

# Integral Encounter Theory (IET) of the reversible reaction $A + A \leftrightarrow C$ , taking into account the force interaction between the reactants

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**Integral Encounter Theory (IET)** – consistent many-particle theory for the derivation of non-Markovian kinetic equations for reactions occurring in the liquid phase

- This theory generalizes the kinetic law of mass action of formal chemical kinetics
- It is the most detailed theory developed and widely used to describe the kinetics of various physical and chemical processes.
- IET allows to establish the basic laws in the course of chemical reactions and is an important step for the further development of non-Markovian theory

## Description of the problem and problem statement

- Initially IET was built neglecting force interaction between reactants, i.e. reactants were considered as point particles. Accounting for the force interaction between the reactants was carried out not consequently, but at the final stage of kinetic equations derivation
- Consistent consideration of the force interaction on an equal basis with the chemical one is non-trivial due to different analytical properties of the reaction and force interaction operators
- The construction of a theory that takes into account chemical and force interaction on an equal basis, starting from a many-particle description of the reacting system, was carried out for irreversible association reactions  $A + A \rightarrow C$  and  $A + B \rightarrow C$ . However, it is difficult to intuitively generalize this result to the reversible reaction  $A + A \leftrightarrow C$

## The purpose of this study

- Consistent derivation of non-Markovian kinetic equations for the reversible reaction  $A + A \leftrightarrow C$ , taking into account the force interaction between the reactants in the framework of IET

## Derivation of IET kinetic equations

Within the framework of the basic concepts of IET, a dilute solution is considered as a gas of reactants placed in an inert solvent medium. The reactivity is described by an elementary rate, and the translational migration, taking into account the force interaction between reactants, is described by a Markov process.

## Microscopic description of the reaction system. Fock Space. Liouville equation

The concept of the Fock space is introduced as the space  $\{\Phi^{N,L}(A^N, C^L, t)\}$  of all possible states of a many-particle reacting system. The evolution of the reacting system in time over these states is governed by Liouville equation which is the balance equation in the Fock space and the starting point to subsequent many-particle derivation

## The thermodynamic limit and the Reduced Distribution Functions (RDF)

The concept of the thermodynamic limit was introduced in physical kinetics to describe the bulk properties of macroscopic systems. In this case, instead of real many-particle systems, some imaginary systems with an infinite number of particles in an infinite volume (systems in the thermodynamic limit) are considered. The thermodynamic limit is the limit  $T - \lim \dots = \lim_{N \rightarrow \infty, V \rightarrow \infty} \dots$

$$\lim_{\substack{N \rightarrow \infty, V \rightarrow \infty \\ N/V = \text{Const} = [A]^N L}} \dots$$

It is postulated that the evolution of systems in the thermodynamic limit coincides with the bulk evolution of real systems, which is not related to the effects due to the presence of walls in real macrosystems. Consideration of systems in the thermodynamic limit greatly simplifies the mathematical description of real many-particle systems.

We introduce the quantity **Distribution Functions (RDF)**  $\varphi_{p,r}(t)$  by

$$\varphi_{p,r}(A^p, C^r, t) = T - \lim \left( \sum_{N, L \in h} \int \frac{dA_{p+1} \dots dA_N dC_{r+1} \dots dC_L}{(N-p)!(L-r)!} \Phi^{N,L}(A_0^N, C_0^L, t) \right).$$

On the basis of this definition and the Liouville equation we get the following equations for one and two particle RDFs

$$(\partial_t - \hat{L}_A) \varphi_{1,0}(A_1, t) = \int dA_2 (\hat{V}_f^{(1,2)} + \hat{L}'_{A_2}) \varphi_{2,0} + \int dC_1 \hat{L}'_{A_1 C_1} \varphi_{1,1} + \int dA_2 \hat{R}_r^{(1,2)} \varphi_{0,1} + \delta(t) \varphi_{1,0}(t=0)$$

$$(\partial_t - \hat{L}_{C_1}) \varphi_{0,1}(C_1, t) = \hat{V}_r^{(1)} \varphi_{0,1} + \hat{R}_f^{(1)} \varphi_{2,0} + \int dA_1 \hat{L}'_{A_1 C_1} \varphi_{1,1} + \int dC_2 \hat{L}'_{C_1 C_2} \varphi_{0,2} + \delta(t) \varphi_{0,1}(t=0)$$

