

## Theory of nonMarkovian reversible dissociation reactions

Noam Agmon and George H. Weiss

Citation: [The Journal of Chemical Physics](#) **91**, 6937 (1989); doi: 10.1063/1.457310

View online: <http://dx.doi.org/10.1063/1.457310>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/91/11?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Theory of reversible diffusion-influenced reactions with non-Markovian dissociation in two space dimensions](#)

J. Chem. Phys. **138**, 104112 (2013); 10.1063/1.4794311

[Non-Markovian theory for the waiting time distributions of single electron transfers](#)

J. Chem. Phys. **131**, 114111 (2009); 10.1063/1.3225244

[Statistical theory of turbulent transport \(non-Markovian effects\)](#)

Phys. Plasmas **6**, 2359 (1999); 10.1063/1.873507

[NonMarkovian theory of activated rate processes. VI. Unimolecular reactions in condensed phases](#)

J. Chem. Phys. **86**, 2734 (1987); 10.1063/1.452076

[NonMarkovian reaction sites and trapping](#)

J. Chem. Phys. **83**, 5670 (1985); 10.1063/1.449691

---

 **APL Materials**

# 2014 Special Topics

 **PEROVSKITES**

 **2D MATERIALS**

 **MESOPOROUS MATERIALS**

 **BIOMATERIALS/  
BIOELECTRONICS**

 **METAL-ORGANIC  
FRAMEWORK  
MATERIALS**

**Submit Today!**

# Theory of non-Markovian reversible dissociation reactions

Noam Agmon<sup>a)</sup> and George H. Weiss

Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Health, Build. 12A, Rm. 2007, Bethesda, Maryland 20892

(Received 22 June 1989; accepted 8 August 1989)

We consider a reversible dissociation–recombination reaction in solution which is described by a distribution of waiting times rather than a single dissociation rate constant. This is a non-Markovian generalization of the backreaction boundary condition. We formulate the new boundary condition in terms of the residence time in the bound state and illustrate the theory by assuming a stable-law density for the residence time. Explicit expressions are found for the Laplace transform of the survival probability in one and three dimensions, which can be inverted analytically for special values of the stable-law parameter  $\alpha$  and numerically for other values of  $\alpha$ . We derive the long-time behavior of the survival probability for arbitrary  $\alpha$ , and note that the survival probability undergoes a first-order phase transition in one dimension, in which its asymptotic value changes abruptly at  $\alpha = 1/2$ . In three dimensions it undergoes a second-order phase transition at  $\alpha = 1$ , in which only the asymptotic slope of the survival probability changes discontinuously.

## I. INTRODUCTION

Much of the traditional literature<sup>1–6</sup> on diffusion-influenced reactions has dealt with irreversible reactions exemplified by geminate recombination and fluorescence quenching. Recently, reversibility has been introduced<sup>7–9</sup> into the theory of diffusion-influenced reactions in the form of the so-called backreaction boundary condition,<sup>7</sup> which generalizes the radiation boundary condition<sup>3</sup> by allowing a dissociated pair to form at the boundary. The resulting theory, which is based on the transient solution of the spherically symmetric Smoluchowski equation,<sup>1</sup> has been applied to the interpretation of experimental data of an aromatic molecule which ejects a proton in its excited state and recombines with it reversibly without quenching.<sup>8</sup>

We can symbolically represent the backreaction boundary condition as a first-order reaction at the boundary of a sphere

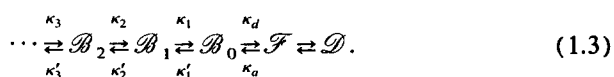


in which  $\mathcal{B}$  represents the state of a particle temporarily trapped,  $\mathcal{F}$  is the state of particles which reach the surface but are not yet bound, and  $\mathcal{D}$  represents diffusion in the space exterior to the sphere. When  $\mathcal{B}$  is a single discrete state, the probability density  $\psi(t)$  for residence in the bound state for a time  $t$  prior to dissociation is

$$\psi(t) = \kappa_d \exp(-\kappa_d t). \quad (1.2)$$

In the general case considered here we allow  $\psi(t)$  to be an arbitrary probability density.

