Deviation from the kinetic law of mass action for reactions induced by binary encounters in liquid solutions

Deviation from the kinetic law of mass action for reactions induced by binary encounters in liquid solutions

Alexander B Doktorov and Alexey A Kipriyanov

Institute of Chemical Kinetics and Combustion, SB RAS, Novosibirsk 630090, Russia
and
Novosibirsk State University, Novosibirsk 630090, Russia

Abstract

In considering the irreversible chemical reaction $A + B \rightarrow C + B$ in liquid solutions two many-particle approaches to the derivation of binary non-Markovian kinetic equations are compared: simple superposition decoupling and a method of extracting 'pair' channels from three-particle correlation evolution. It is shown that both methods provide an almost identical description of this reaction.

However, in studies of reversible reactions in liquid solutions only the channel extraction method gives a correct physically clear description of the reaction though it consists of a sequence of steps: the development of integral encounter theory (IET), effective pairs approximation (EPA), modified encounter theory (MET), and the final regular form (RF) of kinetic equations. It is shown that the rate equations often encountered in the literature correspond to the independence of transient channels of 'scattering' in the bimolecular reversible reaction ($A+B \rightleftarrows C+B$), while the independent transient channel of 'decay' in the reversible reaction $A + B \rightleftarrows C$ is defined solely by time integral convolution. In the general case transient channels in non-Markovian theory are not independent, and their interference manifests itself as a non-Markovian inhomogeneous source in binary non-Markovian kinetic equations in regular form.

Based on the derived equations new universal kinetics (independent of models) of chemical equilibrium attainment have been obtained. It is shown that these kinetics can differ essentially from the kinetics corresponding to the kinetic law of mass action of formal chemical kinetics.

1. Introduction

In formal chemical kinetics [1] the description of a bulk stoichiometric chemical reaction involving reactants A_i:

$$\sum_i \nu_i A_i = 0; \qquad \sum_i \alpha_k A_k - \sum_l \beta_l A_l = 0 \tag{1.1}$$

(where ν_i are stoichiometric coefficients positive $\nu_k = \alpha_k$ for initial reactants and negative $\nu_l = -\beta_l$ for the reaction products) relies on two basic laws. The law of mass action, sometimes called the thermodynamic detailed balancing principle,

$$\frac{\prod_l [A_l]_{eq}^{\beta_l}}{\prod_k [A_k]_{eq}^{\alpha_k}} = K_{eq} \tag{1.2}$$

defines the appropriate relation between equilibrium concentrations $[A_i]_{eq}$ of initial reagents and the products of reaction (1.1) via the rate constant K_{eq} that depends solely on the equilibrium thermodynamic parameters of the system. This law is based on general physical laws of equilibrium thermodynamics; thus it is valid for any reaction system in equilibrium.

The kinetic law of mass action represents reaction (1.1) as

$$\sum_k \alpha_k A_k \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \sum_l \beta_l A_l. \tag{1.3}$$

It defines the variation rate of concentrations $[A_i]_t$ of any of A_i reagents at any instant of time, and, hence, the reaction kinetics, according to kinetic equations

$$\frac{1}{\nu_i} \partial_t [A_i]_t = -k_f \prod_k [A_k]_t^{\alpha_k} + k_r \prod_l [A_l]_t^{\beta_l}. \tag{1.4}$$

Here ∂_t denotes the derivative with respect to time, and k_f and k_r are concentration-independent rate constants of forward and reverse reactions, respectively. In formal chemical kinetics the values of these constants are either assumed to be prescribed, or treated as the fitting parameters in the consideration of experimental kinetics.

Unlike the law of mass action (1.2), the kinetic law of mass action (1.4) does not follow from general physical principles. That is why it needs substantiation. Also the recipes should be given for the determination of rate constants k_f and k_r, the values of which depend essentially on specific properties of a reacting system (the structure of reactants, their reactivity and mobility).

The kinetic coefficients k_f and k_r should satisfy the kinetic detailed balancing principle

$$\frac{k_f}{k_r} = K_{eq} \tag{1.5}$$

that is easily seen to be the consequence of laws (1.2) and (1.4). This principle relates the ratio between the kinetic characteristics (rate constants of reactions in the kinetic law of mass action (1.4)) to the equilibrium characteristic of the reacting system (equilibrium constant).

At rather low concentrations of reagents any stoichiometric reaction (1.1) is commonly a sequence of elementary (in the general case, reversible) reactions (stages) of two types [2].

Bimolecular (exchange) reactions determined by binary encounters of reactants proceed according to the scheme

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D. \tag{1.6}$$

A catalytic conversion of reactant A into reactant C is an important specific case of such an elementary reaction:

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + B. \tag{1.7}$$

Associative–dissociative reactions where the forward reaction is a recombination (or addition) one, and the reverse reaction is dissociation into two initial fragments proceed by a general scheme

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C. \tag{1.8}$$

A particular case of such a reaction is recombination of identical particles with the subsequent dissociation

$$2A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C. \tag{1.9}$$

Here we confine the discussion to elementary reversible reactions (1.7) and (1.8). For them the law of mass action (1.2) and the kinetic detailed balancing principle (1.5) are of the form

$$\frac{[C]_{\text{eq}}}{[A]_{\text{eq}}} = K_{\text{eq}} = \frac{k_f}{k_r} \tag{1.10}$$

and

$$\frac{[C]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}} = K_{\text{eq}} = \frac{k_f}{k_r} \tag{1.11}$$

respectively. In the framework of the kinetic law of mass action the kinetic equations are

$$\partial_t[A]_t = -\partial_t[C]_t = -k_f[B][A]_t + k_r[B][C]_t \tag{1.12}$$

and

$$\partial_t[A]_t = \partial_t[B]_t = -\partial_t[C]_t = -k_f[A]_t[B]_t + k_r[C]_t \tag{1.13}$$

respectively.

Substantiation of the kinetic law of mass action has been performed for the bimolecular reaction (1.6) in rarefied gases [3]. The rate constants k_f and k_r are expressed in terms of effective cross-sections of inelastic scattering from the channel AB into CD and back. It is interesting that in this case the kinetic detailed balancing principle (1.5) follows either from laws (1.2) and (1.4) or from time inversion symmetry [4].

If by a reaction is meant any physico-chemical process of quantum state variation, not only the process accompanied by molecular structure rearrangement, then the deviation from the kinetic law of mass action in rarefied gases has already been taken into account in pressure broadening and dephasing theories [3]. Such deviations manifest themselves as the dependence of the rate constant on time at initial times comparable to the collision time. They affect the Lorentzian wings of the pressure broadened centre of spectral lines. In terms of chemical kinetics this centre corresponds to the kinetic law of mass action. Theories based on this law are called Markovian, while those taking account of the time dependence of the rate constant are called non-Markovian. We shall use this terminology in considering chemical reaction kinetics.

As for the reaction $A + B \rightleftharpoons C$, the forward reaction in gases is only possible in conditions of impact or radiation stabilization. Impact stabilization is caused by collisions with a foreign gas, and radiation stabilization by the spontaneous deactivation of excited states. Compliance

with the kinetic law of mass action calls for maintenance of thermal equilibrium in the process of dissociation.

Though dilute solutions resemble a 'gas' of reactants residing in a chemically inert solvent, reactions in them can proceed differently than in gases. With rare exception [5, 6], a solvent is treated as a continual medium. On the one hand, the interaction with the medium simplifies the quantum dynamics (including the rotational one) of an elementary event of chemical conversion. In particular, it ensures stabilization in reaction (1.8) or reaction (1.9) and forms the rate $w(q)$ of the elementary event. The coordinate q of the configuration space involves the relative-position vector $\vec{r}$, orientation angles of reactants, and internal degrees of freedom (for example, vibration, spin, etc). In principle, the rate of the elementary event of reaction (1.6) depends on four coordinates, and that of reaction (1.8) on three coordinates. It also allows for the change in the coordinates of initial reactants under chemical conversion into products [7]. However, in most traditional theories variation of coordinates is neglected, and the rate w is taken to depend solely on the configuration space coordinates of the initial reactants. In the present contribution we shall primarily restrict ourselves to this approximation. Calculation of the elementary rate is a separate problem of elementary event theories [8, 9]. In developing the kinetic theory of reactions influenced by reactant mobility, the rates $w(q)$ are considered to be given. On the other hand, due to the 'cage' effect the medium complicates the kinematics of collision (among other things, breaking time inversion symmetry) which in this case is the encounter of reactants consisting of re-contacts [10]. This effect (arising in continual consideration of the medium in the case of stochastic motion of reactants) is responsible for long-term space correlations. It complicates the notion of pair encounters that can only be identified in considering the evolution of the Gibbs many-particle ensemble of reactants. Thus the derivation of kinetic equations of chemical reactions in solutions calls for the examination of many-particle reacting systems, i.e., systems with all reactants placed in a continual chemically inert medium.

2. A many-particle approach to the derivation of kinetic equations of chemical reactions in liquid solutions in the framework of superposition decoupling

2.1. Superposition decoupling for the reaction $A + B \rightarrow C + B$

The many-particle approach to the consideration of irreversible reactions $A + B \rightarrow$ product in liquid solutions based on hierarchy closure for reduced distribution functions (RDFs) was first applied by Waite [11, 12] to spatially uniform systems of spherical particles reacting at the contact. Waite realized that, unlike the case with rarefied gases, the derivation of kinetic equations for dilute solutions requires that not only pair distribution functions be considered. In the most general statement taking into account the dependence of the rate $w_{AB}(q)$ of the elementary event on the coordinate q, the lowest RDF hierarchies in a uniform system are as follows:

$$\partial_t [A]_t = -\mathcal{P}_{AB}(t) = -\int w_{AB}(q) f_{AB}(q, t) \, \mathrm{d}q \tag{2.1}$$

where $f_{AB}(q, t)$ is a two-particle RDF in the thermodynamic limit, and

$$\partial_t f_{AB}(q, t) = (\hat{\mathcal{L}}_{AB}(q) - w_{AB}(q)) f_{AB}(q, t) - \int w_{AB'}(q') f_{ABB'}(q, q', t) \, \mathrm{d}q'. \tag{2.2}$$

Here $q = B - A$ and $q' = B' - A$ are relative coordinates (A, B and B' are the coordinates of A, B and B' particles, respectively), and $f_{ABB'}(A, B, B', t) \equiv f_{ABB'}(q, q', t)$ is a three-particle RDF. The functional operator $\hat{\mathcal{L}}_{AB}$ defines the stochastic relative motion of reactants in the medium (often it corresponds to continual diffusion).

4

In the framework of simple superposition decoupling [12] (the analogue of the Kirkwood superposition decoupling in the liquid theory [13]), it is assumed that

$$f_{ABB'}(q, q', t) = \frac{f_{AB}(q, t) f_{AB'}(q', t)}{[A]_t}.$$ (2.3)

This leads to the closure of the equation for the two-particle RDF

$$\partial_t f_{AB}(q, t) = (\hat{\mathcal{L}}_{AB}(q) - w_{AB}(q)) f_{AB}(q, t) - \frac{\mathcal{P}_{AB}(t)}{[A]_t} f_{AB}(q, t)$$ (2.4)

with the initial condition of correlation absence

$$f_{AB}(q; 0) = [A]_0 [B].$$ (2.5)

This equation corresponds to the following physical picture of the bulk reaction course. Any pair of relatively mobile reactants $A + B$ enters into the reaction at the rate $w_{AB}(q)$, and the other B reactants in solution play the role of some uncorrelated 'background'. They bring about the reaction of A particles proceeding at the rate $\mathcal{P}_{AB}(t)/[A]_t$.

Introducing a new pair distribution function $n_{AB}(q, t)$,

$$f_{AB}(q, t) = n_{AB}(q, t)[A]_t [B]$$ (2.6)

brings kinetic equation (2.1) to a regular form similar to the kinetic law of mass action:

$$\partial_t [A]_t = -K_{AB}(t) [A]_t [B].$$ (2.7)

As expected, here the reaction rate constant

$$K_{AB}(t) = \int w_{AB}(q) n_{AB}(q, t) \, dq$$ (2.8)

does not depend on the concentrations of reactants, but depends on time (the non-Markovian rate 'constant'). The pair distribution function $n_{AB}(q, t)$ satisfies the equation

$$\partial_t n_{AB}(q, t) = (\hat{\mathcal{L}}_{AB}(q) - w_{AB}(q)) n_{AB}(q, t) \qquad n_{AB}(q, 0) = 1.$$ (2.9)

Unlike equation (2.4), it describes the evolution of an isolated pair $A + B$. Note that equations (2.7), (2.8) and (2.9) are the exact solution of the many-particle problem for the model of the reaction between immobile A reactant and mobile point (uncorrelated) B reactants [14–16].

2.2. The model of spheres reacting at the contact

For the model of diffusing spheres reacting at the contact

$$w_{AB}(r) = k_f^0 \frac{\delta(r - R)}{4\pi r R}; \qquad \hat{\mathcal{L}}_{AB}(r) = D \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}$$ (2.10)

where $k_f^0 = 4\pi \int_{R-0}^{\infty} w_{AB}(r) r^2 \, dr$ is the reaction constant (intrinsic constant), $R = R_A + R_B$ is the sum of van der Waals radii, and $D = D_A + D_B$ is the relative diffusion coefficient. In this case the solution of equation (2.9) can be found at $w_{AB} \equiv 0$ under the radiation boundary condition, making allowance for the course of the reaction at the contact of reactants [17].