The evolution of one-particle RDFs depends on the evolution of two-particle RDFs. The process of constructing equations for higher order RDFs is infinite. For example, the equation for two-particle RDF has the form

$$(\partial_t - \hat{L}_{A_1} - \hat{L}_{A_2}) \varphi_{2,0}(A_1, A_2, t) = \delta(t) \varphi_{2,0}(t=0) + (\hat{V}_f^{(1,2)} + \hat{L}'_{A_2}) \varphi_{2,0} + \int dA_3 (\hat{V}_f^{(1,3)} + \hat{V}_f^{(2,3)} + \hat{L}'_{A_3} + \hat{L}'_{A_2 A_3}) \varphi_{3,0} + \hat{R}_r^{(1,2)} \varphi_{0,1} + \int dC_1 (\hat{L}'_{A_1 C_1} + \hat{L}'_{A_2 C_1}) \varphi_{2,1} + \int dA_3 \hat{R}_r^{(1,3)} \varphi_{1,1}(A_2, C_1, t) + \int dA_3 \hat{R}_r^{(2,3)} \varphi_{1,1}(A_1, C_1, t)$$

## Correlation patterns (CPs)

According to the general algorithm of nonequilibrium statistical mechanics, the second step in the construction of kinetic equations is the introduction of the concept of correlation patterns. This notion is based on the hierarchical property for RDFs and is introduced as terms in their group decomposition, which is of the form. For example, for one-particle and two-particle RDFs, this partition has the form

$$\varphi_{1,0}(A_1, t) = n_A(A_1, t) = \pi_{1,0}(A_1, t); \quad \varphi_{0,1}(C_1, t) = n_C(C_1, t) = \pi_{0,1}(C_1, t)$$

$$\varphi_{2,0}(A_1, A_2, t) = \pi_{2,0}(A_1 | A_2, t) + \pi_{2,0}(A_1, A_2, t); \quad \varphi_{1,1}(A_1, C_1, t) = \pi_{1,1}(A_1 | C_1, t) + \pi_{1,1}(A_1, C_1, t); \dots$$

Each correlation pattern (CP), including the division of reactants into several groups, is factorized. For example,

$$\pi_{2,0}(A_1 | A_2, t) = \pi_{1,0}(A_1, t) \pi_{1,0}(A_2, t); \quad \pi_{1,2}(A_1, C_1 | C_2, t) = \pi_{1,1}(A_1, C_1, t) \pi_{0,1}(C_2, t)$$

Substituting the group expansion into the kinetic equations for RDFs allows one to obtain equations describing the evolution of one-particle and two-particle completely correlated correlation patterns

$$(\partial_t - \hat{L}_A) n_A(A_1, t) = \delta(t) n_A^0(A_1) + \int dA_2 (\hat{V}_f^{(1,2)} + \hat{L}'_{A_2}) [\pi_{2,0}(A_1, A_2, t) + n_A(A_1, t) n_A(A_2, t)]$$

$$+ \int dC_1 \hat{L}'_{A_1 C_1} [\pi_{1,1}(A_1, C_1, t) + n_A(A_1, t) n_C(C_1, t)] + \int dA_2 \hat{R}_r^{(1,2)} n_C(C_1, t)$$

$$(\partial_t - \hat{L}_{C_1}) n_C(C_1, t) = \delta(t) n_C^0(C_1) + \hat{V}_r^{(1)} n_C(C_1, t) + \hat{R}_f^{(1)} [\pi_{2,0}(A_1, A_2, t) + n_A(A_1, t) n_A(A_2, t)]$$

$$+ \int dA_1 \hat{L}'_{A_1 C_1} [\pi_{1,1}(A_1, C_1, t) + n_A(A_1, t) n_C(C_1, t)] + \int dC_2 \hat{L}'_{C_1 C_2} [\pi_{0,2}(C_1, C_2, t) + n_C(C_1, t) n_C(C_2, t)]$$

