

Alternative Treatment of Diffusion-Controlled Bulk Recombination

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It is shown that the Laplace transform of the diffusion-controlled bimolecular rate kernel can be directly obtained as the solution of a Riccati equation with the annihilation distance as the independent variable. This provides an efficient alternative to solving the Smoluchowski equation. The solution is expanded in powers of the square root of the Laplace variable; for the first time, the question of convergence is discussed and settled, and terms other than the first two are given explicitly and recursively by quadratures.

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A fundamental problem in the theory of diffusion-controlled processes is the calculation of the time-dependent bimolecular rate kernel or rate constant (also called the bulk or the homogeneous rate of recombination). This is the central quantity for a large amount of bulk recombination phenomena, e.g., recombination of electrolytes or radicals in solutions, quenching of fluorescence, and annihilation of excitons or electron-hole pairs in amorphous and solid materials. In the traditional approach¹ the Smoluchowski equation must be solved with an initial Boltzmann distribution and an absorption boundary condition at the annihilation (reaction) distance A . That solution is the time-dependent density profile from which the rate of recombination is calculated as the flux through the annihilation surface with radius A ; this requires knowledge of the first derivative of the solution at A only. Consequently that approach or the equivalent one² based on a calculation of the geminate rate via the backward (adjoint) equation³ contains one superfluous variable and the relevant variable A appears indirectly as the position of the boundary condition. Only for free diffusion has a closed-form solution been given and, perhaps because of the indirect route of calculation in the traditional approach, only few and restrictive approximate solutions have been obtained for more realistic situations. Several authors have constructed perturbation expansions for the Laplace transform of the rate kernel⁴ or of a closely related quantity,^{2,3,5,6} but until now only the first two terms have been given and the range of applicabil-

ity was uncertain. For example, for the important case of a Coulomb interaction an unpredicted divergence appears.⁶ In view of the large amount of applications it seemed desirable to present a simpler approach to the calculation of the rate kernel, to find a systematic way of generating a perturbation expansion, and to investigate its convergence.

In this Letter we present an alternative treatment by showing that the measurable quantity the Laplace transform of the diffusion-controlled rate of bulk recombination $\bar{\kappa}(s, A)$ is determined directly by an initial-value problem defined by a Riccati equation with A as the independent variable. For small s the solution of this equation is given as an expansion in powers of $s^{1/2}$, where we show that each term can be expressed in terms of the previous ones by a simple quadrature, and thus in principle all the terms can easily be calculated successively. Furthermore, we establish that the series is convergent for cut-off and exponentially damped potentials, and that it is asymptotic for inverse-power potentials.

As emphasized previously⁷ no restriction is introduced by considering only the diffusion-controlled limit since this also covers the general case of a partially diffusion-controlled process. In the present work we only consider three-dimensional isotropic systems with continuous diffusion.

Let $\bar{R}(s, r, A)$ be the Laplace transform of the (geminate) rate of recombination at A of a pair of particles with an initial separation r . The Laplace transform of the bulk recombination rate is then equal to^{7,8}

$$\bar{\kappa}(s, A) = \int_A^\infty e^{-\beta U(r)} \bar{R}(s, r, A) 4\pi r^2 dr \quad (1a)$$

$$= -4\pi D(A) A^2 e^{-\beta U(A)} [\partial \bar{R}(s, r, A) / \partial r]_{r=A}, \quad (1b)$$

where $\beta = 1/kT$, $U(R)$ is the potential energy between a pair of recombining particles which vanishes as $r \rightarrow \infty$, and $D(r)$ is the relative diffusion coefficient which may depend on r . The equivalence of the two

expressions follows from Green's theorem.⁸

Since $R(t, r, A)$ can also be interpreted as the density of first arrival times at A starting from r , the renewal equation

$$R(t, r, A) = \int_0^t R(t - \tau, r, y) R(\tau, y, A) d\tau \quad (2)$$

is valid for $r \geq y \geq A$. The Laplace transform of Eq. (2) is

$$\bar{R}(s, r, A) = \bar{R}(s, r, y) \bar{R}(s, y, R). \quad (3)$$

It readily follows from Eqs. (1a) and (3) that the bimolecular rate kernel, defined as⁹

$$\bar{k}(s, r) \equiv s \mathcal{K}(s, r), \quad (4)$$

obeys

$$\bar{k}(s, A) = \bar{k}(s, y) \bar{R}(s, y, A) + s \int_A^y e^{-\beta U(r)} \bar{R}(s, r, A) 4\pi r^2 dr. \quad (5)$$