For an absolutely absorbing ('black') sphere, $k_f^0 \rightarrow \infty$, we obtain the Smoluchowski result [18]

$$K_{AB}(t) = 4\pi R D \left(1 + \frac{R}{\sqrt{\pi D t}}\right)$$ (2.11)

derived by a simple physical approach. As is generally taken, the time dependence of the rate constant corresponds to the initial stage (transient) of the establishment of a quasi-stationary profile of concentrations (non-stationary diffusion). On completion of the transient

($t \gg \tau_e = \tau_D = R^2/D$) the non-Markovian rate constant (2.11) reaches its Markovian limit (equal to diffusion constant)

$$k_f = \lim_{t \to \infty} K_{AB}(t) = k_D = 4\pi R D \qquad (2.12)$$

that corresponds to the kinetic law of mass action.

For a partially absorbing ('grey') sphere we have [17]

$$K_{AB}(t) = \frac{k_f^0 k_D}{k_f^0 + k_D} \left\{ 1 + \frac{k_f^0}{k_D} \exp\left[\left(\frac{k_f^0 + k_D}{k_D} \right)^2 \frac{t}{\tau_D} \right] \mathrm{erfc}\left(\frac{k_f^0 + k_D}{k_D} \sqrt{\frac{t}{\tau_D}} \right) \right\} \qquad (2.13)$$

where $\mathrm{erfc}(x)$ is a complementary error function [19]. In the expression for the Markovian rate constant

$$k_f = \lim_{t \to \infty} K_{AB}(t) = \frac{k_f^0 k_D}{k_f^0 + k_D} \qquad (2.14)$$

two limiting reaction regimes can be distinguished: the kinetic regime at $k_f^0 \ll k_D$ when $k_f \approx k_f^0$, and the diffusion-controlled one, $k_D \ll k_f^0$ when $k_f \approx k_D$ (see equation (2.12)).

Note (compare equations (2.11) and (2.13)) that at the transient the time dependence of the non-Markovian rate constant depends noticeably on the model under consideration (structure and reactivity of reactants).

2.3. Demerits of the superposition approximation

Simple superposition decoupling (2.3) is a specific case of superposition decoupling. It corresponds to the absence of correlations between B reactants. General superposition decoupling was also employed in studies of chemical reactions in liquid solutions [20, 21]. However, when applied to non-uniform irreversibly reacting systems, it gave results that were inconsistent with physical considerations [22]. Application to reversibly reacting systems [23] led to kinetic equations that were difficult to interpret. The reversible reaction kinetics calculated by these equations for model systems failed to coincide with that obtained by numerical simulation [24, 25]. This approximation was criticized in a number of papers [22, 26, 27]. In the late 1980s considerable interest was aroused in many-particle methods for the derivation of kinetic equations. Apart from the existing simple encounter theory [28] and integral encounter theory (IET) [29] and reversible energy transfer kinetics calculated on their basis [28, 30], other techniques were proposed, such as system-size expansion [31], statistical non-equilibrium thermodynamic theory [32], kinetic theory of reactions in liquids [6], modified encounter theory [33–35], etc. However, all these theories were concerned with simple specific models of reactants and their mobility and were limited to uniform reacting systems involving elementary reactions only. Consistent consideration of force interactions between reactants and examination of multistage reactions also present difficulties.

The method based on adapting the Balescu approaches of non-equilibrium statistical mechanics [36] and non-stationary quantum scattering theory [4] to reacting systems placed in an inert continual medium proved to be the most promising technique of treating many-particle reacting systems. On this basis a new method for the derivation of binary non-Markovian kinetic equations for a wide class of chemical reactions in liquid solutions has been developed [22], and new universal kinetic laws of their course have been established [37–40]. The irreversible chemical reaction $A + B \rightarrow C + B$ and reversible chemical reactions $A + B \rightleftarrows C + B$ and $A + B \rightleftarrows C$ serve as examples (see sections 3–6).

3. A new many-particle method for the derivation of binary non-Markovian kinetic equations of chemical reactions in liquid solutions

3.1. Correlation patterns

Adaptation of non-equilibrium statistical mechanics and quantum non-stationary scattering theory methods is necessary, since in the reacting systems under study the motion of reactants is of random walk character, unlike the case with gases where it is dynamic. In particular, time inversion symmetry is broken. The adaptation has made it possible to derive the kinetic equation of integro-differential form [41] typical of non-equilibrium statistical mechanics [36, 42–44] for the irreversible reaction $A + B \rightarrow C + B$. The kernel (memory function) was represented as a sum which was summarized using the diagram technique. The diagrams are to be kept in the binary approximation at small density parameters

$$\xi_i = \tfrac{4}{3}\pi R_{\mathrm{eff}}^3 [A_i] \qquad (i = 1, 2) \tag{3.1}$$

where $[A_i]$ is the ith reagent concentration (in our case $[A_1] = [A], [A_2] = [B]$). The necessary diagrams were chosen by a scaling procedure corresponding to infinite dilution of the solution with increasing timescale [41, 45].

Based on the analysis of the selected diagrams a universal many-particle method for the derivation of binary non-Markovian kinetic equations for a wide class of reactions was devised [22]. The method consists of six steps. The first step is the construction of hierarchies for the RDF (see, e.g., equations (2.1) and (2.2)) in the thermodynamic limit. The second step is passing to hierarchies for correlation patterns, e.g.,

$$f_{AB}(q, t) = [A]_t [B] + \pi_{AB}(q, t) \tag{3.2}$$

in view of correlation loss rules

$$\pi_{AB}(q, t) \xrightarrow[r=|\vec{r}|\to\infty]{} 0. \tag{3.3}$$

Neglecting correlation of B particles ($\pi_{BB} \equiv 0$), we have for the three-particle RDF

$$f_{ABB'}(q, q', t) = [A]_t [B]^2 + \pi_{AB}(q, t)[B] + \pi_{AB'}(q', t)[B] + \pi_{ABB'}(q, q', t). \tag{3.4}$$

Originally reactants were treated as point particles (with a long-range reactivity), i.e., the force interactions of reactants were ignored. This corresponds to making allowance for chemical space correlations only. Force interaction were taken into account after derivation of binary kinetic equations by incorporating them in the reacting pair evolution. However, simultaneous accumulation of chemical and force space correlations on the level of the many-particle problem statement can easily be taken into consideration. This can be done by representing the motion operator $\hat{\mathcal{L}}_{AB}(q)$ as a sum of the motion operator of point particles and the operator involving the force interaction. In operator formulation of the problem (see section 3.3) the second operator can be considered on equal terms with the reaction interaction. For simplicity in this contribution we shall restrict ourselves to the first approach, and the coordinate q will denote space coordinates.

3.2. The integral encounter theory (IET)

The third step in the derivation of kinetic equations is the development of the integral encounter theory (IET) making allowance for pair correlations only. Substitution of equations (3.2) and (3.4) in equations (2.1) and (2.2) neglecting any three-particle correlations gives for the reaction $A + B \rightarrow C + B$

$$\partial_t [A]_t = -\int w_{AB}(q)([A]_t[B] + \pi_{AB}(q, t))\,\mathrm{d}q \tag{3.5}$$

$$(\partial_t - \hat{\mathcal{L}}_{AB}(q) + w_{AB}(q))\pi_{AB}(q, t) = -w_{AB}(q)[A]_t[B]. \tag{3.6}$$

The solution of equation (3.6) is easily found by taking the Laplace transform (denoted by the upper index L) of time. We have (s is the Laplace variable)

$$(s - \hat{\mathcal{L}}_{AB}(q) + w_{AB}(q)) \, \pi_{AB}^{L}(q, s) = -w_{AB}(q)[A]_s^{L}[B]. \tag{3.7}$$

We introduce a spatial Green's function

$$(s - \hat{\mathcal{L}}_{AB}(q) + w_{AB}(q)) \, g_{AB}^{L}(q, q', s) = \delta(q - q'), \tag{3.8}$$

where $\delta(q - q')$ is the Dirac delta function. In the timescale equation (3.8) takes the form

$$(\partial_t - \hat{\mathcal{L}}_{AB}(q) + w_{AB}(q)) g_{AB}(q, q', t) = 0 \qquad g_{AB}(q, q', 0) = \delta(q - q'). \tag{3.9}$$

It follows that $g_{AB}(q, q', t)$ is a conditional survival probability of an A particle at the point q at the instant of time t provided that at the initial instant of time $t = 0$ it was at the point q'. Comparison of equations (3.9) and (2.9) shows

$$n_{AB}(q, t) = \int g_{AB}(q, q', t) \, \mathrm{d}q'. \tag{3.10}$$

Using Green's function $g_{AB}^{L}(q, q', s)$ in the solution of inhomogeneous equation (3.7) and substituting this solution in equation (3.5) for the Laplace transforms, we have

$$s \, [A]_s^{L} - [A]_0 = -[B] \, \Sigma_e^{L}(s) \, [A]_s^{L}, \tag{3.11}$$

where the quantity

$$\Sigma_e^{L}(s) = -\int \int t_{AB}^{L}(q, q', s) \, \mathrm{d}q \, \mathrm{d}q' \tag{3.12}$$

is expressed in terms of the T-matrix

$$t_{AB}^{L}(q, q', s) = -w_{AB}(q) \, \delta(q - q') + w_{AB}(q) \, g_{AB}^{L}(q, q', s) \, w_{AB}(q'), \tag{3.13}$$

which is the analogue of the T-matrix of non-stationary scattering theory [4].

3.3. Operator representation

At the first glance, equation (3.11) written in the timescale is an integro-differential convolution-type equation with the kernel (the memory function) defined by its Laplace transform (3.12). However, the quantities introduced by equations (3.12) and (3.13) are not the Laplace transform of a regular time function, since they do not satisfy the necessary property of tending to zero at $\mathrm{Re}\, s \to \infty$ [19]. This property is inherent in mathematical objects of non-stationary scattering theory. To avoid such difficulties and to obtain the relations between physically measured quantities and the scattering theory objects (those in the timescale included), one should introduce integral operators defined both by their kernels on an extended time interval $-\infty < t < \infty$ and by space coordinates. Extension of the time interval of the measured quantities defined at $t \geqslant 0$ to the entire time axis is performed by multiplication by the Heaviside function $\theta(t)$. Thus the defined quantities are equal to zero at $t < 0$, and coincide with initial quantities at $t > 0$. At $t = 0$ their values become indeterminate, and initial values of physical quantities appear as a source in appropriate differential equations. Such functions fall into a class of generalized functions [46].

We replace the functional operator $\hat{\mathcal{L}}_{AB}(q)$ and the elementary event rate $w_{AB}(q)$ by integral operators $\hat{\mathcal{L}}$ and $\hat{\upsilon}_f$ defined by the kernels

$$\begin{aligned} \mathcal{L}(q, t | q', t') &= \hat{\mathcal{L}}_{AB}(q)\delta(q - q') \, \delta(t - t') \\ \upsilon_f(q, t | q', t') &= -w_{AB}(q) \, \delta(q - q')\delta(t - t'). \end{aligned} \tag{3.14}$$

Instead of conditional probability $g_{AB}(q, q', t - t')$ (see equations (3.9)) we employ the integral operator $\hat{g}$ defined by the kernel

$$g(q, t | q', t') = \theta(t - t') g_{AB}(q, q', t - t'). \tag{3.15}$$

Using equations (3.9) and $\partial_t \theta(t) = \delta(t)$ for the operator $\hat{g}$ gives the operator equation

$$(\partial_t - \hat{\mathcal{L}} - \hat{v}_f)\hat{g} = \hat{I}, \tag{3.16}$$

where $\hat{I}$ is a unit operator with the kernel

$$I(q, t | q', t') = \delta(t - t')\delta(q - q'). \tag{3.17}$$

The operator $\hat{g}$ is the analogue of the non-stationary scattering theory propagator [4, 37]. The free propagator $\hat{g}_0$ corresponds to $\hat{v}_f \equiv 0$ in equation (3.16) and

$$(\partial_t - \hat{\mathcal{L}})\hat{g}_0 = \hat{I}. \tag{3.18}$$

Obviously there is a relation between the propagators [4, 33],

$$\hat{g} = \hat{g}_0 + \hat{g}_0 \hat{v}_f \hat{g} = \hat{g}_0 + \hat{g} \hat{v}_f \hat{g}_0. \tag{3.19}$$

The expression for the T-operator is

$$\hat{t}_f = \hat{v}_f + \hat{v}_f \hat{g} \, \hat{v}_f. \tag{3.20}$$

Operator representations (3.19) and (3.20) easily give important relations

$$\hat{v}_f \, \hat{g} = \hat{t}_f \, \hat{g}_0; \qquad \hat{g} \, \hat{v}_f = \hat{g}_0 \, \hat{t}_f. \tag{3.21}$$

They serve to obtain closed equations for the T-operator from equation (3.20),

$$\hat{t}_f = \hat{v}_f + \hat{v}_f \hat{g}_0 \hat{t}_f = \hat{v}_f + \hat{t}_f \hat{g}_0 \, \hat{v}_f, \tag{3.22}$$

as well as the propagator representation via free propagator and T-operator from equation (3.19),

$$\hat{g} = \hat{g}_0 + \hat{g}_0 \hat{t}_f \hat{g}_0. \tag{3.23}$$

According to equations (3.14) and (3.15), the T-operator kernel depends on the time difference

$$\begin{aligned}
t_f(q, t - t' | q', 0) = {} & -w_{AB}(q)\, \delta(q - q')\, \delta(t - t') \\
& + w_{AB}(q)\, \theta(t - t') g_{AB}(q, q', t - t')\, w_{AB}(q').
\end{aligned} \tag{3.24}$$

Taking the Laplace transform of equation (3.24) within a class of generalized functions of $t - t'$ (generalized Laplace transformation [46]), we obtain equation (3.13). Note that the generalized Laplace transform calls for no restrictions at $\mathrm{Re}\, s \to \infty$ [46]. Besides, the generalized Laplace transformation of the derivative of the generalized function with respect to time corresponds just to multiplication of its generalized Laplace transform by s [46].