To close this system, it is necessary to know the two-particle completely correlated CPs. For example, the equation for two-particle CP  $\pi_{2,0}(A_1, A_2, t)$  has the form

$$(\partial_t - \hat{L}_{A_1} - \hat{L}_{A_2} - \hat{L}'_{A_2} - \hat{V}_f^{(1,2)}) \pi_{2,0}(A_1, A_2, t) = \delta(t) \pi_{2,0}^0(A_1, A_2) + (\hat{V}_f^{(1,2)} + \hat{L}'_{A_2}) \pi_{2,0}(A_1 | A_2, t) + \hat{R}_r^{(1,2)} n_C(C_1, t)$$

$$+ \int dA_3 (\hat{V}_f^{(1,3)} + \hat{L}'_{A_3}) [\pi_{3,0}(A_1 | A_2, A_3, t) + \pi_{3,0}(A_1, A_2 | A_3, t) + \pi_{3,0}(A_1, A_2, A_3, t)]$$

$$+ \int dA_3 (\hat{V}_f^{(2,3)} + \hat{L}'_{A_3}) [\pi_{3,0}(A_1, A_2 | A_3, t) + \pi_{3,0}(A_1, A_3 | A_2, t) + \pi_{3,0}(A_1, A_2, A_3, t)]$$

$$+ \int dC_1 \hat{L}'_{A_1 C_1} [\pi_{2,1}(A_1, A_2 | C_1, t) + \pi_{2,1}(A_1 | A_2, C_1, t) + \pi_{2,1}(A_1, A_2, C_1, t)]$$

$$+ \int dC_1 \hat{L}'_{A_2 C_1} [\pi_{2,1}(A_1, A_2 | C_1, t) + \pi_{2,1}(A_2 | A_1, C_1, t) + \pi_{2,1}(A_1, A_2, C_1, t)]$$

$$+ \int dA_3 \hat{R}_r^{(1,3)} \pi_{1,1}(A_2, C_1, t) + \int dA_3 \hat{R}_r^{(2,3)} \pi_{1,1}(A_1, C_1, t)$$

The resulting equations for CPs serve as a basis for further derivation of the IET kinetic equations. These equations are valid for the general case of spatially homogeneous and inhomogeneous chemical systems and ensure the fulfillment of the balance condition for the number of reactants. It follows from the obtained equations that in

order to calculate the two-particle completely correlated CPs, it is necessary to know the three-particle completely correlated CPs. Thus, there is an infinite hierarchy in the language of correlation patterns, which is equivalent to an infinite hierarchy for RDFs. And, therefore, the evolution of a many-particle system can be considered as the evolution of correlation patterns.

## Approximation of the IET

The simplest kinetic equations describing the evolution of reacting systems were proposed on the basis of the truncation of the infinite hierarchy of CPs when calculating two-particle completely correlated patterns. Such a truncation is valid for small values of the density parameter, when the contributions of three-particle correlations can be neglected.

Thus, after neglecting the contributions of three-particle correlations, the system of coupled equations for two-particle CPs decomposes into three independent inhomogeneous equations

$$(\partial_t - \hat{L}_{A_1} - \hat{L}_{A_2} - \hat{L}'_{A_2} - \hat{V}_f^{(1,2)}) \pi_{2,0}(A_1, A_2, t) = \delta(t) \pi_{2,0}^0(A_1, A_2) + (\hat{V}_f^{(1,2)} + \hat{L}'_{A_2}) \pi_{2,0}(A_1 | A_2, t) + \hat{R}_r^{(1,2)} n_C(C_1, t)$$

