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Competition effect in diffusion-controlled reactions between ions

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Abstract

The first correction to the total flux of charged particles into a sink including the mutual influence of the other sink for the system of two charged static sinks is obtained. It turns out that the correction is negative for a high intrinsic rate constant and positive otherwise. It is shown that for attractive reactants the diffusive interaction effect may be neglected even in the case of fully diffusion-controlled reactions for large enough values of the Onsager length. Moreover the monopole approximation formula is suggested to describe the diffusive interaction between closely located sinks.

1. Introduction

The theory of irreversible bulk diffusion-controlled bimolecular reaction between reactants A and B in an inert solvent $A + B \rightarrow A$ was first developed by Smoluchowski [1]. The Smoluchowski theory uses the diffusion equation without considering intermolecular forces between reactants, and in the diffusion-controlled case it leads to the following steady-state rate coefficient:

$$k_S = 4\pi DR, \quad (1)$$

where $D = D_A + D_B$ is the coefficient of relative diffusion, and D_A and D_B are the diffusion coefficients of particles A and B respectively; $R = R_A + R_B$ is the encounter distance. Later, Debye [2] generalized this result, incorporating in the theory the influence of interparticle interaction potential $U(r)$:

$$k_D = 4\pi D \left[\int_R^\infty \frac{1}{r^2} e^{\beta U(r)} dr \right]^{-1}. \quad (2)$$

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Here $\beta = 1/k_B T$, k_B being the Boltzmann constant; T is the absolute temperature. Hummel [3] made a further generalization using the partially reflecting boundary condition instead of the Smoluchowski one which was used by Debye. In the case of Coulomb interparticle potential, the Hummel rate constant reads

$$k_H = 4\pi D\eta r_c \left[\left(1 + \frac{4\pi\eta r_c D}{k_{in}} \right) \exp(\eta r_c/R) - 1 \right]^{-1}, \quad (3)$$

where r_c is the Onsager length, $r_c = \beta |z_A z_B| e^2 / 4\pi \epsilon_0 \epsilon_r$ (here ϵ_0 is the permittivity of free space, and ϵ_r is the dielectric constant of the medium, e is the electronic charge, and $z_A e$ and $z_B e$ are charges of ions A and B, respectively); $\eta = \text{sgn}(z_A z_B)$; k_{in} is the intrinsic rate constant at the encounter distance. It is well known that these formulae work well for many systems with interparticle interaction [4]. However, they do not depend on the concentration of particles A. Therefore, the validity of equations (2) and (3) for non-dilute systems is questionable.

It is clear that, for example for a fully diffusion-controlled reaction, the local concentration of particles B around each reactive particle A (sink) is affected by the presence of neighbouring sinks. This effect is called competition or diffusive interaction (DI) by analogy to the hydrodynamic interaction [5, 4, 6]. It is worth noting that in the case of different sinks the terms ‘competition’ and ‘diffusive interaction’ may be used as synonyms. We should stress that one cannot consider the total flux of particles into the sinks (divided by bulk concentration) as the reaction rate coefficient, unlike in the case of one test sink for dilute systems. In the case of fully diffusion-controlled reaction into two sinks, this flux is known to decrease when we reduce the distance between the sinks. On the other hand, in the thermodynamic limit of a many-sink system the relevant rate coefficient increases as the mean distance between sinks decreases (i.e., when the concentration increases) [4]. It is also important to note that DI manifests itself in the case of finite values of the reaction radius R and vanishes in the case of $R = 0$ [7]. It is well known that in general the treatment of the competition effects encounters serious theoretical difficulties even for neutral reactants. In this connection the model of diffusion-controlled processes into multiple immobile sinks has been widely investigated by many authors [5, 8–10]. It is worth noting that the reaction-induced fluctuations in the reactant densities play sometimes very important role (see, e.g., the book [11] and references therein). In this approach, spatial correlations of reactants arising due to reaction are taken into account. However, the problem we treated here is not directly related to fluctuation-controlled kinetics.

In the simplest case of DI between two equal stationary uncharged sinks with the Smoluchowski boundary condition on their surfaces, the first correction due to the presence of the other sink to the total flux of diffusing particles into one sink Φ is [12, 6]

$$\Phi(0) = k_S \left(1 - \frac{R}{L} \right), \quad (4)$$

where L is the distance between the sinks. In analogy to the above result one might expect that in the case of ionic particles interacting through the potential of attraction the DI is more profound, and the first correction to the total flux has the form

$$\Phi(U) = k_D \left(1 - \frac{\tilde{R}}{L} \right), \quad (5)$$

where $\tilde{R} = k_D / 4\pi D$ is the so-called ionic reaction length. In this paper we will find the first correction to the flux and show that in the case of Coulomb potential the expression (5) does not hold.