The Laplace transform (3.13) of the kernel can be treated as the kernel of the integral T-operator $\hat{t}_f^{\mathrm{L}}(s)$ defined in the coordinate space and depending parametrically on the Laplace variable s. Similarly, one can consider operators $\hat{\mathcal{L}}^{\mathrm{L}}$, $\hat{v}_f^{\mathrm{L}}$ and $\hat{I}^{\mathrm{L}}$ (with the kernels independent of s due to equations (3.14) and (3.17)) instead of operators $\hat{\mathcal{L}}$, $\hat{v}_f$ and $\hat{I}$, and resolvent operator $\hat{g}^{\mathrm{L}}(s)$ and free resolvent operator $\hat{g}_0^{\mathrm{L}}(s)$ instead of propagators $\hat{g}$ and $\hat{g}_0$. According to equations (3.16) and (3.18), these operators satisfy the equations

$$(s - \hat{\mathcal{L}}^{\mathrm{L}} - \hat{v}_f^{\mathrm{L}})\hat{g}^{\mathrm{L}}(s) = \hat{I}^{\mathrm{L}}; \qquad (s - \hat{\mathcal{L}}^{\mathrm{L}})\hat{g}_0^{\mathrm{L}}(s) = \hat{I}^{\mathrm{L}}. \tag{3.25}$$

For all these operators, relations of (3.19)–(3.23) type hold for any value of s. There are also relations for operator values at two different values of s [37].

Taking the Dirac designations of coordinate functions, we have for the memory function (3.12)

$$\Sigma_e(t - t') = -\langle 1|t_f|1\rangle; \qquad \Sigma_e^L(s) = -\langle 1|t_f^L(s)|1\rangle. \tag{3.26}$$

Using the stationarity condition for the propagator $\hat{g}_0$ [37], we easily find

$$\partial_t \langle 1|\text{kel}\,(\hat{t}_f \hat{g}_0)|1\rangle = \langle 1|t_f|1\rangle \tag{3.27}$$

where $\text{kel}(\cdots)$ means the kernel of the operator between brackets. In view of equations (3.26), (3.21), (3.14), (3.15), (3.10), and (2.8), this gives the relation between the IET kernel and the reaction rate constant (2.8) of the superposition decoupling considered on an extended time axis

$$K_f(t) = \theta(t)\,K_{AB}(t) \tag{3.28}$$

i.e.,

$$\Sigma_e = \partial_t\,K_f(t); \qquad \int_{-0}^{t} \Sigma_e(\tau)\,\mathrm{d}\tau = K_f(t). \tag{3.29}$$

By virtue of equation (2.12) or equation (2.14) at $t \to \infty$, the second relation gives the definition of the Markovian rate constant in terms of the IET kernel

$$k_f = \int_{-0}^{\infty} \Sigma_e(\tau)\,\mathrm{d}\tau \;\equiv\; \Sigma_e^L(0). \tag{3.30}$$

The IET kinetic equation (3.11) is now written within the extended time interval

$$\partial_t[A]_t = \delta(t)\,[A]_0 - [B]\int_{-0}^{t} \Sigma_e(\tau)\,[A]_{t-\tau}\,\mathrm{d}\tau. \tag{3.31}$$

Thus passing from equation (3.11) to equation (3.31) called for using a class of generalized functions.

3.4. Effective pairs approximation (EPA) and modified encounter theory (MET)

The IET binary kinetic equation (3.31) takes account of pair correlations only and has a restricted time range of applicability [33]. To extend this interval, it is necessary to retain three-particle correlations, just as in equation (2.2). Substituting equations (3.2) and (3.4) in equation (2.2) with allowance for equation (2.1) yields

$$(\partial_t - \hat{\mathcal{L}}_{AB}(q) + w_{AB}(q))\pi_{AB}(q, t) = -w_{AB}(q)[A]_t[B]$$
$$- \int w_{AB'}(q')\,\mathrm{d}q'\,[B]\pi_{AB}(q, t) - \int w_{AB'}(q')\,\mathrm{d}q'\,\pi_{ABB'}(q, q', t). \tag{3.32}$$

However, instead of superposition decoupling of the form $\pi_{ABB'}$, its evolution is considered neglecting the influence of all four-particle correlations. In calculating the evolution of the system of three reactants $(A + B + B')$ the analogue of the Faddeev procedure from three-body quantum theory is employed [47]. It consists in extracting pair channels such that in each of the channels the reaction proceeds with only one of the B reactants, while the other moves independently. The essence of the approximation is neglecting the interference of channels [22]. Besides, an approximation of point encounters is used that consists in neglecting the size of the reaction zone at macroscopic distances of the pair evolution [41, 45]. As a result, equation (3.32) gives the so-called effective pairs approximation (EPA) that is the fourth step in the development of the theory.

In operator form the desired equation is

$$(\partial_t - \hat{\mathcal{L}} - \hat{\upsilon}_f)\pi_{AB}(q, t) = \hat{\upsilon}_f[A]_t[B] - k_f[B]\,\pi_{AB}(q, t), \tag{3.33}$$

where k_f is the Markovian rate constant defined by equation (3.30) in terms of the IET kernel.

To make the essence of the approximation more clear, we turn to equation (2.4) of superposition decoupling. In principle, the last term on the right-hand side describes the interaction of three particles (in the pair $A + B$ and with some B' particle of the 'background'). Assuming that in the reaction with B' the B reactant of the pair is rather far removed from A, owing to equation (3.3) $f_{AB}(q, t) \approx [A]_t [B]$ in this term, and equation (2.4) is identically transformed into equation (3.6) of the IET. Making allowance for accumulation of correlations in the pair $A + B$ ($\frac{\mathcal{P}_{AB}(t)}{[A]_t} \pi_{AB}(q, t) \neq 0$), it should be taken that interaction with the 'background' proceeds in a quasi-stationary regime, and (see equations (2.1), (2.6), (2.8), and (2.12) or (2.14))

$$\lim_{t \to \infty} \frac{\mathcal{P}_{AB}(t)}{[A]_t} = k_f [B]. \tag{3.34}$$

Unfortunately, such an interpretation of channel extraction is valid solely for the irreversible reaction $A + B \to C + B$. In more complicated reactions, including reversible ones, superposition decoupling is inapplicable. It does not reduce to EPA which becomes the only basis for the derivation of binary non-Markovian kinetic equations.

In the case of the irreversible reaction $A + B \to C + B$ equation (3.33) describes the evolution of one 'effective' pair. Thus the fifth step can easily be made in the development of the theory: construction of a binary modified encounter theory (MET) that is completely equivalent to EPA. Indeed, solving equation (3.33) in the same way as in the case with the IET, we obtain the integro-differential equation of (3.31) type from equation (3.5) [22]:

$$\partial_t [A]_t = \delta(t)[A]_0 - [B] \int_{-0}^{t} \Sigma_b(\tau)[A]_{t-\tau} \, d\tau, \tag{3.35}$$

where the kernel (MET memory function) is

$$\Sigma_b(t) = \Sigma_e(t) \exp(-k_f [B]t); \qquad \Sigma_b^L(s) = \Sigma_e^L(s + k_f [B]) \tag{3.36}$$

i.e., it is a modification of the IET kernel with the use of the Markovian rate constant k_f defined by the IET kernel itself (see equation (3.30)) [35]. In view of equation (3.30) it is seen that the Markovian rate constant is defined by the root $s = -k_f [B]$ of the expression $[B]\Sigma_b^L(s) + s$ [48].

3.5. Regular form (RF) of binary non-Markovian kinetic equations

The MET kinetic equation (3.35) has a form typical of equations of non-equilibrium statistical mechanics [36, 42–44] and general kinetic theory of reactions in liquids [5]. However, from the standpoint of chemical kinetics and binary equations in general, it has a demerit, namely, the dependence of the kinetic coefficient (memory function (3.36)) on the initial concentration. However, this equation can be brought to a regular form of rate equation (2.7) using the rule of time shift,

$$[A]_{t-\tau} = \exp\left([B] \int_{t-\tau}^{t} K_{AB}(\tau) \, d\tau \right) [A]_t \approx \exp(k_f [B]\tau) \, [A]_t. \tag{3.37}$$

This is a final sixth step in the construction of the binary theory. In the binary approximation in equation (3.37) the kinetics of the concentration rise in the interval $[t - \tau, t]$ is replaced by the Markovian one. Using equation (3.37) in equation (3.35) with allowance for equations (3.36) and (3.29), we have the kinetic equation

$$\partial_t [A]_t = \delta(t)[A]_0 - K_f(t)[B][A]_t. \tag{3.38}$$

It coincides with equation (2.7) on an ordinary time interval in view of equation (3.28). Reducing equation (3.35) to equation (3.37) is possible within the binary interval [33]

$$t \ll \{k_f [B]\xi\}^{-1} \tag{3.39}$$

where ξ is the largest of the density parameters (3.1). A limited character of the binary interval follows at least from the fact that at rather long times the so-called fluctuation asymptote is realized [49–51] which cannot be achieved in the framework of the binary approximation.

Though for the irreversible reaction $A + B \rightarrow C + B$ reproduction of the kinetic equation (2.7) of the superposition approximation calls for a sequence of steps, its evident advantage is the ability to cover a wide class of chemical reactions. Another advantage is the expression of the reaction rate constant $K_f(t)$ in terms of a T-matrix. This allows one to deduce a new universal law of $K(t)$ behaviour and attainment of equilibrium.

Indeed, the binary theory describes the behaviour of dilute systems where the characteristic time of the kinetics significantly exceeds the average encounter time. So a timescale can be chosen where the encounter duration can be neglected ($\tau_e \rightarrow 0$). In gases this corresponds to an impact collision theory (Markovian) that completely ignores the non-Markovian kinetics [3, 52]. However, in liquid solutions one should be more careful [39]. This is because the statistical distribution of encounter times in solutions differs considerably from that of collision times in gases [53]. In any case the approximation is based on the idea that the effective size of reacting particles is negligibly small as compared to the average distance between them (point encounter approximation). However, since the frequency of encounters is proportional to the effective size of reactants, mathematical formulation of the idea can rely solely on the scaling procedure which can be applied to the T-matrix only and gives [39]

$$t_f(q, t|q', 0) = -k_f \left(\delta(t) + \frac{k_f}{4(\pi \bar{D})^{3/2}} \partial_t \frac{\theta(t)}{\sqrt{t}} \right) \delta(q) \delta(q'). \tag{3.40}$$

Using equation (3.40) in equations (3.26) and (3.29) we have

$$K_f(t) = \theta(t) k_f \left(1 + \frac{k_f}{4\pi \bar{D} \sqrt{\pi \bar{D} t}} \right), \tag{3.41}$$

where $\bar{D}$ is a relative macro-diffusion coefficient. Employing formal identification

$$k_f = 4\pi \bar{D} R_{\text{eff}} \tag{3.42}$$

where R_{eff} is the radius of some effective sphere we obtain the expression formally coinciding ($t > 0$) with the Smoluchowski result (2.11) (with $D = \bar{D}$ and $R = R_{\text{eff}}$). However, our result differs essentially from the Smoluchowski one where the second term is traditionally identified with the transient. Any complication of the model (see, e.g., equation (2.13)) affects this term, as must be the case for the transient. In point encounter approximation the transient is neglected; thus the non-Markovian correction is universal, i.e., independent of the specific structure of the reactants and the nature of their microscopic mobility. It depends only on macro-observables k_f and $\bar{D}$. That is why formal 'microscopic' identification (3.42) is rather artificial and has a meaning only for formal representation of the effective sphere [54]. So any non-Markovian correction describing the transient in the end is transformed into a universal non-Markovian correction preserved on macro-times and going through the whole kinetics. In view of equation (3.41), the reaction kinetics is

$$[A]_t = [A]_0 \exp \left(-2[B] \frac{k_f^2}{4(\pi \bar{D})^{3/2}} \sqrt{t} \right) \exp(-k_f[B]t) \tag{3.43}$$

i.e., it is defined by two exponential factors. The second factor corresponds to pure exponential kinetics of the law of mass action, while the first one can be considered as a pre-exponential factor corresponding to the non-Markovian correction to the kinetics. Strictly speaking, pure exponential kinetics never takes place even as a long-term asymptote. This means that the non-Markovian correction permeates the kinetics and is the more important, the longer the time t. Realizing this fact allows us to understand why appropriate fitting of the non-stationary

(non-Markovian), not quasi-stationary (Markovian), kinetics is needed for the interpretation of experimental data on fluorescence quenching by diffusion assisted electron transfer [55] even at very low concentration of quenchers, when the transient of the kinetics is extremely short.