$$(\partial_t - \hat{L}_{A_1} - \hat{L}_{C_1} - \hat{L}'_{A_1 C_1} - \hat{V}_r^{(1)}) \pi_{1,1}(A_1, C_1, t) = \delta(t) \pi_{1,1}^0(A_1, C_1) + \hat{L}'_{A_1 C_1} \pi_{1,1}(A_1 | C_1, t)$$

$$(\partial_t - \hat{L}_{C_1} - \hat{L}_{C_2} - \hat{L}'_{C_1 C_2} - \hat{V}_r^{(1)} - \hat{V}_r^{(2)}) \pi_{0,2}(C_1, C_2, t) = \delta(t) \pi_{0,2}^0(C_1, C_2) + \hat{L}'_{C_1 C_2} \pi_{0,2}(C_1 | C_2, t)$$

The left homogeneous part of these equations describes the evolution of CP due to the evolution in a pair of reactants, the right inhomogeneous part is the source of correlations due either to the initial conditions, or independent encounters of the corresponding reactants in solution, or dissociation. Note that the force and chemical interactions in the evolution of different pairs are included in a non-symmetrical way.

The independence of the evolutions of pairs of reactants among themselves makes it possible to solve these equations for two-particle CPs. After substituting the solutions, we obtain the general IET kinetic equations in terms of T-operators for local concentrations of reactants

$$(\partial_t - \hat{L}_{A_1}) n_A(A_1, t) = \delta(t) n_A^0(A_1) + \int dA_2 \hat{T}_{A_1 A_2} n_A(A_2, t) + \int dA_2 \hat{T}_{A_1 A_2 C_1} n_C(C_1, t)$$

$$+ \int dC_1 \hat{T}_{A_1 C_1} n_C(C_1, t) + \int dA_2 \hat{T}_{A_1 A_2} \hat{G}_{A_1 A_2}^{00} \delta(t) \pi_{2,0}^0(A_1, A_2) + \int dC_1 \hat{T}_{A_1 C_1} \hat{U}_{A_1 C_1}^{00} \delta(t) \pi_{1,1}^0(A_1, C_1)$$

$$(\partial_t - \hat{L}_{C_1}) n_C(C_1, t) = \delta(t) n_C^0(C_1) + \hat{T}_{C_1 | A_1 A_2} n_A(A_1, t) n_A(A_2, t) + \hat{T}_{C_1} n_C(C_1, t)$$

$$+ \int dA_1 \hat{T}_{A_1 C_1} n_A(A_1, t) n_C(C_1, t) + \int dC_2 \hat{T}_{C_1 C_2} n_C(C_2, t) n_C(C_1, t) + \hat{T}_{C_1 | A_1 A_2} \hat{G}_{A_1 A_2}^{00} \delta(t) \pi_{2,0}^0(A_1, A_2)$$

$$+ \int dA_1 \hat{T}_{A_1 C_1} \hat{U}_{A_1 C_1}^{00} \delta(t) \pi_{1,1}^0(A_1, C_1) + \int dC_2 \hat{T}_{C_1 C_2} \hat{U}_{C_1 C_2}^{00} \delta(t) \pi_{0,2}^0(C_1, C_2)$$

The introduced T-operators are renormalized interaction operators in the corresponding pairs. In full agreement with the general kinetic theory, the resulting equations have the form of integro-differential equations with inhomogeneous sources describing the contribution of initial correlations to the evolution of local concentrations.

