

Many-particle peculiarities in the $A + B \rightarrow B$ bimolecular reaction kinetics. The effect of sink spatial distribution

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Abstract. The Kirkwood superposition approximation is used for the study of many-particle effects in the $A+B \rightarrow B$ bimolecular reaction (energy transfer from donors A to unsaturable sinks B). Several spatial distributions of sinks B are considered. It is shown that the theory presented reproduces exact results obtained earlier for particular cases of a random distribution (using the Wigner–Seitz model) and the sink-concentration correction obtained for particle accumulation by means of the mean-field theory.

1. Introduction

The kinetics of bimolecular $A + B \rightarrow B$ reaction continues to attract much attention due to both its fundamental importance and applications in energy transfer, luminescence quenching, void growth in irradiated solids etc ([1–4] and references therein). In this reaction B particles (reactants) play a role of non-saturable sinks (energy acceptors or traps). The first attempt to solve this problem was suggested long ago by Smoluchowski [5]. This approach gives an exact result in the case of mobile non-interacting sinks B and immobile particles A (characterized by the diffusion coefficients $D_A = 0$, $D_B > 0$, the so-called *target problem*) whereas its correctness in the opposite situation ($D_B = 0$, $D_A > 0$, the *trapping problem*) is not clear so far [1]. The problem is that in this case particles A reveal spatial correlations, e.g. when several As compete to recombine some particular sink B.

The purpose of this paper is to apply the *Kirkwood superposition approximation* to the trapping problem, in order to study the effect of the spatial distribution of sinks B on the reaction rate. In section 2 we present a general expression for the reaction rate for an *arbitrary* spatial distribution of sinks B. In section 3 several particular cases (regular, random and correlated sink distributions) for the donor concentration decay are considered. The kinetics of particle accumulation is discussed in section 4. In sections 2 and 3 we test our theory for several particular cases solved earlier [6–11] and demonstrate that Kirkwood's formalism successfully reproduces the relevant concentration dependences of the reaction rate. Unlike other formalisms, our theory is very flexible and could easily be applied to very different cases.

2. Superposition approximation

Following the approach we developed earlier [6, 7], let us consider a macroscopic crystal of volume V containing at $t = 0$ N_B fixed sinks B and N_A mobile particles A. The

spatial distributions of reactants could be described in terms of many-particle densities $\rho_{mm'}(\mathbf{r}_1, \dots, \mathbf{r}_m, \mathbf{r}'_1, \dots, \mathbf{r}'_{m'}, t)$; $\rho_{mm'} d\mathbf{r}_1 \dots d\mathbf{r}'_{m'}$ gives at time t an average number of configurations with m sinks B at coordinates $\mathbf{r}_1, \dots, \mathbf{r}_m$ and m' mobile A particles at $\mathbf{r}'_1, \dots, \mathbf{r}'_{m'}$, respectively. The following hierarchy of kinetic equations for these densities could be easily derived:

$$\begin{aligned} \frac{\partial \rho_A(\mathbf{r}'_1, t)}{\partial t} &= D_A \Delta \rho_A(\mathbf{r}'_1, t) - \int \sigma(\mathbf{r}_1, \mathbf{r}'_1) \rho_{AB}(\mathbf{r}_1, \mathbf{r}'_1, t) d\mathbf{r}_1 \\ \frac{\partial \rho_{AB}(\mathbf{r}_1, \mathbf{r}'_1, t)}{\partial t} &= D_A \Delta \rho_{AB}(\mathbf{r}_1, \mathbf{r}'_1, t) - \sigma(\mathbf{r}_1, \mathbf{r}'_1) \rho_{AB}(\mathbf{r}_1, \mathbf{r}'_1, t) \\ &\quad - \int \sigma(\mathbf{r}_2, \mathbf{r}'_1) \rho_{BBA}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, t) d\mathbf{r}_2. \end{aligned} \quad (1)$$