Nevertheless, after the transient stage the kinetic law of mass action is valid within a bounded time interval with a rather high accuracy [40]. To see this, we introduce the reduced macroscopic time

$$\tau = k_f[B]t. \tag{3.44}$$

Then we have from equation (3.43)

$$[A]_\tau = [A]_0 \exp\left(-2\sqrt{\frac{3\xi\tau}{\pi}}\right) \exp(-\tau) \tag{3.45}$$

where $\xi = \frac{4}{3}\pi R^3_{\text{eff}}[B]$ is one of the density parameters (3.1). Since the parameter is assumed to be rather small, the kinetic law of mass action is a good approximation if

$$\tau \ll \frac{1}{\sqrt{\xi}} \qquad \text{or} \qquad t \ll \left(k_f[B]\sqrt{\xi}\right)^{-1}. \tag{3.46}$$

The non-Markovian correction to the kinetics is fairly small, though it increases on the approach to boundary (3.39) of the binary interval.

4. Unimolecular–bimolecular reversible reaction $A + B \rightleftarrows C$

This reaction is of interest both from the standpoint of the development of modern binary non-Markovian theory of elementary reactions in solutions, and from the point of view of experiments in physical chemistry and biology. The well-known examples of such reactions are reversible recombination of impurities in crystals [56], monomer–eximer kinetics in solutions [57–60], reversible mechanisms in enzyme catalysis [61], and excited-state proton transfer [62].

4.1. IET kinetic equations

As in section 3, we shall deal with uniform reacting systems. The sequence of the above-mentioned steps enables one (at the third step) to derive IET equations that are the generalization to the case of the presence of association (forward irreversible reaction) and dissociation of isolated C molecules into two fragments [63],

$$\partial_t[A]_t - \delta(t)[A]_0 = \partial_t[B]_t - \delta(t)[B]_0 = -\partial_t[C]_t + \delta(t)[C]_0$$
$$= -\int_{-0}^{t} \Sigma_f^e(\tau)[A]_{t-\tau}[B]_{t-\tau}\,d\tau + \int_{-0}^{t} \Sigma_r^e(\tau)\,[C]_{t-\tau}\,d\tau. \tag{4.1}$$

Here $\Sigma_f^e(\tau)$ is the association memory function coinciding with that considered in section 3 (see equations (3.26) and (3.20)) and satisfying relations (3.29) and (3.30). The dissociation memory function is defined similarly to equation (3.26)

$$\Sigma_r(t - t') = -\langle 1|t_d|1\rangle \tag{4.2}$$

in terms of the dissociation T-operator [63, 64]

$$\hat{t}_d = \hat{v}_d + \hat{v}_f\hat{g}\hat{v}_d, \tag{4.3}$$

where $\hat{g}$ is the forward reaction propagator defined by equation (3.16). The dissociation operator $\hat{v}_d$ is defined by analogy with the operator $\hat{v}_f$ in terms of the kernel

$$v_d(q, t|q', t') = -w_C(q)\delta(q - q')\delta(t - t'). \tag{4.4}$$

Here $w_C(q)$ is the rate of dissociation into two fragments, the relative position of which is characterized by the coordinate q. Equations (3.19) and (4.3) give the relation similar to the second equation (3.21),

$$\hat{g}\hat{v}_d = \hat{g}_0\,\hat{t}_d. \tag{4.5}$$

From equation (4.3) we have a closed equation for the operator $\hat{t}_d$,

$$\hat{t}_d = \hat{v}_d + \hat{v}_f\hat{g}_0\hat{t}_d. \tag{4.6}$$

The equation conjugate to (4.6), the analogue of the second equation (3.22), follows from the first relation (3.21) and equation (4.3),

$$\hat{t}_d = \hat{v}_d + \hat{t}_f\hat{g}_0\hat{v}_d, \tag{4.7}$$

and specifies just the relation between dissociation and association T-operators. In connection with this, the physical meaning of the association T-operator differs essentially from that of the dissociation T-operator. According to equation (3.23), the association T-operator is based on the concepts of the scattering theory (encounter of reactants A and B in solution) [64]. The dissociation T-operator describes the evolution of the reaction pair arisen not from the encounter but from reactant C dissociation at the instant of time t' and survived by the moment t. The survival probability $\Omega_{t-t'}$ (considered as the kernel of the operator $\hat{\Omega}_{t-t'}$ in the time space) of such a geminate pair satisfies the operator relation [64]

$$\partial_t\hat{\Omega}_{t-t'} = \langle 1|\hat{I} + \hat{v}_f\hat{g}|\varphi(q)\rangle = \langle 1|\hat{I} + \hat{t}_f\hat{g}_0|\varphi(q)\rangle, \tag{4.8}$$

where

$$\varphi(q) = \frac{w_C(q)}{k_r^0} \qquad k_r^0 = \int w_C(q)\,dq \tag{4.9}$$

is the $A + B$ pair distribution normalized to unity at the instant of time t' of reactant C decay. With equations (4.9) and (4.4) in equation (4.8) in view of equations (4.3) or (4.7), we obtain

$$\partial_t\Omega_{t-t'} = -\langle 1|t_d|1\rangle/k_r^0. \tag{4.10}$$

Taking account of equation (4.2), one has

$$\Sigma_r(t) = k_r^0\partial_t\Omega_t \tag{4.11}$$

i.e., dissociation is represented as an independent decay of reactant C into the pair $A + B$ at the rate k_r^0 with the subsequent recombination at the rate $\partial_t\Omega_t$. We define the Markovian dissociation rate constant similarly to equation (3.30):

$$k_r = \int_{-0}^{\infty}\Sigma_r(\tau)\,d\tau \equiv \Sigma_r^{\mathrm{L}}(0) = k_r^0\Omega_\infty. \tag{4.12}$$

Note that unlike the case with gases, dissociation in solutions is always connected with association, however with a low association rate. This is because of the 'cage' effect. Due to this effect complete dissociation consists of a sequence of elementary decays of reactant C with the subsequent association of fragments until molecular motion causes reactants A and B to escape from the 'cage' to the bulk [65].

The above relation is necessary for the kinetic detailed balancing principle to be valid. Unlike gases, in this case it follows not from the kinetic law of mass action but from the microscopic detailed balancing principle that is a consequence of time inversion symmetry in elementary event theories [63, 64],

$$\frac{w_{AB}(q)}{k_f^0} = \frac{w_C(q)}{k_r^0} \qquad \text{or} \qquad \frac{\hat{v}_f}{k_f^0} = \frac{\hat{v}_d}{k_r^0}. \tag{4.13}$$

Equations (3.20), (4.3) and (4.13) give the operator relation (microscopic detailed balance)

$$\frac{\hat{t}_f}{k_f^0} = \frac{\hat{t}_d}{k_r^0}. \tag{4.14}$$

In view of definitions (3.26), (4.2), (3.30) and (4.12), this gives

$$\frac{\Sigma_f(t)}{k_f^0} = \frac{\Sigma_r(t)}{k_r^0} \qquad \text{or} \qquad \frac{k_f}{k_r} = \frac{k_f^0}{k_r^0}. \tag{4.15}$$

Thus the ratio of memory functions (Markovian rate constants), each depending on A and B mobility, is equal to the ratio of mobility independent intrinsic constants. Since the reaction proceeding in the kinetic regime is described by the kinetic law of mass action, this relation is equal to the equilibrium constant

$$K_{\text{eq}} = \frac{[C]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}} \tag{4.16}$$

i.e., we have the kinetic detailed balancing principle [63, 64]

$$\frac{\Sigma_f(t)}{\Sigma_r(t)} = \frac{k_f}{k_r} = \frac{k_f^0}{k_r^0} \equiv K_{\text{eq}}. \tag{4.17}$$

Note that despite the time interval boundedness, the IET ensures the attainment of correct equilibrium concentrations by virtue of equation (4.1).

4.2. EPA, MET and regular form of binary non-Markovian kinetic equations

A knowledge of IET memory functions allows one to derive Markovian rate constants k_f and k_r from equations (3.30) and (4.12) and develop the effective pairs approximation (EPA) at the fourth step [66]. However, in contrast to the irreversible reaction $A + B \rightarrow C + B$ considered in section 3 (see equation (3.33)), in the case of the reversible reaction $A + B \rightleftarrows C$ the approximation describes interrelated evolutions of six 'effective' pairs [66]. Thus in the general case memory functions of the corresponding kinetic equations cannot be expressed in terms of IET memory functions, and such a theory is not binary, despite the smallness of density parameters (3.1). So the fifth step of the derivation of binary non-Markovian kinetic equations is needed, namely, construction of the modified encounter theory (MET). MET memory functions are modified kernels of IET kinetic equations with the use of macro-observables specified by the kernels themselves.

EPA to MET conversion depends essentially on the ratio between reactant mobility and forward and reverse reaction rates. We consider the case where the rate of dissociation significantly exceeds that of association [40, 64]:

$$k_r/k_f[B]_t \gg 1; \qquad k_r/k_f[A]_t \gg 1. \tag{4.18}$$

It corresponds to the independence of the reaction pair dynamics and collective dynamics in two-particle correlation evolution. The problem of the dynamics relationship will be studied in greater detail in section 5 with the reversible reaction $A + B \rightleftarrows C + B$ as an example.

Passing to a regular form (RF) of binary kinetic equations requires that reactant C be a rather stable chemical particle observed at 'free path' times [40, 64]

$$k_r \tau_e \ll 1 \tag{4.19}$$

where τ_e is the mean encounter time of reactants A and B. This means that the kinetic law of mass action is valid at least within the intermediate time interval after fairly short transient stage. We shall call this situation a reaction regime [67].

Taking into account that the density parameters in equation (3.1) may be represented as $\xi_i = k_f \tau_e [A_i]$ and in view of equation (4.18), conditions (3.1), (4.18) and (4.19) can be written in a unified fashion as

$$\xi_i \ll k_r \tau_e \ll 1 \qquad \text{or} \qquad \xi_i \ll K_{\text{eq}}[A_i]_t \ll 1. \tag{4.20}$$

Binary non-Markovian kinetic equations have the following regular form:

$$\partial_t [A]_t - \delta(t)[A]_0 = \partial_t [B]_t - \delta(t)[B]_0 = -\partial_t [C]_t + \delta(t)[C]_0$$
$$= -K_f(t)[A]_t [B]_t + \int_{-0}^{t} \Sigma_r(\tau)[C]_{t-\tau} \, d\tau. \tag{4.21}$$

Under conditions (4.20) the reaction proceeds by independent association and dissociation channels that may be presented by kinetic schemes [64, 68]

$$A + B \rightleftarrows A \ldots B \Rightarrow C; \qquad A + B \leftarrow A \ldots B \rightleftarrows C \tag{4.22}$$
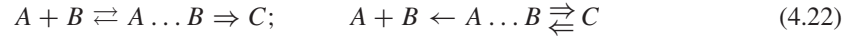
respectively. Here thin arrows correspond to the exchange between 'collision complex' pairs and free pairs in solution due to the relative motion of reactants. Thick arrows denote the elementary chemical conversion of the 'collision complex' to the reactant, or, vice versa, the elementary decay of this reactant into a pair of 'collision complex'. The radical difference between 'scattering' and decay channels is evident.

Note that the rate constants of the kinetic law of mass action calculated from these schemes at diffusion motion of reactants (quasi-stationary 'complex' concentration)

$$k_f = \frac{k_f^0 k_D}{k_f^0 + k_D}; \qquad k_r = \frac{k_r^0 k_D}{k_f^0 + k_D} \tag{4.23}$$

(k_D is defined in equation (2.12)) coincide with Markovian rate constants calculated by equations (3.30) and (4.12) for the model of hard spheres reversibly reacting at the contact.

Equations (4.21) are of 'differential' form for the association channel, i.e., the change in concentration due to association is determined by the rate constant $K_f(t)$ (see equation (3.29)). However, these equations are 'integral' for the dissociation channel, i.e., the change in concentrations due to dissociation is determined by time convolution. Although the kernel of this convolution coincides with the kernel for the decay of isolated reactant C [65], the derived equations take into account the effect of a 'competitive binding' [69], i.e., competition between bulk reactants for reactants of the pair arisen from reactant C decay. This effect appears to be included in the association channel.