The problem discussed above is important in understanding the origin of the competition effects and it will allow us to investigate the concentration dependence of the rate coefficient, since this dependence arises from the competition effects.

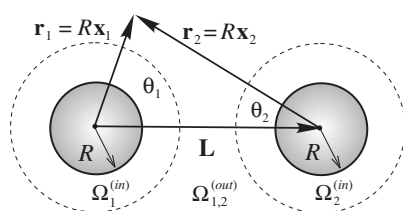


Figure 1. Two competing sinks of radii R with separation L .

The main goal of the present paper is to treat the DI between two immobile charged sinks absorbing charged reactants. We find simple formulae to estimate the effect of the DI in the system under consideration. In particular, for the fully diffusion-controlled regime we will show that in the case of ions the DI effect on diffusion-controlled reactions is weaker than in the case of uncharged particles. The outline of the paper is as follows. In section 2 we pose the boundary value problem describing the recombination of ions subjected to the partially reflecting condition on the reaction surface. Section 3 presents an approximate solution of the posed problem with the help of matching asymptotic expansions and the reflection method. Here we obtain the first correction due to the presence of the other sink. Some results obtained are discussed in section 4. In section 5 the main conclusions of the paper are given.

2. Statement of the problem

Let us treat the motion of diffusing negative ions B^- carrying the charge $z_B e < 0$ around two immobile positive ions A^+ (sinks) carrying the charge $z_A e > 0$. For the sake of simplicity we assume a case of equal sinks of the same radii, i.e., $R_1 = R_2 = R$, and let L be the distance between sinks. We also assume that the B^- ion concentration is small enough to neglect the dynamical interaction between ions. Thus any ion B^- diffuses under the action of the following potential,

$$\beta U(\mathbf{r}) = -r_c \left(\frac{1}{r_1} + \frac{1}{r_2} \right), \quad (6)$$

where r_1 and r_2 are the radial coordinates of ion B^- with respect to the spherical coordinates associated with sink I and II, respectively, where we take the z axis along the direction of the vector \mathbf{L} connecting the centres of the sinks (see figure 1).

As is known, at short times the effect of reaction appears only in a close neighbourhood of each sink and, therefore, the sinks do not ‘feel’ each other for the initial time period. In the course of time, however, the influence of the neighbouring sink appears, and becomes stronger and stronger. Thus, it is clear that the diffusive interaction becomes profound at the steady state [13]. This allows us to estimate the maximum of the DI effect using the relevant steady-state Debye–Smoluchowski equation (DSE),

$$D \nabla (\nabla n_B + n_B \nabla \beta U) = 0. \quad (7)$$

Apparently for the model at issue $D = D_B$.

We assume that the recombination occurs when ions A^+ and B^- approach the encounter distance R . Therefore, in a partially diffusion-controlled regime the following boundary condition is assumed to be posed:

$$4\pi R^2 D \left(\frac{\partial n_B}{\partial r} + n_B \beta \frac{\partial U}{\partial r} \right) \Big|_{r_i=R} = k_{in} n_B |_{r_i=R}. \quad (8)$$

In a fully diffusion-controlled regime ($k_{\text{in}} \rightarrow \infty$) the corresponding boundary condition reads

$$n_{\text{B}}|_{r_i=R} = 0. \quad (9)$$

At infinity, n_{B} approaches its bulk value n_0 , i.e.,

$$n_{\text{B}}|_{r_i \rightarrow \infty} \rightarrow n_0. \quad (10)$$

In equations (8)–(10) and hereafter $i = 1, 2$. From the mathematical point of view for the problems associated with the DI it is convenient to write the posed boundary-value problem in terms of the function $n = 1 - n_{\text{B}}/n_0$, which vanishes at infinity. Moreover, it is convenient for the further asymptotic solution to proceed to the dimensionless radial variables $x_i = r_i/R$. Thus the posed boundary-value problem (7)–(10) takes the form

$$\nabla_x^2 n + \nabla_x n \nabla_x \beta U = 0, \quad (11)$$

$$\left. \frac{\partial n}{\partial x_i} \right|_{x_i=1} = (r_c^* - h)(1 - n|_{x_i=1}), \quad (12)$$

$$n|_{x_i \rightarrow \infty} \rightarrow 0, \quad (13)$$

where $r_c^* = r_c/R$ is the dimensionless Onsager length and $h = k_{\text{in}}/k_{\text{S}}$ is the dimensionless intrinsic rate constant. For a fully diffusion-controlled regime the boundary condition (12) is simplified to

$$n|_{x_i=1} = 1. \quad (14)$$

Note that in many works on diffusion-controlled reactions between ions the spatial scale is usually chosen as r_c . For Coulomb interacting particles this seems inconvenient because in this case r_c has no relation to the space characteristic of the diffusion process [14]. The value of r_c makes the only physical sense as the distance where electrostatic energy is equal to the thermal one.

