Diffusion-Controlled Reactions with Mobile Traps

Attila Szabo,[a] Robert Zwanzig,[a] and Noam Agmon[b]
National Institutes of Health, Bethesda, Maryland 20892
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A density expansion is obtained for the time dependence of the survival probability of diffusing particles in the presence of randomly distributed diffusing traps. The coefficients are expressed in terms of the exact survival probabilities in the presence of one trap, two traps, and so on. Its leading term coincides with the well-known Smoluchowski result which is shown to be exact for static particles and noninteracting mobile traps. As an application, the first correction term is calculated for a one-dimensional system and arbitrary ratios of particle and trap diffusion coefficients.

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In recent years much effort has been devoted to the formulation of rigorous many-body treatments of diffusion-controlled reactions.[1-11] Considerable attention has been directed to annihilation and coalescence reactions,[1-7] and to trapping problems with static traps.[9-11] For these systems, rigorous results for the survival probability have been obtained, at least in one dimension (1D). Experiments on quasi-1D conductors were performed to check the static-trap limit.[10] Relatively little was done on trapping reactions (written symbolically as $A+B\rightarrow B$) when both particles (A) and traps (B) are mobile.[8] As a physical example,[12] A can be an excited-state molecule which upon collision with another molecule B gets quenched to its ground electronic state.

The Smoluchowski approach[12] to approximating the time dependence of the survival proability (fractional concentration), $\langle S(t)\rangle$, of such an excited molecule in a random distribution of quenchers is based on solving the rate equation

$$d\langle S(t)\rangle/dt=-ck(t)\langle S(t)\rangle \tag{1}$$

with a *time-dependent* rate coefficient, $k(t)$, obtained from the reactive diffusive flux into a single trap with an initial uniform distribution of A particles and a diffusion coefficient which is the sum of the two diffusion coefficients. The time-invariant concentration of B particles is denoted by c.

In this Letter we introduce a density expansion for the survival probability. The leading term involves independent particle-quencher pairs and coincides with the Smoluchowski result. The first correction term is a measure of the accuracy of this approximation. We calculate this term in 1D and show how it leads to an improved estimate of the survival probability.

Consider a system containing random walkers (particles), with diffusion coefficient D_w, and N traps (quenchers), with diffusion coefficient D_t, in a volume V in a d-dimensional space. We assume that the particles have a finite size but that the traps can be idealized as points and hence are ignorant of each other. When the concentration of the walkers is sufficiently low so that excluded volume interactions between them are negligible, it suffices to focus on a single walker.

Let $\mathbf{x}_0$ and $\mathbf{x}_i$, $i=1,\ldots,N$ be the (vectorial) coordinates of the walker and traps, respectively, in this d-dimensional space at $t=0$. The survival probability of the walker for the given initial positions of the traps, $S_N(t\,|\,\mathbf{x}_0,\mathbf{x}_1,\ldots,\mathbf{x}_N)$, satisfies a many-body diffusion equation

$$\partial S_N/\partial t=\left[D_w\nabla_0^2+D_t\sum_{i=1}^{N}\nabla_i^2\right]\times S_N(t\,|\,\mathbf{x}_0,\mathbf{x}_1,\ldots,\mathbf{x}_N)\,, \tag{2}$$

which is to be solved subject to the initial condition that $S_N(t=0)=1$ and the boundary conditions that $S_N=0$ whenever the particle comes in contact with any one of the traps. Note that while the diffusion equation is separable in these coordinates, the boundary conditions are not. This makes the problem hard. By introducing relative coordinates $\mathbf{r}_i=\mathbf{x}_i-\mathbf{x}_0$, Eq. (2) is transformed into

$$\partial S_N/\partial t=\left[(D_w+D_t)\sum_{i=1}^{N}\nabla_i^2+D_w\sum_{i\neq j=1}^{N}\nabla_i\cdot\nabla_j\right]\times S_N(t\,|\,\mathbf{r}_1,\ldots,\mathbf{r}_N)\,. \tag{3}$$

Now the boundary conditions are separable, but if $D_w\neq 0$, the diffusion equation is not separable. The problem is still hard.

Ultimately we wish to calculate the survival probability in the presence of uniformly distributed traps. This average is denoted by brackets and obtained by integration over the volume accessible to the traps:

$$\langle S_n(t)\rangle=V^{-N}\int\cdots\int d\mathbf{r}_1\cdots d\mathbf{r}_N\,S_N(t\,|\,\mathbf{r}_1,\ldots,\mathbf{r}_N)\,. \tag{4}$$

The survival probability for a concentration c, denoted by $\langle S(t)\rangle$, is the limit of the above $d\times N$-dimensional integral as $N\rightarrow\infty$, and $V\rightarrow\infty$, taken in such a way that $c=N/V$ is constant.

Our starting point is a density expansion analogous to one used by Haan and Zwanzig[13] in treating the migration of excitons between randomly distributed sites. This expansion is a generalization of the cluster expansion in equilibrium statistical mechanics to dynamical processes. It is formally exact even when the traps interact, but its utility depends on whether the coefficients are well behaved as V and t approach infinity. To the order considered here, there are no difficulties.