The kinetic principle of detailed balancing follows from equations (4.17) and (3.29) [64],

$$\frac{\partial_t K_f(t)}{\Sigma_r(t)} = \frac{k_f}{k_r} = \frac{k_f^0}{k_r^0} = K_{\text{eq}}. \tag{4.24}$$

Taking into consideration material balance conditions

$$[A]_t - [B]_t = [A]_0 - [B]_0; \qquad [A]_t + [C]_t = [A]_0 + [C]_0;$$
$$[B]_t + [C]_t = [B]_0 + [C]_0 \tag{4.25}$$

following from equations (4.21) and (4.16), we find, in view of (4.20), equilibrium concentrations up to the first non-vanishing terms

$$[A]_{\text{eq}} \approx [A]_0 + [C]_0; \qquad [B]_{\text{eq}} \approx [B]_0 + [C]_0$$
$$[C]_{\text{eq}} \approx K_{\text{eq}}([A]_0 + [C]_0)([B]_0 + [C]_0)) \tag{4.26}$$

that identically satisfy relation (4.16).

Let us introduce the deviation from equilibrium concentrations

$$\Delta[A]_t = [A]_t - \theta(t)\,[A]_{\text{eq}}; \qquad \Delta[B]_t = [B]_t - \theta(t)\,[B]_{\text{eq}};$$
$$\Delta[C]_t = [C]_t - \theta(t)[C]_{\text{eq}}. \tag{4.27}$$

As is readily seen from equations (4.25) and the same equations at equilibrium ($t \to \infty$), they are related to one another in a simple fashion:

$$\Delta[A]_t = \Delta[B]_t = -\Delta[C]_t \equiv [\Delta]_t. \tag{4.28}$$

Then using equations (4.27), (4.28) and (4.24), we obtain from equations (4.21) the only equation for $[\Delta]_t$,

$$\partial_t[\Delta]_t = \delta(t)[\Delta]_0 - K_f(t)\{[\Delta]_t^2 + ([A]_{\text{eq}} + [B]_{\text{eq}})[\Delta]_t\} - \int_0^t \Sigma_r(t-\tau)[\Delta]_\tau \, \mathrm{d}\tau, \tag{4.29}$$

describing the attainment of equilibrium concentrations by any of the reactants. Now we establish a universal kinetic law of equilibrium attainment with the use of expression (3.41) for $K_f(t)$ on a large timescale (point encounter approximation). To derive the kernel $\Sigma_r(t)$, we need only use the kinetic principle of detailed balancing (4.24):

$$\Sigma_r(t) = \frac{k_r}{k_f}\partial_t K_f(t) = k_r\left(\delta(t) + \frac{k_f}{4(\pi\bar{D})^{3/2}}\partial_t\frac{\theta(t)}{\sqrt{t}}\right). \tag{4.30}$$

The solution of equation (4.29) can be found by the perturbation theory method considering the non-Markovian correction terms (resulting from the second (non-Markovian) terms in equations (3.41) and (4.30)) as a perturbation [40, 41].

Let us introduce the Markovian rate [40]

$$k = k_f([A]_{\text{eq}} + [B]_{\text{eq}}) + k_r \tag{4.31}$$

and a small (under condition (4.20)) dimensionless parameter [39, 40]

$$\varepsilon_r = \frac{k_f\sqrt{k_r}}{4\pi\bar{D}^{3/2}} \ll 1. \tag{4.32}$$

Then in the first-order approximation in parameters $K_{\text{eq}}[\Delta]_0$ and ε_r we have [40]

$$[\Delta]_t = [\Delta]_0\{\mathrm{e}^{-kt} - K_{\text{eq}}[\Delta]_0\mathrm{e}^{-kt}(1 - \mathrm{e}^{-kt}) + \mathcal{P}_r(t)\}, \tag{4.33}$$

where

$$\mathcal{P}_r(t) = \varepsilon_r\sqrt{\frac{k_r}{\pi k}}\left\{2\sqrt{kt}(kt-1) + (1-2kt)\int_0^t \mathrm{d}y\,\sqrt{y}\exp(y-kt)\right\} \tag{4.34}$$

that satisfies the condition

$$\int_{-0}^\infty \mathcal{P}_r(t)\,\mathrm{d}t = 0 \tag{4.35}$$

and demonstrates the following short-term ($kt \ll 1$) and long-term ($kt \gg 1$) behaviour:

$$\mathcal{P}_r(t) \underset{t\to 0}{\sim} 2\varepsilon_r\sqrt{\frac{k_r t}{\pi}} \qquad \mathcal{P}_r(t) \underset{t\to\infty}{\sim} \frac{\varepsilon_r}{\sqrt{4\pi}(kt)^{3/2}}. \tag{4.36}$$

Thus we have that the kinetics is a sum of the Markovian and non-Markovian terms. Although for irreversible association (section 3) the kinetics can be formally represented in the same fashion, the results differ radically. In the first case the universal non-Markovian correction describes the deviation from the kinetic law of mass action. In the second case the leading term of expansion in equation (4.33) is changed for another: the Markovian terms disappear with time and the non-Markovian term becomes the leading one. Thus the kinetics demonstrates a universal power law $\sim t^{-3/2}$ in contradiction to the kinetic law of mass action. Note that since

the kinetics investigated is binary, this long-term kinetics is not a well-known fluctuation one, though it has some features of the fluctuation kinetics that is commonly associated with the manifestation of macroscopic many-particle correlations in reacting systems [49].

Thus the time range of the validity of the law of mass action becomes essentially narrower than the binary interval (3.39). The correct description of the irreversible reaction $A + B \rightleftarrows C$ over the entire binary range requires that the non-Markovian corrections be taken into account even in the most rough approximation.

5. Reversible reaction $A + B \rightleftarrows C + B$

Among reversible bimolecular reactions, the reaction $A + B \rightleftarrows C + B$ is the simplest one. It makes it possible to reveal some regularities in the course of other bimolecular reversible reactions; besides, it is interesting from the standpoint of catalytic chemistry.

5.1. IET kinetic equations

As before, we shall deal with uniform reacting systems. In this case the construction of the IET may be based on the conception of 'effective' particles [70], i.e., instead of two A and C species we can consider some R particle the 'internal' states of which correspond either to A or to C reactant. Then the encounter of the R particle with reactant B 'switches on' the reaction Liouvillian that affects the populations of 'internal' states. The process resembles the course of irreversible reaction (section 3). The difference is that instead of one state population (concentration $[A]_t$), populations of two states are changed. Accordingly, a two-component column-vector of concentrations may be introduced [70, 71]:

$$[R]_t = \begin{bmatrix} [A]_t \\ [C]_t \end{bmatrix}. \tag{5.1}$$

For its variation we can write the matrix analogue of kinetic equation (3.31) [70, 71]:

$$\partial_t [R]_t = \delta(t)[R]_0 - [B] \int_{-0}^{t} \Sigma^e(\tau)[R]_{t-\tau} \, d\tau. \tag{5.2}$$

Here $\Sigma^e(\tau)$ is a matrix (2×2) memory function expressed in terms of the kernel of the matrix T-operator t similarly to equation (3.26):

$$\Sigma^e(t - t') = -\langle 1|t|1 \rangle. \tag{5.3}$$

As before, angle brackets denote integration over coordinates. Equation (3.20) assumes a matrix form,

$$\hat{t} = \hat{v} + \hat{v}\hat{g}\hat{v}, \tag{5.4}$$

just as equation (3.16) for the matrix propagator,

$$(\partial_t - \hat{\mathcal{L}} - \hat{v})\hat{g} = \hat{I}. \tag{5.5}$$

Here $\hat{I}$ is a unit matrix-integral operator defined by the matrix kernel

$$I(q, t|q', t') = \delta(q - q')\delta(t - t')E_2, \tag{5.6}$$

where E_2 is a unit matrix (2×2). The matrix functional operator $\hat{\mathcal{L}}$ specifies the relative motion in the pair $R + B$, i.e., in pairs $A + B$ and $C + B$, while the matrix reaction operator (the Liouvillian) defines the reactions in these pairs:

$$\hat{\mathcal{L}} = \begin{bmatrix} \hat{\mathcal{L}}_{AB} & 0 \\ 0 & \hat{\mathcal{L}}_{CB} \end{bmatrix}; \qquad \hat{v} = \begin{bmatrix} \hat{v}_f & -\hat{v}_r \\ -\hat{v}_f & \hat{v}_r \end{bmatrix}. \tag{5.7}$$

Here $\hat{\mathcal{L}}_{AB}$, $\hat{v}_f$ and $\hat{\mathcal{L}}_{CB}$, $\hat{v}_r$ are operators for the pairs $A + B$ and $C + B$, respectively (i.e., forward and reverse reactions), defined in accordance with equations (3.14). In view of the structure of matrix operators (5.7) and equation (5.4), we easily establish the general structure of operators $\hat{g}$ and $\hat{t}$

$$\hat{g} = \begin{bmatrix} \hat{g}_{AA} & \hat{g}_{AC} \\ \hat{g}_{CA} & \hat{g}_{CC} \end{bmatrix}; \qquad \hat{t} = \begin{bmatrix} \hat{t}_f & -\hat{t}_r \\ -\hat{t}_f & \hat{t}_r \end{bmatrix}, \tag{5.8}$$

where

$$\hat{t}_f = \hat{v}_f + \{\hat{v}_f(\hat{g}_{AA} - \hat{g}_{AC}) + \hat{v}_r(\hat{g}_{CC} - \hat{g}_{CA})\}\hat{v}_f$$
$$\hat{t}_r = \hat{v}_r + \{\hat{v}_f(\hat{g}_{AA} - \hat{g}_{AC}) + \hat{v}_r(\hat{g}_{CC} - \hat{g}_{CA})\}\hat{v}_r \tag{5.9}$$

are T-operators of forward and reverse reactions, respectively. Note that the structure of the T-operator of the forward reaction differs considerably from that (see equation (3.20)) for the irreversible reaction and forward reaction in the reaction $A + B \rightleftarrows C$. Both T-operators are similar in structure, since they describe similar scattering processes (reactions). It is essential that each of the T-operators involves both reaction operators $\hat{v}_f$ and $\hat{v}_r$.

According to equation (5.3), the matrix memory function has the same matrix structure as $\hat{t}$ (5.8), and

$$\Sigma_f^e(t - t') = -\langle 1|t_f|1\rangle; \qquad \Sigma_r^e(t - t') = -\langle 1|t_r|1\rangle. \tag{5.10}$$

Equation (5.2) gives the non-Markovian kinetic equations of the IET:

$$\partial_t[A]_t - \delta(t)[A]_0 = -\partial_t[C]_t + \delta(t)[C]_0$$
$$= -[B] \int_{-0}^t \Sigma_f^e(\tau)[A]_{t-\tau} \, d\tau + [B] \int_{-0}^t \Sigma_r^e(\tau)[C]_{t-\tau} \, d\tau. \tag{5.11}$$

The Markovian rate constants are defined in an ordinary way (see equation (3.30)):

$$k_f = \int_{-0}^\infty \Sigma_f^e(\tau) \, d\tau; \qquad k_r = \int_{-0}^\infty \Sigma_r^e(\tau) \, d\tau. \tag{5.12}$$

We use the microscopic detailed balancing principle for elementary event rates [72],

$$\frac{w_{AB}(q)}{k_f^0} = \frac{w_{CB}(q)}{k_r^0} \qquad \text{or} \qquad \frac{\hat{v}_f}{k_f^0} = \frac{\hat{v}_r}{k_r^0}, \tag{5.13}$$

where k_f^0 and k_r^0 are intrinsic constants of the forward and reverse reactions, respectively, defined in terms of $w_{AB}(q)$ and $w_{CB}(q)$ (by analogy with the second equation (4.9)). Then equations (5.9) yield the microscopic detailed balancing principle for T-operators:

$$\frac{\hat{t}_f}{k_f^0} = \frac{\hat{t}_r}{k_r^0}. \tag{5.14}$$

In view of equations (5.10), (5.12) and arguments used in the derivation of equation (4.17), we obtain the kinetic principle of detailed balancing [72]:

$$\frac{\Sigma_f^e(t)}{\Sigma_r^e(t)} = \frac{k_f}{k_r} = \frac{k_f^0}{k_r^0} = K_{\text{eq}} \equiv \frac{[C]_{\text{eq}}}{[A]_{\text{eq}}}. \tag{5.15}$$

5.2. EPA kinetic equations

Following the logic of the previous subsection, we write for the reaction $A + B \rightleftarrows C + B$ (instead of equation (3.33) for irreversible reactions) [70]

$$(\partial_t - \hat{\mathcal{L}} - \hat{v} + k[B])\pi = \hat{v}[R]_t[B]. \tag{5.16}$$

Here $\boldsymbol{\pi}$ is a column-vector of correlation patterns, and $\boldsymbol{k}$ is the matrix composed of Markovian rate constants (5.12) and defining the kinetics corresponding to the kinetic law of mass action

$$\partial_t[\boldsymbol{R}]_t = -\boldsymbol{k}[B][\boldsymbol{R}]_t \tag{5.17}$$

i.e.,

$$\boldsymbol{\pi}(q,t) = \begin{bmatrix} \pi_{AB}(q,t) \\ \pi_{CB}(q,t) \end{bmatrix}; \qquad \boldsymbol{k} = \begin{bmatrix} k_f & -k_r \\ -k_f & k_r \end{bmatrix}. \tag{5.18}$$

We seek the solution of the inhomogeneous equation (5.16) using the matrix propagator of effective pairs satisfying the equation

$$(\partial_t - \hat{\mathcal{L}} - \hat{\boldsymbol{v}} + \boldsymbol{k}[B])\hat{G} = \hat{\boldsymbol{I}}. \tag{5.19}$$

Then the EPA kernel will be expressed via the effective pair T-operator

$$\hat{M} = \hat{\boldsymbol{v}} + \hat{\boldsymbol{v}}\hat{G}\hat{\boldsymbol{v}} \tag{5.20}$$

defined similarly to the T-operator t (5.4) but with the effective pair propagator $\hat{G}$ instead of $\hat{g}$.