3. Solution of the problem

Obviously, due to complicated geometry (we have the problem in a periphractic domain with two disconnected boundaries), it is not feasible to reduce the given DSE in the region outside the sinks to an equation with separable or \mathcal{R} -separable variables. Moreover, in contrast to the pure diffusion case [6] or diffusion in an external electric field [15], the relevant DSE cannot be solved analytically even in the relevant local coordinates. However, if we limit ourselves to the calculation of the first correction due to the DI to the Debye or Hummel results (equation (2) or (3), respectively) the problem may be quite easily solved with the help of the matching asymptotic expansions [16] and reflections method in the dimensionless reciprocal distance $\varepsilon = R/L \ll 1$ [6, 15].

It is convenient to separate the space outside the i th sink into two parts: $\Omega_i^{(\text{in})}$ and $\Omega_i^{(\text{out})}$ (see figure 1). The domains $\Omega_i^{(\text{in})} = \{x_i \in \mathbf{R}^3 : 1 < x_i < O(\varepsilon^{-1})\}$ and $\Omega_i^{(\text{out})} = \{x_i \in \mathbf{R}^3 : O(\varepsilon^{-1}) \leq x_i\}$ are called the inner and outer regions corresponding to the i th sink, respectively. The relevant asymptotic solutions we shall denote as $n_i^{(\text{in})}$ and $n_i^{(\text{out})}$, and $\Omega_{1,2}^{(\text{out})} = \Omega_1^{(\text{out})} \cap \Omega_2^{(\text{out})}$.

It is evident (see figure 1) that in the local spherical coordinates system associated with the i th sink

$$U^*(\mathbf{x}) = -r_c^* \left(\frac{1}{x_i} + \frac{1}{x_j} \right) = -r_c^* \left(\frac{1}{x_i} + \frac{1}{\sqrt{x_i^2 + \varepsilon^{-2} - 2x_i \varepsilon^{-1} \cos \theta_i}} \right). \quad (15)$$

Hereafter $i, j (\neq i) = 1, 2$ and θ_i is the corresponding polar angle for the i th sink. Using the well-known property of a generating function of Legendre polynomials $P_\nu(\mu_i)$ [17]

$$\frac{1}{\sqrt{x_i^2 + \varepsilon^{-2} - 2x_i\varepsilon^{-1}\mu_i}} = \varepsilon \sum_{\nu=0}^{\infty} (\varepsilon x_i)^\nu P_\nu(\mu_i), \tag{16}$$

where $\mu_i = \cos \theta_i$, we see that in the local coordinates system associated with the i th sink the DSE reads

$$\begin{aligned} \nabla_{x_i}^2 n_i^{(in)} + r_c^* \left[\frac{1}{x_i^2} - \varepsilon^2 \sum_{\nu=0}^{\infty} (1 + \nu) (\varepsilon x_i)^\nu P_{\nu+1}(\mu_i) \right] \frac{\partial n_i^{(in)}}{\partial x_i} \\ - \varepsilon^2 \frac{r_c^*}{x_i^2} \left[\sum_{\nu=1}^{\infty} \varepsilon^{\nu-1} x_i^\nu \frac{d}{d\mu_i} P_\nu(\mu_i) \right] (1 - \mu_i^2) \frac{\partial n_i^{(in)}}{\partial \mu_i} = 0, \end{aligned} \tag{17}$$

where

$$\nabla_{x_i}^2 = \frac{1}{x_i^2} \frac{\partial}{\partial x_i} \left(x_i^2 \frac{\partial}{\partial x_i} \right) + \frac{1}{x_i^2} \frac{\partial}{\partial \mu_i} \left[(1 - \mu_i^2) \frac{\partial}{\partial \mu_i} \right].$$

Taking into account the condition of uniform convergence of the series (16) one can conclude that equation (17) holds when $\varepsilon x_i < 1$ (or $r_i < L$), i.e., it is evident that equation (17) is valid everywhere in $\Omega_i^{(in)}$.