Differentiation of this equation with respect to y at $y=A$ and use of Eq. (1b) leads to the Riccati equation

$$\frac{d\bar{k}(s, y)}{dy} = -4\pi y^2 e^{-\beta U(y)} s + \frac{\bar{k}(s, y)^2}{4\pi D(y) y^2 e^{-\beta U(y)}}. \quad (6)$$

In deriving Eq. (6) $\bar{R}(s, y, y) = 1$ was used, which is true only for a diffusion-controlled process. Since $U(r) \rightarrow 0$ and $D(r) \rightarrow D_\infty$ for $r \rightarrow \infty$, $\bar{k}(s, y)$ must approach the free-diffusion expression for $r \rightarrow \infty$. Thus we obtain the following boundary condition:

$$\bar{k}(s, y) \rightarrow 4\pi D_\infty y [1 + y(s/D_\infty)^{1/2}] \text{ for } y \rightarrow \infty. \quad (7)$$

It can be shown¹⁰ that \bar{R} and hence \bar{k} are analytic functions of $q = \sqrt{s}$, in the half-plane $\text{Re}(q) > -\gamma$ for exponentially screened potentials $U(r) = \exp(-\gamma r)/r^n$, and in the whole complex plane for cut-off potentials. For these potentials the solution can therefore be written as a power-series expansion of the form

$$\bar{k}(s, y) = \sum_{n=0}^{\infty} q^n k_n(y) \quad (q = \sqrt{s}). \quad (8)$$

For other potentials the series does not converge but it still constitutes an asymptotic expansion in q , i.e., only a small number of terms should be kept.

By inserting the expansion (8) into Eq. (6) one readily finds that the k_n 's satisfy the following *closed* system of first-order differential equations:

$$\frac{dk_n}{dy} = -4\pi y^2 e^{-\beta U(y)} \delta_{n,2} + \frac{e^{+\beta U(y)}}{4\pi D(y) y^2} \sum_{i=0}^n k_i(y) k_{n-i}(y). \quad (9)$$

Equation (9) is linear for $n > 0$ and can be linearized for $n=0$ by using $1/k_0$ as the dependent variable. Hence it can be solved successively for all n . The boundary condition (7) implies that $k_0 \rightarrow 4\pi D_\infty y$, $k_1 \rightarrow 4\pi D_\infty^{1/2} y^2$, and $k_n \rightarrow 0$ for $y \rightarrow \infty$ and $n \geq 2$.

The first two terms are simply given in terms of quadratures as

$$k_0(y) = \left(\int_y^\infty \frac{e^{\beta U(x)} dx}{4\pi D(x) x^2} \right)^{-1}, \quad (10)$$

$$k_1(y) = k_0(y)^2 / 4\pi D_\infty^{3/2}. \quad (11)$$

The expression (10) for the steady-state rate constant $k_0(y)$ is of course identical to that obtained by calculating steady-state fluxes and concentra-

tion profiles.¹¹ The expression (11) for the lowest-order contribution to the time dependence is identical to that obtained by asymptotic perturbation theory² and agrees with the less general formulas obtained by matched perturbation expansions.^{4,5}

For the purpose of calculating the higher terms, which have not previously been given, it is convenient to introduce a new set of unknown functions f_n , defined as

$$f_n = k_n / k_0^2. \quad (12)$$

This eliminates the $k_0 k_n$ terms on the right-hand side of Eq. (9), yielding an explicit expression for any f_n in terms of the previous ones by the

following quadrature:

$$f_n(y) = - \int_y^\infty \left(k_0'(x) \sum_{i=1}^{n-1} f_i(x) f_{n-i}(x) - \frac{\delta_{n,2}}{D(x)k_0'(x)} \right) dx, \quad n \geq 2; \quad (13)$$

the prime indicates differentiation with respect to x . The second and third terms may be written as

$$k_2(y) = -k_0(y)^2 \int_y^\infty \left(\frac{k_0'(x)}{(4\pi)^2 D_\infty^3} - \frac{1}{D(x)k_0'(x)} \right) dx, \quad (14)$$

$$k_3(y) = \frac{k_0(y)^2}{2\pi D_\infty^{3/2}} \int_y^\infty [k_0(x) - k_0(y)] \left(\frac{k_0'(x)}{(4\pi)^2 D_\infty^3} - \frac{1}{D(x)k_0'(x)} \right) dx. \quad (15)$$

