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Smoluchowski Theory as the Leading Term of Reversible Geminate Dissociation Kinetics[*]

by A.V. Popov[**] and N. Agmon[***]

Department of Physical Chemistry and the Fritz Haber Research Center,
The Hebrew University, Jerusalem 91904, Israel

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The significance of the Smoluchowski theory transcends its initial goal of depicting pseudo-unimolecular irreversible kinetics. We show that a generalized Smoluchowski theory (GST) provides a short-time description for reversible geminate dissociation reactions even in the presence of a potential of interaction. Using this property, we succeed in constructing an excellent approximation for the whole time dependence, in which the GST is the leading term. We discuss the implication of these observations to experimental data, particularly for excited-state proton transfer to solvent.

Key words: diffusion, geminate recombination, reversible kinetics, Smoluchowski theory

In 1917 the Polish scientist von Smoluchowski published a seminal paper [1], solving the kinetics of an *irreversible* pseudo-unimolecular diffusion influenced reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_a} \mathrm{C} \tag{1}$$

This theory was later shown [2–5] to be the exact solution for the many body problem, in which a single static spherical A molecule can react upon collision (association rate coefficient k_a) with initially randomly distributed, point particles B of concentration c, which are diffusing in solution (diffusion coefficient D). The B-particles may have a spherically-symmetric potential of interaction with the central A-molecule, but they should not interact with each other. This allows to apply the theory to ionic reactions by utilizing the mean-field Debye-Hückel potential [6], in which each A–B interaction is screened by all other B's.

For many years, efforts to verify the Smoluchowski theory experimentally have centered on fluorescence quenching by either neutral [7] or charged molecules [8,9]. Unfortunately, it proved difficult to obtain conclusive evidence for the initial non-exponential phase of the reaction kinetics as predicted by Smoluchowski [10,11].

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[*] Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

[**] Permanent address: Technological Institute, Kemerovo 650060, Russia.

[***] Corresponding author. FAX: +972-2-6513742; e-mail: agmon@fh.huji.ac.il

This situation has changed recently [12–14], for acid-base reactions carried out in the excited electronic state (S_1)

$$R^*OH + B^- \xrightarrow{k_a} R^*O^- + BH \tag{2}$$

Here the photoacid, ROH, is a hydroxyaryl such as a naphthol or a hydroxypyrene derivative (the asterisk denotes its S_1 state). The base, B^-, was taken as highly concentrated (say, 2 M) acetate. At such high concentrations, the initial acid–base distances are small, and they can be covered by diffusion before the R*OH molecule has had a chance to dissociate spontaneously (see below). By adding a viscous cosolvent (glycerol) to water, it was possible to slow down diffusion (D) with little effect on the reaction rate constant, k_a. As the ratio k_a/D increased, the initial non-exponential phase became more and more dominant [12–14], just as predicted by the theory (see Figure 1 below).

This belated triumph of the Smoluchowski theory also highlights its generality. It is not a specialized theory for fluorescence quenching, but rather for *any* pseudo-unimolecular reaction. The conditions under which conventional exponential kinetics fail are not esoteric, because high viscosity conditions exist in many living organelles. High concentrations are also prevalent in biological systems. For example, neuro-transmitters are highly concentrated within phospholipid vesicles. As these vesicles are rele-

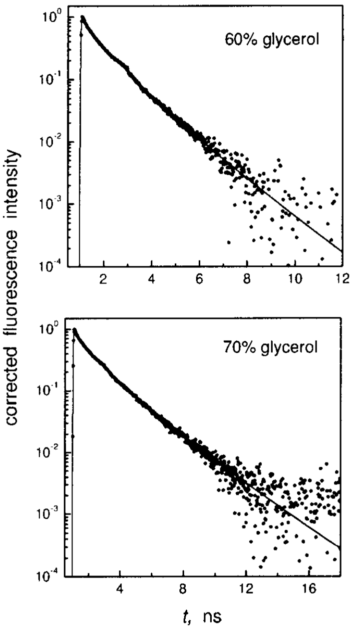

Figure 1. Non-exponential kinetics in proton transfer between excited (S_1) 2-naphthol-6-sulfonate and 2 M acetate in water-glycerol mixtures of the indicated volume %. The fluorescence signal from the photoacid was corrected for background and lifetime effects, and fitted to the solution of the Smoluchowski kinetics of eq 9 which was convoluted with the experimental instrument response function. Adapted from Fig. 6 of Ref. 13.

ased in the synaptic cleft [15], the emitted transmitter molecules diffuse and bind to receptors (and/or to enzymes such as acetyl-cholinesterase), and this initial binding phase is probably also depicted by Smoluchowski kinetics.