In the outer domain $\Omega_i^{(out)}$ it is convenient to introduce the outer ‘compressed’ variables (ξ_i, μ_i^*) , in such a way that $\xi_i = \varepsilon x_i, \mu_i^* = \mu_i$. The corresponding outer equation in terms of outer variables may be obtained from (11) with the help of the expression (15):

$$\nabla_{\xi_i}^2 n_i^{(out)} + \varepsilon r_c^* \left[\frac{1}{\xi_i^2} + \frac{(\xi_i - \mu_i)}{x_j(\xi_i)^3} \right] \frac{\partial n_i^{(out)}}{\partial \xi_i} - \varepsilon \frac{r_c^*}{\xi_i^2} \frac{(1 - \mu_i^2)}{x_j(\xi_i)^3} \frac{\partial n_i^{(out)}}{\partial \mu_i} = 0. \tag{18}$$

It is clear from equation (13) that one should pose the following condition at infinity:

$$n_i^{(out)}|_{\xi_i \rightarrow \infty} \rightarrow 0. \tag{19}$$

We will look for the inner and outer expansions of the solution in the form

$$n_i^{(in)} = n_{i0}^{(in)}(x_i, \mu_i) + \alpha_1^{(in)}(\varepsilon) n_{i1}^{(in)}(x_i, \mu_i) + \dots \tag{20}$$

$$n_i^{(out)} = n_{i0}^{(out)}(\xi_i, \mu_i) + \alpha_1^{(o)}(\varepsilon) n_{i1}^{(out)}(\xi_i, \mu_i) + \dots, \tag{21}$$

where $\alpha_1^{(in)}(\varepsilon) \rightarrow 0, \alpha_1^{(o)}(\varepsilon) \rightarrow 0$ as $\varepsilon \rightarrow 0$. The matching condition of the inner expansion (20) and outer one (21) is

$$n_i^{(in)}(x_i, \mu_i)|_{x_i \rightarrow \infty} = n_i^{(out)}(\xi_i, \mu_i)|_{\xi_i \rightarrow 0}. \tag{22}$$

According to the procedure we start from the outer solution of the zeroth order, satisfying (19), which is trivial:

$$n_{i0}^{(out)}(\xi_i, \mu_i) = 0. \tag{23}$$

Now we should find the inner solution of the zeroth order which matches this solution. Substitution of the expansion (20) into (17) gives

$$\frac{d^2 n_{i0}^{(in)}}{dx_i^2} + \left(\frac{2}{x_i} + \frac{r_c^*}{x_i^2} \right) \frac{dn_{i0}^{(in)}}{dx_i} = 0. \tag{24}$$

Therefore the functions $n_{i0}^{(in)}$ do not depend on an angular variable. It is clear that the function $n_{i0}^{(in)}$ satisfies the boundary condition (12), i.e.,

$$\left. \frac{\partial n_{i0}^{(in)}}{\partial x_i} \right|_{x_i=1} = (r_c^* - h)(1 - n_{i0}^{(in)}|_{x_i=1})$$

or in the fully diffusion-controlled case

$$n_{i0}^{(in)}|_{x_i=1} = 1$$

and, moreover, in order to match (23) the functions $n_{i0}^{(in)}$ should vanish at infinity. Hence it is evident that the zeroth-order inner approximation is

$$n_{i0}^{(in)}(x_i) = A_i^{(0)}[1 - \exp(r_c^*/x_i)], \tag{25}$$

where

$$A_i^{(0)} = \left[1 - \left(1 - \frac{r_c^*}{h} \right)^{-1} e^{r_c^*} \right]^{-1}.$$

It is easy to see that

$$\begin{aligned} 0 \leq A_i^{(0)} \leq 1 & \quad \text{if } h \leq r_c^*, \\ |A_i^{(0)}| < (e^{r_c^*} - 1)^{-1} & \quad \text{if } h > r_c^*, \end{aligned}$$

and we can consider $A_i^{(0)} = O(1)$ as $\varepsilon \rightarrow 0$.

Let us represent the zeroth-order inner solution (25) in terms of outer ‘compressed’ variable ξ_i and expand it in powers of ε , assuming that $\xi_i = O(1)$ as $\varepsilon \rightarrow 0$, i.e.,

$$n_{i0}^{(in)}(\xi_i) = A_i^{(0)}[1 - \exp(\varepsilon r_c^*/\xi_i)] \sim -\varepsilon A_i^{(0)} r_c^* \frac{1}{\xi_i}. \tag{26}$$

It follows from this equation that $\alpha_1^{(0)}(\varepsilon) = \varepsilon$. Provided we substitute function $\varepsilon n_{i1}^{(out)}$ into equation (18) and retain terms $O(\varepsilon)$, we get

$$\nabla_{\xi_i}^2 n_{i1}^{(out)} = 0. \tag{27}$$

The general solution of this equation vanishing at infinity is

$$n_{i1}^{(out)} = \sum_{l=0}^{\infty} B_l \xi_i^{-(l+1)} P_l(\mu_i)$$

and the matching condition (22) for the inner $n_{i0}^{(in)}$ and outer $n_{i1}^{(out)}$ solutions yields the expression for the unknown constants:

$$B_0 = -A_i^{(0)} r_c^*, \quad B_l = 0 \quad (l = \overline{1, \infty}).$$

Thus we get

$$n_{i1}^{(out)}(\xi_i, \mu_i) = -A_i^{(0)} r_c^* \frac{1}{\xi_i}. \tag{28}$$

Therefore, solution (25) is uniformly valid in the whole domain when $x_i > 1$.