Thus the EPA equations will have the form of equation (5.11) but with EPA kernels instead of IET ones.

$$\Sigma_f(t - t') = -\langle 1|M_f|1\rangle; \qquad \Sigma_r(t - t') = -\langle 1|M_r|1\rangle. \tag{5.21}$$

As the structure of $\hat{M}_f$ and $\hat{M}_r$ is identical to equations (5.9), the kinetic principle of detailed balancing is valid for EPA kernels. It differs from equation (5.15) only in the substitution of EPA kernels for IET ones.

5.3. Specific case $\hat{\mathcal{L}}_{AB} = \hat{\mathcal{L}}_{CB} = \hat{\mathcal{L}}$

In this case, in view of equations (5.13) and (5.15), the matrix $\boldsymbol{k}$ in equation (5.19) commutes with all other operators. Thus the kernel of the matrix propagator of effective pairs is obtained from the matrix propagator kernel by multiplication by $\exp(-\boldsymbol{k}[B](t - t'))$. Then the same relation exists between the kernel of the matrix operator of effective pairs and the kernel of the matrix T-operator, and

$$\Sigma(\tau) = \Sigma^e(\tau)\exp(-\boldsymbol{k}[B]\tau). \tag{5.22}$$

EPA equation

$$\partial_t[\boldsymbol{R}]_t = \delta(t)[\boldsymbol{R}]_0 - [B]\int_{-0}^{t} \Sigma(r)[\boldsymbol{R}]_{t-\tau}\,\mathrm{d}\tau \tag{5.23}$$

is a binary equation of MET, since kernel (5.22) is defined by the IET kernel and its characteristic $\boldsymbol{k}$.

Using the rule of time shift similar to equation (3.37) (see equation (5.17)),

$$[\boldsymbol{R}]_{t-\tau} \approx \exp(\boldsymbol{k}[B]\tau)[\boldsymbol{R}]_t, \tag{5.24}$$

we have a regular form of binary non-Markovian kinetic equations

$$\partial_t[\boldsymbol{R}]_t = \delta(t)[\boldsymbol{R}]_0 - [B]\int_{-0}^{t} \Sigma^e(\tau)\,\mathrm{d}\tau\,[\boldsymbol{R}]_t \tag{5.25}$$
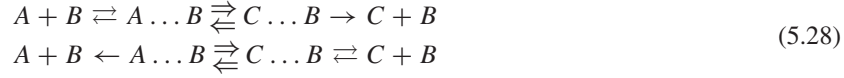
or, in expanded form,

$$\partial_t[A]_t - \delta(t)[A]_0 = -\partial_t[C]_t + \delta(t)[C]_0 = -K_f(t)[B][A]_t + K_r(t)[B][C]_t, \tag{5.26}$$

where the time-dependent rate constants are

$$K_f(t) = \int_{-0}^{t} \Sigma_f^e(\tau)\,\mathrm{d}\tau; \qquad K_r(t) = \int_{-0}^{t} \Sigma_r^e(\tau)\,\mathrm{d}\tau. \tag{5.27}$$

These constants satisfy the kinetic principle of detailed balancing (5.15). It follows from equation (5.12) that their limits at $t \to \infty$ are the Markovian rate constants introduced earlier. Thus binary non-Markovian equations written in a regular form (5.26) are the rate equations of the Smoluchowski–Waite equations type [11, 18] in both directions of the reaction. This case (just as that considered in section 4 (the reaction $A + B \rightleftarrows C$)) corresponds to the independence of channels that can be represented as simple kinetic schemes [30]

$$A + B \rightleftarrows A \ldots B \stackrel{\rightarrow}{\rightleftharpoons} C \ldots B \to C + B$$
$$A + B \leftarrow A \ldots B \stackrel{\rightarrow}{\rightleftharpoons} C \ldots B \rightleftarrows C + B \tag{5.28}$$

with the same arrow designations as in scheme (4.22) for the reaction $A + B \rightleftarrows C$. It is seen that both 'scattering' channels are symmetric about the reaction directions. However, they differ radically from the 'scattering' channel in the reaction $A + B \rightleftarrows C$. Each channel (5.28) involves elementary chemical conversion in both directions that corresponds to reversible conversion in a 'collision complex'. So the rate constant $K_f(t)$ in equation (5.26) does not coincide with the rate constant (3.28) appearing in equation (3.38) of the irreversible reaction and equation (4.21) of the reversible reaction $A + B \rightleftarrows C$.

Note that as in the reaction $A + B \rightleftarrows C$, the rate constants of the kinetic law of mass action calculated by scheme (5.28)

$$k_f = \frac{k_f^0}{1 + \frac{k_f^0}{k_{D_{AB}}} + \frac{k_r^0}{k_{D_{CB}}}} \qquad k_r = \frac{k_r^0}{1 + \frac{k_f^0}{k_{D_{AB}}} + \frac{k_r^0}{k_{D_{CB}}}} \tag{5.29}$$

($k_{D_{AB}}$ and $k_{D_{CB}}$ are defined similarly to equation (2.12) using the corresponding diffusion coefficients) at $k_{D_{AB}} = k_{D_{CB}} \equiv k_D$ coincide with the Markovian values of rate constants (5.27) of the kinetic equation (5.26) calculated for the model of hard spheres reversibly reacting at the contact.

With the use of material balance conditions following from equation (5.26)

$$[A]_t + [C]_t = [A]_{eq} + [C]_{eq} = [A]_0 + [C]_0 \tag{5.30}$$

and equation (5.15), we find the equilibrium concentrations

$$[A]_{eq} = \frac{1}{1 + K_{eq}}([A]_0 + [C]_0); \qquad [C]_{eq} = \frac{K_{eq}}{1 + K_{eq}}([A]_0 + [C]_0). \tag{5.31}$$

We introduce deviations from equilibrium concentrations

$$\Delta[A]_t = [A]_t - \theta(t)[A]_{eq}; \qquad \Delta[C]_t = [C]_t - \theta(t)\,[C]_{eq}. \tag{5.32}$$

It follows from equation (5.30) that

$$\Delta[A]_t = -\Delta[C]_t \equiv [\Delta]_t. \tag{5.33}$$

Using the kinetic principle of detailed balancing (see equations (5.15)), with $K_f(t)$ and $K_r(t)$ instead of $\Sigma_f^e(t)$ and $\Sigma_r(t)$, we obtain the kinetic equation from equations (5.26),

$$\partial_t[\Delta]_t = \delta(t)[\Delta]_0 - (K_f(t) + K_r(t))[B][\Delta]_t, \tag{5.34}$$

that formally coincides with equation (3.38) of the irreversible reaction.

To derive a universal asymptotic kinetic law of equilibrium attainment, we need only note that in the point encounter approximation (see section 5.4)

$$t_f(q, t|q', 0) + t_r(q, t|q', 0) = -(k_f + k_r)\left\{\delta(t) + \frac{k_f + k_r}{4(\pi\bar{D})^{3/2}}\partial_t \frac{\theta(t)}{\sqrt{t}}\right\}\delta(q)\delta(q'). \tag{5.35}$$

This gives (see equations (5.10) and (5.27))

$$K_f(t) + K_r(t) = \theta(t)(k_f + k_r)\left\{1 + \frac{k_f + k_r}{4\pi\bar{D}\sqrt{\pi\bar{D}t}}\right\}. \tag{5.36}$$

Thus comparison of equation (3.38) where the rate constant $K_f(t)$ is given by expression (3.41) with equation (5.34) where the sum of rate constants $K_f(t) + K_r(t)$ is given by expression (5.36) shows that studies of the equilibrium attainment kinetics in the reversible reaction $A + B \rightleftarrows C + B$ are equivalent to examination of the kinetics of the irreversible reaction $A + B \rightarrow C + B$ (see equations (3.43) and (3.45)), where the Markovian rate constant k_f of the reaction $A + B \rightarrow C + B$ is replaced by the sum $k_f + k_r$ of Markovian rate constants in the forward and reverse directions of the reversible reaction $A + B \rightleftarrows C + B$. This is in full agreement with the theorem of the correspondence between the above kinetics proved in the literature [73].

5.4. Independence and separation of pair dynamics and collective dynamics. MET binary non-Markovian equations

In the specific case of identical mobility in the pairs $A + B$ and $C + B$ (see the preceding subsection) the EPA kernel was at the same time an MET kernel. It was divided into the product of an IET kernel describing the pair dynamics on micro- and meso-timescales and a co-factor defining the collective dynamics (on meso- and macro-scales). Such representations correspond to the independence of these dynamics which in a regular form of the equation manifests itself as the independence of forward and reverse reaction 'channels'. In the general case of different mobility such a separation of dynamics does not take place. As a result, an 'interference' of channels occurs which is determined by collective dynamics developing on mean timescales between reactant encounters but corresponding to non-Markovian kinetics. Thus the EPA can be reduced to MET by representing the EPA kernel as a sum of expression (5.22) and the additional term that can be considered on the macro-timescale. This is most reliably achieved by scaling [41, 45] of this term.

To obtain such a representation, we use a matrix analogue of equation (3.22) both for the T-operator $\hat{M}$ of effective pairs and the T-operator t of the pair

$$\hat{M} = \hat{v} + \hat{v}\hat{G}^0\hat{M}; \qquad \hat{t} = \hat{v} + \hat{t}\hat{g}^0\hat{v}, \tag{5.37}$$

where $\hat{G}^0$ and $\hat{g}^0$ are free propagators of effective pairs and the reaction pair obeying equation (5.19) and (5.5) at $\hat{v} \equiv \mathbf{0}$, respectively. Eliminating the operator $\hat{v}$ from equations (5.37), we have

$$\hat{M} = \hat{t} + \hat{t}(\hat{G}^0 - \hat{g}^0)\hat{M}. \tag{5.38}$$

Writing equation (5.38) for operator kernels necessary for the calculation of memory functions, we obtain

$$M(q, t|q', 0) = t(q, t|q', 0) + \hat{t}(\hat{G}^0 - \hat{g}^0)M(q, t|q', 0) \tag{5.39}$$

or, identically,

$$M(q, t|q', 0) = t(q, t|q', 0)\exp(-k[B]t) + t(q, t|q', 0)(E_2 - \exp(-k[B]t))$$
$$+ \hat{t}(\hat{G}^0 - \hat{g}^0)M(q, t|q', 0). \tag{5.40}$$

Equation (5.40) corresponds to the desired representation of the EPA kernel. It is easily seen that the second ('interference') term is actually different from zero on macro-timescales. To estimate the third term, we need scaling [41, 45] which shows that the required values of the quantity $\hat{G}^0 - \hat{g}^0$ contain the non-Markovian part only. The motion of reactants can be treated as macro-diffusion on the scales considered (these propagators will be denoted by the upper index D). Using the T-matrix in the point encounter approximation

$$t(q, t|q', 0) = -k\left\{\delta(t) + \frac{1}{4\pi^{3/2}}\left(\frac{k_f}{\bar{D}_{AB}^{3/2}} + \frac{k_r}{\bar{D}_{CB}^{3/2}}\right)\partial_t \frac{\theta(t)}{\sqrt{t}}\right\}\delta(q)\delta(q') \tag{5.41}$$

which is the generalization of equation (3.40) we obtain for the MET memory function

$$\Sigma^b(t) = \Sigma^e(t)\exp(-k[B]t) + \Lambda_m(t). \tag{5.42}$$

Here

$$\Lambda_m(t) = \frac{1}{4\pi^{3/2}}\left(\frac{k_f}{\bar{D}_{AB}^{3/2}} + \frac{k_r}{\bar{D}_{CB}^{3/2}}\right)\partial_t\frac{\theta(t)}{\sqrt{t}}k(E_2 - \exp(-k[B]t)) + \Lambda(t), \tag{5.43}$$

where

$$\Lambda(t) = \lim_{q\to 0}k(g^D(q,t|0,0) - G^D(q,t|0,0))k. \tag{5.44}$$

Note that in using (5.41) in the second term of equation (5.39) and in the third term of equation (5.40) only the Markovian part should be taken into account. The Markovian part of the operator $\hat{M}$ obviously coincides with the Markovian part of $\hat{t}$. The first expression in equation (5.39) also points to another possibility of representing the MET kernel as a sum corresponding to separation of the above dynamics,

$$\Sigma^b(t) = \Sigma^e(t) + \Lambda(t). \tag{5.45}$$

This representation is more universal in studies of MET kernel transformation to the limiting cases (see below). The components of the matrix Σ^b according to equations (5.42) and (5.45) are

$$\Sigma_f^b(t) = \Sigma_f^e(t)\exp(-(k_f + k_r)[B]t) + k_f(k_f + k_r)\Lambda_m(t) = \Sigma_f^e(t) + k_f(k_f + k_r)\Lambda(t) \tag{5.46}$$

$$\Sigma_r^b(t) = \Sigma_r^e(t)\exp(-(k_f + k_r)[B]t) + k_r(k_f + k_r)\Lambda_m(t) = \Sigma_r^e(t) + k_r(k_f + k_r)\Lambda(t) \tag{5.47}$$

where $\Lambda_m(t)$ and $\Lambda(t)$ are given in the appendix. As is seen, they do depend on macro-observables defined by the IET memory function.

