Corrections to the Law of Mass Action and Properties of the

Asymptotic $t = \infty$ State for Reversible Diffusion-Limited

Reactions

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On example of diffusion-limited reversible $A + A \rightleftharpoons B$ reactions we re-examine two fundamental concepts of classical chemical kinetics - the notion of "Chemical Equilibrium" and the "Law of Mass Action". We consider a general model with distance-dependent reaction rates, such that any pair of $A$ particles, performing standard random walks on sites of a $d$-dimensional lattice and being at a distance $\mu$ apart of each other at time moment $t$, may associate forming a $B$ particle at the rate $k_+ (\mu)$. In turn, any randomly moving $B$ particle may spontaneously dissociate at the rate $k_- (\lambda)$ into a geminate pair of $A$'s "born" at a distance $\lambda$ apart of each other. Within a formally exact approach based on Gardiner’s Poisson representation method we show that the asymptotic $t = \infty$ state attained by such diffusion-limited reactions is generally not a true thermodynamic equilibrium, but rather a non-equilibrium steady-state, and that the Law of Mass Action is invalid. The classical concepts hold only in case when the ratio $k_+ (\mu)/k_- (\mu)$ does not depend on $\mu$ for any $\mu$.

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I. INTRODUCTION

"Chemical Equilibrium" (CE) and the "Law of Mass Action" (LMA) are two central concepts of classical chemical kinetics (see, e.g., Refs. [1, 2]). In virtually every text-book one finds, regarding, for instance, the behavior of reversible association/dissociation reaction of the form

\[ A + A \xleftrightarrow{K_+} K_- B, \]  

where \( K_+ \) and \( K_- \) are the forward and the backward rate constants, respectively, that the asymptotic state achieved in closed systems at \( t = \infty \) is the state of Chemical Equilibrium - state with no net change in activity, or concentration with time \( t \). Thermodynamically, the condition of CE is the condition in which the driving forces of the reaction in Eq. (1) (or any other reversible reaction) are equal and opposite. This condition implies that no spontaneous change is observed and that, according to the zeroth principle of thermodynamics, the net Gibbs free energy change of a mixture of reactants and products vanishes. Kinetically, the condition of CE is the condition in which the rates of the forward, \( K_+ a_\infty \), and the backward, \( K_- b_\infty \), reactions are equal and opposite, such that \( a_\infty \) and \( b_\infty \) - the "equilibrium" concentrations of \( A \) and \( B \) species, obey the LMA:

\[ -K_+ a_\infty^2 + K_- b_\infty = 0 \quad \text{or} \quad \frac{a_\infty^2}{b_\infty} = \frac{K_-}{K_+} = K_{eq}, \]  

with \( K_{eq} \) being the "equilibrium" constant, dependent only on the thermodynamic properties of the reactive system [1, 2]. It is important to remark that once the CE is achieved, the forward and backward reactions continue to run. It is just at equilibrium, since the rates are equal, there is no visible or measurable change in the system.

In this paper we re-examine these two fundamental concepts, serving to define the composition of reactive mixtures (as well as general trends in reactive systems), in case of reversible reactions which involve diffusive particles and products, i.e. the so-called diffusion-limited reactions [3, 4, 5, 6, 7, 8]. Our focal questions here are whether for such diffusion-limited reactions taking place in closed systems the CE is always a true thermodynamic equilibrium state (TES), and whether the LMA in Eq. (2) always holds. We emphasize that it

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does not mean that the principles of thermodynamics are contested: according to the zeroth principle, for a closed system the CE always exists and is by definition the thermodynamic equilibrium state. What is meant here by true thermodynamic equilibrium state, is much more restrictive: within the conventional picture it designates a state fully described by the thermodynamical, as opposed to dynamical, quantities, and which satisfies the detailed balance equilibrium. The fact that the CE is not, in some cases described below, a TES is therefore fully compatible with the laws of thermodynamics. Note that in particular the LMA is not a law of thermodynamics, since it relies on an ideal gas approximation which is not necessarily always the case.

We concentrate on a particular reaction scheme - the simple association/dissociation reaction in Eq.(1), but our analysis can be readily generalized for any other type of reversible reaction. We consider here a rather general lattice model of reactions in Eq.(1), which was first studied analytically by Zeldovich and Ovchinnikov [18]. In this model the A particles and products B perform standard random walks on sites of a d-dimensional hypercubic lattice and the elementary reaction rates are long-ranged and dependent on the instantaneous distance between any two A particles; that is, any pair of As may associate (forming a B particle) at any moment of time $t$ at rate $k_+(\mu)$, where $\mu$ is the instantaneous distance separating these two particles. In turn, any B particle may spontaneously dissociate at rate $k_-(\lambda)$ giving birth to a geminate pair of As separated by a distance $\lambda$. In our analysis we suppose that the bimolecular elementary reaction rate $k_+(\mu)$ and the unimolecular elementary reaction rate $k_-(\lambda)$ are arbitrary (integrable) functions of $\mu$ and $\lambda$. Note also that we have chosen the lattice formulation just for the convenience of exposition; an analogous continuous-space formulation can be readily worked out. For this model, in terms of a formally exact approach based on Gardiner’s Poisson representation method [9], we obtain exact non-linear Langevin equations describing the time evolution of complex-valued Poisson fields, whose mean values determine the A and B particles’ mean concentrations. Solutions of these Langevin equations in the asymptotic $t = \infty$ state are obtained by two different approaches: via a) a certain decoupling approximation and b) a systematic diagrammatic expansion. From these solutions, which coincide in the leading order, we deduce a general criterion determining the conditions when the classical LMA in Eq.(2) holds and when the asymptotic $t = \infty$ state is a true thermodynamic equilibrium. We show that this may only happen when the distance-dependent elementary reaction rates obey a rather strong (and
apparently unrealistic) condition: the ratio \( k_+(\mu)/k_-(\mu) \) does not depend on \( \mu \) for any \( \mu \)!

In case when this microscopic restriction is violated even at a single point, one can show that the detailed balance is broken. Here we demonstrate that this violation of the detailed balance at the microscopic scale has macroscopic consequences: the LMA in Eq. (2) is violated, particles’ concentrations are spatially correlated, the correlation length is macroscopically large, and, remarkably, the CE is not a true thermodynamic equilibrium but rather a non-equilibrium steady-state, depending on dynamical properties such as the particles’ diffusion coefficient. The profound reason of these spectacular macroscopic effects is that the breaking of detailed balance generates a non-vanishing probability current which modifies and sustains the fluctuations. In turn these fluctuations correlate the particles’ concentrations, perturbate the rate of the forward reaction and thus displace the equilibrium concentrations, breaking the LMA. Note that such a current occurs in the phase space and there is no net transport in the real space. We remark that this non-equilibrium steady-state breaking the detailed balance provides an example of irreversible circulation of fluctuations - a notion put forward in Ref. [10]. Using system size expansion method, Tomita and Tomita [10] have demonstrated that for statistical physics systems a non-vanishing probability current can be generated by breaking of the detailed balance (a state which they call a "cyclic balance").

We note parenthetically that appearance of a non-equilibrium steady state is generic for open reaction-diffusion systems, as first suggested by Kuramoto [11] and subsequently elaborated in Refs. [12, 13, 14, 15]. Under certain conditions, it may also take place for reactions in which the particles number is not explicitly conserved [16]. We emphasize that here such a non-equilibrium steady-state emerges in a closed system with strictly conserved overall concentration of particles and products, without any external inflow of particles! This gives a striking example of a steady state breaking the detailed balance equilibrium, characterized by non-vanishing probability currents in the phase space.

We note that despite the common belief that in closed systems the CE is a true TES and that the LMA may be taken for granted, there are some good reasons which might make our questions legitimate. Indeed, the classical kinetic picture has already been proven to be inadequate in many situations and a number of significant deviations from the text-book behavior has been discovered. These deviations concern primarily the kinetic behavior. For example, for reversible reactions conventional chemical kinetics predicts an exponential approach toward the CE state. It has been realized, however, that this is not the case
for reversible reactions involving diffusive species; here, the concentrations approach the asymptotic state $t \to \infty$ only as a power law ($t^{-d/2}$ in $d$ dimensions)! Such a behavior stems out of many particle and non-linear effects. Because of the bimolecular (non-linear) forward reaction, the time evolution of observables - particles mean concentrations, appears to be coupled to the evolution of the pairwise correlation functions. In turn, long-time decay of correlations is dominated by existence of the conserved values, e.g., the overall concentration of particles and products, which are not affected by reactions and thus represent purely diffusive modes of the system. Theoretically, the power law approach to the asymptotic state has been first predicted in Ref.

\[ \text{[17]} \] using physical arguments based on the analysis of spatial concentration fluctuations, and subsequently elucidated in terms of more elaborated approaches \[ \text{[18, 19, 20, 21, 22, 23, 24, 25, 26]} \]. In some cases, exact dynamical many-particle solutions have been obtained \[ \text{[27, 28, 29]} \]. As well, this power law behavior has been indeed observed in excited state proton transfer reactions \[ \text{[30, 31]} \], and also seen in numerical MC simulations \[ \text{[32]} \].