These properties of the obtained kinetic equations distinguish them from the rate equations of the law of mass action of formal chemical kinetics. Nevertheless, it can be shown that the equilibrium concentrations obtained from both these approaches coincide, which confirms the correctness of our truncation in the CPs hierarchy

## Equations for volume averaged concentrations

When calculating volume-averaged concentrations in the general case of spatially inhomogeneous systems, the resulting equations are simplified

$$\partial_t [A]_t = \delta(t) [A]_0 + \lim_{v \rightarrow \infty} \int \frac{dA_1 dA_2}{v} \hat{T}_{A_1 A_2} n_A(A_1, t) n_A(A_2, t)$$

$$+ \lim_{v \rightarrow \infty} \int \frac{dA_1 dA_2}{v} \hat{T}_{A_1 A_2 C_1} n_C(C_1, t) + \lim_{v \rightarrow \infty} \int \frac{dA_1 dA_2}{v} \hat{T}_{A_1 A_2} \hat{G}_{A_1 A_2}^{00} \delta(t) \pi_{2,0}^0(A_1, A_2)$$

$$\partial_t [C]_t = \delta(t) [C]_0 + \lim_{v \rightarrow \infty} \int \frac{dC_1}{v} \hat{T}_{C_1 | A_1 A_2} n_A(A_1, t) n_A(A_2, t)$$

$$+ \lim_{v \rightarrow \infty} \int \frac{dC_1}{v} \hat{T}_{C_1} n_C(C_1, t) + \lim_{v \rightarrow \infty} \int \frac{dC_1}{v} \hat{T}_{C_1 | A_1 A_2} \hat{G}_{A_1 A_2}^{00} \delta(t) \pi_{2,0}^0(A_1, A_2)$$

In this case, it can be seen that evolution in pairs in which there is no chemical interaction between the reactants (i.e., AC and CC pairs) does not affect the kinetics of volume-averaged concentrations

## Spatially homogeneous systems

In the case of spatially homogeneous systems, the average concentration of the reactants coincides with the local concentration, and all two-particle CPs depend on the difference in the coordinates of the reactants in the pair

$$n_A(A, t) = [A]_t; \quad n_C(C, t) = [C]_t; \quad \pi_{2,0}(A_1, A_2, t) = \pi_{2,0}(A_1 - A_2, t), \dots$$

In the case of spatially homogeneous systems, the kinetic equations for local concentrations are simplified and take the form of time equations of the memory function type

$$\partial_t [A]_t = \delta(t) [A]_0 - 2 \int_{-0}^t dt_0 \Sigma_f^0(t-t_0) [A]_{t_0}^2 + 2 \int_{-0}^t dt_0 \Sigma_r(t-t_0) [C]_{t_0} - 2 J_{init}(t)$$

In the case of a microscopic scale of initial correlations, the kinetic equations can be rewritten into homogeneous ones with the corresponding redefinition of the kinetic coefficients, just as was done for the irreversible reaction  $A + A \rightarrow C$

$$\partial_t [A]_t = \delta(t) [A]_0 - 2 \int_{-0}^t dt_0 \Sigma_f(t-t_0) [A]_{t_0}^2 + 2 \int_{-0}^t dt_0 \Sigma_r(t-t_0) [C]_{t_0}$$

Thus, the IET kinetic equations for spatially homogeneous systems, taking into account the force interaction between reactants, can be obtained from the equations for point reactants by appropriately redefining the kinetic coefficients.

## Conclusion and results

- Within the framework of the many-particle approach under discussion, a hierarchy of equations for one-particle and two-particle correlation patterns is obtained in the thermodynamic limit
- Solving the equations neglecting the contributions of three-particle correlations made it possible to obtain closed non-Markovian kinetic equations for local concentrations within the framework of the Integral Encounter Theory (IET) for the general case of spatially inhomogeneous systems
- In full accordance with the principles of the general kinetic theory, these equations have an integro-differential form and contain inhomogeneous sources that describe the decay of the initial pair correlations. Despite the fact that the obtained non-Markovian kinetic equations are valid in a narrow time interval, they have the correct Markovian limit corresponding to the kinetic law of mass action, ensure the fulfillment of the particle number balance law, and lead to correct equilibrium concentrations
- The presence of force interaction in pairs of reactants, in which there is no pairwise chemical interaction, does not affect the kinetics of volume-average concentrations
- Kinetic equations of IET for spatially homogeneous systems, taking into account the force interaction between reactants, can be obtained from the equations for point reactants by appropriately redefining the kinetic coefficients