It is clear that the inner domain of the j th sink belongs to the outer domain of the i th sink (i.e., $\Omega_j^{(in)} \subset \Omega_i^{(out)}$). Hence in the local coordinates associated with the j th sink one can rewrite equation (28) as follows:

$$\varepsilon n_{i1}^{(out)}(x_j) \sim -\varepsilon A_i^{(0)} r_c^* \left[\sum_{v=0}^{\infty} (\varepsilon x_j)^v P_v(\mu_j) \right].$$

If we substitute this function into the corresponding DSE written in the local coordinates associated with the j th sink it satisfies the equation with accuracy up to $O(\varepsilon^2)$. Therefore, the terms $o(\varepsilon)$ in this expansion may be omitted. It is now clear that in a neighbourhood of the j th sink the function $\alpha_1^{(in)}(\varepsilon) = \varepsilon$.

According to the method of reflections we have in a neighbourhood of the j th sink the two-term solution for the domain $\Omega_j^{(in)}$:

$$n_j^{(in)} = n_{j0}^{(in)}(x_j) + \varepsilon n_{j1}^{(in)}(x_j, \mu_j), \tag{29}$$

where

$$n_{j1}^{(in)}(x_j, \mu_j) = n_{j1}^{(1)}(x_j, \mu_j) + n_{i1}^{(out)}(x_j).$$

We can interpret the term $\varepsilon n_{j1}^{(1)}$ as the first reflection of the field $n_{i1}^{(out)}(x_j)$ near the j th sink [6, 15], which compensates a change in the boundary condition on the surface of the j th sink. In this way function $n_j^{(in)}$ should be responsible for the DI between sinks.

Substitution of the function $n_j^{(in)}$ into equation (17) yields the general solution for $n_{j1}^{(1)}$:

$$n_{j1}^{(1)}(x_i) = A_j^{(1)}[1 - \exp(r_c^*/x_j)], \tag{30}$$

where $A_j^{(1)}$ is a constant to be determined by the boundary condition. It is clear that if one changes $j \rightarrow i$ the expression (29) holds in the domain $\Omega_i^{(in)}$ as well. Now we can find the unknown constant $A_j^{(1)}$ in the formula (30) which, due to the symmetry of the problem, is equal to $A_i^{(1)}$.

As was pointed out above, the function $n_{j1}^{(in)}$ describes the influence of the i th sink on the j th one, and in order to obtain $A_j^{(1)}$ we should pose the following boundary condition:

$$\varepsilon \frac{\partial n_{j1}^{(in)}}{\partial x_j} \Big|_{x_j=1} = -(r_c^* - h)(1 - \varepsilon n_{j1}^{(in)}|_{x_j=1}). \tag{31}$$

Particularly for the fully diffusion-controlled recombination condition, (31) gives the usual condition in the method of reflections [6, 15]

$$(n_{i1}^{(out)} + n_{j1}^{(in)})|_{x_j=1} = 0. \tag{32}$$

One can see that the condition (31) leads to

$$A_j^{(1)} = A_i^{(1)} = (A_j^{(0)})^2 r_c^*.$$

Thus we have derived a simple two-term expression approximately describing the concentration field in a neighbourhood of the j th sink within accuracy $O(\varepsilon)$:

$$n_j^{(in)} = n_{j0}^{(in)} - \varepsilon A_j^{(0)} r_c^* (1 - n_{j0}^{(in)}). \tag{33}$$

Formula (33) allows us to find an approximation for the total flux of diffusing ions B^- into the j th sink, divided by $n_0 k_S$, i.e.,

$$\Phi(r_c^*, \varepsilon) = \left[-\frac{\partial n_j^{(in)}}{\partial x_j} + r_c^*(1 - n_j^{(in)}) \right] \Big|_{x_j=1} = \Phi(r_c^*, 0)(1 + \varepsilon A_j^{(0)} r_c^*). \tag{34}$$

Here

$$\Phi(r_c^*, 0) = \frac{k_H(r_c^*)}{k_S} = \frac{r_c^*}{1 - (1 - \frac{r_c^*}{h}) \exp(-r_c^*)} \tag{35}$$

is the dimensionless Hummel rate coefficient for the attractive Coulomb potential [3].