The question whether in closed systems the LMA in Eq.\((2)\) is valid for the reversible diffusion-limited reactions at $t = \infty$ has already been raised in Refs.\[ \text{[18]} \text{ and [21, 22]} \]. In Refs.\[ \text{[18]} \] an approximate approach has been proposed to describe kinetics of reversible association/dissociation reactions in Eq.\((1)\) with distance-dependent elementary reaction rates. In this approach, the evolution of the reactive system has been reduced to the evolution of a mixture of two quantum Bose gases, which was solved by extraction of the condensate and approximate second quantization method, similar to the Bogolyubov’s theory of a weakly non-ideal Bose gas \[ \text{[33]} \]. In Refs.\[ \text{[18]} \], some corrections to the LMA non-vanishing in the limit $t \to \infty$ have been found. Corrections to the LMA have also been obtained in Ref.\[ \text{[21]} \] in terms of a suitably extended Smoluchowski approach for reversible, microscopically inhomogeneous contact reactions, such that the reaction radius $R$ of the forward reaction is unequal to the radius $\lambda$ of pairs appearing within the course of the backward reaction. In three dimensions, it was found that in the asymptotic $t = \infty$ state the particles concentration obey

\[ \frac{a^2}{b_{\infty}} = \frac{K_-}{K_+} \left[ 1 + \frac{K_+}{4\pi DR} \left( 1 - \frac{R}{\lambda} \right) \right], \tag{3} \]

where $D$ is particles diffusion coefficient. Note that according to Eq.\((3)\), particles concentrations in the asymptotic $t = \infty$ state are dependent on such "kinetic" parameter as $D$, which could be quite alarming, if Eq.\((3)\) were derived in terms of a more reliable approach.
Further on, Refs. [22] have pursued a different *uncontrollable* approach analyzing the temporal evolution of several contact diffusion-limited reactions in terms of reaction-diffusion equations for local concentrations. In these equations, the stochastic nature of particles transport and reactions have been incorporated by random source terms, derived within the framework of a hydrodynamic-level stochastic description of number densities for a dilute, chemically reacting system Ref. [34]. Solving the resulting non-linear Langevin equations under an assumption that the concentration fields are Gaussian (which implies an automatic decoupling of fourth-order correlations and hence, insures that the third-order correlations vanish), Refs. [22] predicted not only non-vanishing corrections to the LMA, but also shown that in the asymptotic $t = \infty$ state particles’ spatial distributions are correlated. Moreover, it has been realized that the correlation length depends on particles’ diffusion coefficients, which rules out, of course, that the CE is a true TES, but rather represents a non-equilibrium steady-state.

On the other hand, formally *exact solutions* obtained in Refs. [27] and [29] for several reversible diffusion-limited reactions have demonstrated that the LMA in Eq. (2) is strictly valid at $t = \infty$, and that the asymptotic $t = \infty$ state has a Poissonian spatial distribution of concentrations, which signifies that the CE is a true TES. Consequently, approximate [18, 21, 22] and rigorous [27, 29] approaches, although agree on the dynamical behavior, are at some odds concerning the properties of the asymptotic $t = \infty$ state.

Both exact approaches [27, 29], however, focused on contact diffusion-limited reactions with some rather restrictive conditions imposed on the elementary reaction acts. More specifically, in Ref. [27], which considered a continuous-space model of different reversible reactions and made use of suitably generalized quantum field theory techniques of Refs. [35, 36, 37], the forward reaction radius and the radius of the geminate pair born in the backward reaction act were both set equal to zero. In Ref. [29], which used a lattice formulation ingeniously extending the Poisson representation method of Gardiner [9], it was stipulated that the forward reaction takes place when both species occupy simultaneously the same lattice site, while the dissociation of the reaction product produces a geminate pair of reactants born at the *same* lattice site. We note parenthetically that for this particular case both Refs. [18] and [21], Eq. (3), predict that corrections to the LMA vanish as $t \to \infty$ and thus the LMA obeys its classical form in Eq. (2).

Strictly speaking, reaction events are not describable within the framework of a classical
theory only; an elementary reaction act results from an interplay of many factors and is influenced by solvent structure, potential interactions, a variety of particles’ energies and angular orientations, quantum processes of different origin and etc. [38, 39, 40, 41, 42, 43]. At such scales, a notion of a fixed ”reaction radius” $R$ does not make much sense - a ”reactive” boundary condition, imposed at a fixed distance $R$ separating the reactants, is just a mathematical trick employed to obtain a tractable formalism and to circumvent enormous technical difficulties. This technical breakthrough is achieved, however, at expense of introducing a certain degree of arbitrariness regarding the choice of the value of $R$ and of the reaction rate itself, which both, in consequence, are rather ill-defined. In this regard, for a more adequate description of an elementary reaction act, (still being, however, in a reasonable compromise between either too restrictive or too complicated theoretical model) it is appropriate to introduce, as it has been done, in particular, in Ref.[18], a distance $\mu$ dependent elementary reaction rates for both forward and backward reactions. Note that an account for the long-range distance-dependent character of elementary reaction rates is indispensable for the analysis of kinetics of reaction including remote electron or proton transfer [44, 45], for which the contact approximation is meaningless. It appears, as well, that it is indispensable also in the general case for the analysis of such a delicate issue as the nature of the asymptotic $t = \infty$ state. The meaning of this statement will become clearer as we proceed.

This paper is outlined as follows. In section 2 we formulate the model, write down the master equation describing particles reactions and diffusion on the microscopic many particle level, and, within the framework of Gardiner’s Poisson representation method [9], derive non-linear Langevin equations describing the time evolution of the Poisson fields. In section 3 we discuss solutions of the non-linear Langevin equations using a certain decoupling approximation. Within this approach, we define a criterion determining the conditions when the classical LMA in Eq.(2) holds and when the asymptotic $t = \infty$ state is a true thermodynamic equilibrium. Focusing next on a particular case of microscopically inhomogeneous contact reactions, we determine explicitly corrections to the LMA. Further on, in section 4, we set up a systematic approximation scheme previously developed for contact reactions in Ref.[27]. We show, within this mathematically rigorous approach, that the criterion obtained in section 3 is exact. Moreover, we demonstrate that for microscopically inhomogeneous contact reactions, the corrections to the LMA obtained in section 3 within
the decoupling approximation, as well as the result in Eq. (3) obtained in Ref. [21] within a suitably extended Smoluchowski approach, are exact in the linear order in deviation from the equilibrium. Besides, we present here several explicit results for exponential reaction rates. Finally, we conclude in section 5 with a brief summary of results and discussion.

II. MODEL AND EVOLUTION EQUATIONS

Consider an infinite $d$-dimensional hypercubic lattice of spacing $\ell$, containing particles of two types - $A$ and $B$, which perform unconstrained (an arbitrary number of particles can occupy any lattice site) random walks between neighboring sites. Any two $A$ particles, being at a distance $\mu$ from each other, may enter into reaction at the rate $k_+(\mu)$ forming a single $B$ particle, placed at the half-distance between two $A$s. Further on, any $B$ particle at any moment of time may spontaneously dissociate at the rate $k_-(\lambda)$ producing a geminate pair of $A$ particles born (with a random orientation) at a distance $\lambda$ apart of each other. Note that the true reaction constants, (those entering Eq. (2)) are determined as $K_+ = \sum_\mu k_+(\mu)$ and $K_- = \sum_\lambda k_-(\lambda)$ [18]. Most of our analysis will be performed supposing that $k_+(\mu)$ and $k_-(\lambda)$ are arbitrary integrable functions of $\mu$ and $\lambda$.

In what follows, we will distinguish between two situations:

(i) the case of microscopically homogeneous elementary reactions, when $k_+(\mu)$ is strictly proportional to $k_-(\mu)$ (or, in other words, when the ratio $k_+(\mu)/k_-(\mu)$ is independent of $\mu$ for any $\mu$)

(ii) the general case of microscopically inhomogeneous reactions, where $k_+(\mu)/k_-(\mu)$ is $\mu$-dependent, at least in some region of space.

The criterium of microscopically homogeneous reactions has an important interpretation. Indeed, for microscopically inhomogeneous reactions, any steady distribution of the concentrations of the species A and B breaks the detailed balance equilibrium. This is due to the fact that in this case the equilibrium constant $k_-(\mu)/k_+(\mu)$ is space dependent: equilibrium can not be satisfied at each point for homogeneous concentrations. We will show below that this violation of the detailed balance has important implications at the macroscopic scale.

The state of the system at time $t$ is determined by the time-dependent numbers $A(x)$ and $B(x)$ of $A$ and $B$ particles at site $x$ of the lattice. The set of such numbers is denoted as \{A\} and \{B\} and $P[A, B, t]$ stands for the probability of finding the system at time moment $t$
in the \( \{A\} \) and \( \{B\} \) state.

Our analytical approach is based on the formally exact Poisson representation method, proposed originally by Gardiner [9], and subsequently generalized in Ref. [29] for the description of the fluctuation-induced kinetics of reversible, microscopically homogeneous contact diffusion-limited reactions. Extension of this approach to the case of distance-dependent reactions is straightforward and here we merely outline the steps involved.

