Non-Markovian kinetic effects in the liquid-phase reaction A + A ↔ C

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Statement of the problem

A consistent derivation of non-Markovian kinetic equations for the reversible reaction A + A ↔ C was carried out in a previous work within the Integral Encounter Theory (IET)

However, these equations have a narrowed time interval of applicability due to the inability of the method to describe the macroscopic correlations that arise during the reaction itself. These results were obtained earlier, in particular, for the irreversible reactions A + A → C and A + B → C.

Modified Encounter Theory (MET) is a further development of the many-particle method for deriving non-Markovian kinetic equations and describes non-Markovian effects more accurately than IET, thus expanding the time interval of the theory's applicability

The purpose of this study

Application of Modified Encounter Theory methods to study non-Markovian effects in reversible reaction A + A ↔ C

Used assumptions

In this study, we restrict ourselves to consideration of point particles, i.e. we will neglect the force interaction between the reactants. This will allow:

- significantly simplify mathematical calculations
- focus on the evolution of correlations between reactants, occurred due only to the chemical reaction

For further derivation, let us turn to the basic equations for the Correlation Patterns (CP) obtained in the previous work, neglecting the force interactions

$$\left(\partial_t - \hat{L}_{A_1}\right)n_A\left(A_1,t\right) = \delta\left(t\right)n_A^0\left(A_1\right) + \int dA_2 \hat{V}_f^{(1,2)}\left[\pi_{2,0}\left(A_1,A_2,t\right) + n_A\left(A_1,t\right)n_A\left(A_2,t\right)\right] + \int dA_2 \hat{R}_r^{(1,2|1)}n_C\left(C_1,t\right)$$

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

The equations for two-particle correlation patterns have the form

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

$$+\int dA_3 \hat{V}_f^{(1,3)}\left[\pi_{3,0}\left(A_1\,|\,A_2,A_3,t\right) + \pi_{3,0}\left(A_1,A_2\,|\,A_3,t\right) + \pi_{3,0}\left(A_1,A_2,A_3,t\right)\right]$$

$$+\int dA_3 \hat{V}_f^{(2,3)}\left[\pi_{3,0}\left(A_1,A_2\,|\,A_3,t\right) + \pi_{3,0}\left(A_1,A_3\,|\,A_2,t\right) + \pi_{3,0}\left(A_1,A_2,A_3,t\right)\right]$$

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

Despite the fact that only the two-particle correlation pair of reactants AA is included in the equation for local concentrations, the calculation of others is necessary due to the relationship of this CP with other CPs

$$\left(\partial_t - \hat{L}_{A_1} - \hat{L}_{C_1} - \hat{V}_r^{(1)}\right)\pi_{1,1}\left(A_1,C_1,t\right) =$$

$$+\int dA_2 \hat{V}_f^{(1,2)}\left[\pi_{2,1}\left(A_1,A_2,C_1,t\right) + \pi_{2,1}\left(A_1\,|\,A_2,C_1,t\right) + \pi_{2,1}\left(A_2\,|\,A_1,C_1,t\right)\right]$$

$$+\hat{R}_f^{(1|2,3)}\left[\pi_{3,0}\left(A_1,A_2,A_3,t\right) + \pi_{3,0}\left(A_2\,|\,A_1,A_3,t\right) + \pi_{3,0}\left(A_3\,|\,A_1,A_2,t\right)\right] + \int dA_2 \hat{R}_r^{(1,2|2)}\pi_{0,2}\left(C_1,C_2,t\right)$$

$$\left(\partial_t - \hat{L}_{C_1} - \hat{L}_{C_2} - \hat{V}_r^{(1)} - \hat{V}_r^{(2)}\right)\pi_{0,2}\left(C_1,C_2,t\right) =$$

$$+\hat{R}_f^{(1|1,2)}\left[\pi_{2,1}\left(A_1\,|\,A_2,C_2,t\right) + \pi_{2,1}\left(A_2\,|\,A_1,C_2,t\right) + \pi_{2,1}\left(A_1,A_2,C_2,t\right)\right]$$

$$+\hat{R}_f^{(2|1,2)}\left[\pi_{2,1}\left(A_1\,|\,A_2,C_1,t\right) + \pi_{2,1}\left(A_2\,|\,A_1,C_1,t\right) + \pi_{2,1}\left(A_1,A_2,C_1,t\right)\right]$$

Effective Pair Approximation (EPA)