Here Δ is the Laplace operator and $\sigma(\mathbf{r}_1, \mathbf{r}'_1)$ is the reaction (trapping) rate for a particle A at \mathbf{r}'_1 with a sink B at \mathbf{r}_1 . The equation set (1) is infinite; the next equation for the three-particle densities ρ_{BBA} contains four-particle densities, etc. Due to a crystal homogeneity one-particle densities are nothing but coordinate-independent macroscopic concentration

$$\rho_B(\mathbf{r}_1) = \rho_B(\mathbf{r}_2) = n_B(t) \quad \rho_A(\mathbf{r}'_1, t) = n_A(t) \quad (2)$$

whereas the joint densities depend only on the relative coordinates, $r = |\mathbf{r}_1 - \mathbf{r}'_1|$ and $r^* = |\mathbf{r}_1 - \mathbf{r}_2|$:

$$\begin{aligned} \rho_{BA}(\mathbf{r}'_1, \mathbf{r}_1, t) &= n_A n_B Y(r, t) \\ \rho_{BB}(\mathbf{r}_1, \mathbf{r}_2, t) &= n_B^2 X_B(r^*, t). \end{aligned} \quad (3)$$

In equation (3) we introduced for simplicity the *correlation functions* X_B, Y for pairs of sinks (traps B–B) and for donor–trap pairs (A–B). The advantage of their use is that these correlation functions do not depend on the macroscopic concentrations n_A and n_B . For the random (Poisson) particle distribution the correlation functions are equal to unity, thus their deviation from unity characterizes non-uniform relative spatial distribution of reactants.

In order to handle practically the infinite set of equations, the so-called superposition approximation [8] is widely used, as suggested first by Kirkwood:

$$\rho_{BBA}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, t) \approx X_B(r^*, t) Y(r, t) Y(r', t) n_B^2(t) n_A(t). \quad (4)$$

This approximation presents three-particle correlation $B_1 B_2 A$ through three relative pair correlations: $B_1 B_2, B_1 A, B_2 A$.

For the case of a contact reaction at the sphere of radius r_0 described by $\sigma(r) = \beta \delta(r - r_0) / 4\pi r_0^2$ (β is the rate parameter) and using equations (1)–(4), one can easily describe the kinetics under study in terms of the macroscopic concentrations and the joint correlation functions:

$$\frac{dn_A(t)}{dt} = -k(t) n_A(t) n_B(t) \quad (5)$$

where the *reaction rate* is described by a flux of particles A over the reaction sphere:

$$k(t) = 4\pi D_A r_0^2 \left[\frac{\partial Y(r, t)}{\partial r} \right]_{r=r_0} = \beta Y(r_0, t). \quad (6)$$

The joint correlation ‘sink-particle’ function obeys the following kinetic equation:

$$\frac{\partial Y(r, t)}{\partial t} = D_A \Delta Y(r, t) + k(t) n_B Y(r, t) [1 - Z(r, r_0)] \quad (7)$$

where in the 3D case the functional reads [6, 7]

$$Z(r, r_0) = \frac{1}{2rr_0} \int_{r-r_0}^{r+r_0} X_B(r', t) r' dr'. \quad (8)$$

Since sinks B are immobile, their spatial distribution function does not depend on time, $X_B(r, t) \equiv X_B(r)$. In the quasi-steady-state regime reached after some transient period, the relevant reaction rate k_{qs} and the correlation function Y_{qs} become time independent. One can see that many-particle effects are incorporated into the kinetic equation (7) through the second, non-linear term on the right-hand side containing the reaction rate and the functional of the correlation function of traps. If traps were not spatially correlated (homogeneous distribution of sinks), $X_B(r, t) \equiv 1$, the term in square brackets on the right-hand side of equation (7) turns out to be zero and these corrections disappear. This immediately results in the quasi-steady-state reaction rate derived for diluted systems by Smoluchowski, $k_0 = 4\pi D_A r_0$ (see also [7, 12]).