The starting point of our analysis is the following master equation describing the time evolution of \( P[A, B; t] \):

\[
\partial_t P[A, B; t] = \mathcal{L} P[A, B; t],
\]

where \( \mathcal{L} \) is an operator, accounting for the reaction and diffusion processes on the microscopic, many particle level. Explicitly, the right-hand-side of Eq. (4) reads:

\[
\mathcal{L} P[A, B; t] = \frac{D}{\ell^2} \sum_x \sum_{e_x} \left[ (A(e_x) + 1) P[A(x) - 1, A(e_x) + 1, B, t] - A(x) P[A, B, t] \right] + \frac{D}{\ell^2} \sum_x \sum_{e_x} \left[ (B(e_x) + 1) P[A, B(x) - 1, B(e_x) + 1, t] - B(x) P[A, B, t] \right] - \sum_{\mu} k_+ (\mu) \sum_x \left[ \left( A(x - \frac{\mu}{2}) + 1 + \delta_{\mu,0} \right) \left( A(x + \frac{\mu}{2}) + 1 \right) \times P[A(x - \frac{\mu}{2}) + 1 + \delta_{\mu,0}, A(x + \frac{\mu}{2}) + 1 + \delta_{\mu,0}, B(x) - 1, t] - A(x - \frac{\mu}{2})(A(x + \frac{\mu}{2}) - \delta_{\mu,0}) P[A, B, t] \right] + \sum_{\mu} k_- (\mu) \sum_x \left( B(x) + 1 \right) P[A(x - \frac{\mu}{2}) - 1 - \delta_{\mu,0}, A(x + \frac{\mu}{2}) - 1 - \delta_{\mu,0}, B(x) + 1, t] - \sum_{\mu} k_- (\mu) \sum_x B(x) P[A, B, t],
\]

where \( D = \ell^2/2d\tau \) is \( A \) and \( B \) particles diffusion coefficient, \( \tau \) is a characteristic hopping time, while the symbol \( \sum_{e_x} \) denotes summation over all possible orientations of the lattice vector \( e_x \). As the initial condition to Eq. (5), we choose an uncorrelated Poisson distribution on each site and for each species:

\[
P[A, B, t = 0] = e^{-A_0 - B_0} \prod_x \frac{A_0^{A(x)} B_0^{B(x)}}{A(x)! B(x)!},
\]

where \( A_0 \) and \( B_0 \) are mean occupation numbers of \( A \) and \( B \) particles per lattice site.
The next step consists in projecting the particles numbers on sites \( x \) onto the Poisson states \( \Psi \):

\[
P[A, B, t] = \int \prod_x d\alpha(x) d\beta(x) \frac{\exp(-\alpha(x)) \alpha(x)^A(x)}{A(x)!} \times \]

\[
\times \frac{\exp(-\beta(x)) \beta(x)^B(x)}{B(x)!} F[\alpha(x), \beta(x), t]
\]

Existence of such a transformation (and of the inverse one) is well established \[9\]. As a matter of fact, the factorial moments of particles’ numbers, say of \( A(x) \), are related to the Poisson fields \( \alpha(x) \) and \( \beta(x) \) via a simple formula:

\[
\langle A(x) \rangle_n \equiv \left\langle A(x) \right\rangle \left( A(x) - 1 \right) \ldots \left( A(x) - (n - 1) \right) = \int \prod_x d\alpha(x) d\beta(x) \alpha^n(x) F[\alpha(x), \beta(x), t] = \langle \alpha^n(x) \rangle,
\]

where the angle brackets denote the probabilistic average stemming out of stochastic reaction processes. Note, however, that the Poisson fields \( \alpha(x) \) and \( \beta(x) \) may be complex-valued; consequently, \( F[\alpha(x), \beta(x), t] \) may admit negative values and hence can not be interpreted as a probability distribution.

Defining next the generating function

\[
G[u(x), v(x), t] = \sum_{a,b} \prod_x u(x)^a v(x)^b P[A, B, t]
\]

one represents \( G[u(x), v(x), t] \) as

\[
G[u(x), v(x), t] = \int \prod_x d\alpha(x) d\beta(x) \exp[(u(x) - 1)\alpha(x)] \times \exp[(v(x) - 1)\beta(x)] F[\alpha(x), \beta(x), t],
\]

which yields, eventually, the following Fokker-Planck equation determining evolution of \( F[\alpha(x), \beta(x), t] \):

\[
\partial_t F[\alpha(x), \beta(x), t] = -\sum_x \sum_\mu \left\{ \frac{\partial}{\partial \alpha(x)} C_1[\alpha, \beta] + \frac{\partial}{\partial \beta(x)} C_2[\alpha, \beta] - \frac{1}{2} \frac{\partial^2}{\partial \alpha(x - \mu/2) \partial \alpha(x + \mu/2)} C_3[\alpha, \beta] \right\} F[\alpha(x), \beta(x), t]
\]

where

\[
\begin{align*}
C_1[\alpha, \beta] &= -k_+(\mu)\alpha(x)\left(\alpha(x - \mu) + \alpha(x + \mu)\right) + k_-(\mu)\left(\beta(x - \mu) + \beta(x + \mu)\right) + D\Delta \alpha, \\
C_2[\alpha, \beta] &= k_+(\mu)\alpha(x - \mu/2)\alpha(x + \mu/2) - k_-(\mu)\beta(x) + D\Delta \beta, \\
C_3[\alpha, \beta] &= k_+(\mu)\alpha(x + \mu/2)\alpha(x - \mu/2) - k_-(\mu)\beta(x).
\end{align*}
\]
where $\Delta$ is the second finite difference operator.

Note that Eq.(11) can not be, of course, solved exactly. On the other hand, we are in position to draw one important conclusion directly from the form of Eq.(11). By inspection, one may verify that because of the presence of ”mixed” derivatives $\partial^2/\partial\alpha(x - \mu/2)\partial\alpha(x + \mu/2)$..., in the microscopically inhomogeneous case, when $k_+(\mu)/k_-(\mu)$ is $\mu$-dependent, this Fokker-Planck equation does not admit any stationary solution of the form:

$$F[\alpha(x), \beta(x), t] = \prod_x \delta[\alpha(x) - \langle \alpha \rangle] \delta[\beta(x) - \langle \beta \rangle] \tag{13}$$

Therefore, if $k_+(\mu)/k_-(\mu)$ depends on $\mu$, the stationary distribution $P[A, B, t]$ is not a product of uncorrelated Poisson distributions, as one obtains in case of contact, microscopically homogeneous reactions. This implies, in turn, that the detailed balanced is not satisfied, which hints us that here the asymptotic $t = \infty$ state might be rather particular. Indeed, below we will demonstrate that the fact that $F[\alpha(x), \beta(x), t]$ does not factorize into the product $\prod_x f[\alpha(x), \beta(x), t]$, where each multiplier $f[\alpha(x), \beta(x), t]$ depends only on the Poisson fields $\alpha(x)$ and $\beta(x)$ on the site $x$, implies that the CE state is not a true equilibrium state and that the pairwise correlations in particles’ spatial distribution exist, which, in consequence, results in violation of the LMA in Eq.(2).

Using Itô’s equivalence, we find the following Langevin equations corresponding to equation (11):

$$\begin{align*}
\partial_t \alpha(x) &= \sum_\mu C_1[\alpha, \beta] + \zeta(x, t), \\
\partial_t \beta(x) &= \sum_\mu C_2[\alpha, \beta],
\end{align*} \tag{14}$$

where $\zeta(x, t)$ is a Gaussian noise with zero mean value, whose correlation is given by

$$\begin{align*}
\langle \zeta(x, t)\zeta(x + x', t') \rangle &= \delta(t - t') \left[ k_-(x') \langle \beta(x') \rangle \\
&\quad - k_+(x') \langle \alpha(x - x'/2)\alpha(x + x'/2) \rangle \right]. \tag{15}
\end{align*}$$

Before we proceed further, some comments are in order. We first remark that exactly the same Langevin equations can be obtained extending to the general case with distance-dependent elementary reaction rates the field theoretical technique, developed in Ref.[27] for contact microscopically homogeneous reactions. We believe, however, that the approach used here is more simple and transparent. Second, we note that contrary to the situation with contact microscopically homogeneous reactions (see Eqs.(12) and (13) in Ref.[27]), in
the general case when the ratio $k_+(\mu)/k_-(\mu)$ is $\mu$-dependent, the amplitude of the noise correlation can not be expressed as a time derivative of $<\alpha(x)>$; hence, noise correlation does not vanish as $t \to \infty$. Finally, we note that non-linear Langevin equations have been already used in Refs.\[21, 22\] to analyze the temporal evolution of several contact diffusion-limited reactions. Noise terms, employed in this approach, were previously derived within the hydrodynamic-level stochastic approach in Ref.\[34\]. Our Eqs.(14) and (15) have essentially the same structure as those used in Refs.\[21, 22\] with two notable exceptions:

(i) Eqs.(14) and (15) are obeyed by the Poisson fields, which are not physical concentrations, and moreover, the noise is complex-valued, while the corresponding Langevin equations in Refs.\[21, 22\] are formulated for the true local concentrations.

(ii) the noise terms used in Refs.\[21, 22\] contain an additional, compared to our Eq.(15), term $\sim D\nabla_x A(x)\nabla_x \delta(x)$, which does not vanish as $t \to \infty$. This is apparently incorrect and represents an evident shortcoming of the hydrodynamic-level stochastic approach in Ref.\[34\]. Moreover, this is precisely the reason why the deviations from the LMA were obtained in Refs.\[21, 22\] for microscopically homogeneous contact reactions.

### III. THE ASYMPTOTIC $t = \infty$ STATE: DECOUPLING APPROXIMATION.

For convenience, we turn from now on to the continuous-space limit ($\ell \to 0$), consider $x$ as a continuous variable and operate with particles’ concentrations $a(x) = A(x)/l^d$ and $b(x) = B(x)/l^d$, instead of particles’ numbers. Note also that for an accurate ”passage” to such a limit, one has to introduce the rescaled reaction rates $k_+ \to k_+\ell^{-1}$ and $k_- \to k_-\ell^{-1}$, noise $\zeta \to \zeta/l^d$, as well as the Poisson fields $\alpha(x) \to \alpha(x)/l^d$ and $\beta(x) \to \beta(x)/l^d$\[27\].

Taking into account that, in virtue of Eq.(13), we have $<\alpha(x)> = <\alpha(x)> = a$ and $<\beta(x)> = <\beta(x)> = b$, we write the Poisson fields as follows:

$$\alpha(x,t) = a + \delta\alpha(x,t),$$

$$\beta(x,t) = b + \delta\beta(x,t)$$

where $a$ and $b$ are (time-dependent) particles’ mean concentrations, while $\delta\alpha(x,t)$ and $\delta\beta(x,t)$ denote local deviations of the Poisson fields from their mean values. Hence, by definition, $<\delta\alpha(x,t)> = <\delta\beta(x,t)> = 0$.