In effect the single bound state in Eq. (1.1) will be replaced by a bound state characterized by a possibly infinite number of internal states



In this scheme  $\psi(t)$ , the probability density for residence

time in the set of bound states, will not be a single exponential as in Eq. (1.2), but can rather be expressed as a sum of exponentials

$$\psi(t) = \sum_{n=0}^{\infty} \rho_n \exp(-\lambda_n t), \quad (1.4)$$

where the  $\rho_n$  and  $\lambda_n$  depend on both initial condition and rate parameters of Eq. (1.3). When one does not keep detailed account of transitions between internal states, but rather lumps the bound states into a single  $\mathcal{B}$  state, the resulting process will be non-Markovian.<sup>10,11</sup> For example, an electronically excited molecule may dissociate most effectively from high vibrational states. When such a molecule is highly vibrationally excited it decays, as a function of time, to its ground vibrational state, thus making dissociation less probable. In a description involving only the mutual separation distance but not the vibrational state, the dissociation coefficient will appear to decrease with time. This effect can be mimicked by the functions  $\psi(t)$ , characterized by a long time tail, that are discussed in this work.

In the present work we consider the effects of using a non-Markovian model for the kinetics of a pair of reversibly binding particles whose motion is described by a spherically symmetric diffusion equation.<sup>1</sup> We will show that, for the class of  $\psi(t)$  to be considered, the probability of finding a bound pair undergoes a “phase transition” in one dimension, as the parameter characterizing this function is changed, while in three dimensions we find only a “second order” phase transition in the rate of approaching the ultimately dissociated state.

## II. GENERAL ANALYSIS

We restrict our analysis of non-Markovian pair kinetics to the case of force-free diffusion (although this can be generalized) and model the system in terms of two molecules, one a fixed sphere of radius  $a$ , and the second mobile particle assumed to be a point. The resulting system is spherically symmetric with respect to an origin fixed at the center of the sphere. We also restrict the analysis to an initially bound

<sup>a)</sup> Present address: Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel.

pair, denoted below by an asterisk, but the case of a pair initially dissociated to a separation distance  $r_0$  can also be dealt with. The evolution equation for the probability density,  $p(r, t | *)$ , for the position  $r$  of the point particle at time  $t$  in a  $d$ -dimensional space will be assumed to be the spherically symmetric diffusion (Smoluchowski<sup>1</sup>) equation

$$\begin{aligned} \frac{\partial p(r, t | *)}{\partial t} &= -\gamma_d^{-1} r^{1-d} \frac{\partial}{\partial r} J(r, t | *) \\ &= r^{1-d} \frac{\partial}{\partial r} D r^{d-1} \frac{\partial}{\partial r} p(r, t | *), \quad r \gg a, \end{aligned} \quad (2.1)$$

where  $\gamma_d$  is a geometric factor,  $\gamma_d \equiv 2\pi^{d/2}/\Gamma(d/2) = 2, 2\pi$ , and  $4\pi$  for  $d = 1, 2$ , and  $3$ , respectively,  $D$  is a constant diffusion coefficient and  $J$  is the diffusional flux. Since particles may be either bound or free, the initial condition for  $r > a$  is

$$p(r, 0 | *) = 0. \quad (2.2)$$

This implies that at  $t = 0$  the pair is bound.

### A. Markovian dissociation

In the Markovian limit, Eq. (2.1), in unbounded space, is to be solved subject to the backreaction boundary condition, usually<sup>7-9</sup> written as a relation between the flux at contact ( $r = a$ ) and the probability that the particle is not bound,  $S(t | *)$ , as

$$J(a, t | *) = -\kappa_a p(a, t | *) + \kappa_d [1 - S(t | *)]. \quad (2.3)$$

In this equation  $\kappa_a$  and  $\kappa_d$  are the association and dissociation rate parameters at contact, respectively. For the sake of subsequent comparison with Ref. 8, note that in  $3d$   $\kappa_a = 4\pi a^2 \kappa_r$ , where  $\kappa_r$  is the intrinsic recombination rate defined there.<sup>8</sup> When  $\kappa_d = 0$ , Eq. (2.3) reduces to the well known radiation boundary condition<sup>3</sup> and when, in addition,  $\kappa_a = \infty$  it becomes an absorbing boundary condition,<sup>1</sup>  $p(a, t | *) = 0$ .

$S(t | *)$  can be expressed in terms of  $p(r, t | *)$  as

$$S(t | *) = \gamma_d \int_a^\infty p(r, t | *) r^{d-1} dr \quad (2.4)$$

while  $1 - S(t | *)$  is the fraction in the bound state. In the ordinary (Markovian) case the dissociation rate is proportional to this fraction at any instant in time. The flux at contact,  $J(a, t | *)$ , is related to  $S(t | *)$  by

$$J(a, t | *) = \partial S(t | *) / \partial t. \quad (2.5)$$

This relation, which follows formally by integration of Eq. (2.1) over space, states that the number of particles in the free state can only change due to dissociation and recombination events.