However, many chemical reactions are reversible, and their initial conditions sometimes involve geminate pairs rather than a uniform distribution. Under such conditions [16–18], the Smoluchowski theory is not expected to hold. Yet, curiously enough, we have recently demonstrated that a generalized Smoluchowski theory (GST) provides the leading term for the kinetics of the most general type of pseudo-unimolecular reversible reaction [19,20]. Most remote from the conditions of the Smoluchowski theory are geminate reversible reactions, where both the initial condition (a fixed distance within the pair) and the boundary condition (that of “back-reaction” [21]) differ from those considered above. Yet these conditions are relevant in experiment.

For example, in the absence of high base concentrations, the photoacid in eq 2 undergoes a reaction of proton-transfer to solvent (PTTS),

$$\mathrm{R^*OH} \underset{k_a}{\overset{k_d}{\rightleftarrows}} \mathrm{R^*O^-} + \mathrm{H^+} \tag{3}$$

The dissociated, solvated proton diffuses (*via* the “Grotthuss mechanism” [22]) and is steered back by the Coulomb interaction with the photobase ($\mathrm{R^*O^-}$) into collision, which leads to reversible association in the excited state [23–29]. It is well known that in this case the initial temporal (t) decay of the photoacid concentration is exponential, $\exp(-k_d t)$, while ultimately it switches into a power-law decay, $K_{\mathrm{eq}}/(4\pi Dt)^{3/2}$ (where K_{eq} is the equilibrium constant for the PTTS reaction in the association direction) [24,25,30].

The surprising result of the present work is that the short-time kinetics is more accurately depicted by a GST term than as $\exp(-k_d t)$. The generalization [31] is in having the concentration replaced by K_{eq}^{-1}. Furthermore, we show that the exact geminate kinetics in either the absence [17,18] or presence of an interaction potential [32] can be accurately represented by a GST term plus a correction term. The latter accounts for the long-time kinetics. Thus even when the original Smoluchowski assumptions do not hold, his theory is an important ingredient of the complete solution.

THEORY

A. Smoluchowski kinetics: Smoluchowski has assumed [1] that for the reaction in eq 1, the probability of observing the A-molecule at time t, denoted $P_{\mathrm{A}}(t)$, obeys a rate equation

$$dP_{\mathrm{A}}(t)/dt = -ck(t)P_{\mathrm{A}}(t) \tag{4}$$

albeit with a *time-dependent* rate-function, $k(t)$. The latter is obtained as the reactive flux from a diffusion problem involving an initial equilibrium distribution in (infinite) space [33]. Its Laplace transform, $\tilde{k}(s) = \int_0^\infty k(t)\exp(-st)dt$, is given by

$$\tilde{k}(s) = \frac{k_a'}{s\tilde{F}_{\rm gem}(s)} \tag{5}$$

In the presence of a spherically-symmetric A–B potential of interaction, $V(r)$ (in units of $k_{\rm B}T$, r being the A–B distance), one has

$$k_{\rm a}' = k_{\rm a}\, e^{-V(a)}$$

$$\tilde{F}_{\rm gem}(s) = 1 + k_a\, g(s) \tag{6}$$

Here a is the A–B contact (or collision) distance where reaction occurs, and $g(s)$ is the solution of the corresponding unreactive problem (*i.e.*, imposing a reflective boundary condition at $r = a$), and starting at $r = a$.

When $V(r) = 0$, the reflective solution (in three-dimensions) is well-known,

$$g(s)^{-1} = k(\infty)\left(1 + a\sqrt{s/D}\right) \tag{7}$$

where the long-time limit of $k(t)$ may be found even with a potential:

$$\frac{1}{k(\infty)} = \frac{1}{k_a'} + \frac{1}{k_D'},$$

$$k_D' = 4\pi D\left(\int_a^\infty e^{V(r)} r^{-2} dr\right)^{-1} \tag{8}$$

Hence, when $V(r) = 0$, eq 5 can be inverted analytically to yield $k(t)$ [33]. In the presence of a potential, $g(s)$ and thus $k(t)$ can be found only approximately [4]. An excellent approximation for $g(s)$ was suggested by Zharikov and Shokhirev [32]. In either case, $\tilde{F}_{\rm gem}(s) \to 1$ at short times (when $s \to \infty$), so that $k(t) \to k_a'$. At long times the reaction slows down, because the initially closely separated A–B molecules have been eliminated by reaction, and $k(t) \to k(\infty)$.