Substituting next expressions in Eq.(16) into Langevin Eqs.(14), averaging the resulting equations and using the definition of the overall reaction constants $K_\pm = \int\mu \, k_\pm(\mu) \, d\mu$, we
find that particles' mean concentrations obey:

\[
\begin{align*}
\partial_t a &= -2K_+ a^2 + 2K_+ b + 2\Omega(0), \\
\partial_t b &= K_+ a^2 - K_+ b - \Omega(0),
\end{align*}
\]  

(17)

where

\[
\Omega(0) \equiv - \int d\mu k_+(\mu) \sigma_{\alpha\alpha}(\mu),
\]

(18)

and \(\sigma_{\alpha\alpha}(\mu)\) is the pairwise correlation function,

\[
\sigma_{\alpha\alpha}(\mu) = \langle \delta \alpha(x - \mu/2, t) \delta \alpha(x + \mu/2, t) \rangle,
\]

(19)

of the fluctuations in the Poisson fields. The corresponding correlation function for the fluctuations in particles concentrations in the asymptotic \(t = \infty\) state can be readily expressed in terms of \(\sigma_{\alpha\alpha}(\mu)\):

\[
c(\mu)_{\infty} = \langle (a_{\infty} - a(x, t = \infty))(a_{\infty} - a(x + \mu, t = \infty)) \rangle = \sigma_{\alpha\alpha}(\mu)_{\infty} + a_{\infty} \delta(\mu)
\]

(20)

Note that Eqs. (17) are formally exact for any \(t\). These equations show that the time evolution of observables - the particles' mean concentrations, is ostensibly coupled to the evolution of pairwise correlations in the reaction-diffusion system under study.

Turning next to the infinite time limit, \(t \to \infty\), we get, slightly rearranging Eqs. (17), that the particles' mean concentrations obey:

\[
a_{\infty}^2 / b_{\infty} = K_- / K_+ + \Omega(0)_{\infty} / K_- b_{\infty},
\]

(21)

where the subscript \(\infty\) signifies that we deal with the asymptotic \(t = \infty\) solution.

Note that Eq. (21) resembles the classical Law of Mass Action in Eq. (2), but differs from it due to an extra term \(\Omega(0) / K_+ b_{\infty}\), which is dependent on the pairwise correlation function \(\sigma_{\alpha\alpha}(\mu)_{\infty}\) and embodies all non-trivial physics associated with the fluctuation effects. Therefore, one may judge directly from Eq. (21) that the classical LMA holds only if \(A\) particles distribution is spatially uncorrelated in the asymptotic \(t = \infty\) state, i.e. \(\sigma_{\alpha\alpha}(\mu)_{\infty} \equiv 0\).

Now, our aim is to determine the pair correlation function \(\sigma_{\alpha\alpha}(\mu)\). This turns out to be, however, quite a complicated problem. More specifically, when one writes the evolution equations obeyed by pairwise correlations, he gets that these are coupled to the third-order correlations and etc, which is a signature of a genuine many particle problem.
In this section we resort to an approximate approach, while some exact results will be presented in the next section. Our approach here is based on the assumption that the deviations $\delta \alpha(x, t)$ and $\delta \beta(x, t)$ are Gaussian random fields, which implies an automatic decoupling of fourth-order correlations into the product of pairwise ones, and hence, truncation of the hierarchy of coupled reaction-diffusion equations on the level of third-order correlations. Such an approach has been first employed in Ref. [46] to obtain the $t^{-d/4}$-law describing the fluctuation-induced kinetics of irreversible $A + B \rightarrow 0$ reactions, and subsequently generalized in Refs. [21] and [22] for other irreversible and reversible reactions.

Within this approach, we find that pairwise correlations obey the following system of equations:

$$
\partial_t \sigma_{\alpha\alpha}(\mu) = 2D\Delta_\mu \sigma_{\alpha\alpha}(\mu) - 2a \int d\lambda k_+(\lambda) \left( 2\sigma_{\alpha\alpha}(\mu) + \sigma_{\alpha\alpha}(\mu - \lambda) + \sigma_{\alpha\alpha}(\mu + \lambda) \right)
+ 2 \int d\lambda k_-(\lambda) \left( \sigma_{\alpha\beta}(\mu - \lambda) + \sigma_{\alpha\beta}(\mu + \lambda) \right) + k_-(\mu)b - k_+(\mu)a^2 - k_+(\mu)\sigma_{\alpha\alpha}(\mu),
$$

(22)

$$
\partial_t \sigma_{\alpha\beta}(\mu) = 2D\Delta_\mu \sigma_{\alpha\beta}(\mu) - \left( 2aK_+ + K_- \right) \sigma_{\alpha\beta}(\mu) - a \int d\lambda k_+(\lambda) \left( \sigma_{\alpha\beta}(\mu + \lambda) + \sigma_{\alpha\beta}(\mu - \lambda) \right)
+ a \int d\lambda k_+(\lambda) \left( \sigma_{\alpha\alpha}(\mu + \frac{\lambda}{2}) + \sigma_{\alpha\alpha}(\mu - \frac{\lambda}{2}) \right) +
+ \int d\lambda k_-(\lambda) \left( \sigma_{\beta\beta}(\mu + \lambda) + \sigma_{\beta\beta}(\mu - \lambda) \right),
$$

(23)

and

$$
\partial_t \sigma_{\beta\beta}(\mu) = 2D\Delta_\mu \sigma_{\beta\beta}(\mu) - 2K_- \sigma_{\beta\beta}(\mu) + 2a \int d\lambda k_+(\lambda) \left( \sigma_{\alpha\beta}(\mu + \frac{\lambda}{2}) + \sigma_{\alpha\beta}(\mu - \frac{\lambda}{2}) \right),
$$

(24)

where the "$\alpha\beta$" and "$\beta\beta$" pair correlation functions are defined as

$$
\sigma_{\alpha\beta}(\mu) = \langle \delta \alpha(x - \mu/2, t)\delta \beta(x + \mu/2, t) \rangle,
$$

(25)

and

$$
\sigma_{\beta\beta}(\mu) = \langle \delta \beta(x - \mu/2, t)\delta \beta(x + \mu/2, t) \rangle.
$$

(26)

Further on, introducing a pair of Fourier transforms:

$$
f(p) = \int d\mu \, e^{i(p \cdot \mu)} f(\mu), \quad \text{and} \quad f(\mu) = \frac{1}{(2\pi)^d} \int dp \, e^{-i(p \cdot \mu)} f(p),
$$

(27)
we get from Eqs. (22) to (24) that \( \sigma_{kl}(p), (k, l = \alpha, \beta) \), obey:

\[
\begin{align*}
\partial_t \sigma_{\alpha\alpha}(p) &= -2\left( Dp^2 + 2aK_+ + 2ak_+(p) \right) \sigma_{\alpha\alpha}(p) \\
&\quad + 4k_-(p)\sigma_{\alpha\beta}(p) + k_-(p)b - k_+(p)a^2 + \Omega(p), \\
\partial_t \sigma_{\alpha\beta}(p) &= -\left( 2Dp^2 + 2aK_+ + K_- + 2ak_+(p) \right) \sigma_{\alpha\beta}(p) \\
&\quad + 2ak_+(p/2)\sigma_{\alpha\alpha}(p) + 2k_-(p)\sigma_{\beta\beta}(p), \\
\partial_t \sigma_{\beta\beta}(p) &= 4ak_+(p/2)\sigma_{\alpha\beta}(p) - 2\left( Dp^2 + K_- \right) \sigma_{\beta\beta}(p),
\end{align*}
\]

where we have assumed that \( k_+(\mu) \) and \( k_-(\mu) \) depend only on the absolute value of \( \mu \), and denoted

\[
\Omega(p) = -\int d\mu e^{i(p\mu)}k_+(\mu)\sigma_{\alpha\alpha}(\mu).
\]

Turning now to the asymptotic limit \( t = \infty \), we get from Eqs. (28) to (30) that \( \sigma_{\alpha\alpha}(p)_{\infty} \) is determined as the solution of the following equation:

\[
\sigma_{\alpha\alpha}(p)_{\infty} = F(p) \left[ \Omega(p)_{\infty} - \epsilon(p)_{\infty} \right],
\]

where

\[
F(p) = \frac{X_2(p)(X_1(p) + X_2(p)) - X_3(p)}{2(X_1(p)X_2(p) - X_3(p))(X_1(p) + X_2(p))},
\]

\[
X_1(p) = Dp^2 + 2K_+a_{\infty} + 2k_+(p)a_{\infty},
\]

\[
X_2(p) = Dp^2 + K_-,
\]

\[
X_3(p) = 4k_+(p/2)k_-(p)a_{\infty},
\]

and

\[
\epsilon(p)_{\infty} = k_+(p)a_{\infty}^2 - k_-(p)b_{\infty}.
\]

Note that Eq. (32) only implicitly defines \( \sigma_{\alpha\alpha}(p)_{\infty} \), since the term \( \Omega(p)_{\infty} \) on the right-hand-side of this equation is itself dependent on \( \sigma_{\alpha\alpha}(p)_{\infty} \), Eq. (31). Therefore, Eq. (32) is an integral equation and its solution may be found only if we specify \( k_+(\mu) \) and \( k_-(\mu) \).

### A. Criterion of validity of the LMA and of the True Thermodynamic Equilibrium: Decoupling Approximation.

Despite the fact that \( \sigma_{\alpha\alpha}(p)_{\infty} \) has been so far only implicitly defined, and in order to get some explicit results we have to fix \( k_+(\mu) \) and \( k_-(\mu) \), we are in position now to deduce a
general criterion specifying when the LMA in Eq. (2) holds and when it is violated. To do this, we have merely to define conditions when \( \sigma_{\alpha \alpha}(p)_{\infty} \neq 0 \).