It is easily verified that k_2 and all higher terms vanish identically for free diffusion as required. For a Coulomb potential the integral in Eq. (14) diverges logarithmically. Thus, as expected, no convergent series in powers of $s^{1/2}$ can be found in this case. However, the first two terms still constitute a useful, asymptotic approximation, cf. Table I. For a power potential r^{-n} the first divergent term is k_{n+1} .

The accuracy of the expansion was investigated for a Debye-Hückel interaction

$$U(r) = \exp[-\kappa(r-A)]/[kT\epsilon(1+\kappa A)r]$$

for different values of the screening constant κ and the dielectric constant ϵ . "Exact" values of the rate kernel $\tilde{k}(s, A)$ were obtained numerically with an accuracy of five digits. The coefficients k_0 , k_1 , k_2 , and k_3 were calculated by numerical integration of the relevant integrals up to a distance r_{\max} while the tail contribution was evaluated by analytical integration of the asymptotic expansions of the integrands. Note that k_2 and k_3 can be calculated simultaneously and thus there is no point in going to second order only. The relative errors of the first-order and third-order expansions of $\tilde{k}(s, A)$ are displayed in Table I for

various values of κ and the dimensionless Laplace variable $\sigma \equiv sA^2/D$. The important case of a pure Coulomb field ($\kappa=0$) is also included but only as a first-order expansion since the higher-order coefficients diverge. For $\sigma^{1/2} < \kappa A$, i.e., within the region of convergence, the accuracy of the expansion is increased by a factor of 5 to 1000 by going from first to third order, e.g., for $\kappa=10^{-1}$, $\sigma=10^{-1}$ the first-order error of 80% is reduced to 1% by including the second- and third-order terms. The accuracy of the expansion and the improvement due to the higher-order corrections, which both depend on the strength of the potential, decrease near the convergence limit, but the third-order results continue to be more accurate than the first-order results up to $\sigma \simeq \kappa A(10)^{1/2}$ from which point on the expansion ceases to be useful.

The long-time behavior of $k(t)$ follows immediately from the expansion (8) which can be inverted term by term.¹² If, however, many terms are required or the expansion diverges it may be necessary to solve Eq. (6) directly by a numerical technique. This can be done very quickly and efficiently since Eqs. (6) and (7) represent a sim-

TABLE I. Relative errors of the expansion Eq. (8) for a screened Coulomb potential. Upper and lower entries refer to first- and third-order expansions, respectively. Empty entries indicate numbers smaller than 5×10^{-5} , the accuracy of the present numerical calculation.

σ	$\kappa=0$		$\kappa=10^{-1}$		$\kappa=1$	
	$\epsilon=10$	$\epsilon=30$	$\epsilon=10$	$\epsilon=30$	$\epsilon=10$	$\epsilon=30$
10^{-5}	9×10^{-3}	10^{-4}	8×10^{-4}
			$< 10^{-4}$
10^{-3}	4×10^{-1}	7×10^{-3}	8×10^{-2}	4×10^{-3}	7×10^{-4}	2×10^{-4}
			$< 10^{-4}$
10^{-1}	1	2×10^{-1}	8×10^{-1}	2×10^{-1}	5×10^{-2}	10^{-2}
			10^{-2}	5×10^{-2}	10^{-4}	10^{-4}
1	1	4×10^{-1}	1	4×10^{-1}	2×10^{-1}	6×10^{-2}
			10^{-1}	1	6×10^{-3}	5×10^{-3}

ple one-point initial-value problem, but of course the solution must then be Laplace inverted numerically, which significantly decreases the accuracy. An accurate numerical solution of $k(t)$ is not trivially obtained.