Given $k(t)$, the rate equation 4 can be integrated analytically to yield

$$P_{\rm A}(t) = \exp\left[-c\int_0^t k(t')dt'\right] \tag{9}$$

As stated above, one can show that this result is *exact* when A is a spherical static molecule, whereas the B's are point particles that can interact only with A [2–4]. When A is mobile this becomes an approximation, though arguably a rather good one [5].

An experimental demonstration of Smoluchowski kinetics for excited-state proton transfer reaction, eq 2, is shown in Fig. 1. Due to the small diffusion coefficients ($2–4 \cdot 10^{-7}$ cm^2/s) in concentrated glycerol solutions, $k_D' << k_a'$, so that the reaction in these solvents is diffusion-controlled, $k(\infty) \approx k_D'$. However, because $k(t)$ converges very slowly to $k(\infty)$, as $t^{-1/2}$, the exponential asymptotic limit of the kinetics is not reached here. In this case the whole observed time-dependence is within the early non-exponential phase of the Smoluchowski kinetics.

B. Geminate kinetics: Consider now a bound geminate pair (state C), which reacts according to

$$\mathrm{C} \underset{k_a}{\overset{k_d}{\rightleftarrows}} \mathrm{A} + \mathrm{B} \tag{10}$$

It dissociates with a rate constant k_d, and subsequently may associate again with a rate constant k_a. The pair can undergo several rebinding cycles, but eventually it will separate diffusively to such large distances from which it will never return. Therefore the probability of observing the initially prepared C-molecule, $P_{\rm C}(t)$, decays to zero with time, but this decay is non-exponential. An important example for such behavior is given by PTTS reactions, eq 3, as demonstrated in numerous publications [23–29].

Starting from the Smoluchowski equation with the "back-reaction" boundary condition [21] (or with dissociation and association "sink terms"), one can show that the Laplace transformed probability, $\widetilde{P}_C(s)$, is given by the simple relation [16]

$$\widetilde{P}_C(s) = \frac{\widetilde{F}_{\text{gem}}(s)}{s\widetilde{F}_{\text{gem}}(s) + k_d} \tag{11}$$

with $\widetilde{F}_{\text{gem}}(s)$ from eq 6. For $V(r) = 0$, this provides an exact result that can be inverted analytically [17]. This treatment can be extended [18] to the excited-state reaction in eq 3. However, these analytic solutions in the time domain are rather complex, and will not be reproduced herein. For $V(r) \neq 0$, $\widetilde{F}_{\text{gem}}(s)$ depends on a good approximation [32] for the reflective Green function, $g(s)$.

Since $\widetilde{F}_{\text{gem}}(s) \to 1$ when $s \to \infty$, $\widetilde{P}_C(s) \to (s + k_d)^{-1}$. Therefore $\widetilde{P}_C(t) \to \exp(-k_d t)$ when $t \to 0$ [24,25,30]. However, this initial exponential decay may hold only for extremely short times. We now show that an improved description of the short-time behavior of the geminate pair is given by an appropriate version of Smoluchowski kinetics.

C. Smoluchowski kinetics depict the short-time behavior of geminate pairs: We claim that for an initially-bound geminate pair at short times, $P_C(t)$ is given by eq 9 with c replaced by $K_{\text{eq}}^{-1} = k_d/k_a'$. Specifically, we suggest that $P_C(t) \to P_{\text{GST}}(t)$ as $t \to 0$, where

$$P_{\text{GST}}(t) = \exp\left[-K_{\text{eq}}^{-1} \int_0^t k(t')dt'\right] \tag{12}$$

This approximation may nevertheless hold to significantly longer times than the $\exp(-k_d t)$ decay. Equation 12 is a special limit of the modified rate equation suggested by Szabo for pseudo-unimolecular reversible reactions [31], and of the generalized Smoluchowski theory (GST) presented in Refs. 19 and 20.