We proceed as follows. First, we set in Eq. (32) \( \sigma_{\alpha \alpha}(p)_{\infty} \equiv 0 \) (i.e. \( \sigma_{\alpha \alpha}(\mu)_{\infty} \equiv 0 \)). This implies that \( \Omega(p)_{\infty} \equiv 0 \), and hence, in order to have \( \sigma_{\alpha \alpha}(p)_{\infty} \equiv 0 \), the following relation should hold as an identity:

\[
k_-(p)b_{\infty} \equiv k_+(p)a_{\infty}^2 \quad \text{for any } p,
\]

or, in the \( \mu \)-domain,

\[
k_-(\mu)b_{\infty} \equiv k_+(\mu)a_{\infty}^2 \quad \text{for any } \mu.
\]

Note that in this only case the amplitude of the noise-noise correlation in Eq. (15) is proportional to \( \partial_t a \) and hence, vanishes as \( t \to \infty \).

Now, one readily verifies that the identities in Eqs. (36) and (37) may hold only if the reactions rates are identic functions of \( \mu \), i.e. the elementary reactions are microscopically homogeneous. If this condition is violated, even at least at a single point, pair correlations \( \sigma_{\alpha \alpha}(\mu)_{\infty} \) are non-zero, and hence, in virtue of Eq. (21), the LMA in Eq. (2) is violated. Hence, we find that the conventional LMA in Eq. (2) is always violated for microscopically inhomogeneous reactions.

Next, for microscopically inhomogeneous reactions, we estimate the decay of pairwise correlations in the limit \( \mu \to \infty \). In the limit \( p \to 0, \mu \to \infty \), the kernel \( F(p) \) in Eq. (33) attains the form:

\[
F(p) \sim \frac{2D^2p^4 + Dp^2(4K_+a_{\infty} + 3K_-) + K_-^2}{2Dp^2(Dp^2 + 4K_+a_{\infty} + K_-)(2Dp^2 + 4K_+a_{\infty} + K_-)}
\]

Now, let \( \Lambda_r \) be the characteristic decay length of \( k_+(\mu) \). Since this property is usually of a range of a few interparticle separations, one may expect that \( \sigma_{\alpha \alpha}(\mu)_{\infty} \) varies with \( \mu \) much more slowly than \( k_+(\mu) \). This assumption will be checked for consistency afterwards. Hence, we may approximate \( \Omega(p)_{\infty} \) in Eq. (31) as

\[
\Omega(p)_{\infty} \sim -\sigma_{\alpha \alpha}(\mu = 0)_{\infty}k_+(p)
\]

Substituting the latter representation into Eq. (32) and performing straightforward calculations, we get that in the limit \( \mu \to \infty \), the pairwise correlations in the asymptotic \( t = \infty \) state obey

\[
\sigma_{\alpha \alpha}(\mu)_{\infty} \sim \exp \left( -\frac{\mu}{\Lambda_{corr}} \right)/\mu,
\]
where
\[ \Lambda_{corr} = \sqrt{\frac{D}{4K_+a_\infty + K_-}}. \] (41)

The approximation underlying the derivation of Eqs. (40) and (41) is thus justified when \( \Lambda_{corr} \gg \Lambda_r \), or, in other words, when \( \tau_{chem} = (4K_+a_\infty + K_-)^{-1} \gg \tau_{diff} = \Lambda_r^2/D \).

Hence, pairwise correlations in \( A \) particles distributions are long-ranged for microscopically inhomogeneous reactions. A salient feature of the result in Eq. (40) is that the characteristic decay length \( \Lambda_{corr} \) of pairwise correlations depends on such ”kinetic” parameter as \( D \), the particles diffusion coefficient, which signifies that the asymptotic state achieved by reversible diffusion-limited reactions with microscopically inhomogeneous elementary reaction rates at \( t = \infty \) is not a true equilibrium state, but rather a non-equilibrium steady-state. We note finally that \( \Lambda_{corr} \) is, of course, \( D \)-dependent for arbitrary relation between \( \tau_{chem} \) and \( \tau_{diff} \). Note also that for microscopically inhomogeneous reactions \( \Lambda_{corr} \) does not vanish as \( D \to 0 \); in this case, the particles may perform random excursions in space just because in the break-up of \( B \) a pair of \( A \)s is not forced to be born at their initial locations, at which they have entered the reaction forming the \( B \) particle. It is also interesting to remark that in the limit \( \tau_{chem} = (4K_+a_\infty + K_-)^{-1} \gg \tau_{diff} = \Lambda_r^2/D \) the correlation length \( \Lambda_{corr} \) equals the distance travelled by a diffusive particle within its typical life-time between the reaction processes, i.e. the so-called Kuramoto length. Remarkably, precisely this length sets the scale of spatial correlations in out of equilibrium open chemical systems [11, 12, 13, 14, 15].

**B. ”Contact reaction” approximation for microscopically inhomogeneous reactions.**

In this subsection we consider, within the framework of the decoupling procedure, the properties of the asymptotic \( t \to \infty \) state for reversible diffusion-limited reactions in ”contact approximation”. This will allow us to illustrate the statement made in the Introduction that this approximation entails a somewhat ambiguous definition of the properties of the asymptotic \( t = \infty \) state, as well as to present some explicit results on the corrections to the LMA in Eq. (2).

Suppose that \( k_+(\mu) \) and \( k_-\mu(\mu) \) are some bell-shaped functions centered around their most probable values \( R \) and \( \lambda \), and the thicknesses of the distributions are negligibly small, such that the forward and the backward distance-dependent reaction constants can be deemed as delta-functions: \( k_+(\mu) = \gamma_d^{-1}(R)K_+\delta^d(|\mu| - R) \) and \( k_-\mu(\mu) = \gamma_d^{-1}(\lambda)K_-\delta^d(|\mu| - \lambda) \), where the
normalization factor $\gamma_d(R) = A_d R^{d-1}, \ A_d$ being the volume of a $d$-dimensional unit sphere, $A_d = 2\pi^{d/2}/\Gamma(d/2)$, and $\Gamma(x)$ - the Gamma-function.

For such a choice of the reaction rates, we get from Eq. (32) that

$$\sigma_{\alpha\alpha}(p)_\infty = F(p) \left( k_- (p) b_\infty - k_+ (p) a_\infty^2 - k_+ (p) \sigma_{\alpha\alpha}(|\mu| = R)_\infty \right),$$

(42)

which implies

$$\sigma_{\alpha\alpha}(\mu)_\infty = J_- (\mu, \lambda) b_\infty - J_+ (\mu, R) a_\infty^2 - J_+ (\mu, R) \sigma_{\alpha\alpha}(|\mu| = R)_\infty,$$

(43)

where

$$J_- (\mu, \lambda) = \frac{1}{(2\pi)^d} \int dp \ e^{-i(p \cdot \mu)} F(p) k_- (p),$$

(44)

and

$$J_+ (\mu, R) = \frac{1}{(2\pi)^d} \int dp \ e^{-i(p \cdot \mu)} F(p) k_+ (p).$$

(45)

Next, setting $|\mu| = R$ in Eq. (43), we obtain the following equation determining the value of the pairwise correlation function $\sigma_{\alpha\alpha}(\mu)$ at distance equal to the direct reaction radius:

$$\sigma_{\alpha\alpha}(|\mu| = R)_\infty = \frac{J_- (|\mu| = R, \lambda) b_\infty - J_+ (|\mu| = R, R) a_\infty^2}{1 + J_+ (|\mu| = R, R)}$$

(46)

Consequently, taking advantage of Eqs. (21) and (46), we find that for reactions in contact approximation particles’ mean concentrations $b_\infty$ and $a_\infty$ obey:

$$\frac{a_\infty^2}{b_\infty} = \frac{K_-}{K_+} \left( 1 + J_+ (|\mu| = R, R) - \frac{K_+}{K_-} J_- (|\mu| = R, \lambda) \right).$$

(47)

Note now that setting $R \equiv \lambda$, we get that $J_+ (|\mu| = R, R) = K_+ J(R)$ and $J_- (|\mu| = R, \lambda = R) = K_- J(R)$, which immediately implies that Eq. (47) simplifies to the conventional LMA in Eq. (2) and signifies that the chemical equilibrium state is a true thermodynamic equilibrium. If we, however, take into account dispersions around most probable values, which should be generally different for unimolecular backward and bimolecular forward elementary reactions, we would immediately obtain that the particles’ mean concentrations do not obey the LMA and that the chemical equilibrium state is not a true equilibrium. The situation becomes even more ambiguous if the elementary reaction rates $k_+ (\mu)$ and $k_- (\mu)$ are not simple bell-shaped, but more realistic complicated functions of $\mu$ having minima and maxima (see, e.g., Refs. [40, 43]). As we have already remarked in the Introduction, for such $k_+ (\mu)$ and $k_- (\mu)$ the choice of $R$ and $\lambda$, at which the reactive boundary condition is imposed, has a
large degree of arbitrariness, but its consequences are grave: when one constrains himself to "contact approximation" and supposes, as it has been done in Refs. [27] and [29], that two ill-defined reaction radii are equal to each other, one finds that there are no corrections to the LMA as $t \to \infty$ and that the CE is a true TES. On contrary, letting $R$ and $\lambda$ be different on an arbitrarily small but fixed value, one gets that Eq. (47) is always different from Eq. (2), and that both $a_\infty$ and $b_\infty$ are dependent on such "kinetic" parameter as particles diffusion coefficient $D$. Which, in turn, implies that the asymptotic $t = \infty$ state is not a true thermodynamic equilibrium, but rather a non-equilibrium steady-state.