A formal solution to the Smoluchowski equation for either Markovian or non-Markovian dynamics can be found in terms of Laplace transforms. Denote the Laplace transform of a function  $f(t)$  by  $\hat{f}(s) \equiv \int_0^\infty f(t) \exp(-st) dt$ . Since  $S(0 | *) = 0$ , the transform of Eq. (2.5) is

$$\hat{J}(a, s | *) = s \hat{S}(s | *). \quad (2.6)$$

This allows us to write<sup>9</sup> the boundary condition, Eq. (2.3), as

$$\hat{J}(a, s | *) = \frac{\kappa_d - s \kappa_a \hat{p}(a, s | *)}{s + \kappa_d}. \quad (2.7)$$

It has been shown<sup>9</sup> that the Laplace transform of  $S(t | *)$  for the boundary condition in Eq. (2.3) can be expressed in terms of  $\hat{p}_{\text{ref}}(a, s | a)$ , the solution of the Laplace transformed diffusion equation subject to a reflecting boundary condition,  $\hat{J}(a, s | *) = 0$ , as

$$s \hat{S}(s | *) = \frac{\kappa_d}{\kappa_d + s [1 + \kappa_a \hat{p}_{\text{ref}}(a, s | a)]}. \quad (2.8)$$

The functions  $\hat{p}_{\text{ref}}(a, s | a)$  are known<sup>2</sup> in one and three dimensions to be

$$\hat{p}_{\text{ref}}(0, s | 0) = 1/\sqrt{Ds}, \quad d = 1 \quad (2.9a)$$

$$\hat{p}_{\text{ref}}(a, s | a) = 1/[4\pi Da(a\sqrt{s/D} + 1)], \quad d = 3. \quad (2.9b)$$

Equation (2.8) can be inverted explicitly when these forms are used.<sup>8(c),9</sup>

### B. Non-Markovian dissociation

In our derivation of the non-Markovian analog of Eq. (2.3) we need not change the first term in the right-hand side since, in the reaction scheme of Eq. (1.3), we have retained the assumption of first order kinetics for the binding step. We make the further assumption that  $t = 0$  marks the beginning of a sojourn in the bound state. For the second term we can argue that if dissociation occurs for the first time at time  $t$  either the initial sojourn time in the bound state is exactly equal to  $t$ , with a probability density  $\psi(t)$ , or else recombination has occurred at time  $t' < t$ . In the latter case the subsequent sojourn time for the fraction  $\kappa_a p(a, t' | *) dt'$  which has recombined between  $t'$  and  $t' + dt'$  is  $t - t'$ . These two possibilities allows us to express the flux in terms of  $p(a, t | *)$  as

$$\begin{aligned} J(a, t | *) &= -\kappa_a p(a, t | *) + \psi(t) \\ &\quad + \kappa_a \int_0^t p(a, t' | *) \psi(t - t') dt'. \end{aligned} \quad (2.10)$$

In Laplace space the convolution integral corresponds to a product of the transforms, allowing us to write

$$\hat{J}(a, s | *) = \hat{\psi}(s) - \kappa_a [1 - \hat{\psi}(s)] \hat{p}(a, s | *). \quad (2.11)$$

Indeed, for the exponential waiting time distribution in Eq. (1.2),  $\hat{\psi} = \kappa_d/(s + \kappa_d)$  and Eq. (2.11) reduces to the boundary condition in Eq. (2.7).

The generalization of the solution (2.8) for  $\hat{S}(s | *)$  to the non-Markovian boundary (2.11) follows by similar techniques

$$s \hat{S}(s | *) = \frac{\hat{\psi}(s)}{1 + \kappa_a [1 - \hat{\psi}(s)] \hat{p}_{\text{ref}}(a, s | a)}. \quad (2.12)$$

While a closed form inverse of Eq. (2.8) can be found for the expressions for  $\hat{p}_{\text{ref}}$  in Eq. (2.9) i.e., for the Markovian case, one cannot, for general forms of  $\hat{\psi}(s)$ , find the inverse of Eq. (2.12). However, it is possible in some cases of interest to find asymptotic properties of  $S(t | *)$  in terms of the small- $s$

behavior of  $\hat{\psi}(s)$  using arguments based on Tauberian theorems.<sup>12</sup>

We next consider possible forms of  $\psi(t)$  that may be regarded as generalizing the multiexponential expression in Eq. (1.4). When the number of internal  $\mathcal{B}$  states is very large one can approximate the sum in that equation by an integral

$$\psi(t) = \int_0^\infty \rho(\lambda) \exp(-\lambda t) d\lambda. \quad (2.13)$$