The construction of the effective pair approximation is based on separating the contribution of binary channels to the evolution of three particles. As shown in a number of papers, this approach reduces to the fact that in equations for two-particle CPs it is necessary to exclude completely correlated three-particle CPs from consideration, and in equations that take into account the remaining three-particle CPs, renormalize the reaction operators corresponding to the transition to the T-operators obtained in previous work

$$\hat{V}_f^{(1,2)} \rightarrow \hat{T}_{A_1A_2} = \hat{V}_f^{(1,2)} + \hat{L}'_{A_1A_2} + \left(\hat{V}_f^{(1,2)} + \hat{L}'_{A_1A_2}\right)\hat{G}_{A_1A_2}\left(\hat{V}_f^{(1,2)} + \hat{L}'_{A_1A_2}\right)$$

$$\hat{R}_f^{(1|1,2)} \rightarrow \hat{T}_{C_1|A_1A_2} = \hat{R}_f^{(1|1,2)} + \hat{R}_f^{(1|1,2)}\hat{G}_{A_1A_2}\left(\hat{V}_f^{(1,2)} + \hat{L}'_{A_1A_2}\right)$$

$$\hat{V}_r^{(1)} \rightarrow \hat{T}_{C_1} = \hat{V}_r^{(1)} + \hat{R}_f^{(1|1,2)}\hat{G}_{A_1A_2}\hat{R}_r^{(1,2|1)}$$

$$\hat{R}_r^{(1,2|1)} \rightarrow \hat{T}_{A_1A_2|C_1} = \hat{R}_r^{(1,2|1)} + \left(\hat{V}_f^{(1,2)} + \hat{L}'_{A_1A_2}\right)\hat{G}_{A_1A_2}\hat{R}_r^{(1,2|1)}$$

Further, to simplify mathematical calculations, we turn to the consideration of spatially homogeneous systems. In that case, 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

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

For T-operators we use their point approximations. As a result, we obtain a closed system of equations for correlation patterns in relative coordinates, corresponding to the Effective Pair Approximation (EPA)

$$\begin{cases}\left(\partial_t - \hat{L}_{AA} - \hat{v}_f + 8k_f n_A\left(t\right)\right)\pi_{2,0}\left(\vec{r},t\right) = \hat{v}_f n_A^2\left(t\right) - \hat{v}_d n_C\left(t\right) + 4k_r\pi_{1,1}\left(\vec{r},t\right)\\ \left(\partial_t - \hat{L}_{AC} + k_r + 4k_f n_A\left(t\right)\right)\pi_{1,1}\left(\vec{r},t\right) = 2k_f\pi_{2,0}\left(\vec{r},t\right)n_A\left(t\right) + 2k_r\pi_{0,2}\left(\vec{r},t\right)\\ \left(\partial_t - \hat{L}_{CC} + 2k_r\right)\pi_{0,2}\left(\vec{r},t\right) = 4k_f\pi_{1,1}\left(\vec{r},t\right)n_A\left(t\right)\end{cases}$$

Thus, taking into account the contribution of binary channels to the evolution of three-particle correlation patterns significantly complicates the exchange of correlations between different pairs of reactants even in the absence of force interactions between them. This fact significantly distinguishes the equations obtained from the equations for correlation patterns within the framework of IET, where the contribution from three-body correlations is ignored.

Although the system of equations for the correlation patterns is linear, its exact solution is very difficult, since the equations contain unknown concentrations nA(t) and nC(t) in their coefficients. Moreover, the solution of this system depends on the translational mobility of the reactants not only in the AA pair, but also in the AC and CC pairs, i.e., has a many-particle (rather than two-particle) character. Below we present the formal solution of the resulting system of equations and the MET equation in general form

Formal solution of the EPA equations

We introduce matrix quantities according to the definition

$$\hat{\mathbf{L}} = \begin{pmatrix}\hat{L}_{AA} & 0 & 0\\ 0 & \hat{L}_{AC} & 0\\ 0 & 0 & \hat{L}_{CC}\end{pmatrix};\, \boldsymbol{\pi}\left(\vec{r},t\right) = \begin{pmatrix}\pi_{2,0}\left(\vec{r},t\right)\\ \pi_{1,1}\left(\vec{r},t\right)\\ \pi_{0,2}\left(\vec{r},t\right)\end{pmatrix};\, \hat{\mathbf{v}}_f = \begin{pmatrix}\hat{v}_f & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix};\, \hat{\mathbf{v}}_d = \begin{pmatrix}\hat{v}_d & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$$