Consider next the explicit form of corrections to the LMA in Eq. (47) for microscopically inhomogeneous contact reactions in three dimensional systems. Here, we have for the Fourier transformed reaction constants:

$$k_+(p) = K_+ \frac{\sin(pR)}{pR}, \quad \text{and} \quad k_-(p) = K_- \frac{\sin(p\lambda)}{p\lambda},$$

and consequently,

$$J_+ (|\mu| = R, R) - \frac{K_+}{K_-} J_-(|\mu| = R, \lambda) = \frac{K_+}{2\pi^2 R} \int_0^{\infty} p dp \sin(pR) F(p) \left( \frac{\sin(pR)}{pR} - \frac{\sin(p\lambda)}{p\lambda} \right).$$

Expanding next $F(p)$ in Eq. (48) into elementary fractions and performing the resulting integrals, we find that for sufficiently small $R$ and $\lambda$ ($\lambda > R$),

$$J_+ (|\mu| = R, R) - \frac{K_+}{K_-} J_-(|\mu| = R, \lambda) \approx \frac{K_+}{4\pi DR} (1 - \frac{R}{\lambda}).$$

Substituting the last equation into Eq. (47), we arrive eventually at the result presented in Eq. (3), which has been previously obtained in Ref. [21] in terms of a suitably extended heuristic Smoluchowski approach. In the next section we will show using a systematic diagrammatic expansion that, curiously enough, this equation is exact in the linear order in deviation from the equilibrium.

**IV. THE ASYMPTOTIC $t = \infty$ STATE: EXACT RESULTS.**

In this section we will analyze behavior of the pairwise correlation function $\sigma_{aa}(\mu)$ entering Eq. (21) in terms of a systematic diagrammatic expansion. In terms of this expansion, we will derive, in the linear with respect to the deviation from equilibrium approximation, an integral equation obeyed by $\sigma_{aa}(\mu)$. We proceed to show then that our criterion of the
validity of the LMA and of the thermodynamic equilibrium, obtained in the previous section within the decoupling procedure, is exact. Moreover, we will define corrections to the LMA in Eq. (2) for microscopically inhomogeneous reactions with contact and exponential reaction rates.

We start by rewriting the Langevin equations (14) in the following matricial form:

\[
M \cdot \begin{pmatrix}
\delta \alpha(x, t) \\
\delta \beta(x, t)
\end{pmatrix} = \begin{pmatrix}
u_1 - 2 \epsilon_0 + \zeta \\
u_2 + \epsilon_0
\end{pmatrix} \tag{51}
\]

where \(\delta \alpha = \delta \alpha(x, t)\) and \(\delta \beta = \delta \beta(x, t)\) are local deviations from the stationary values, \(\zeta = \zeta(x, t)\), \(\epsilon_0 \equiv \epsilon(p = 0) \infty\), the functionals \(u_{1,2}\) are given by:

\[
\begin{cases}
u_1(x, t) = -\int d\mu k_+ (\mu) \delta \alpha(x, t)(\delta \alpha(x - \mu, t) + \delta \alpha(x + \mu, t)), \\
u_2(x, t) = \int d\mu k_+ (\mu) \delta \alpha(x - \mu/2, t) \delta \alpha(x + \mu/2, t),
\end{cases} \tag{52}
\]

while the linear operator \(M\) is defined in the Laplace-Fourier space of parameters \(s, p\) as:

\[
M(s, p) = \int d\mu dt e^{-st} + i(p \cdot \mu) M(\mu) = 
\begin{pmatrix}
s + Dp^2 + 2a_\infty (K_+ + k_+(p)) & -2k_-(p) \\
-2a_\infty k_+(p) & s + Dp^2 + K_-
\end{pmatrix}. \tag{53}
\]

Note that in Eq. (53), we have supposed, as in the previous section, that \(k_\pm(\mu)\) depend only on the absolute value of \(\mu\) and hence, that \(k_\pm(p) = k_\pm(-p)\).

Denoting next the propagator \(G\) as an inverse of the matrix \(M\), \(G = M^{-1}\), and taking the inverse Laplace transform, we find that the Fourier-transformed pair correlation function \(\sigma_{\alpha\alpha}(\mu), \text{Eq. (19)},\) obeys:

\[
\sigma_{\alpha\alpha}(p) = \langle |G_{\alpha\alpha}(p, t) \ast (u_1(p, t) - 2\epsilon_0 \delta(p) + \zeta(p, t) + \delta \alpha_0(p) \delta(t))|^2 \rangle \\
+ \langle |G_{\alpha\beta}(p, t) \ast (u_2(p, t) + \epsilon_0 \delta(p) + \delta \beta_0(p) \delta(t))|^2 \rangle \\
+ 2 \langle |G_{\alpha\alpha}(p, t) \ast (u_1(p, t) - 2\epsilon_0 \delta(p) + \zeta(p, t) + \delta \alpha_0(p) \delta(t))| \\
\times |G_{\alpha\beta}(p, t) \ast (u_2(p, t) + \epsilon_0 \delta(p) + \delta \beta_0(p) \delta(t))| \rangle, \tag{54}
\]

where the symbol " \(\ast\)" denotes the time convolution, while \(\delta \alpha_0\) and \(\delta \beta_0\) stand for the initial values of the Fourier spectra of fluctuations \(\delta \alpha(x, 0)\) and \(\delta \beta(x, 0)\). Note, however, that \(\delta \alpha_0\) and \(\delta \beta_0\) give rise to exponentially decreasing terms and are insignificant for both
the asymptotic state and for the long-time kinetic behavior. Eq. (54) is complimented by
the following equation determining the noise-noise correlation, Eq. (15), in time–momentum
space:
\[ \langle \zeta(p, t)\zeta(-p, t') \rangle = -\delta(t - t') (\varepsilon(p) - \Omega(p)) \]  

(55)
where \( \varepsilon \) and \( \Omega \) have been defined in the previous section.

Now, following Refs. [27] and [35], we set up a systematic diagrammatic expansion of the
pairwise correlation function \( \sigma_{\alpha\alpha}(p) \), defined by Eqs. (54) and (55). This expansion can be
obtained either from the analysis of the action of the field theory describing the model [35]
or more directly by iterating Eq. (54) and collecting the different terms appearing during this
procedure. The propagators and vertices corresponding to such an expansion are defined in
figure 1. The two first kinds of vortices (of coordinance 3) arise because of the coupling of
the quadratic term in \( u_1 \) and \( u_2 \) either with \( \delta\alpha \) or with \( \delta\beta \); the next one is due to the noise
term \( \zeta \) and the last one to the \( \varepsilon_0 \) term.

\[ \delta\alpha \delta\alpha \delta\alpha \delta\alpha \delta\alpha \delta\beta \delta\beta \delta\beta \delta\beta \]

\[ \leq \text{time} \]
\[ \delta\alpha \delta\beta \delta\alpha \delta\alpha \delta\alpha \delta\alpha \delta\alpha \delta\alpha \delta\alpha \delta\alpha \delta\alpha \delta\alpha \delta\beta \delta\beta \delta\beta \delta\beta \]

FIG. 1: Set of propagators (upper part) and vertices involved in the diagrammatic expansion of
the correlation function \( \sigma_{\alpha\alpha}(\mu) \).

\[ \langle \delta\alpha^2 \rangle = \]
\[ + \]
\[ + \]
\[ + \]
\[ + \]
\[ + \]

FIG. 2: Diagrammatic expansion of the correlation function \( \sigma_{\alpha\alpha}(p) \).

A direct summation of these diagrams is impossible, of course. We will therefore deem
this expansion as a perturbative development around the homogeneous situation, that is, an
expansion around a configuration of the elementary reaction rates satisfying \( \varepsilon(p)_{\infty} \equiv 0 \). The
small parameter in such an expansion will be the norm (supremum, for instance, denoted
as $|\epsilon|)$ of the function $\epsilon(p)$. First order contribution can be obtained as follows: Note that a vortex $\epsilon_0$ in figure 11 corresponding to the term $\epsilon_0$ in Eq.(54), is of order $|\epsilon|$: likewise, following Eq.(55), one has that a vortex $\zeta$ is also of order $|\epsilon|$. The first diagram of figure (2) is therefore of order 1, the second of order 2, and all the following diagrams are of higher order in $|\epsilon|$. Consequently, in the linear order in deviation from the equilibrium, we obtain the following relation:

$$
\sigma_{\alpha\alpha}(p) = - \int_0^t dt' G_{\alpha\alpha}^0(p, t-t')^2 [\epsilon(p) - \Omega(p)],
$$

(56)

where $G_{\alpha\alpha}^0(p, t)$ is the 0–order propagator, which can be readily obtained in an explicit form from Eq.(53):

$$
G_{\alpha\alpha}^0(p, t) = \frac{(K_- - q^-)}{q^+ - q^-} e^{-(Dp^2 + q^-) t} + \frac{(K_- - q^+)}{q^- - q^+} e^{-(Dp^2 + q^+) t}
$$

(57)

where

$$
q^\pm = \left[ K_- + 2a_\infty \left( K_+ + k_+(p) \right) \right] \pm \sqrt{q}/2,
$$

(58)

$$
q = \left[ K_- + 2a_\infty \left( K_+ + k_+(p) \right) \right]^2 - 8a_\infty \left( K_- (K_+ + k_+(p)) - 2k_+(p)k_-(p) \right).
$$

(59)

Turning next to the limit $t \to \infty$, making use of Eq.(21) and denoting

$$
\mathcal{F}^0(p) = \int_0^\infty dt' G_{\alpha\alpha}^0(p, t')^2,
$$

(60)

we get the following system of implicit equations:

$$
\begin{cases}
\sigma_{\alpha\alpha}(p) = \mathcal{F}^0(p) \left[ \Omega(p) - \epsilon(p) \right], \\
\epsilon_0 - \Omega(0) = 0
\end{cases}
$$

(61)

Note now that Eq.(61) has the same form as Eq.(32), obtained in section 3 within the framework of the decoupling approximation. The only difference is in the form of the kernel $\mathcal{F}^0(p)$, which is a little bit more complicated than $F(p)$ in Eq.(32) but has exactly the same poles. Note, however, that this difference does not affect the criterium we have formulated in the previous section. One may immediately deduce from Eq.(61) that $\sigma_{\alpha\alpha}(\mu) \equiv 0$, which implies that the LMA in Eq.(2) is valid, if and only if $\epsilon(p)$ equals 0, which holds only for systems with microscopically homogeneous reactions. This condition can be generalized to all orders and solves exactly our original problem in a very general framework for reactions
in Eq. (1): the chemical equilibrium is a true thermodynamic equilibrium and the LMA in Eq. (2) holds only for microscopically homogeneous diffusion-limited reversible reactions. If the reaction is not microscopically homogeneous, the asymptotic \( t = \infty \) state \((a_\infty, b_\infty)\) in the linear with respect to deviation from equilibrium approximation is described in a closed form by the system in Eqs. (61).