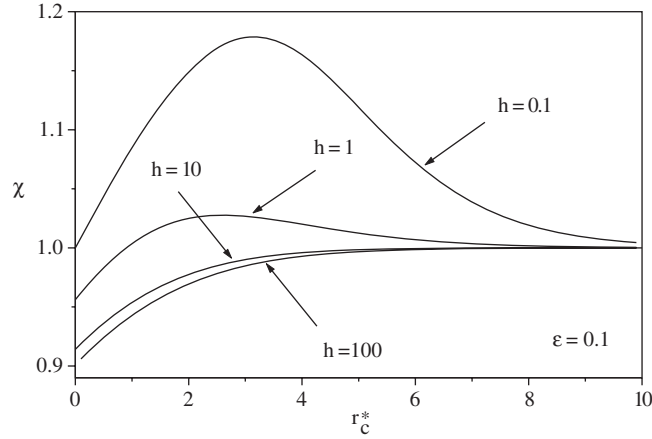


Figure 2. Plots of the first approximation to the correction factor χ as a function of the dimensionless Onsager length r_c^* and different reactivity h at $L = 10R$.

4. Discussion

4.1. Partially diffusion-controlled recombination

We can rewrite the obtained formula (34) in a more convenient form:

$$\chi(r_c^*, h, \varepsilon) = 1 + \varepsilon A_j^{(0)} r_c^*. \quad (36)$$

Here we have introduced the function $\chi(r_c^*, h, \varepsilon) = \Phi(r_c^*, \varepsilon)/\Phi_0$, where $\Phi_0 = \Phi_0(r_c^*, 0)$ is the dimensionless total flux unperturbed by the other sink. It is clear that this function characterizes the strength of the DI (see figure 2).

In the case of very small reactivity, i.e., as $h \rightarrow 0$, we have $n_{j0}^{(in)} \rightarrow 1 - \exp(r_c^*/x_j)$, and $A_j^{(0)} \rightarrow 1$. So the general formula (33) is reduced to

$$n_B = n_0(1 + \varepsilon r_c^*) \exp(r_c^*/x_j)$$

and, therefore, $n_B \rightarrow n_0(1 + \varepsilon r_c^*)$ as $x_j \rightarrow \infty$. It is important to note that in this case the concentration of particles B^- increases near the boundary of the sinks.

One can see from figure 2 that the function $\chi(r_c^*, h, \varepsilon)$ for any fixed values of ε and h has a maximum in the region where the correction due to the DI is positive. The dependence of the location of this maximum on the value of h is presented in figure 3.

If $r_c^* < h$ the correction due to the DI is always negative and $\chi < 1$. The case $r_c^* = h$ is critical, because for this case the DI disappears completely. Provided $r_c^* > h$ we have a positive correction, which due to the exponent $\exp(r_c^*)$ in $A_j^{(0)}$ tends to zero as $r_c^* \rightarrow \infty$ (see figure 2).

In both cases due to the presence of the other sink the background concentration $n_\infty^{(in)} = \lim_{x_i \rightarrow \infty} n^{(in)}$ changes: for high reactivity ($h \gg 1$) it is less than the bulk concentration value n_0 and for low reactivity ($h < 1$) it is more than n_0 . Therefore, for these two cases this leads to a decreasing of the diffusive flux ($\propto \partial n / \partial x_i$) because the concentration n_B differential $|n_B|_{x_i=1} - n_\infty^{(in)}|$ becomes smaller. However, in the case of high reactivity this flux is towards the reaction surface and the DI decreases the flux into the i th sink but in the case of low reactivity the diffusive flux is outwards from the reaction surface and the DI increases the flux into the i th sink (see figure 4).

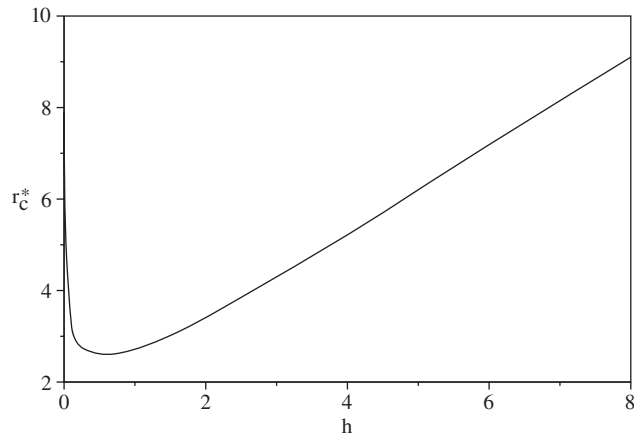


Figure 3. The location r_c^* of the maximum of the first approximation to the correction factor χ as a function of h .