To prove the above statement, note that for small times the integrand in eq 12 is small, so that $P_C(t)$ may be Taylor-expanded as $1 - K_{\text{eq}}^{-1} \int_0^t k(t')\,dt'$. Therefore, in Laplace space

$$\widetilde{P}_C(s) \approx \frac{1}{s}\left(1 - \frac{k_d}{s\widetilde{F}_{\text{gem}}(s)}\right) \tag{13}$$

where we have substituted eq 5 for $\widetilde{k}(s)$, but we *do not* take the $s \to \infty$ limit of $\widetilde{F}_{\text{gem}}(s) \to 1$, which leads to the exponential decay. Let us now rewrite the geminate solution from eq 11 as

$$\widetilde{P}_C(s) = \frac{1}{s}\left(1 + \frac{k_d}{s\widetilde{F}_{\text{gem}}(s)}\right)^{-1} \tag{14}$$

When $k_d/s\widetilde{F}_{\text{gem}}(s)$ is small (*e.g.*, for large s), the two expressions coincide, which completes our proof. Near the irreversible limit (small k_d) we thus expect that the approximation in eq 12 holds to longer times (when it will also be closer to exponential). Since our proof is independent of the exact form of $g(s)$, it is valid also for a spherically-symmetric interaction potential $V(r)$.

D. Smoluchowski kinetics as the leading term of geminate kinetics: We now show that the exact solution in eq 11 can be written in the time domain approximately as

$$P_C(t) \approx P_{\text{GST}}(t) + \Delta P(t) \tag{15}$$

for *all* times. $P_{\text{GST}}(t)$ is given in eq 12, whereas $\Delta P(t)$ is a correction-term which produces the correct long-time behavior [20]. We determine it as follows.

Moving to Laplace space, let us define

$$\widetilde{F}_{\text{GST}}(s) = \frac{k_d}{\widetilde{P}_{\text{GST}}(s)^{-1} - s} \tag{16}$$

This makes the relation between $\tilde{P}_{\mathrm{GST}}(s)$ and $\tilde{F}_{\mathrm{GST}}(s)$ the same as in eq 11. Subsequently, we define $\Delta F(s)$ as

$$\Delta F(s) = \tilde{F}_{\mathrm{gem}}(s) - \tilde{F}_{\mathrm{GST}}(s) \tag{17}$$

Substituting $\tilde{F}_{\mathrm{gem}}(s)$ from the above equation into eq 11, expanding for small $\Delta F(s)$ and neglecting the $\Delta F(s)^2$ term, gives

$$\tilde{P}_{\mathrm{C}}(s) \approx \frac{\tilde{F}_{\mathrm{GST}}(s)}{s\tilde{F}_{\mathrm{GST}}(s) + k_d}\left(1 + \frac{k_d \Delta F(s)}{s\tilde{F}_{\mathrm{GST}}(s) + k_d}\right) \tag{18}$$

The leading term inverts analytically to yield $P_{\mathrm{GST}}(t)$, whereas the correction term on the right hand side (rhs) has to be inverted numerically to give $\Delta P(t)$.

RESULTS AND DISCUSSION

We test the Smoluchowski presentation of geminate kinetics (eqs 12 and 15) in Figs. 2 and 3. In the first case, there is no potential of interaction, $V(r) = 0$, and the diffusion constant, D, is varied. In the second case we apply an attractive Coulomb potential, $V(r) = -r_c/r$, with different values for r_c. (In water at room-temperature, $r_c =$ 7.1 and 21.3 Å correspond to the case of a proton interacting with a singly and triply charged anionic bases, respectively). In both cases we have chosen rate-parameters which are typical to excited-state PTTS [23–29].

For Fig. 2, the exact solution can be obtained by Laplace inverting eq 11 either numerically, or analytically [17]. Its long-time asymptotic solution [16,25], $P_{\mathrm{C}}(t) \sim K_{\mathrm{eq}}/(4\pi Dt)^{3/2}$, is depicted as dashed lines on a log-log scale. The larger D, the faster the dissociated pair separates. The probability of geminate recombination then diminishes, and the initial kinetics approaches more closely the exponential decay, $\exp(-k_d t)$ [30], depicted by the dash-dot line. This description, which is independent of D, becomes progressively worse as D decreases. The GST in eq 12 then depicts the short-time behavior much better (dashed lines). Moreover, it actually constitutes the leading term of the transient behavior, see eq 15. Calculating the correction term, $\Delta P(t)$, by Laplace inversion of the second term on the rhs of eq 18, we obtain excellent agreement with the exact kinetics for all times (circles). We were not able to reproduce such an agreement by using alternate leading terms, such as $\exp(-k_d t)$.