A. "Contact reactions" approximation revisited.

In this subsection we turn back to the "contact reaction" case and re-examine it in within the framework of Eqs. (61), which are exact in linear with respect to deviation from equilibrium approximation. As in section 3, we take the reaction rates in form of delta-functions: 
\[ k_+ (\mu) = \gamma_+^{-1}(R)K_+ \delta^d(|\mu| - R) \]
\[ k_- (\mu) = \gamma_-^{-1}(\lambda)K_- \delta^d(|\mu| - \lambda) \]
and suppose that \( \lambda > R \).

From Eq. (57), we have that the Fourier-transformed 0-order propagator:
\[ G_{0\alpha}^0 (p, t) = \frac{K_-}{4K_+ a_\infty + K_-} e^{-Dp^2t} + \frac{4K_+ a_\infty}{4K_+ a_\infty + K_-} e^{- (Dp^2 + 4K_+ a_\infty + K_-)t} \]  
(62)

Integrating Eq. (62) over the time variable, we get that the kernel \( F^0(p) \) in Eq. (61) is given explicitly by:
\[ F^0(p) = \frac{1}{(4K_+ a_\infty + K_-)^2} \left( \frac{K_-^2}{2Dp^2} + \frac{16K_+^2 a_\infty^2}{2(Dp^2 + 4K_+ a_\infty + K_-)} + \frac{8K_+ K_- a_\infty}{2Dp^2 + 4K_+ a_\infty + K_-} \right) \]  
(63)

Note that this function of \( p \), in the limit \( p \to 0 \), has exactly the same poles and shows exactly the same asymptotic behavior as \( F(p) \), Eq. (33), obtained using an uncontrollable decoupling procedure. Solving next Eqs. (61), we find that in three-dimensions particles mean concentrations \( a_\infty \) and \( b_\infty \) obey
\[ \frac{a_\infty^2}{b_\infty} = \frac{K_-}{K_+} \left[ 1 + \frac{K_+}{4\pi DR} \left( 1 - \frac{R}{\lambda} \right) + O((\lambda - R)^2) \right] \]  
(64)

This relation between the particles mean concentrations is obtained in an exact and controllable way. Quite surprisingly, in the linear with the respect to the difference \((\lambda - R)\) approximation, it coincide with Eq. (3), obtained in Ref. [21] within the framework of a suitably extended heuristic Smoluchowski approach.
Similar to Eq. (64), results can be also obtained for low-dimensional systems. Performing straightforward calculations, we find then that $a_\infty$ and $b_\infty$ obey:

$$\frac{a_\infty^2}{b_\infty} = \frac{K_-}{K_+} \left[ 1 + \frac{K_+}{4\pi D R} (\lambda - R) + O((\lambda - R)^2) \right],$$

(65)

and

$$\frac{a_\infty^2}{b_\infty} = \frac{K_-}{K_+} \left[ 1 + \frac{K_+}{4D} (\lambda - R) + O((\lambda - R)^2) \right]$$

(66)

for two- and one-dimensional systems, respectively.

B. Long-range, exponential reaction probabilities.

Here we estimate corrections to the LMA for a particular example of long-range distance-dependent rates, characterized by an exponential dependence on the interparticle separation for the forward bimolecular reaction, and an exponential dependence on the radius of a geminate pair born in the elementary act of the unimolecular backward reaction. We focus on three-dimensional systems in which $k_+ (\mu)$ and $k_- (\lambda)$ obey:

$$k_+ (\mu) = \frac{K_+}{8\pi R^3} e^{-\mu/R} \quad \text{and} \quad k_- (\mu) = \frac{K_-}{8\pi \lambda^3} e^{-\mu/\lambda}$$

(67)

For such a choice of reaction probabilities, we are not in position to solve our implicit equation (61) exactly and we have to resort to an approximate scheme. We thus develop an approximate approach, supposing that $R$ and $\lambda$ are sufficiently small, such that the characteristic length $\Lambda_{corr}$ of correlations in particles distributions emerging due to ongoing microscopically inhomogeneous elementary reactions in Eq. (67), is much greater than $R$ and $\lambda$. This is precisely the approximation used in section 3 to analyze behavior of correlations in general case of distance-dependent reactions. Under such an assumption, we may expect that $\sigma_{\alpha\alpha} (\mu)_\infty$ varies much slower than $k_+ (\mu)$ and $\Omega (p)_\infty$ can be represented as in Eq. (39). This implies that

$$\sigma (p)_\infty \approx b_\infty K_- F^0 (p) \left[ \frac{1}{(1 + p^2 \lambda^2)^2} - \frac{1}{(1 + p^2 R^2)^2} \right]$$

(68)

Evaluating next

$$\Omega (0)_\infty \approx -K_+ \int \frac{d^3 p}{(2\pi)^3} \sigma (p)_\infty,$$

(69)

we get, using Eq. (21), that particles mean concentrations $a_\infty$ and $b_\infty$ obey

$$\frac{a_\infty^2}{b_\infty} \approx \frac{K_-}{K_+} \left[ 1 + \frac{K_+}{16\pi D R} \left( 1 - \frac{R}{\lambda} \right) \right],$$

(70)
which holds for $R$ and $\lambda$ sufficiently small. Note that corrections to the LMA in case of long-range reactions rates in Eq.(67) appear to be smaller than in the ”contact” case.

Now, in order to verify that our approximation is self-consistent, we have to evaluate the form of pairwise correlation function $\sigma_{\alpha\alpha}(\mu)$ in $\mu$-space. Performing the inverse Fourier transformation of $\sigma_{\alpha\alpha}(p)\infty$ in Eq.(68), we find that for sufficiently small $R$ and $\lambda$ the pairwise correlations follow:

$$
\sigma(\mu)\infty = \frac{b_\infty K_-(\lambda^2 - R^2)}{4\pi D^2 \mu} \left[ \frac{16K_+^2a_\infty^2}{4K_+a_\infty + K_-} e^{-\mu/\Lambda_{\text{corr}}} + \frac{4K_+K_-a_\infty}{2(4K_+a_\infty + K_-)} e^{-\mu/\sqrt{2}\Lambda_{\text{corr}}} \right] + C_R e^{-\mu/R} + C_\lambda e^{-\mu/\lambda}
$$

(71)

where $C_R$ and $C_\lambda$ are $\mu$-independent constant and $\Lambda_{\text{corr}}$ has been defined in section 3, Eq.(41) in terms of the decoupling procedure. Therefore, our assumption underlying the derivation of the result in Eq.(71) is justified when $\Lambda_{\text{corr}} \gg R$, i.e., for sufficiently slow reactions such that the chemical time $\tau_{\text{chem}} = (4K_+a_\infty + K_-)^{-1}$ is much larger than the time necessary to diffuse on distance $R$. Note also that the dependence of the correlation length on the diffusion coefficient is symptomatic of a non-equilibrium state.

V. CONCLUSIONS.

To conclude, in this paper we re-examined two fundamental concepts of classical chemical kinetics - the notion of ”Chemical Equilibrium” and the ”Law of Mass Action” - on example of diffusion-limited reversible $A + A \rightleftharpoons B$ reactions. We have considered a rather general lattice model of such reactions, in which the elementary reaction rates are long-ranged and dependent on the instantaneous distance between particles. This model has been first analyzed by Zeldovich and Ovchinnikov [18] and pertains to chemical reactions between excited molecules or reactions involving transport of a proton or of an electron. It may be also viewed as a model of elementary reactions taking into account, albeit in an idealized fashion, different ”microscopic” effects such as solvent structure, different angular orientations of reactive molecules, energy distributions and etc. In this model any pair of $A$ particles, which perform standard random walks on sites of a $d$-dimensional hypercubic lattice may associate forming a $B$ particle at any moment of time $t$ with the rate $k_+(\mu)$, where $\mu$ is the instantaneous distance separating these two particles. In the reverse reaction elementary
act, a mobile $B$ particle may spontaneously dissociate with the rate $k_-(\lambda)$ giving birth to a geminate pair of $A$s separated by a distance $\lambda$. In our analysis we supposed that long-range rate $k_+(\mu)$ of bimolecular forward reaction and the rate $k_-(\lambda)$, describing the birth of a geminate pair of $A$ particles born at the distance $\lambda$ apart of each other within the elementary act of the unimolecular backward reaction, are arbitrary (integrable) functions of $\mu$ and $\lambda$. In terms of a formally exact approach based on Gardiner’s Poisson representation method \[9\], we have obtained exact non-linear Langevin equations describing the time evolution of complex-valued Poisson fields, whose mean values determine the $A$ and $B$ particles’ mean concentrations. Solutions of these Langevin equations in the asymptotic $t = \infty$ state were obtained via a certain decoupling approximation and a systematic diagrammatic expansion.