5.5. Regular form of binary non-Markovian kinetic equations

To go to a regular form, one should employ again the time shift rule (5.24). However, as mentioned above, application of this rule requires that the time of rate constant attainment of its Markovian limit be essentially less than the average time between the encounters defined by the inverse value of the reaction rate (see equations (2.11) or (3.41)). Since, according to equation (5.34), the equilibrium attainment rate is defined by the sum of rate constants, just this quantity should be studied. According to equation (5.41) and the definition of rate constants, it is

$$K_f(t) + K_r(t) = -(k_f + k_r)\left\{1 + \frac{1}{4\pi^{3/2}}\left(\frac{k_f}{\bar{D}_{AB}^{3/2}} + \frac{k_r}{\bar{D}_{CB}^{3/2}}\right)_t\frac{1}{\sqrt{t}}\right\}. \tag{5.48}$$

The required condition is as follows:

$$[B]\frac{(k_f + k_r)}{16\pi^3}\left(\frac{k_f}{\bar{D}_{AB}^{3/2}} + \frac{k_r}{\bar{D}_{CB}^{3/2}}\right)^2 \ll 1. \tag{5.49}$$

It is readily seen that for diffusion coefficients of the same order it is equivalent to the smallness of the density parameter (3.1) where the effective radius is equal to the sum of radii in the forward and reverse reaction channels, and concentration $[A_i] = [B]$. However, the situation is changed if

$$(\bar{D}_{CB}/\bar{D}_{AB})^{\frac{3}{2}} \gg k_r/k_f. \tag{5.50}$$

Equation (5.49) immediately gives

$$\xi_{AB}(1 + k_r/k_f) \ll 1 \tag{5.51}$$

where the density parameter ξ_{AB} is defined by the effective radius in the forward channel. For the irreversible reaction ($k_r = 0$), criterion (5.51) coincides with (3.1). However, at $k_f \gg k_r$ it imposes more rigid restrictions on the density parameter for the forward channel. It is interesting that in this case it can easily be recast as

$$k_r[B]\frac{(R_{eff}^{AB})^2}{3D} \equiv k_r[B]\tau_e^{AB} \ll 1. \tag{5.52}$$

This condition means that the depth of the fast reverse reaction should be small during the time of quasi-stationary profile attainment in the slow forward reaction channel. It is quite similar to criterion (4.19) of the reaction regime in the reaction $A + B \rightleftarrows C$. The reason will become clear in section 6.

Let us apply the time shift rule to the MET integro-differential equation with kernel (5.42). For the non-Markovian term $\Lambda_m(t)$ we can restrict ourselves to the Markovian part of the kinetics. This gives a binary non-Markovian equation in a regular form,

$$\partial_t[\boldsymbol{R}]_t - \delta(t)[\boldsymbol{R}]_0 = -\boldsymbol{K}(t)[B][\boldsymbol{R}]_t - J(t)\boldsymbol{k}[B][\boldsymbol{R}]_0, \tag{5.53}$$

where $\boldsymbol{K}(t)$ is defined in an ordinary fashion in terms of the IET matrix kernel, and

$$J(t) = -(k_f + k_r)\int_{-0}^{t}\Lambda_m(t - \tau)\exp(-(k_f + k_r)[B]\tau)\,d\tau. \tag{5.54}$$

For concentrations $[A]_t$ and $[C]_t$, equation (5.53) is

$$\begin{aligned}\partial_t[A]_t - \delta(t)[A]_0 &= -\partial_t[C]_t + \delta(t)[C]_0 \\ &= -K_f(t)[B][A]_t + K_r(t)[B][C]_t + J(t)[B](k_f[A]_0 - k_r[C]_0)\end{aligned} \tag{5.55}$$

and for deviations $[\Delta]_t$ (5.33) from equilibrium concentrations,

$$\partial_t[\Delta]_t - \delta(t)[\Delta]_0 = -(K_f(t) + K_r(t))[B][\Delta]_t + J(t)(k_f + k_r)[B][\Delta]_0. \tag{5.56}$$

An important difference between the derived equations and conventional rate equations is that they involve an inhomogeneous non-Markovian term related to channel interference. This term will be discussed in detail in section 6.

Now we establish a universal kinetic law of equilibrium attainment in view of equations (5.48) and (5.54) and considering non-Markovian corrections as a perturbation. This gives the expression

$$[\Delta]_t = [\Delta]_0(\exp(-(k_f + k_r)[B]t) + \mathcal{P}(t)) \tag{5.57}$$

similar in structure to equation (4.33), where

$$\begin{aligned}\mathcal{P}(t) = -(k_f + k_r)[B]\int_{-0}^{t}dt_1\int_{-0}^{t_1}dt_0\,\exp(-[B](k_f + k_r)(t - t_0)) \\ \times\left[(k_f + k_r)\Lambda(t) + \frac{\partial_t(\theta(t)t^{-1/2})}{4\pi^{3/2}}\left(\frac{k_f}{\bar{D}_{AB}^{3/2}} + \frac{k_r}{\bar{D}_{CB}^{3/2}}\right)\right].\end{aligned} \tag{5.58}$$

The function $\mathcal{P}(t)$ shows the following short-term behaviour:

$$\mathcal{P}(t) \underset{t\to 0}{\sim} -2\varepsilon\sqrt{\tau/\pi}, \tag{5.59}$$

where

$$\tau = [B](k_f + k_r)t \qquad \varepsilon = \frac{\sqrt{[B](k_f + k_r)}}{4\pi}\left(\frac{k_f}{\bar{D}_{AB}^{3/2}} + \frac{k_r}{\bar{D}_{CB}^{3/2}}\right). \tag{5.60}$$
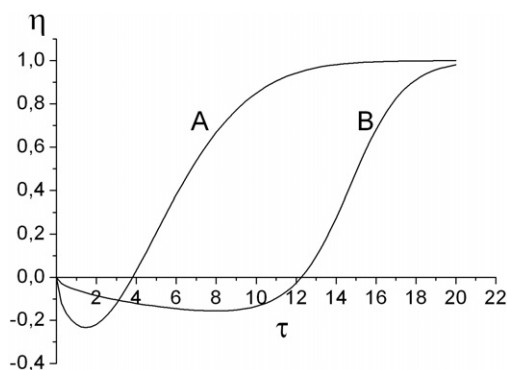
Figure 1. Relative deviation η of kinetics (5.57) from the Markovian kinetics for the following parameters: for curve A $\varepsilon = 0.2$, $D_{AB}/D_{CB} = 24$; for curve B $\varepsilon = 0.05$, $D_{AB}/D_{CB} = 3/2$. For both curves $k_f/k_r = 2$.

The long-term behaviour is

$$\mathcal{P}(t) \underset{t \to \infty}{\sim} \frac{15}{8\sqrt{\pi}} \varepsilon \frac{k_f k_r}{(k_f + k_r)\left(\frac{k_f}{\bar{D}_{AB}^{3/2}} + \frac{k_r}{\bar{D}_{CB}^{3/2}}\right)} \frac{(\bar{D}_{AB} - \bar{D}_{CB})^2}{(D_1 \tau)^{7/2}}, \tag{5.61}$$

where

$$D_1 = \frac{k_r}{k_f + k_r} \bar{D}_{AB} + \frac{k_f}{k_f + k_r} \bar{D}_{CB}. \tag{5.62}$$

Thus, just as kinetics (4.33), kinetics (5.57) is a sum of the Markovian and the non-Markovian terms and shows the change in the leading term with time. So the kinetics demonstrates the universal power law $\sim t^{-7/2}$ in contradiction to the kinetic law of mass action. Figure 1 presents the relative deviation η of kinetics (5.57) from the Markovian kinetics $[\Delta_m]_t = [\Delta]_0 \exp(-(k_f + k_r)[B]t)$

$$\eta = \frac{[\Delta]_t - [\Delta_m]_t}{[\Delta]_t} = \frac{\mathcal{P}(t)}{\exp(-[B](k_f + k_r)t) + \mathcal{P}(t)} \tag{5.63}$$

for the parameters given in the figure caption.

6. Interference of transient channels

6.1. Transient channels

Note that 'channels' considered in the previous sections do not completely correspond to the concepts of channels in non-stationary quantum scattering theory [4] and the theory of multistage reactions (IET) developed in [72]. In these theories a channel means a set of chemical compound fragments. That is why the reaction $A + B \rightleftarrows C + B$, for example, involves the channel AB of initial reactants and the channel CB of forward reaction products (and vice versa). The notions introduced in this contribution and in [30, 64] correspond to transient channels, and it is these channels that the simple kinetic schemes (4.22) and (5.28) refer to. Strictly speaking, any of these definitions are the concepts of the Markovian theory. So, for instance, expressions (5.29) derived by schemes (5.28) do not necessarily correspond to $D_{AB} = D_{CB}$ in reaction pairs.

Traditionally notions of transient channels are extended to the non-Markovian theory by taking account of the time dependence of reaction rate constants [11, 12, 23, 26]. As is shown

in section [3], for the irreversible reaction $A + B \rightarrow C + B$, such an approach agrees with the many-particle derivation of binary non-Markovian kinetic equations. This reaction has only one (forward) transient channel of 'scattering'.

Examination of the reversible reaction $A + B \rightleftarrows C$ (under conditions (4.20) given in section [4]) shows that the time-dependent reaction rate constant describes just the forward reaction (transient channel of 'scattering'). As for the reverse transient channel of reactant C 'decay', here integral convolution of the memory function with the reactant C kinetics is observed. In the reversible reaction $A + B \rightleftarrows C + B$, the equations are of rate equation character for both transient channels of 'scattering'. It has been shown that both situations correspond to independence of the reaction pair dynamics and collective dynamics. So it can be concluded that transient channels of 'scattering' in binary non-Markovian kinetic equations in a regular form are always characterized by time-dependent reaction rate constants, while the 'decay' transient channel is characterized by integral convolution. It is the interference of transient channels appearing in the non-Markovian theory as an extra non-Markovian source which brings such situations into agreement (see below). Physically the above interference means that on binary encounter of reactants a two-particle space correlation arises described by a two-particle correlation pattern. Though this correlation decays effectively at the average encounter time τ_e, it lives for an infinitely long time, and can only be terminated by the third particle colliding with one of the correlated reactants. Taking account of this fact is the essence of the IET modification in the development of MET of the irreversible reaction $A+B \rightarrow C+B$. In the case of the reversible reaction the third particle both breaks the binary encounter once and for all, and causes the interference of the forward and reverse transient channels.

6.2. Transformation of transient channels

The different form of the manifestation of 'decay' and 'scattering' transient channels in non-Markovian theory leads to the ambiguous extraction of the interference source in binary non-Markovian kinetic equations in a regular form. To see this, consider the specific case of the reaction $A + B \rightleftarrows C + B$. According to channel kinetic schemes (5.28) and the corresponding expressions (5.29) for Markovian rate constants, at $D_{CB} \rightarrow \infty$ they reduce to expressions

$$k_f = \frac{k_f^0 k_{D_{AB}}}{k_f^0 + k_{D_{AB}}}; \qquad k_r = \frac{k_r^0 k_{D_{AB}}}{k_f^0 + k_{D_{AB}}} \tag{6.1}$$

formally coinciding with equations (4.23) for the reaction $A + B \rightleftarrows C$. This means that at $D_{CB} \rightarrow \infty$ the reaction $A + B \rightleftarrows C + B$ may be treated as the reaction $A + B \rightleftarrows C$ (in excess of reactant B) with the reverse reaction ('decay') rate equal to $k_r[B]$. It is easily seen that this correspondence also takes place in non-Markovian IET at infinitely rapid relative mobility in the pair $C + B$. Such a mobility corresponds to the equality of the free propagator $\hat{g}_{CB}^0$ to zero in the expression for the T-operator (5.37), since in the case of infinite mobility the reactants instantaneously leave the reaction zone. Then equation (5.37) goes into equations (3.22) and (4.7). Preservation of the above correspondence in MET that uses just IET kernels and characteristics obtained on their basis allows one to establish the form of MET memory functions of the reaction $A + B \rightleftarrows C$ by passing to the limit $D_{CB} \rightarrow \infty$ in MET kernels of the reaction $A + B \rightleftarrows C + B$,

$$\Sigma_f^b(t) \equiv \frac{k_f}{k_r} \Sigma_r^b(t) = \Sigma_f^e(t) + k_f^2 (1 - \exp(-[B]k_f t))(4\pi D_{AB} t)^{-3/2}. \tag{6.2}$$

The time shift rule (5.24) is used to change from integro-differential binary equations of MET with kernels (6.2) to binary non-Markovian kinetic equations in a regular form. For deviations

from equilibrium concentrations $[\Delta]_t$ they give the kinetic equation

$$\partial_t[\Delta]_t - \delta(t)[\Delta]_0 = -K_f(t)[B][\Delta]_t - [B]\int_{-0}^{t}\Sigma_r^b(t-\tau)[\Delta]_\tau\,\mathrm{d}\tau + J'(t)[\Delta]_0. \qquad (6.3)$$

It corresponds to equation (4.29) of the reaction $A + B \rightleftarrows C$ in excess of B reactants and under appropriate redefinition of the 'decay' rate but in the general case contains the source

$$J' = \frac{[B]k_f^2}{(4\pi\bar{D}_{AB})^{3/2}}\int_{-0}^{t}\frac{\mathrm{d}\tau}{\tau^{3/2}}(H_{AA}(\tau) - \exp(-[B]k_f\tau))\exp(-[B](k_f + k_r)(t - \tau)), \qquad (6.4)$$

where the matrix element of the propagator of equation (5.17)

$$H_{AA}(\tau) = (\exp(-[B]\mathbf{k}\tau))_{AA} = \frac{k_r}{k_f + k_r} + \frac{k_f}{k_f + k_r}\exp(-[B](k_f + k_r)\tau). \qquad (6.5)$$

Retention of this source as compared to equation (4.29) (in excess of B reactants) is due to the fact that equation (4.29) is obtained under the additional condition (4.18) according to which the reaction rate by the reverse transient channel ('decay') considerably exceeds the rate of forward reaction of association. However, using the limit

$$\lim_{\alpha\to\infty}(\theta(t)\alpha\exp(-\alpha t)) = \delta(t) \qquad (6.6)$$

it is readily seen that $J' = 0$ at $k_r \to \infty$. It is interesting to note that in the reverse limiting case $k_f \gg k_r$ the contribution of channel interference into the deviation from the kinetics corresponding to the kinetic law of mass action is also negligibly small. Note that at $k_r \gg k_f$, equation (5.51) gave condition (5.52) corresponding to condition (4.19) of the reaction regime necessary for conversion from MET equations to their regular form. Thus really the initial interference source can go to zero on redefinition of transient channels.