If we suppose that the density function has the limiting behavior

$$\rho(\lambda) \sim A\lambda^{-\alpha} \quad (2.14)$$

for  $\lambda \rightarrow 0$ , where  $A$  is a constant, the representation of  $\psi(t)$  as the Laplace transform in Eq. (2.13) implies that as  $t \rightarrow \infty$

$$\psi(t) \sim A \frac{\Gamma(1+\alpha)}{t^{1+\alpha}}, \quad (2.15)$$

where  $\Gamma(x)$  is a gamma function.<sup>13</sup> This asymptotic behavior implies that when  $0 < \alpha < 1$  no finite integer moments of  $\psi(t)$  exist beyond the zeroth. By an Abelian theorem for Laplace transforms<sup>12</sup> it also follows that  $\hat{\psi}(s)$  can be expanded to lowest order in powers of  $s$  as

$$\hat{\psi}(s) \sim 1 - (s\tau)^\alpha, \quad (2.16)$$

where  $\tau$  is a constant with dimensions of time. Hence  $\psi(t)$  behaves asymptotically like a stable-law density function.<sup>14</sup> This form of a waiting time distribution has been used extensively by Montroll and co-workers.<sup>10,11</sup>

In the present work, it will prove convenient to consider the particular class of waiting time densities whose transform is

$$\hat{\psi}(s) = 1/[1 + (s\tau)^\alpha], \quad 0 < \alpha \leq 1. \quad (2.17)$$

In the limit of small  $s$  Eq. (2.17) has the expansion in Eq. (2.16), so that the long time behavior of  $\psi(t)$  is that given in Eq. (2.15), while for  $\alpha = 1$  (with  $\tau \equiv 1/\kappa_d$ ) Eq. (2.17) is indeed the Laplace transform of Eq. (1.2). For  $\alpha < 1$ ,  $\psi(t)$  decays slower than an exponential. For example, if  $\alpha = 1/2$

$$\psi(t) = \sqrt{\tau/\pi t} - \exp(t/\tau) \operatorname{erfc}(\sqrt{t/\tau}), \quad (2.18)$$

where  $\operatorname{erfc}(x)$  is the complementary error function.<sup>13</sup> The asymptotic behavior of the error function<sup>13</sup> implies that  $\psi(t)$  in Eq. (2.18) decays asymptotically as  $t^{-3/2}$ , in agreement with Eq. (2.15).

Use of the explicit expressions for  $\hat{\psi}(s)$  and  $\hat{p}_{\text{ref}}(a, s|a)$  given in Eqs. (2.17) and (2.9) enables us to write  $\hat{S}(s|*)$  of Eq. (2.12) as

$$s \hat{S}(s|*) = 1/\{1 + (s\tau)^\alpha [1 + (\theta_1 s)^{-1/2}]\}, \quad d = 1 \quad (2.19a)$$

$$s \hat{S}(s|*) = \frac{1 + \sqrt{\theta_3 s}}{[1 + \sqrt{\theta_3 s}][1 + (s\tau)^\alpha] + \mu(s\tau)^\alpha}, \quad d = 3, \quad (2.19b)$$

where the parameters  $\theta_1$ ,  $\theta_3$ , and  $\mu$  are defined by

$$\theta_1 \equiv D/\kappa_a^2, \quad d = 1 \quad (2.20a)$$

$$\theta_3 \equiv a^2/D, \quad \mu \equiv \kappa_a/(4\pi Da), \quad d = 3. \quad (2.20b)$$

Both  $\theta_1$  and  $\theta_3$  have dimensions of time (note that  $\kappa_a$  will

have different units depending on dimensionality) while  $\mu$  is dimensionless. Equation (2.19) will be the starting point of our analysis.

### III. SOME SPECIAL CASES

While neither of the Laplace transforms in Eq. (2.19) can be inverted explicitly for all values of  $\alpha$ , it is nevertheless instructive to perform the inversions for two special cases in which it is possible to find expressions for  $S(t|*)$  valid for all  $t$ . The cases to be considered are  $\alpha = 1$ , which is the Markovian case, and  $\alpha = 1/2$ . In addition, we obtain the asymptotic behavior at long times for all  $\alpha$  and observe that while a first order phase transition is obtained in  $d = 1$  as a function of  $\alpha$ , only a second order transition exists in three dimensions.