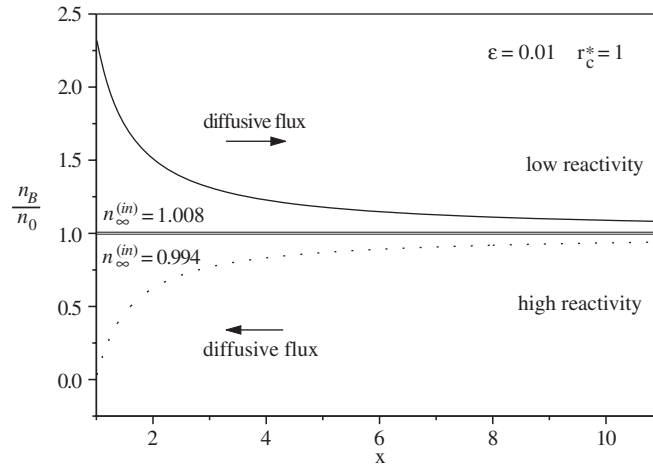


Figure 4. The local concentration distribution in a neighbourhood of a sink at $L = 100R$ and $r_c^* = 1$ for low reactivity $h = 0.1$ (solid line) and high reactivity $h = \infty$ (dotted line).

4.2. Fully diffusion-controlled recombination

In the case of fully diffusion-controlled recombination, equation (36) may be written in an alternative form:

$$\chi(r_c^*, \varepsilon) = 1 - \frac{k_D(-r_c^*)}{4\pi DL}, \quad (37)$$

where

$$k_D(r_c^*) = \frac{k_S r_c^*}{1 - \exp(-r_c^*)} \quad (38)$$

is the Debye rate constant (2) for the attractive Coulomb potential. In expression (37) we used the fact that for the Coulomb potential the following identity holds:

$$k_D(-r_c^*) = k_D(r_c^*)e^{-r_c^*}.$$

It is worth noting that $k_D(-r_c^*)$ corresponds to the case of repulsive potential with the same Onsager length r_c^* .

It follows from (37) that for fully diffusion-controlled recombination the DI should be important when $r_c^* \ll 1$. Otherwise one can ignore the DI and calculate the total flux by the Debye formula (38).

4.3. Monopole approximation

Keeping dipole-type terms of $O(\varepsilon^2)$ in the potential expansion (16), equation (17) may be written as follows:

$$\nabla_{x_i}^2 n + \left(\frac{r_c^*}{x_i^2} - \varepsilon^2 r_c^* \mu_i \right) \frac{\partial n}{\partial x_i} - \varepsilon^2 r_c^* (1 - \mu_i^2) \frac{1}{x_i} \frac{\partial n}{\partial \mu_i} = 0. \quad (39)$$

One can see that this equation is of the form of the DSE (11) with the ‘effective potential’

$$\beta U_{\text{eff}} = -\frac{r_c^*}{x_i} - \varepsilon^2 r_c^* x_i \mu_i.$$

Equation (39) as applied to reactions in an external electric field was comprehensively investigated in [18]. It was shown there that increasing the value $\varepsilon^2 r_c^*$ leads to the increasing of the total flux into the i th sink. It is worth noting that the drift term in equation (39) arises from the presence of the other sink. Therefore the inclusion of dipole-type terms leads to the decrease of the DI effect. Thus in order to estimate the maximum of the DI one should consider the monopole approximation for the potential (16), i.e., the corresponding DSE is simplified to (24). Furthermore, the latter equation may be studied more thoroughly and we can find the renormalized flux into the i th sink taking into account all reflections for the local concentration indirectly. This procedure is equivalent to partial summation of the regular perturbation series, and usually leads to an improved approximation [6].

In order to derive the monopole approximation we consider solutions vanishing at infinity and uniformly valid outside the sinks:

$$n = A_i [1 - \exp(r_c^*/x_i)] + A_j [1 - \exp(r_c^*/x_j)], \quad (40)$$

where A_i and A_j are some unknown constants (it is evident due to the symmetry of the problem that $A_i = A_j$). In a neighbourhood of the i th sink for the monopole approximation, (40) yields

$$n_{\text{mon}} = A_i [1 - \exp(r_c^*/x_i) - \varepsilon r_c^*]. \quad (41)$$

Using the boundary condition (12) we can find the constant A_i :

$$A_i = \left[(1 - r_c^* \varepsilon) - \left(1 - \frac{r_c^*}{h} \right)^{-1} \exp(r_c^*) \right]^{-1}$$

and therefore the total flux is

$$\Phi_{\text{mon}}(r_c^*, \varepsilon) = \frac{\Phi(r_c^*, 0)}{1 + (1 - \frac{r_c^*}{h}) \exp(-r_c^*) \Phi(r_c^*, 0) \varepsilon}. \quad (42)$$

Using this approximate formula we can obtain the exact first correction due to the DI given by equation (34) that lends support to its validity.

