rightarrow \infty}{\sim} \tilde{t}_{BB}^{0ps}(\mathbf{r}, t|\mathbf{r}_0, t_0) \underset{\gamma \rightarrow \infty}{\sim} O(\gamma^{-10}). \end{aligned} \tag{C.2}$$

First let us scale the matrix element  $(\hat{\mathbf{t}}^{MET})_{12}$  defined in (6.5). Expressing the action of integral operators explicitly in terms of their kernels, and making the scaling procedure by rule (C.1), we have

$$\begin{aligned} (\tilde{\mathbf{t}}^{MET})_{12}(\mathbf{r}, t|\mathbf{r}_0, t_0) &= \text{ker} \left[ \hat{t}_{AB}^{ps}(\widehat{\mathbf{g}}_{eff}^{00D})_{12} \hat{t}_{AA}^{0ps} \right] (\mathbf{r}, t|\mathbf{r}_0, t_0) \\ &\equiv \int \hat{t}_{AB}^{ps}(\gamma \mathbf{r}, \gamma^2 t|\mathbf{r}_1, t_1) d\mathbf{r}_1 dt_1 (\mathbf{g}_{eff}^{00D})_{12}(\mathbf{r}_1, t_1|\mathbf{r}_2, t_2) d\mathbf{r}_2 dt_2 \hat{t}_{AA}^{0ps}(\mathbf{r}_2, t_2|\gamma \mathbf{r}_0, \gamma^2 t_0). \end{aligned} \tag{C.3}$$

Here notation *ker* means the kernel of integral operator in square brackets. Performing the substitution  $\mathbf{r}_i \rightarrow \gamma \mathbf{r}_i, t_i \rightarrow \gamma^2 t_i$ , where  $i = 1, 2$ , and using the property  $d\mathbf{r}_i \rightarrow \gamma^3 d\mathbf{r}_i$  we get

$$(\tilde{\mathbf{t}}^{MET})_{12}(\mathbf{r}, t|\mathbf{r}_0, t_0) = \gamma^{10} \text{ker} \left[ \hat{t}_{AB}^{ps}(\hat{\mathbf{g}}_{eff}^{00D})_{12} \hat{t}_{AA}^{0ps} \right] (\mathbf{r}, t|\mathbf{r}_0, t_0). \tag{C.4}$$

The free propagator kernel of the effective pair on macroscopic space-time scales has the following estimate in the parameter  $\gamma$  [36, 59]

$$\tilde{\mathbf{g}}_{eff}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0) \underset{\gamma \rightarrow \infty}{\sim} \gamma^{-3} \mathbf{g}_{eff}^{00D}(\mathbf{r}, t|\mathbf{r}_0, t_0). \tag{C.5}$$

The action of point operators  $\hat{t}_{AB}^{ps}$  and  $\hat{t}_{AA}^{0ps}$  from the left and from the right on the propagator  $\hat{\mathbf{g}}_{eff}^{00D}$ , respectively, means that the motion of reactants described by this propagator takes place in a restricted area: initial and final points of reactant motion are at zero. Thus direct substitution of estimate (C.5) in expression (C.4) is not quite correct, and leads to nonintegrable singularity. For the calculation to be correct, it is sufficient to make initial and final points differ by a small value. The corresponding scaling parameter estimate is of the form

$$\tilde{\mathbf{g}}_{eff}^{00D}(0, t|0 + 0, t_0) \underset{\gamma \rightarrow \infty}{\sim} \frac{\gamma \mathbf{g}_{eff}^{00D}(0, t|0 + 0, t_0)}{\gamma^3} = \gamma^{-2} \mathbf{g}_{eff}^{00D}(0, t|0 + 0, t_0). \tag{C.6}$$

So in view of relations (6.11), (C.2), and (C.6), from (C.4) we obtain the required estimate of the matrix element  $(\hat{t}^{MET})_{12}$  in (6.10). Estimation for the matrix element  $(\hat{t}^{MET})_{13}$  is made by analogy. Note that the second term of the matrix element  $(\hat{t}^{MET})_{11}$  is structurally similar to  $(\hat{t}^{MET})_{12}$ . That is why it is scaled in a similar way. However, the action of point  $T$ -operators on the difference between propagators  $(\hat{g}_{eff}^{00D})_{11} - \hat{g}_{AB}^{00D}$  is well-defined, thus the following estimation is valid

$$(\hat{g}_{eff}^{00D})_{11}(0, t|0, t_0) - \hat{g}_{AB}^{00D}(0, t|0, t_0) \underset{\gamma \rightarrow \infty}{\sim} \gamma^{-3} \left( (\hat{g}_{eff}^{00D})_{11}(0, t|0, t_0) - \hat{g}_{AB}^{00D}(0, t|0, t_0) \right). \tag{C.7}$$

This gives the required estimate of the matrix element  $(\hat{t}^{MET})_{11}$  in Eq. (6.10).

To get the scaling estimate for the source  $J_{init}^{MET}(t)$  (6.4) we take into account that the initial correlations are of microscale. This means that initial correlations can be considered only in a limited area and on macroscopic scale are reduced to a point. Therefore they have  $\delta(\mathbf{r})$ -shaped character. To scale  $\delta$ -shaped functions we use the property

$$\delta(Cx) = \frac{\delta(x)}{C}, \tag{C.8}$$

where  $C$  is constant,  $x$  is variable. Generalizing the expression for initial correlations in pair  $AB$  (4.10) to other pairs  $AA$  and  $BB$ , taking into account Eq. (C.8) and the property

$$[\widetilde{A}]_0 \sim \gamma^{-2}[A]_0 ; [\widetilde{B}]_0 \sim \gamma^{-2}[B]_0, \tag{C.9}$$

we have the following estimate in the parameter  $\gamma$  for the initial correlations

$$\tilde{\pi}_0(\mathbf{r}) \underset{\gamma \rightarrow \infty}{\sim} \gamma^{-7} \delta(\mathbf{r}). \tag{C.10}$$

Using the recipe described in obtaining the expression (C.4), we can easily obtain the following estimate for the source  $J_{init}^{MET}(t)$  (6.4)

$$\tilde{J}_{init}^{MET}(t) \underset{\gamma \rightarrow \infty}{\sim} \gamma^{13} \int d\mathbf{r} \left( (\hat{t}^{MET})_{11}; (\hat{t}^{MET})_{12}; (\hat{t}^{MET})_{13} \right) \hat{g}_{eff}^{00} \delta(\tilde{t}) \tilde{\pi}^0(\mathbf{r}). \tag{C.11}$$

Using the property (C.8), Eqs. (6.10), (C.6) and (C.10) in expression (C.11), we get the desired scaling estimate of the source (6.13).

Let us scale the kinetic equation MET (6.14). Using Eqs. (C.8), (C.9) we get for the first term in Eq. (6.14)

$$\delta(\tilde{t})[\widetilde{A}]_0 \sim \gamma^{-4} \delta(t)[A]_0 \tag{C.12}$$

For the scaling of the second term in Eq. (6.14) take into account expressions (C.9), (6.10), (6.11) and (6.12). As a result, taking into account the first two terms in the parameter  $\gamma$  we get

$$\widetilde{\partial_t[A]}_t \sim \gamma^{-4} \delta(t) [A]_0 - \gamma^{-4} k[A]_t [B]_t + O(\gamma^{-5}). \quad (\text{C.13})$$

Leading order in the parameter  $\gamma$  corresponds to the law of mass action (2.3) (i.e., a Markovian description). Accounting next order is essential in the construction of non-Markovian theory. Its form is not explicitly specified here, because it is considered in detail Sect. 5.

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