#### A. One dimensional reactions

In one dimension for  $\alpha = 1$  (the usual Markovian limit) one has<sup>7(b),8(c)</sup>

$$\begin{aligned} \hat{S}(s|*) &= \{s[1 + \tau\sqrt{s/\theta_1} + s\tau]\}^{-1} \\ &= \frac{\theta_1}{\tau s} \{[\sqrt{\theta_1 s} + \frac{1}{2}(1 - \Delta)][\sqrt{\theta_1 s} + \frac{1}{2}(1 + \Delta)]\}^{-1} \\ &= (\theta_1/\Delta\tau s) \{[\sqrt{\theta_1 s} + \frac{1}{2}(1 - \Delta)]^{-1} \\ &\quad - [\sqrt{\theta_1 s} + \frac{1}{2}(1 + \Delta)]^{-1}\}, \end{aligned} \quad (3.1)$$

where  $\Delta^2 \equiv 1 - 4\theta_1/\tau$ . Equation (3.1) is easily inverted<sup>2,12,13</sup> leading to

$$\begin{aligned} 1 - S(t|*) &= \frac{1}{2\Delta} \{ (1 + \Delta)f[\frac{1}{2}(1 - \Delta)\sqrt{t/\theta_1}] \\ &\quad - (1 - \Delta)f[\frac{1}{2}(1 + \Delta)\sqrt{t/\theta_1}] \}, \end{aligned} \quad (3.2)$$

where  $f(x)$  is the ubiquitous function

$$f(x) \equiv \exp(x^2) \operatorname{erfc}(x). \quad (3.3)$$

For later convenience we also define the function  $g(x) \equiv 1 - f(x)$ . Equation (3.2) is identical with Eq. (C8) in Ref. 8(c). When  $\Delta$  is complex it is necessary to evaluate a complex error function.<sup>13</sup> The asymptotic behavior of  $S(t|*)$  can be obtained either from that of the error function<sup>13</sup> or by inverting the expansion of Eq. (3.1) near  $s = 0$ . As  $t \rightarrow \infty$  one finds<sup>8(c)</sup>

$$S(t|*) \sim 1 - \frac{\tau}{\sqrt{\pi\theta_1 t}}. \quad (3.4)$$

Hence the ultimate escape probability,  $S(\infty|*)$ , for a reversible reaction is unity, in contrast to an irreversible reaction in 1d for which the ultimate escape probability vanishes (return to the origin is certain). Note also that this limiting value is approached very slowly. This power-law behavior should be contrasted with the exponential decay predicted from a scheme of first-order chemical rate equations.<sup>8(c)</sup>

We consider next non-Markovian dissociation in 1d with  $\alpha = 1/2$ . From Eq. (2.19a) we find

$$\hat{S}(s|*) = \{s[1 + \sqrt{\tau/\theta_1} + \sqrt{s\tau}]\}^{-1}. \quad (3.5)$$

Inversion in terms of the function  $g(x)$  defined earlier yields the expression

$$S(t|*) = \frac{g(\sqrt{t/\tau} + \sqrt{t/\theta_1})}{1 + \sqrt{t/\theta_1}}. \quad (3.6)$$

Unlike the  $\alpha = 1$  case, where the ultimate escape probability is unity, for  $\alpha = 1/2$  the asymptotic behavior for  $t \rightarrow \infty$  is

$$S(t|*) \sim \frac{\sqrt{\theta_1}}{\sqrt{\tau} + \sqrt{\theta_1}} \left\{ 1 - \frac{\sqrt{\theta_1}}{\sqrt{\tau} + \sqrt{\theta_1}} \sqrt{\frac{\tau}{\pi t}} \right\} \quad (3.7)$$

so that the system tends towards an equilibrium state in which a fraction of the population is dissociated while the rest remains bound.

To investigate this point further, we consider the asymptotic behavior of Eq. (2.19a) for arbitrary  $0 < \alpha < 1$ . We find that there is an interesting phase transition at  $\alpha = 1/2$ : For  $\alpha > 1/2$  the small  $s$  expansion of Eq. (2.19a) is

$$s \hat{S}(s|*) \sim 1 - \frac{\tau^\alpha}{\sqrt{\theta_1}} s^{\alpha-1/2} \quad (3.8)$$

from which we infer that as  $t \rightarrow \infty$

$$S(t|*) \sim 1 - \frac{\tau^\alpha}{\Gamma(3/2 - \alpha)\sqrt{\theta_1}} t^{-(\alpha-1/2)}. \quad (3.9)$$

Hence the probability of finding a bounded particle decays asymptotically as  $t^{-(\alpha-1/2)}$ . As in the Markovian case,  $\alpha = 1$ , the ultimate escape probability is unity. The situation is qualitatively different for  $\alpha$  less than  $1/2$ , where we have

$$\hat{S}(s|*) \sim \frac{\sqrt{\theta_1}}{\tau^\alpha} s^{-(\alpha+1/2)} \quad (3.10)$$

which, in the time domain, corresponds to the asymptotic behavior

$$S(t|*) \sim \frac{\sqrt{\theta_1}}{\Gamma(1/2 + \alpha)\tau^\alpha} t^{-(1/2-\alpha)}. \quad (3.11)$$

In this limit all pairs eventually recombine and therefore the function  $S(t|*)$  decays as  $t^{-(1/2-\alpha)}$ . Thus, there is a phase transition as a function of  $\alpha$  at  $\alpha = 1/2$ . When  $\alpha < 1/2$  particles at long time remain in the bound state, while the condition  $\alpha > 1/2$  ensures that all of the particles eventually escape into the unbound state. Only at the transition value of  $\alpha = 1/2$  are particles distributed asymptotically between both bound and unbound states.