From these solutions, which coincide in the leading order, we have deduced a general criterion determining the conditions when the classical LMA holds and when the asymptotic $t = \infty$ state is a true thermodynamic equilibrium. We have shown that this may only happen when the distance-dependent elementary reaction rates obey a very restrictive condition of microscopic homogeneity: the ratio $k_+(\mu)/k_-(\mu)$ does not depend on $\mu$ for any $\mu$. It seems that such a condition may be considered as apparently unrealistic since the bimolecular forward and unimolecular backward reactions are supported by different physical processes of classical and quantum origin. At present time, no general argument exists that it should be always the case. In case when $k_+(\mu)/k_-(\mu)$ is $\mu$-dependent, i.e. the elementary reactions are microscopically inhomogeneous, it appears that the detailed balance is broken, the LMA does not hold, particles’ concentrations are spatially correlated and, remarkably, both correlation length and particles mean concentrations do depend on such kinetic parameter as the diffusion coefficient. This implies that the CE is not a true thermodynamic equilibrium but rather a non-equilibrium steady-state. Diffusion coefficient $D$-dependent corrections to the LMA have been calculated explicitly in several particular cases.

Consequently, for diffusion-limited reversible reactions the diffusional relaxation of the system is not fast enough to offset the perturbative effect of ongoing microscopically inhomogeneous elementary reactions (breaking the detailed balance) even in the asymptotic $t = \infty$ state. This results in a non–vanishing current which modifies the structure of fluctuations and globally changes asymptotic concentrations. We emphasize that such a non-equilibrium steady-state emerges in a closed system with conserved overall concentration of particles and products, without any external inflow of particles. It might be also worthy to remark
that the diffusion-limited reactions provide thus a nice example of physical systems in which an arbitrarily small but finite difference (of classical or quantum origin) between the microscopic rates $k_+(\mu)$ and $k_-(\mu)$ entails a fundamental change in the asymptotic behavior of a many particle system.

It is important to remark that our work does not contest any principle of thermodynamics, and in particular the zeroth principle. Indeed, in our model the system reaches a steady state, which can be described as the stationary point of a thermodynamical potential $G$, in agreement with the zeroth principle. Our work shows that $G$ does depend on dynamical quantities such as the diffusion coefficient $D$, which implies that the entropic contribution to $G$ can not be postulated a priori, but has to be defined using kinetic approaches taking into account dynamical effects. On the other hand, the LMA itself is not a law of thermodynamics, but rather a law of an ideal gas, since it relies on the hypothesis of infinitely fast mixing of the reaction bath. Consequently, there is no surprise that the classic LMA does not hold for systems with microscopically inhomogeneous reactions and diffusion as the limiting transport process.

Finally, we note that the analysis presented in our work may be extended in several directions. In particular, the question of the corrections to the LMA may be addressed for other types of reaction schemes, including, e.g., reactions between excited molecules, in which case particles possess an intrinsic life-time. As well, one may expect that the effects observed here will become more pronounced for photochemical, ionization and electrochemical reactions.

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[1] J.Keizer, *Statistical Thermodynamics of Nonequilibrium Processes*, (Springer-Verlag, New York, 1987)

[2] R.J.Silbey and R.A.Alberty, *Physical Chemistry*, (John Wiley and Sons, 2000)
[3] G.Wilemski and M.Fixman, J. Chem. Phys. 58, 4009 (1973); ibid. 60, 866, 878 (1974)

[4] D.F.Calef and J.M.Deutch, Diffusion-Controlled Reactions, Ann. Rev. Phys. Chem. 34, 493 (1983)

[5] S.A.Rice, in: Diffusion-Limited Reactions, Comprehensive Chemical Kinetics Vol. 25, eds.: C.H.Bamford, C.F.H.Tipper, and R.G.Compton (Elsevier, New York, 1985)

[6] B.U.Felderhof and R.B.Jones, J. Chem. Phys. 103, 10201 (1995); J. Chem. Phys. 106, 954, 967, 5006 (1997)

[7] S.Lee and M.Karplus, J. Chem. Phys. 86, 1883 (1987)

[8] K.L.Ivanov, N.N.Lukzen, A.B.Doktorov, and A.I.Burshtein, J. Chem. Phys. 114, 1754, 1763, 5682 (2001)

[9] C.W.Gardiner, Handbook of Stochastic Methods, (Springer, Berlin, 1990)

[10] K.Tomita and H.Tomita, Prog. Theor. Phys. 51, 6 (1974)

[11] Y. Kuramoto, Prog. Theor. Phys. 49, 1782 (1973); 52, 711 (1974)

[12] G.Nicolis and M.Mansour, Phys. Rev.A 29, 2845 (1984)

[13] K.Kitahara, K.Seki and S.Suzuki, J. Phys. Soc. Japan 59, 2309 (1990); K.Seki and K.Kitahara, J. Mol. Liq. 65/66, 293 (1995)

[14] J.Gorecki, K.Kitahara, K.Yoshikawa, and I.Hanazaki, Physica A 211, 327 (1994)

[15] J.Wakou and K.Kitahara, Physica A 281, 318 (2000)

[16] F.C.Alcaraz, M.Droz, M.Hankel, and V.Rittenberg, Ann. Phys. 230, 250 (1994)

[17] Ya.B.Zeldovich and A.A.Ovchinnikov, Sov. Phys. JETP Lett. 26, 440 (1977)

[18] Ya.B.Zeldovich and A.A.Ovchinnikov, Sov. Phys. JETP 47, 829 (1978)

[19] M.Tachiya, Proceedings of Ann. Meeting of Japanese Photochem. Assoc., Mie, Japan, October 1980.

[20] S.Redner and K.Kang, Phys. Rev. A 32, 435 (1985)

[21] G.Oshanin, S.F.Burlatsky, and A.A.Ovchinnikov, Sov. J. Chem. Phys. 9, 588 (1991)

[22] S.F.Burlatsky, A.A.Ovchinnikov, and G.Oshanin, Sov. Phys. JETP 68, 1153 (1989); J. Phys. A 22, 973, 977 (1989); Chem. Phys. 152, 13 (1991); G.Oshanin, Sov. J. Chem. Phys. 8, 395 (1991); G.Oshanin, A.Mogutov, M.Moreau, and S.F.Burlatsky, J. Mol. Liquids 63, 175 (1995)

[23] A.Szabo, J. Chem. Phys. 95, 2481 (1991); A.Szabo and R.Zwanzig, J. Stat. Phys. 65, 1057 (1991)

[24] J.Sung, K.J.Shin, and S.Lee, J. Chem. Phys. 107, 9418 (1997); M.Yang, S.Lee, and K.J.Shin,
[25] W.Naumann, N.V.Shokhirev, and A.Szabo, Phys. Rev. Lett. 79, 3074 (1997)
[26] I.V.Gopich, A.A.Ovchinnikov, and A.Szabo, Phys. Rev. Lett. 86, 922 (2001)
[27] P.-A.Rey and J.Cardy, J. Phys. A 32, 1585 (1999)
[28] I.V.Gopich and N.Agmon, Phys. Rev. Lett. 84, 2730 (2000); N.Agmon and I.V.Gopich, J. Chem. Phys. 112, 2863 (2000)
[29] I.V.Gopich and A.Szabo, Chem. Phys. 284, 91 (2002)
[30] D.Huppert, S.Y.Goldberg, A.Masad, and N.Agmon, Phys. Rev. Lett. 68, 3932 (1992); K.M.Solntsev, D. Huppert, and N.Agmon, J. Phys. Chem. A 105, 5868 (2001)
[31] D.Pines and U. Pines, J. Chem. Phys. 115, 951 (2001)
[32] N.Agmon and A.L.Edelstein, J. Chem. Phys. 100, 4181 (1994); A.L.Edelstein and N.Agmon, J. Mol. Liquids 64, 241 (1995); J. Phys. Chem. 99, 5389 (1995)
[33] N.N.Bogolybov, Lectures on Quantum Statistic, (Gordon and Breach, New York, 1976)
[34] S.Grossmann, J. Chem Phys. 65, 2007 (1976); J.Keizer, J. Chem. Phys. 67, 1473 (1977); see also Ch.6.5 in Ref.[1].
[35] M.Droz and A.McKane, J. Phys. A 27, 467 (1994)
[36] M.Doi, J. Phys. A 9, 1465, 1479 (1976)
[37] L.Peliti, J. Physique 46, 1469 (1985)
[38] S.H.Northrup and J.T.Hynes, Chem. Phys. Lett. 54, 244, 248 (1978); J. Chem. Phys. 69, 5246, 5261 (1978); ibid. 71, 871, 884 (1979)
[39] B. Gaveau, J. T. Hynes, R. Kapral, and M. Moreau, J. Stat. Phys. 56, 879, 894 (1989)
[40] P.Hänggi, P.Talkner, and M.Borkovec, Reaction-Rate Theory: Fifty Years After Kramers, Rev. Mod. Phys. 62, 251 (1990)
[41] W.Naumann and A.Molski, J. Chem. Phys. 103, 3474 (1995)
[42] K.Seki, A.V.Barzykin, and M.Tachiya, J. Chem. Phys. 110, 7639 (1999)
[43] G.J.Moro and M.G.Severin, J. Chem. Phys. 114, 4565 (2001)
[44] S.Murata, S.Y.Matsuzaki, and M.Tachiya, J. Phys. Chem. 99, 5345 (1995); S.Murata and M.Tachiya, J. Chem. Phys. 100, 4064 (1996)
[45] A.I.Burshtein, A.A.Zharikov, and N.V.Shokhirev, J. Chem. Phys. 96, 1951 (1992)
[46] S.F.Burlatsky, Theor. Exp. Chem. 14, 483 (1978)
[47] A.I.Burshtein and K.L.Ivanov, J. Phys. Chem. A 105, 3158 (2001); A.I.Burshtein,
A.A. Neufeld, and K.L. Ivanov, J. Chem. Phys. 115, 2652 (2001)