In other words, many-particle correlations are important for the non-uniform trap distributions and large reactant (trap) concentrations entering as co-factor in right-hand side of equation (7). One of the sources for such correlation is a finite size of sinks B: two sinks could not be closer to each other than at the distance of $2r_0$ where r_0 is a sink radius (the so-called *effect of excluded volume*). If at some distance a around a given sink B there are no other sinks, $X_B(r < a) = 0$, it is equivalent to the positive source for the correlation function of dissimilar particles in the interval $r_0 < r < a$ described by the second term on the right-hand side in equation (7). This results in an increase of the reaction rate, $k_{qs} > k_0$. At $r > a$ the sink correlation vanishes and the correlation function of dissimilar particles obeys the Smoluchowski steady-state equation, $D_A \Delta Y(r, t) = 0$. This equation contains no reaction terms; the reaction rate is defined through the gradient of the correlation function of dissimilar particles, equation (6). In contrast, if sinks are clustered at short relative distances, $X_B(r < a) > 1$, this means additional *negative* reaction term in equation (6) which results in a *reduced* reaction rate, $k_{qs} < k_0$.

After these qualitative arguments we consider in detail several kinds of important trap distribution: a random distribution of sinks B, a regular distribution, a pair distribution and a cluster distribution.

3. Particular trap distributions

(i) Consider first the effect of excluded volume described by the steplike (Heaviside) correlation function

$$X_B(r) = \Theta(r - 2r_0). \quad (9)$$

Using equations (7) and (8), and introducing a new function $w(x) = Y_{qs}(x) x r_0$ where $x = r/r_0$, we obtain the following kinetic equations:

$$\frac{d^2 w}{dx^2} + \frac{4\pi r_0^3}{\bar{R}^3} \left(\frac{1}{2} - \frac{x}{4} + \frac{3}{4x} \right) w = 0 \quad 1 \leq x \leq 3 \quad (10)$$

$$\frac{d^2 w}{dx^2} = 0 \quad x \geq 3 \quad (11)$$

where $\bar{R} = n_B^{-1/3}$ is the mean distance between traps.

For a small volume fraction occupied by sinks, $\Phi = \frac{4}{3}\pi r_0^3 n_B \ll 1$, equations (10) and (11) could be solved iteratively. The first approximation for w yields the reaction rate correction linear in sink concentration,

$$k_{qs} \approx 4\pi D r_0 [1 + 1.53\Phi]. \quad (12)$$

(We neglected here higher-order terms in Φ .)

(ii) Let us consider now a more general sink distribution described by the function $X_B(r, 0) = \Theta(r - a)$ where a is a parameter whose magnitude can vary from $2r_0$ (the effect of excluded volume) to the mean distance between traps, \bar{R} .

From the above one obtains the following kinetic equations:

$$\begin{aligned} D_A \Delta Y_{qs}(r) + k_{qs} n_B Y_{qs}(r) &= 0 & r_0 \leq r \leq a \\ D_A \Delta Y_{qs}(r) &= 0 & r > a. \end{aligned} \quad (13)$$

When deriving these equations, we took into account that $Y_{qs}(r)$ is close to zero as r is close to r_0 and the functional $Z(r, r_0)$, equation (8), is close to a step function of the parameter a . Solution of equations (13) could be presented in the form

$$k_{qs} = \frac{k_0}{\cos\{\sqrt{k_0 n_B / D_A}(a - r_0)\}}. \quad (14)$$

Taking into account that $r_0 \ll \bar{R}$, one obtains from equation (14) the steady-state reaction rate

$$k_{qs} = k_0 \left(1 + C \Phi^{1/3} \left(\frac{a - r_0}{\bar{R}} \right)^2 \right) \quad (15)$$

where $C = 2\pi / (\frac{4}{3}\pi)^{1/3} = 3.9$. The second term on the right-hand side of equation (15) demonstrates the many-particle corrections due to competition between several sinks B for the reaction with some approaching donor A.