The above results are illustrated in Fig. 1. The full curves were found by numerical inversion<sup>15</sup> of Eq. (2.19a), while the dashed curves represent the analytical asymptotic behavior from Eqs. (3.4), (3.7), (3.9), and (3.11). To emphasize the long-time behavior, these are plotted in a log-log (base 10) scale as  $\log(1-S)$  vs  $\log t$ . The phase transition is clearly evident from the figure, namely, for  $\alpha > 1/2$  the ultimate escape probability is unity, for  $\alpha < 1/2$  the ultimate recombination probability is unity and for  $\alpha = 1/2$  both escape and recombination probabilities are finite. The rate of convergence towards the long-time asymptotic limit varies with  $\alpha$ , as is evident from the plotted results. For  $\alpha > 1/2$  the asymptotic limit is approached from below while for  $\alpha < 1/2$  it is approached from above. Another interesting property is that at short times the order of the curves is reversed and that

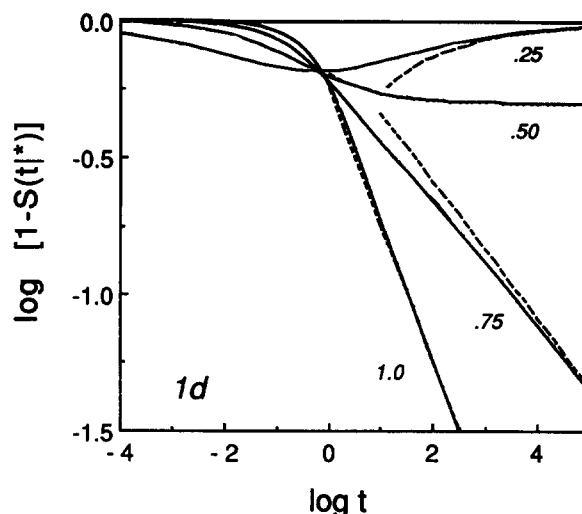


FIG. 1. The survival probability for a one dimensional, reversible diffusion influenced reaction on a log-log (base 10) plot. Full curves were obtained from the numerical inversion (Ref. 15) of Eq. (2.19a). Dashed curves are the long-time asymptotic behavior from results derived in the text. Four values of  $\alpha$  are indicated in the figure,  $\alpha = 1$  being the Markovian limit (Ref. 8).

there is a point where (at least approximately) all curves intersect.

## B. Three dimensional reactions

The exactly invertible cases in  $d = 3$  appear also to be restricted to  $\alpha = 1/2$  and 1, and their inverse may again be written in terms of the function  $g(x)$  introduced following Eq. (3.3).

In the case  $\alpha = 1$  Eq. (2.19b) becomes

$$s \hat{S}(s|*) = \frac{1 + \sqrt{\theta_3}s}{1 + \sqrt{\theta_3}s + (\mu + 1)\tau s + \tau\sqrt{\theta_3} 1s^{3/2}}. \quad (3.12)$$

If we regard the denominator as a cubic equation in  $\sqrt{s}$  and denote its three roots by  $-R_a$ ,  $-R_b$ , and  $-R_c$  then, following the derivation in Eq. (3.1), we find

$$\begin{aligned} \tau\sqrt{\theta_3} S(t|*) &= \frac{1 - R_a\sqrt{\theta_3}}{R_a(R_b - R_a)(R_c - R_a)} g(R_a\sqrt{t}) \\ &+ \frac{1 - R_b\sqrt{\theta_3}}{R_b(R_a - R_b)(R_c - R_b)} g(R_b\sqrt{t}) \\ &+ \frac{1 - R_c\sqrt{\theta_3}}{R_c(R_a - R_c)(R_b - R_c)} g(R_c\sqrt{t}). \end{aligned} \quad (3.13)$$

In this case  $S(\infty|*) = (\tau\sqrt{\theta_3}R_aR_bR_c)^{-1} = 1$  so that, as in 1d, escape is certain. As  $t \rightarrow \infty$  we find

$$S(t|*) \sim 1 - \mu\tau\sqrt{\frac{\theta_3}{4\pi t^3}} \quad (3.14)$$

in agreement with a result first found in Ref. 8(c).