Depending on the experimental conditions either $\bar{k}(s)$ or $k(t)$ is needed for the interpretation of experimental data. In a *steady-state* fluorescence-quenching experiment the fluorescence intensity is measured as a function of the concentration of an impurity that quenches the fluorescence, e.g., by acting as an irreversible trap for the mobile excitation. When the decay of the fluorescent state is mainly radiative, the fluorescence intensity depends linearly upon $[Q]\bar{k}(1/\tau_0)$ where $[Q]$ is the concentration of the quencher and τ_0 is the natural lifetime of the fluorescent state. The same quantity $\bar{k}(1/\tau_0)$ is also needed for a calculation of the "sensitized" fluorescence yield of the impurity, which for example is a central quantity for rare-earth laser and energy up-conversion materials. In most *time-resolved* experiments one or more types of (quasi) particles are created by a delta pulse at time zero. The rate of disappearance of the particles due to bulk recombination at a later time is given by the well-known kinetic equation

$$dn_1/dt = -\kappa(t)n_1(t)n_2(t). \quad (16)$$

If the particles are charged and, for example, only particles of type 1 are mobile, then the measured transient conductivity is directly proportional to $n_1(t)$. An example of this is provided by the transient photoconductivity of amorphous semiconductors. If in addition to the recombination process there is a dominant monomolecular decay, then for "long times" the rate of bulk recombination is again given by Eq. (16) but now with $\kappa(t)$ replaced by $\bar{k}(s)$, where s is equal to the monomolecular decay rate.¹³ An example of this is found in molecular crystals where the triplet-triplet exciton annihilation gives rise to "delayed" fluorescence with a time-dependent intensity proportional to dn_1/dt .

Compared with the traditional method the present approach has several advantages: (1) It is simpler and more direct, e.g., explicit expressions for the expansion coefficients in terms of quadratures follow trivially from Eq. (13) and

thus for the first time terms higher than first order have been given. Inclusion of the second- and third-order terms significantly improves the accuracy of the expansion. For strong potentials the obtained improvement of the accuracy by a factor of 100 or more is in fact necessary for the expansion to be useful. (2) The question of the convergence of the series is discussed and settled here for the first time. (3) It reformulates the problem in a way that is convenient for numerical purposes. Finally, we note that the treatment can easily be extended to include geminate recombination. Consequently, all quantities of interest for diffusion-controlled recombination processes can be found by solving the Riccati equation (6) rather than the Smoluchowski equation.

¹T. R. Waite, Phys. Rev. **107**, 463 (1957).

²J. B. Pedersen and P. Sibani, J. Chem. Phys. **75**, 5368 (1981).

³M. Tachiya, J. Chem. Phys. **70**, 238 (1979).

⁴K. M. Hong and J. Noolandi, J. Chem. Phys. **68**, 5172 (1978).

⁵J. L. Magee and A. B. Tayler, J. Chem. Phys. **56**, 3061 (1972).

⁶S. Raaen and P. C. Hemmer, J. Chem. Phys. **76**, 2569 (1982).

⁷J. B. Pedersen, J. Chem. Phys. **72**, 3904 (1980).

⁸V. Gösele, Chem. Phys. Lett. **69**, 332 (1980).

⁹S. H. Northrup and J. T. Hynes, Chem. Phys. Lett. **54**, 224 (1978).

¹⁰In dimensionless form $\tilde{R}(s, y, A)$ can be written as $\tilde{R}(s, x, 1) = C(x, 1)u(x, s)/u(1, s)$, where $C(x, 1)$ is a functional of the potential $U(x)$ and $u(x, s)$ is the homogeneous solution of $u'' + b(x)u - su = 0$ that decreases exponentially for $x \rightarrow \infty$; cf. Ref. 2. The function $b(x)$ is related to the potential by $b(x) = U''/2 - (U'/2)^2 + U'/x$. By realizing that $u(x, s)$ satisfies the Volterra equation

$$u(x, q) = e^{-qx} - (1/q) \int_x^\infty \sinh[q(x-x')] b(x') u(x', s) dx'$$

(where $q = s^{1/2}$) the analytic properties of u and hence of \tilde{R} and $\tilde{\kappa}$ follow by standard arguments; cf. those given by R. G. Newton, *Scattering Theory of Waves and Particles* (Springer-Verlag, New York, 1982), pp. 336-339.

¹¹P. Debye, Trans. Electrochem. Soc. **82**, 265 (1943).

¹²G. Doetsch, *Introduction to the Theory and Application of the Laplace Transformation* (Springer-Verlag, New York, 1974), Chap. 37.

¹³A. Suna, Phys. Rev. B **1**, 1716 (1970).