For a *regular array* of sinks B characterized by $a \approx \bar{R}$ and $r_0 \approx 0$ one obtains the reaction rate

$$k_{qs} = k_0 [1 + 3.9\Phi^{1/3}]. \quad (16)$$

Note that for $\Phi = \frac{4}{3}\pi r_0^3 n_B \ll 1$ these sink-concentration corrections are much larger than those for the excluded volume, equation (12). This result could be also derived using not a continuum but a discrete distribution of sinks in the form

$$X_B(r) = v_B \sum_{i=1}^n \frac{z_i \delta(r - R_i)}{4\pi R_i^2} \quad (17)$$

where the volume per sink is $v_B = 1/\bar{R}^3$, z_i is a number of sinks at radius R_i from a sink at the coordinate origin, and sinks are arranged in the form of a regular cubic structure with the lattice constant \bar{R} . The reaction rate obeys the following equation:

$$k_{qs}^n = k_0 \left[1 + \frac{2\pi r_0}{\bar{R}} \left(C_{n+1}^2 - \sum_{i=1}^n \frac{z_i}{c_i} \right) \right] \quad (18)$$

where the coefficients $C_i = R_i/\bar{R}$. In the limit of an infinite number of sinks, $n \rightarrow \infty$, one obtains equation (16).

Ham [9] presented an exact solution for such a regular sink distribution in terms of the Wigner-Seitz (cell) model

$$k_{qs} = k_0 [1 + 1.85\Phi^{1/3}]. \quad (19)$$

Despite different numerical co-factors of $\Phi^{1/3}$ in equations (16) and (19), Kirkwood's superposition approximation gives the same functional dependence of the reaction rate on the sink concentration, $n_B^{1/3}$. Moreover, our equation (16) would coincide with the exact solution, equation (19), if one estimates the mean distance between traps as $a = 0.69\bar{R}$. This estimate is more correct than just $a = \bar{R}$ since *each* trap is surrounded by the reaction sphere.

To demonstrate the abilities of Kirkwood's formalism, let us consider now several other sink distributions $X_B(r)$.

(iii) It has been shown in [13] that reaction rate k_{qs} for a pair of sinks B separated by a distance l has the following dependence on l (as $l \gg r_0$)

$$k_{qs} = \frac{4\pi Dr_0}{1 + r_0/l}. \quad (20)$$

In [13] the steady-state equation for a pair of sinks was exactly solved in bi-spherical coordinates. However, this method cannot be generalized for more complicated cases whereas our approach does not have such restrictions. For a pair of sinks we choose $X_B(r)$ in the form

$$X_B(r) = \frac{\delta(r-l)}{4\pi r^2} v \quad (21)$$

where $v = n_B^{-1}$. For $\bar{R} \gg l$ determination of k_{qs} through the equations (7) and (8) results in the solution of a set of the following equations:

$$\frac{d^2 w}{dx^2} = 0 \quad 1 < x \leq x_l - 1 \quad (22)$$

$$\frac{d^2 w}{dx^2} - \frac{1}{2x_l} w = 0 \quad x_l - 1 \leq x \leq x_l + 1 \quad (23)$$

$$\frac{d^2 w}{dx^2} = 0 \quad x_l + 1 \leq x. \quad (24)$$

Here we have changed variables in the steady-state equations (7) and (8) for $x = r/r_0$, $x_l = l/r_0$ and introduced $w = Y_{qs}(r)xr_0$. Taking into account that $w(x=1) = 0$ and $w(x \rightarrow \infty) \rightarrow x$, and internal boundary conditions, we obtain from the definition of the one-dimensional reaction rate, $k_{qs} = 4\pi D dw/dx|_{x=1}$ [14]

$$k_{qs} = 4\pi Dr_0 \left[1 - \frac{1}{x_l} + \frac{1}{2x_l} \ln \left(\frac{x_l + 1}{x_l - 1} \right) \right]. \quad (25)$$

As clearly seen from a comparison of (20) and (25), both equations lead to the same result for large $l \gg r_0$. Their maximum difference takes place at $l = 2r_0$. It can be shown that in the case of contact of two sinks $k_{qs} = 4\pi Dr_0 \times 0.816$. Its deviation from the exact value of $k_{qs} = 4\pi Dr_0 \cdot \ln 2$ could be explained by the fact that in the superposition approximation the averaging over angles was performed before solving equations (7) and (8), thus assuming the spherical symmetry of the function $X_B(r)$.