In Fig. 3, an attractive Coulomb potential is added. Now an analytic solution is not available, not even in Laplace space. It may nevertheless be easily calculated from the numerical solution of the corresponding Smoluchowski equation with "back-reaction" boundary condition [21] (squares) *e.g.*, using the Windows application for solving the Spherically Symmetric Diffusion Problem (SSDP ver. 2.66 [34]). An analytic solution depends on the reflective Green function, $g(s)$. Zharikov and Shokhirev have provided an excellent approximation for this function (eq 20 in Ref. 32). By using their result in eq 11 and inverting, we obtain an excellent agreement with the exact numerical result (full lines).

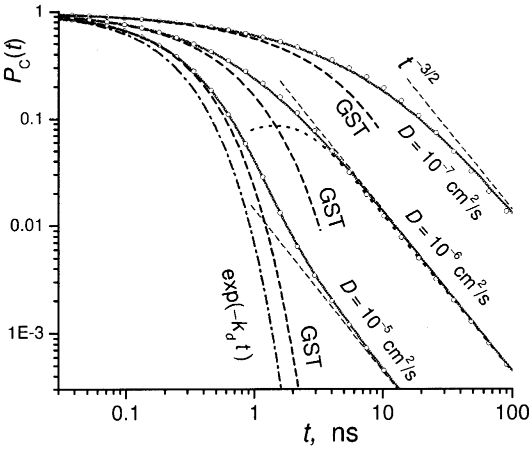

Figure 2. Reversible geminate dissociation reaction, eq 10, in the absence of a potential of interaction. Full lines are exact result, dashed lines depict the long time $t^{-3/2}$ asymptotics and the short-time GST term, eq 12. Dash-dot curve is the exponential decay, which is common to all three cases. Dotted line (shown only for the intermediate D value) is $\Delta P(t)$. It is added to the GST to give the approximation in eq 18, shown as circles. Rate parameters are common to all three cases: $k_a/(4\pi a^2) = 10$ Å/ns, $k_d = 5$ ns^{-1} and $a = 5$ Å.

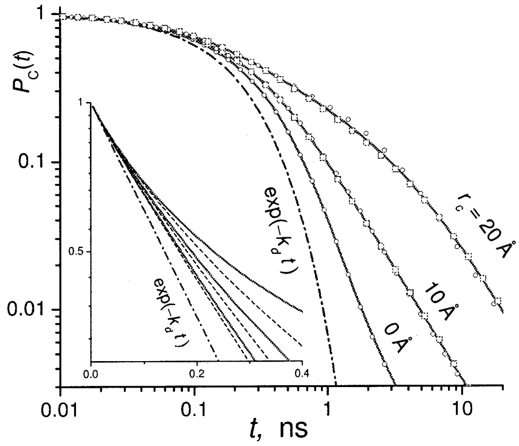

Figure 3. Reversible geminate dissociation reaction, eq 10, in the presence of a potential of interaction, with $D = 1 \cdot 10^{-5}$cm^2/s and the same rate parameters as in Fig. 2. Squares are exact numerical results, using SSDP ver. 2.66 [34]. Full curves are from the inversion of eq 11 with $g(s)$ from the Zharikov-Shokhirev approximation [32]. Circles are the approximation in eq 18. The inset shows the initial time behavior on a semi-log scale, comparing the exponential decay (dash-dot line) with the GST behavior (dash lines) [32].

The stronger the attraction (larger r_c), the more pronounced the geminate recombination process, and thus the worse the exponential approximation, $\exp(-k_d t)$, becomes. In contrast, the GST still gives the correct initial behavior, as depicted in the inset (dashed lines). The approximation in eq 15 (circles) again provides good agreement with the exact results for all times (the small deviation for $r_c = 20$ Å is due predominantly to our neglect of the ΔF^2 term in eq 18). The GST is thus the leading term of the reversible geminate kinetics even in the presence of an interaction potential.

Our observations question the procedure by which the dissociation rate-constant is sometimes extracted from experimental data *e.g.*, for the excited-state PTTS in eq 3. Some workers are either incapable of obtaining the full time dependence or simply ignore the complexity of geminate reversible reactions, assigning the initial slope of the decay curve on a semi-logarithmic scale to k_d [35]. This can lead to errors in the determination of k_d, when either D is small, or r_c large.