In the three dimensional case with  $\alpha = 1/2$ , we rewrite Eq. (2.19b) as

$$s \hat{S}(s|*) = \frac{1 + \sqrt{\theta_3 s}}{1 + [\sqrt{\theta_3} + (\mu + 1)\sqrt{\tau}] \sqrt{s} + \sqrt{\tau \theta_3} s} \quad (3.15)$$

and again the solution may be written in terms of the roots  $-Q_a$  and  $-Q_b$ ,  $Q_a Q_b = \sqrt{\tau \theta_3}$ , of the denominator of Eq. (3.15) regarded as a quadratic polynomial in  $\sqrt{s}$ . Hence we find

$$\begin{aligned} \sqrt{\tau \theta_3} (Q_b - Q_a) S(t|*) &= (1 - Q_a \sqrt{\theta_3}) g(Q_a \sqrt{t}) / Q_a \\ &\quad - (1 - Q_b \sqrt{\theta_3}) g(Q_b \sqrt{t}) / Q_b. \end{aligned} \quad (3.16)$$

In contrast to the one dimensional case, Eq. (3.7), we find that in 3d  $S(\infty|*) = 1$ , just as for  $\alpha = 1$ . The asymptotic behavior of Eq. (3.16) as  $t \rightarrow \infty$  is

$$S(t|*) \sim 1 - (\mu + 1) \sqrt{\frac{\tau}{\pi t}}. \quad (3.17)$$

Hence, while for  $\alpha = 1/2$  all particles escape recombination, they do so more slowly than for  $\alpha = 1$ .

For arbitrary  $\alpha$ , the long-time asymptotic behavior in 3d can be gotten from Eq. (2.19b). We find that for  $s \rightarrow 0$

$$s \hat{S}(s|*) \sim 1 - (\mu + 1) (s\tau)^\alpha \quad (3.18)$$

which for  $\alpha < 1$  can be inverted as

$$S(t|*) \sim 1 - \frac{\mu + 1}{\Gamma(1 - \alpha)} \left( \frac{\tau}{t} \right)^\alpha. \quad (3.19)$$

Hence in 3d the escape probability is unity for all  $\alpha$ . The qualitative difference between one and three dimensional systems undoubtedly arises because one dimensional systems are recurrent (return to the origin occurs with probability one) while three dimensional systems are transient. Nevertheless, 3d systems show a second order phase transition as a function of  $\alpha$  at  $\alpha = 1$ . This is seen by comparing Eqs. (3.19) with (3.14): While  $1 - S$  decays as  $t^{-\alpha}$  for  $\alpha < 1$  it decays as  $t^{-3/2}$  when  $\alpha = 1$ . This is demonstrated in Fig. 2. Introduction of infinitesimally small memory results in finite slowing down of the asymptotic decay. One also notes from Fig. 2 that convergence to the asymptotic behav-

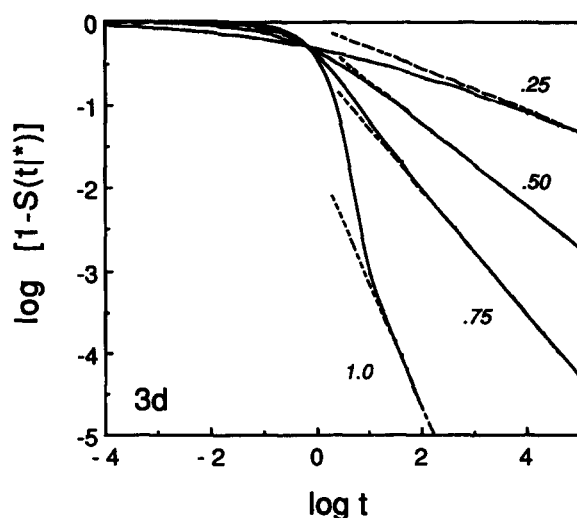


FIG. 2. Same as Fig. 1 for a three-dimensional system.

ior while fastest for  $\alpha = 1/2$ , is rather slow for  $\alpha = 1$ . In contrast to the one-dimensional case (Fig. 1) convergence to the limiting (dashed) curves is from above for  $\alpha > 1/2$  and from below for  $\alpha < 1/2$ . Again, all curves seem to intersect at one point and their order is reversed at short times.

