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Temporal evolution of an ion pair with a perfectly reflecting recombination sphere

A.P. Tyutnev *, R.Sh. Ikhsanov, V.S. Saenko

National Research University Higher School of Economics, 20 Miasnitskaya Ulitsa, Moscow 101000, Russia

ABSTRACT

We have examined the temporal evolution of an ion pair with fully suppressed geminate recombination. For this purpose, the Smoluchowski–Debye equation for a pure Coulomb potential with a reflecting boundary condition on the recombination sphere has been solved numerically and analytically (in the last case, only approximately). It has been shown that the probability of the pair non-dissociation decreases in time roughly as a power law. We also discussed the applicability of the conductivity method for studying the non-Langevin recombination in low mobility solids. An example of such an analysis is given for one technical polymer. The relation of these results to the concept of the coulombic traps has also been discussed.

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1. Introduction

The standard approach in chemical physics for treating slow apparent reaction rates for neutral reactants or recombination rates for charge carriers in liquids or disordered solids in the diffusive transport regime is to introduce a partially reflective boundary condition at the reaction (recombination) sphere into the Smoluchowski–Debye equation [1–4]. We have extensively investigated this problem regarding an evolution of isolated ion pairs due to the Langevin recombination or the geminate conductivity due to their polarization in an applied electric field [5–10] including the case of the totally suppressed geminate recombination [7]. In papers [5–7] this problem has been treated analytically while in papers [8–10] the Smoluchowski–Debye equation has been solved numerically.

Despite the fact that Ref. [3] already reported some results relating to the perfectly reflecting boundary for a Coulomb potential (Eqs. (45)–(47) in the paper), we believe that a more detailed analysis of this problem concerning the time evolution of the dissociation of ion pairs into free charge carriers is still appropriate. It is even more so as Ref. [3] did not discuss the relation of this problem to the notion of the coulombic trap and more specifically, to the kinetics of carrier trapping and detrapping from such traps.

Recently, we discussed this problem in connection with the studies on the recombination of charge carriers in molecularly doped polymers [11]. As we show below, the results of this analysis depend heavily on the consistent interpretation of the experimental evidence presented in the last paper.

We intend to investigate the latter process in detail but in the absence of an external electric field. There are several reasons for choosing such an approach. First, it allows reducing an axially symmetric 2D-problem to a 1D radial differential equation, thus greatly simplifying its general analysis. It is important that theoretical results obtained in this way still retain physical substance. Time-resolved conductivity experiments could be conducted at a small electric field when its influence on the recombination process itself is really negligible, yet the information gained relates directly to the recombination mechanism. Second, theoretical data obtained in a 1D radial differential equation (that is in the absence of the applied electric field) presents an upper bound on the expected ion-pair non-dissociation times since an applied electric field tends only to shorten them. This time is an important methodological constraint as an experimental time in the conductivity method (both photo- and radiation induced) should greatly exceed it for preparing an appropriate initial population of the free charge carriers to investigate the mechanism of the bulk recombination (the Langevin versus non-Langevin). And finally, it allows one to develop an approximate but rather informative analytical treatment of the general problem and specifically to elucidate the nature of the coulombic traps and their dynamic properties.

2. Numerical calculations and results

We consider the classical formulation of the problem based on the diffusion equation for the mobile hole undergoing diffusive

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* Corresponding author.
  E-mail address: aptyutnev@yandex.ru (A.P. Tyutnev).

motion in the presence of a pure Coulombic field due to an immobile electron placed at the center of the spherical coordinate system for appropriate initial and boundary conditions. The equation is well-known [2]

$$\partial w / \partial t = D[\partial^2 w / \partial r^2 + (2/r + r_c/r^2)\partial w / \partial r], \tag{1}$$

where $w(r, t)$ is the time and spatial density of the positive charge, D – the diffusivity, and r_c – the so-called Onsager radius. At this distance, the potential energy of an electron–hole pair equals an average thermal energy. Initial condition is taken to be spherically symmetric with a unit positive charge uniformly distributed over a sphere of radius r_0

$$w(r, 0) = \frac{\delta(r - r_0)}{4\pi r_0^2}. \tag{2}$$

The first boundary condition stipulates that the reaction sphere with radius $r_a \leqslant r_c$ acts as a totally reflecting surface, so that diffusion and drift currents cancel each other at any moment and no accumulation of charge takes place on this sphere

$$(\partial w / \partial r + w r_c / r^2)\big|_{r=r_a} = 0. \tag{3}$$

The second boundary condition stipulates that at all times $w \to 0$ as $r \to \infty$.

For a case of $r_0 = r_a$, we actually mean that the former is infinitesimally larger than the latter.

To proceed further, we use dimensionless units $\tau = Dt/r_c^2$ and $\xi = r/r_c$ for time and coordinate respectively.

Now, Eq. (1) becomes universal

$$\partial \omega / \partial \tau = \partial^2 \omega / \partial \xi^2 + (2/\xi + \xi^{-2})\partial \omega / \partial \xi \tag{4}$$

with the initial condition ($\xi_0 = r_0/r_c$)

$$\omega(\xi, 0) = \frac{\delta(\xi - \xi_0)}{4\pi \xi_0^2}. \tag{5}$$

The boundary condition takes the form

$$(\partial \omega / \partial \xi + \omega / \xi^2)\big|_{\xi=\xi_a} = 0. \tag{6}$$

Here $\omega = r_c^3 w$ is the dimensionless charge density and $\xi_a = r_a/r_c$.