The dependence of the corresponding function χ describing by formulae (34) and (42) is presented in figures 5 and 6. It is worth noting that for the case of low reactivity the local concentration of particles B^- around the sinks increases, and therefore the monopole approximation (34) as well as correction (42) is not valid for short distances between sinks. In

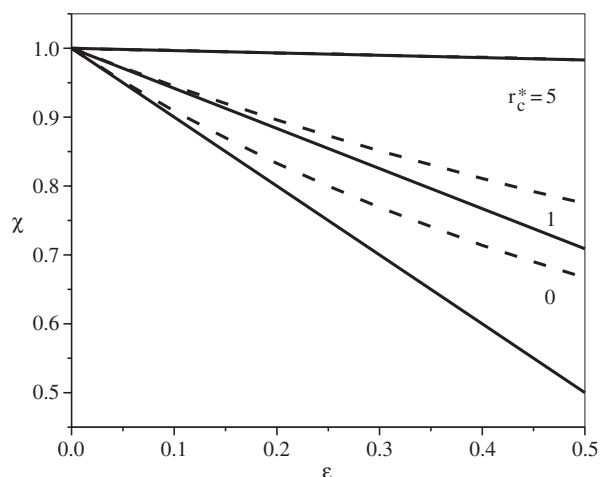


Figure 5. Correction factor for the first correction (34) (solid lines) and the monopole approximation (42) (dashed lines) in the case of full diffusion control at different values of the dimensionless Onsager length r_c^* .

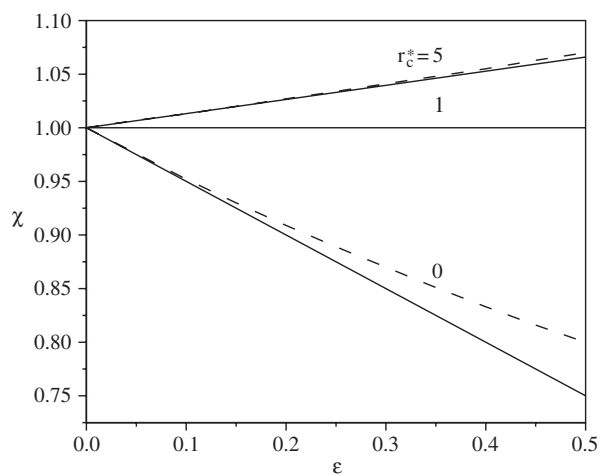


Figure 6. Correction factor for the first correction (34) (solid lines) and the monopole approximation (42) (dashed lines) in the case of $h = 1$ at different values of the dimensionless Onsager length r_c^* .

fact, in order for the total flux $\Phi_{\text{mon}}(r_c^*, \varepsilon)$ to be positive at least the following inequality should hold true:

$$\left| 1 - \frac{r_c^*}{h} \right| \exp(-r_c^*) \Phi(r_c^*, 0) \varepsilon < 1;$$

but at low reactivity this is violated for finite values of r_c^* and ε .

In the fully diffusion-controlled case, the monopole approximation (42) yields

$$\Phi_{\text{mon}}(r_c^*, \varepsilon) = \frac{k_D(r_c^*)}{1 + \varepsilon k_D(-r_c^*)}. \tag{43}$$

It is worth noting that for uncharged particles we get from this equation the known formula of Deutch *et al* [8]

$$\Phi_{\text{mon}}(0, \varepsilon) = \frac{1}{1 + \varepsilon}.$$

5. Concluding remarks

In this paper we have extended the Debye–Hummel theory of diffusion-controlled reactions between charged reactants A^+ and B^- to the situation when the particles A^+ (sinks) are mutually closely located. We have derived a simple expression for the total flux of particles B^- into a sink including the first correction due to the presence of the other sink. We have shown that: (a) in the case of very large values of the intrinsic rate constant this correction is always negative and the diffusive interaction decreases the flux into a sink; (b) in the case of small values of the intrinsic rate constant the above correction changes its sign for sufficiently large Onsager length, becoming positive, and thus the diffusive interaction increases the flux into a sink (see figure 2). Moreover, for the fully diffusion-controlled case we have proved that for large values of the Onsager length the effect due to diffusive interaction becomes unimportant and the well-known Debye formula works well even for non-dilute systems of sinks. A monopole approximation has been suggested to describe the higher-order correction to the diffusive interaction. However, for the case of low reactivity it works only for large enough distances between sinks. Based on the present study we reach the conclusion that the local concentration field is screened for the Coulomb potential and it becomes long ranged for short-range dynamic potentials.

Future extension of the present study may include the numerical solution of the relevant boundary value problem in order to find the range in which the analytical formulae obtained are valid [19].

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