7. Summary

The consistent many-particle derivation of binary non-Markovian kinetic equations is a sequence of steps. First we obtain integro-differential kinetic equations of integral encounter theory (IET), the kernels of which (memory functions) describe the dynamics of the reacting pairs. IET serves as a basis for the calculation of Markovian constants of the kinetic law of mass action further employed to develop an effective pairs approximation (EPA) involving, along with reaction pair dynamics, collective dynamics. The necessity of developing the EPA is due to the existence of long-range space–time correlation in the reacting pair which can only be terminated by the third reactant. In dilute solutions these dynamics have different characteristic space–time scales; this leads to their separation in the binary approximation. As a result, we have binary non-Markovian integro-differential kinetic equations of the modified encounter theory (MET). Their kernels (memory functions) are defined by IET memory functions and macro-observables (Markovian rate constants and macro-diffusion coefficients) which are also the characteristics of IET kernels. In most cases just these binary equations are reduced to their final regular form of binary non-Markovian equations of chemical kinetics. In these equations independence of dynamics manifests itself in the fact that the kinetic coefficients are defined by IET kernels. Th time-dependent reaction rate constant (integral of IET kernel) corresponds to independent transient channels of 'scattering', while the independent transient channel of 'decay' is still the integral convolution with the IET kernel. The dependence of the dynamics corresponds to transient channel interference; this gives rise to the inhomogeneous term (non-Markovian source) in the above-mentioned kinetic equations.

Since taking account of collective dynamics is essential only at macro-times, binary non-Markovian kinetic equations give new unusual universal (model-independent) kinetics

of equilibrium concentration attainment that can differ considerably from the kinetics corresponding to the kinetic law of mass action of formal chemical kinetics.

Acknowledgments

Appendix

Quantity $\Lambda_m(t)$ in equations (5.46) and (5.47) is

$$\Lambda_m(t) = \frac{\exp(-(\bar{k}_f + \bar{k}_r)t)}{(4\pi t)^{3/2}(\bar{k}_f + \bar{k}_r)}\left(\frac{k_f}{\bar{D}_{AB}^{3/2}} + \frac{k_r}{\bar{D}_{CB}^{3/2}}\right) - \int \frac{k^2\,\mathrm{d}k}{2\pi^2}\varphi(k,t),$$

where

$$\bar{k}_f = [B]k_f; \qquad \bar{k}_r = [B]k_r$$

$$\varphi(k,t) = \frac{k_r}{2(\bar{k}_f + \bar{k}_r)\Delta}\left[\mathrm{e}^{-\mu_1 t}\frac{(2\bar{k}_r - z - \Delta)^2}{z + \Delta} + \mathrm{e}^{-\mu_2 t}\frac{(2\bar{k}_f - z + \Delta)^2}{\Delta - z}\right].$$

Here we introduced the parameters

$$\mu_1 = 2^{-1}[k^2(\bar{D}_{AB} + \bar{D}_{CB}) + \bar{k}_f + \bar{k}_r - \Delta];$$
$$\mu_2 = 2^{-1}[k^2(\bar{D}_{AB} + \bar{D}_{CB}) + \bar{k}_f + \bar{k}_r + \Delta];$$
$$\Delta^2 = z^2 + 4\bar{k}_f\bar{k}_r; \qquad z = k^2(\bar{D}_{AB} - \bar{D}_{CB}) + \bar{k}_f - \bar{k}_r.$$

Quantity $\Lambda(t)$ in equations (5.46) and (5.47) is

$$\Lambda(t) = \frac{1}{(4\pi t)^{3/2}(\bar{k}_f + \bar{k}_r)}\left(\frac{k_f}{\bar{D}_{AB}^{3/2}} + \frac{k_r}{\bar{D}_{CB}^{3/2}}\right) - \int \frac{k^2\,\mathrm{d}k}{2\pi^2}\varphi(k,t).$$

References

[1] Eyring H, Lin S H and Lin S M 1980 *Basic Chemical Kinetics* (New York: Wiley)
[2] Keizer J 1987 *Statistical Thermodynamics of Nonequilibrium Processes* (New York: Springer)
[3] Sobelman I I 1963 *Introduction to the Theory of Atomic Spectra* (Moscow: Fizmatgiz)
[4] Taylor J R 1972 *Scattering Theory* (New York: Wiley)
[5] Kapral R 1981 *Adv. Chem. Phys.* **48** 71
[6] Yang M, Lee S and Shin K J 1998 *J. Chem. Phys.* **108** 9069
[7] Entelis S G and Tiger R P 1973 Reaction kinetics in liquid phase *Quantitative Account of the Medium Influence* (Moscow: Khimiya)
[8] Kramers H A 1940 *Physica* **7** 284
[9] Marcus R A 1964 *Annu. Rev. Phys. Chem.* **15** 155
[10] Noyes R M 1956 *J. Am. Chem. Soc.* **78** 5486
[11] Waite T R 1957 *Phys. Rev.* **107** 463
[12] Waite T R 1958 *J. Chem. Phys.* **28** 103
[13] Kirkwood J G 1935 *J. Chem. Phys.* **3** 300
[14] Anderson P W 1949 *Phys. Rev.* **76** 647
[15] Steinberg I Z and Katchalski E 1968 *J. Chem. Phys.* **48** 2404
[16] Tachiya M 1983 *Radiat. Phys. Chem.* **21** 167
[17] Collins F G and Kimbal G E 1949 *J. Colloid Interface Sci.* **4** 425
[18] Smoluchowski M V 1917 *Z. Phys. Chem.* **92** 129
[19] Korn G A and Korn T M 1968 *Mathematical Handbook for Scientists and Engineers* (New York: McGraw-Hill)

[20] Kuzovkov V N and Kotomin E A 1980 *J. Phys. C: Solid State Phys.* **13** 499
[21] Kuzovkov V N and Kotomin E A 1981 *Phys. Status Solidi* b **108** 37
[22] Kipriyanov A A, Igoshin O A and Doktorov A B 1999 *Physica* A **268** 567
[23] Lee S and Karplus M 1987 *J. Chem. Phys.* **86** 1883
[24] Sung J, Shin K J and Lee S Y 1997 *J. Chem. Phys.* **107** 9418
[25] Yang M, Lee S and Shin K J 1998 *J. Chem. Phys.* **108** 8557
[26] Szabo A 1991 *J. Chem. Phys.* **95** 2481
[27] Naumann W and Szabo A 1997 *J. Chem. Phys.* **107** 402
[28] Doktorov A B and Burshtein A I 1976 *Sov. Fiz.—JETP* **41** 671
[29] Kipriyanov A A, Doktorov A B and Burshtein A I 1983 *Chem. Phys.* **76** 149
[30] Lukzen N N, Doktorov A B and Burshtein A I 1986 *Chem. Phys.* **102** 289
[31] Naumann W 1993 *J. Chem. Phys.* **98** 2353
[32] Molski A and Keizer J 1992 *J. Chem. Phys.* **96** 1391
[33] Kipriyanov A A, Gopich I V and Doktorov A B 1994 *Chem. Phys.* **187** 241
[34] Kipriyanov A A, Gopich I V and Doktorov A B 1994 *Chem. Phys.* **187** 251
[35] Kipriyanov A A, Gopich I V and Doktorov A B 1995 *Chem. Phys.* **191** 101
[36] Balescu R 1975 *Equilibrium and Nonequilibrium Statistical Mechanics* (New York: Wiley)
[37] Kipriyanov A A and Doktorov A B 1996 *Physica* A **230** 75
[38] Kipriyanov A A and Doktorov A B 1995 *Chem. Phys. Lett.* **246** 359
[39] Kipriyanov A A and Doktorov A B 2003 *Physica* A **317** 63
[40] Doktorov A B, Kadetov A A and Kipriyanov A A 2004 *J. Chem. Phys.* **120** 8662
[41] Kypriyanov A A, Gopich I V and Doktorov A B 1998 *Physica* A **255** 347
[42] Zwanzig R 1960 *J. Chem. Phys.* **33** 1338
[43] Mory H 1965 *Prog. Theor. Phys.* **33** 423
[44] Mory H 1965 *Prog. Theor. Phys.* **34** 399
[45] Kipriyanov A A, Gopich I V and Doktorov A B 1999 *Chem. Phys.* **244** 361
[46] Vladimirov V S 1981 *Equations of Mathematical Physics* (Moscow: Nauka)
[47] Schmid E and Ziegelmann H 1978 *The Quantum Mechanical Three-body Problem* (Braunschweig: Pergamon)
[48] Kipriyanov A A and Doktorov A B 2005 *Chem. Phys.* **320** 21
[49] Zeldovich Ya B and Ovchinnikov A A 1977 *Pis. Zh. Eksp. Teor. Fiz.* **26** 588
[50] Gopich I V, Ovchinnikov A A and Szabo A 2001 *Phys. Rev. Lett.* **86** 922
[51] Oshanin G, Ovchinnikov A A and Burlatsky S F 1989 *J. Phys. A: Math. Gen.* **22** L977
[52] Doktorov A B 1978 *Physica* A **90** 109
[53] Tunitzky N N 1970 *Diffusion and Random Processes* (Novosibirsk: Nauka)
[54] Doktorov A B and Kipriyanov A A 1996 *Mol. Phys.* **88** 453
[55] Gladkikh V S, Burshtein A I, Tavernier H L and Fayer M D 2002 *J. Phys. Chem.* A **106** 6982
[56] Peak D, Greenlaw D C and Schick L A 1990 *Phys. Rev.* A **41** 5362
[57] Martinho J M G and Winnik M A 1987 *J. Phys. Chem.* **91** 3640
[58] Siencki K and Winnik M A 1987 *J. Chem. Phys.* **87** 2766
[59] Andre J C, Baros F and Winnik M A 1990 *J. Phys. Chem.* **94** 2942
[60] Vogelsang J and Hauses M 1990 *J. Phys. Chem.* **94** 7488
[61] Laidler K J and Bunting P S 1973 *The Chemical Kinetics of Enzyme Action* 2nd edn (Oxford: Clarendon)
[62] Huppert D, Goldberg S V, Masad A and Agmon N 1992 *Phys. Rev. Lett.* **68** 3932
[63] Doktorov A B and Kipriyanov A A 2003 *Physica* A **319** 253
[64] Doktorov A B and Kipriyanov A A 2003 *Physica* A **317** 41
[65] Berg O G 1978 *Chem. Phys.* **31** 47
[66] Kipriyanov A A and Doktorov A B 2003 *Physica* A **326** 105
[67] Gopich I V and Doktorov A B 1996 *J. Chem. Phys.* **105** 2320
[68] Naumann W 1991 *Chem. Phys.* **150** 187
[69] Agmon N and Szabo A 1990 *J. Chem. Phys.* **92** 5270
[70] Ivanov K L, Lukzen N N, Doktorov A B and Burshtein A I 2001 *J. Chem. Phys.* **114** 1754
[71] Gopich I V, Kipriyanov A A and Doktorov A B 1999 *J. Chem. Phys.* **110** 10888
[72] Ivanov K L, Lukzen N N, Kipriyanov A A and Doktorov A B 2004 *PCCP* **6** 1706
[73] Gopich I V, Kipriyanov A A and Doktorov A B 1995 *Chem. Phys. Rep.* **14** 1443