Since recombination in an ion pair is suppressed, the total amount of positive charge in the outer region ($r \geqslant r_a$) is always equal to unity. We choose as an observable quantity the amount of positive charge still residing in the Onsager sphere ($\xi_a \leqslant \xi \leqslant 1$), which effectively defines the ion pair non-dissociation probability

$$\Omega_{in}(\tau) = 4\pi \int_{\xi_a}^1 \xi^2 \omega(\xi, \tau) d\xi. \tag{7}$$

As τ goes to a positive infinity, $\Omega_{in}(\tau \to \infty) \to 0$ (diffusion will finally separate an ion pair). As a check of the consistency of numerical calculations, we used the conservation restraint

$$4\pi \int_{\xi_a}^\infty \xi^2 \omega(\xi, \tau) d\xi \equiv 1. \tag{8}$$

This boundary-value problem has been solved numerically as reported earlier in [8] but this time using the Comsol Multiphysics 3.5 package. The second boundary condition at $r \to \infty$ was realized at r_{inf} (effective infinity) which was chosen in such a way that further increasing of r_{inf} did not change the results within accuracy of 1%. The computation time of a typical variant was about 10 s.

Fig. 1 presents typical curves showing an effect of ξ_a on the time variation of Ω_{in} under condition that $\xi_0 = \xi_a$. The critical value $\Omega_{in} = 0.01$ defines an effective ion-pair dissociation time $\tilde{\tau}$. During this time, 99% of the initial charge (equal to unity) escapes from
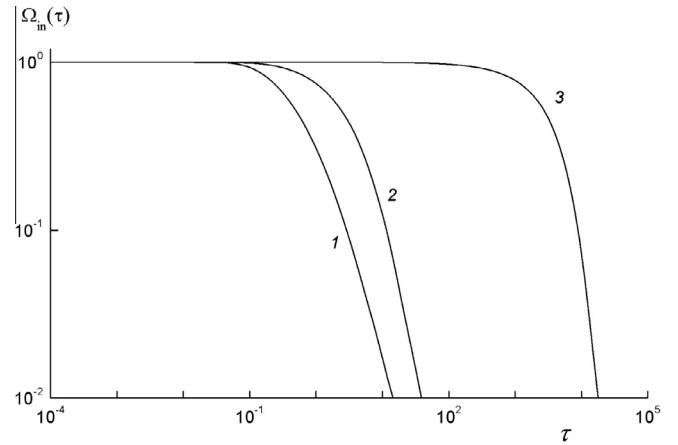

Fig. 1. Time dependence of the positive charge in the Onsager sphere. Parameter ξ_a is equal to 0.2 (1), 0.1 (2) and 0.05 (3). Also, $\xi_a = \xi_0$.

the Onsager sphere. According to Fig. 1, it sharply rises from about 14 ($\xi_a = 0.2$) through 40 ($\xi_a = 0.1$) to almost 1.6×10^4 ($\xi_a = 0.05$). One could also see that the steepness of the probability decay appreciably increases as ξ_a gets smaller.

We have investigated how the size of the integration sphere (which now replaces the original Onsager sphere) would influence the results presented on Fig. 1. As can be seen from Fig. 2, the effect of an integration sphere (its radius progressively increases by a factor of 1, 2 and 3 compared to the Onsager radius) is not that large (the critical time rises by no more than twofold). This result proves that choosing the Onsager sphere as a test-bed for evaluating time evolution of an ion pair seems justified.

The influence of the initial position of the generation sphere (ξ_0 changes) on the time evolution of an ion pair is illustrated on Fig. 3. It is only natural that the larger is the generation radius the less is the time when perceptible changes in Ω_{in} do appear. An important observation is that starting from $\tau = 100$ all curves merge and exhibit an asymptotic behavior $\Omega_{in} \propto t^{-1.5}$ predicted by theory [3].

It is instructive to give this problem an analytical consideration based on the quasi-stationary approximation. It is easy to check that a steady-state solution to Eq. (4) is

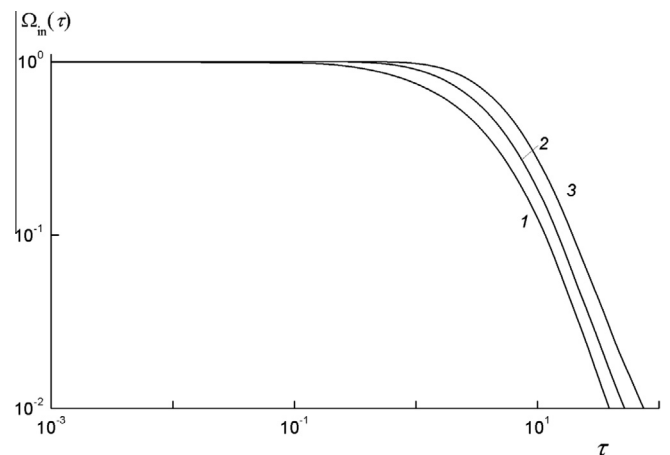$$\omega(\xi) = A \exp(1/\xi). \tag{9}$$

Fig. 2. Time dependence of the positive charge still remaining within integration sphere whose radius (in units of r_c) progressively increases: 1 (1), 2 (2) and 3 (3). Parameter ξ_a is equal to 0.1. Also, $\xi_a = \xi_0$.