Then the EPA equations in matrix form take the form

$$\left(\partial_t - \hat{\mathbf{L}} - \hat{\mathbf{v}}_f + \begin{pmatrix}8k_f n_A\left(t\right) & -4k_r & 0\\ -2k_f n_A\left(t\right) & k_r + 4k_f n_A\left(t\right) & -2k_r\\ 0 & -4k_f n_A\left(t\right) & 2k_r\end{pmatrix}\right)\boldsymbol{\pi}\left(\vec{r},t\right) = \hat{\mathbf{v}}_f\begin{pmatrix}1\\0\\0\end{pmatrix}n_A^2 - \hat{\mathbf{v}}_d\begin{pmatrix}1\\0\\0\end{pmatrix}n_C$$

The solution of which can be formally represented as

$$\boldsymbol{\pi}\left(\vec{r},t\right) = \hat{\mathbf{g}}_{eff}\left(\hat{\mathbf{v}}_f\begin{pmatrix}1\\0\\0\end{pmatrix}n_A^2 - \hat{\mathbf{v}}_d\begin{pmatrix}1\\0\\0\end{pmatrix}n_C\right)$$

The propagator of effective pair obeys the equation

$$\left(\partial_t - \hat{\mathbf{L}} - \hat{\mathbf{v}}_f + \begin{pmatrix}8k_f n_A\left(t\right) & -4k_r & 0\\ -2k_f n_A\left(t\right) & k_r + 4k_f n_A\left(t\right) & -2k_r\\ 0 & -4k_f n_A\left(t\right) & 2k_r\end{pmatrix}\right)\hat{\mathbf{g}}_{eff} = \hat{\mathbf{I}}$$

Substituting the formal solution of the EPA equation into the matrix equation for the concentration yields the EPA kinetic equation

$$\partial_t n_A\left(t\right) = \delta\left(t\right)n_A^0 + \int d\vec{r}\left(\hat{\mathbf{t}}_f^{eff}\right)_{11}n_A^2\left(t\right) - \int d\vec{r}\left(\hat{\mathbf{t}}_d^{eff}\right)_{11}n_C\left(t\right)$$

The matrix T-operators of an effective pair are defined by the relations

$$\hat{\mathbf{t}}_f^{eff} = \hat{\mathbf{v}}_f + \hat{\mathbf{v}}_f\hat{\mathbf{g}}_{eff}\hat{\mathbf{v}}_f;\, \hat{\mathbf{t}}_d^{eff} = \hat{\mathbf{v}}_d + \hat{\mathbf{v}}_f\hat{\mathbf{g}}_{eff}\hat{\mathbf{v}}_d$$

To obtain the MET kinetic equation, we use the approximate solution for the matrix T-operators of the effective pair

$$\hat{\mathbf{t}}_f^{eff} \simeq \hat{\mathbf{t}}_f^{MET} = \hat{\mathbf{t}}_f + \hat{\mathbf{t}}_f^{ps}\left(\hat{\mathbf{g}}_{eff}^{0D} - \hat{\mathbf{g}}^{0D}\right)\hat{\mathbf{t}}_f^{ps};\quad \hat{\mathbf{t}}_d^{eff} \simeq \hat{\mathbf{t}}_d^{MET} = \hat{\mathbf{t}}_d + \hat{\mathbf{t}}_f^{ps}\left(\hat{\mathbf{g}}_{eff}^{0D} - \hat{\mathbf{g}}^{0D}\right)\hat{\mathbf{t}}_d^{ps}$$

Note that the obtained approximate expressions for T-operators as a sum of two terms reflect the physics of the phenomenon. The first terms are essential at the initial stage of the reaction and are completely determined by the pair T-operators. It is the second terms that distinguish the obtained MET equations from the IET equations and appear at long times due to the accumulation and decay of correlations between reactants in the course of reactions. These correlations are due to the dependence of paired encounters in solutions through the influence of the third particle from the volume on them.

Conclusion and results

- On the basis of a hierarchy of equations for correlation patterns in the thermodynamic limit and T-operators obtained earlier, a procedure for extracting the contributions from binary channels (two-particle correlations) into the evolution of three-particle completely correlated patterns is carried out.
- This made it possible to obtain non-Markovian kinetic equations in the Effective Pair Approximation (EPA). Further calculation of the evolution of effective pairs made it possible to obtain non-Markovian integro-differential kinetic equations MET in a general form.
- Obtained formal solution for T-operators of Modified Encounter Theory confirmed the effect of the dependence of pair encounters of reactants in solution, the presence of which are of great importance in binary theory.