Consider the deprotonation of 8-hydroxypyrene-1,3,6-trisulfonate (HPTS) in a 1:1 water-methanol mixture [28]. In this solvent the proton diffusion-constant is less than half its abnormally large value in water [22], whereas the Coulomb attraction is exceedingly large, $r_c = 34.5$ Å, because of the 4-times charged anion and the low dielectric constant of the methanolic component. Moreover, the reaction rates slow down with alcohol addition, so that the initial decay is not masked by the instrument response function of the time-correlated single-photon counting system. This is the main reason for choosing this particular example.

Figure 4 demonstrates the initial part of the kinetics, theory (line) *vs.* experiment (circles) [28]. There is very good agreement with the solution of the time-dependent Smoluchowski equation, either using SSDP (line) [34] or the Zharikov-Shokhirev approximation (dotted line) [32]. Focussing on the initial behavior, we note that only about the first 30% of the decay goes as $\exp(-k_d t)$. Thereafter, the kinetics slow down

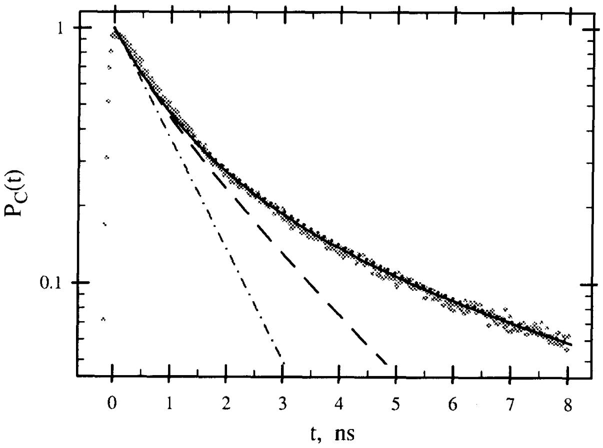

Figure 4. Initial decay of HPTS fluorescence in a 50% (v) water-methanol solution (room temperature), due to the PTTS reaction in eq 3. Figure prepared within SSDP 2.66 [34]. Gray circles depict the experimental data (from Fig. 4 of Ref. 28), after multiplication by $\exp(t/\tau)$, where $\tau = 5.4$ ns is the excited-state lifetime. Full line is the solution of the Debye-Smoluchowski equation, with the parameters [28]: $k_a/(4\pi a^2) = 1.8$ Å/ns, $k_d = 1.0$ ns^{-1}, $a = 6.0$ Å, $D = 3.8 \cdot 10^{-5}$ cm^2/s and $r_c = 34.5$ Å. The Zharikov-Shokhirev approximation [32] (dotted-line) is nearly indistinguishable from it. These were not convoluted with the instrument response function (*ca.* 0.1 ns in width), in order not to alter the theoretical short-time behavior. The dash-dot line depicts the exponential decay $\exp(-k_d t)$, whereas the dashed curve is the generalized Smoluchowski expression in eq 12. Note the semi-logarithmic scale.

appreciably, and remain within reasonable agreement with the GST until about 60% of the decay has occurred. By this time, the kinetics still appear linear on the semi-log scale, but the average slope is less than k_d. Thus when only the initial part of the decay is available for analysis (and not the long-time $t^{-3/2}$ tail), it may be preferable to fit the data to the GST expression in eq 12.

CONCLUSIONS

Sometimes one embarks on a modest mission which, by serendipity, turns out to produce far-reaching results. This occurred to King Saul 3,000 years ago. It also characterizes the development of the Smoluchowski theory. Initially suggested as an approximation for *irreversible* pseudo-unimolecular reactivity [1], it was subsequently realized to be the *exact* solution of the many-body problem when the minority particle is immobile [2–5]. More recently, a generalization thereof was seen to depict the short-time behavior of *reversible* pseudo-unimolecular reactions [19,20].

The present work demonstrated how this holds also in the most pathological case for the theory, that of reversible geminate dissociation reactions, eq 10. Here the generalization involves replacement of the concentration by the equilibrium constant for dissociation. It then provides the correct short-time behavior and also the leading term in an expansion, which shows accurate agreement with the exact transient kinetics, as obtained from the solution of the Smoluchowski equation. Whenever diffusion is slow or A–B attraction is large, the initial decay will deviate significantly from an exponential $\exp(-k_d t)$ decay, and is thus preferably fitted to the generalized Smoluchowski theory in eq 12.

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