#### IV. CONCLUSION

We have seen that for a reversible, diffusion influenced dissociation-recombination reaction the introduction of memory into the dissociation process alters the time dependence of the probability  $S(t|*)$ . In particular, we observe a phase transition as a function of the parameter  $\alpha$  introduced in the text. In one dimension, there is a first-order phase transition in which the asymptotic limit of the escape probability undergoes a discontinuous change at  $\alpha = 1/2$ . In three dimensions, there is only a second-order phase transition. The escape probability is always unity but the long-time slope of the survival probability changes discontinuously at  $\alpha = 1$ .

The above property may help us in analyzing experimental results. For the reversible proton dissociation reaction discussed in Ref. 8 the experimental value for the asymptotic slope is<sup>8(c),8(f)</sup>  $1.5 \pm 0.1$ . Since these error bars exclude values of  $\alpha < 1$ , dissociation in this case is consistent with an exponential lifetime distribution, i.e., a Markovian model. Indeed, in the case of the above reaction one can argue<sup>8(b)</sup> that vibrational relaxation, which might give rise to non-Markovian effects, is extremely fast compared to the dissociation rate.

In contrast to the above mentioned reaction, the rate of the ultrafast, diffusion-controlled recombination of iodine atoms in solutions is known to depend both on electronic and vibrational relaxation.<sup>16</sup> Unfortunately, the reaction is irreversible. Once the iodine atoms recombine, they do not dissociate on the time scale of the experiment. Nevertheless, we expect that with the development of femtosecond laser methods<sup>17</sup> in solution chemistry, ultrafast reversible reactions whose course is influenced by both diffusion and relaxation may be discovered. The present theory may provide a useful approximate treatment for such processes.

#### ACKNOWLEDGMENTS

We are grateful to James E. Kiefer for helping with the numerical Laplace inversion and to Attila Szabo for carefully reading the manuscript.

<sup>1</sup>M. von Smoluchowski, Z. Phys. Chem. **92**, 129 (1917).

<sup>2</sup>H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed. (Clarendon, Oxford, 1959).

<sup>3</sup>F. C. Collins and G. E. Kimball, J. Colloid Sci. **4**, 425 (1949).

<sup>4</sup>U. M. Gösele, Prog. React. Kinet. **13**, 63 (1984).

<sup>5</sup>S. A. Rice, in *Diffusion-Limited Reactions*, edited by C. H. Bamford, C. F. H. Tipper and R. G. Compton, Comp. Chem. Kinet. **25** (Elsevier, Amsterdam, 1985).

<sup>6</sup>A. Szabo, J. Phys. Chem. **93**, 6929 (1989).

<sup>7</sup>(a) F. C. Goodrich, J. Chem. Phys. **22**, 588 (1954); (b) N. Agmon, *ibid.* **81**, 2811 (1984).

<sup>8</sup>(a) E. Pines and D. Huppert, Chem. Phys. Lett. **126**, 88 (1986); (b) E. Pines, D. Huppert and N. Agmon, J. Chem. Phys. **88**, 5620 (1988); (c) N. Agmon, E. Pines and D. Huppert, *ibid.* **88**, 5631 (1988); (d) N. Agmon,

- ibid.* **88**, 5639 (1988); *ibid.* **89**, 1524 (1988); (e) E. Pines and D. Huppert, *J. Am. Chem. Soc.* **111**, 4096 (1989); (f) D. Huppert, E. Pines, and N. Agmon (submitted for publication).
- <sup>9</sup>N. Agmon and A. Szabo (submitted for publication).
- <sup>10</sup>E. W. Montroll and G. H. Weiss, *J. Math. Phys.* **6**, 167 (1965); G. H. Weiss and R. J. Rubin, *Adv. Chem. Phys.* **52**, 363 (1983).
- <sup>11</sup>H. Scher and M. Lax, *Phys. Rev. B* **7**, 4491, 4502 (1973); H. Scher and E. W. Montroll, *Phys. Rev. B* **12**, 2455 (1975); M. F. Shlesinger, *Annu. Rev. Phys. Chem.* **39**, 269 (1988).
- <sup>12</sup>G. Doetsch, *Theorie und Anwendungen der Laplace Transformation* (Dover, New York, 1943).
- <sup>13</sup>M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).
- <sup>14</sup>A. Stuart and J. K. Ord, *Kendall's Advanced Theory of Statistics*, 5th ed. (Oxford University, New York, 1987).
- <sup>15</sup>K. S. Crump, *J. Assoc. Comp. Mach.* **23**, 89 (1976).
- <sup>16</sup>A. L. Harris, J. K. Brown and C. B. Harris, *Annu. Rev. Phys. Chem.* **39**, 341 (1988), and references therein.
- <sup>17</sup>M. A. Kahlou, W. Jarzeba, T. P. DuBruil, P. F. Barbara, *Rev. Sci. Instrum.* **59**, 1098 (1988), and references therein.