Note that having chosen sink distribution function in the form (21), we actually have considered isolated sink pairs neglecting the weaker ($k_{qs} \propto \Phi^{1/3}$) effect of competition between different pairs appearing at larger reaction times.

It is not difficult to obtain that for several *equidistant groups* of B particles, each containing z particles,

$$k_{qs} = 4\pi Dr_0 \left[1 - \frac{(z-1)r_0}{l} \left(1 - \frac{r_0}{l} \right) \right].$$

Lastly, for a *clustered* sink distribution chosen in the form

$$\begin{aligned} X_B(r) &= b & 0 < r \leq r_1 \\ X_B(r) &= 1 & r_1 < r \end{aligned} \quad (26)$$

one easily obtains (at $br_1^2 r_0 n_B \ll 1$) that the reaction rate

$$k_{qs} = 4\pi D r_0 [1 - 2\pi r_0 n_B b (r_1 - r_0)^2]. \quad (27)$$

As one can see, in this case k_{qs} is *decreased* compared to the Smoluchowski reaction rate k_0 as a result of the screening effect of close B sinks. The proof that sink clustering acts to reduce the reaction rate also follows from the variational principle [4].

4. Accumulation kinetics

For the homogeneous creation of donors A with the rate p per unit volume and time the steady-state ($t \rightarrow \infty$) kinetic equations (5) and (7) transform into

$$\begin{aligned} p &= k_{qs} n_B n_A(\infty) \\ D_A \Delta Y_{qs}(r) + \frac{p}{n_A(\infty)} (1 - Y_{qs}(r)) + k_{qs} n_B Y_{qs}(r) [1 - Z(r, r_0)] &= 0 \end{aligned} \quad (28)$$

where $n_A(\infty) = n_A(t \rightarrow \infty)$ is the *saturation concentration* of mobile particles A.

In the same way as we calculated above the reaction rate for the concentration decay, one obtains for the rate of the accumulation kinetics

$$k_{qs} = k_0 \left[1 - \frac{3\Phi}{2} + \frac{(3\Phi)^{1/2} + 1.5\Phi d^2 + 0.5\Phi(3\Phi)^{1/2}(d^3 - 1)}{1 + (3\Phi)^{1/2}(d - 1)} \right] \quad (29)$$

where $d = a/r_0$ describes as earlier the sink correlation effect at $r < a$. Retaining here only the term leading at $\Phi \ll 1$, one obtains for homogeneous sink distribution, $d \rightarrow 1$, that k_{qs} obeys the law derived earlier in terms of the *mean-field theory* [1, 2]:

$$k_{qs} \approx k_0 [1 + (3\Phi)^{1/2}]. \quad (30)$$

On the other hand, it could be shown that the reaction rate for the regular trap array with particle accumulation ($a = \bar{R}/r_0$), equation (29), transforms into equation (15), i.e. the correction factor describing the sink competition effect is proportional to $\Phi^{1/3}$ rather $\Phi^{1/2}$.

A similar result was obtained in [11] for a discrete-lattice model of sink distribution:

$$k_{qs} = \frac{k_0}{1 - m\Phi^{1/3}} \approx k_0 (1 + m\Phi^{1/3}) \quad (31)$$

with $\Phi \ll 1$ and $m=1.76, 1.79$ for sc and fcc lattices, respectively (see also [10, 15]).

5. Conclusion

We have demonstrated that use of the Kirkwood superposition approximation allows us to study the many-particle (sink concentration) effects in the bimolecular $A + B \rightarrow B$ reaction. Study of different trap distributions permitted us to reproduce easily several particular results for the reaction rate derived earlier by means of different methods, including the Wigner–Seitz model and the mean-field theory. It is shown that the Kirkwood formalism, which is a kind of mean-field theory, is very flexible and able to treat easily arbitrary spatial distribution of sinks, including their pairs and clusters.

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