For the present problem, the survival probability of Eq. (4) admits the expansion

$$\langle S_N(t)\rangle = 1+\frac{N}{V}a_1(t)+\frac{N(N-1)}{2V^2}a_2(t)+\frac{N(N-1)(N-2)}{3!V^3}a_3(t)+\cdots . \tag{5}$$

The unknown coefficients $a_k(t)$ are determined by our requiring Eq. (5) to be exact for $1,2,\ldots,N$ traps successively. In this way we find that

$$\begin{aligned} a_1(t) &= \int d\mathbf{r}_1[S_1(t\,|\,\mathbf{r}_1)-1]\,,\\ a_2(t) &= \int\int d\mathbf{r}_1 d\mathbf{r}_2[S_2(t\,|\,\mathbf{r}_1,\mathbf{r}_2)-2S_1(t\,|\,\mathbf{r}_1)+1]\,,\\ a_3(t) &= \int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3[S_3(t\,|\,\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-3S_2(t\,|\,\mathbf{r}_1,\mathbf{r}_2)+3S_1(t\,|\,\mathbf{r}_1)-1]\,,\end{aligned} \tag{6}$$

and so on. To obtain $\langle S(t)\rangle$ we take the limit of large N and V but finite $c=N/V$. To improve convergence we exponentiate the series to obtain

$$\langle S(t)\rangle = \exp[cb_1(t)+c^2b_2(t)/2!+c^3b_3(t)/3!+\cdots]\,. \tag{7}$$

This is a cumulantlike expansion of the many-particle survival probability in terms of the few-body dynamics that determine the coefficients b_k, which are like Ursell functions. By demanding that the series expansions of Eqs. (5) and (7) agree up to the appropriate power of c, we get

$$b_1(t) = \int d\mathbf{r}_1[S_1(t\,|\,\mathbf{r}_1)-1]\,, \tag{8a}$$

$$b_2(t) = \int\int d\mathbf{r}_1 d\mathbf{r}_2[S_2(t\,|\,\mathbf{r}_1,\mathbf{r}_2)-S_1(t\,|\,\mathbf{r}_1)S_1(t\,|\,\mathbf{r}_2)]\,, \tag{8b}$$

$$b_3(t) = \int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3[S_3(t\,|\,\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-3S_1(t\,|\,\mathbf{r}_1)S_2(t\,|\,\mathbf{r}_2,\mathbf{r}_3)+2S_1(t\,|\,\mathbf{r}_1)S_1(t\,|\,\mathbf{r}_2)S_1(t\,|\,\mathbf{r}_3)]\,. \tag{8c}$$

Expansion (7) is not necessarily valid for all times when truncated at an arbitrary level. The lowest-order truncation,

$$\langle S(t)\rangle \approx \exp[cb_1(t)] = \exp\left\{-c\int[1-S_1(t\,|\,\mathbf{r})]d\mathbf{r}\right\}, \tag{9}$$

is expected to be valid at short times, since initially reaction takes place only with (initially) nearby traps. To demonstrate the equivalence with the Smoluchowski approach, we differentiate Eq. (9) with respect to t. It follows that the above $\langle S(t)\rangle$ solves Eq. (1) with

$$k(t) = -db_1(t)/dt = \int d\mathbf{r}[dS_1(t\,|\,\mathbf{r})/dt]\,.$$

This is indeed the reactive flux for a trap-particle pair with a relative diffusion coefficient D_w+D_t.

In the limit of a static particle ($D_w=0$) the cross terms in Eq. (3) vanish. In the absence of trap-trap excluded-volume interactions, the survival probability factorizes as

$$S_N(t\,|\,\mathbf{r}_1,\ldots,\mathbf{r}_N) = \prod_{i=1}^{N} S_1(t\,|\,\mathbf{r}_i)\,.$$

From Eq. (8) it follows that $b_k=0$ for all $k\geq 2$ and Eq. (7) reduces to Eq. (9). An alternative way, analogous to the treatment of static acceptors,[14] is to first average the above expression to obtain $\langle S_N(t)\rangle = \langle S_1(t)\rangle^N$. Taking the limit $N,V\to\infty$, $N/V=c$, of the logarithm expanded to first order gives Eq. (9).

We conclude that the first term in the expansion is exact for arbitrary diffusion coefficients at short times, for a static particle with noninteracting traps at all times, and that it precisely equals the Smoluchowski result in all dimensions. Equation (7) provides a systematic approach for improvement upon this approximation and can also be used to estimate the errors involved in such an approximation.

One expects the Smoluchowski result for mobile traps and particles to improve as the dimensionality increases. Hence it is of interest to examine the worst case of diffusion in 1D. This may also be relevant to certain experimental systems.[10] To find the leading correction term in 1D as a function of $\mu\equiv D_w/(D_w+D_t)$, we rewrite Eq. (7) as

$$\begin{aligned}\langle S(t)\rangle &\approx \exp[cb_1(t)][1+\tfrac{1}{2}c^2b_2(t)]\\ &= \exp(-f_1\sqrt{\tau})[1+f_2\tau]\,,\end{aligned} \tag{10}$$

where $\tau\equiv c^2(D_w+D_t)t$ and the f_k's are related to the

b_k's of Eq. (7). The distance between the ith trap and the particle is denoted by y_i. The operator ∇_i in Eq. (3) becomes a partial derivative $\partial/\partial y_i$.

The known[15] result for an absorbing boundary at the origin

$$S_1(t\,|\,y) = \mathrm{erf}\{y/[4(D_w+D_t)t]^{1/2}\}, \quad y>0 \tag{11}$$

(erf is the error function) allows us to evaluate f_1 from (twice) the integral of $1-S_1$ over y from 0 to ∞. This gives $f_1 = 4/\sqrt{\pi}$. We obtain f_2 by rewriting Eq. (3) for one particle, two traps, and positive y_i:

$$\partial S_2^{\pm}/\partial t = (D_w+D_t)(\partial^2/\partial y_1^2 + \partial^2/\partial y_2^2 \pm 2\mu\, \partial^2/\partial y_1 \partial y_2) S_2^{\pm}(t\,|\,y_1,y_2)\,. \tag{12}$$

The cross term is positive for two traps on the same side of the particle (denoted by +) and negative for the two-sided (−) configuration. $f_2^{\pm}$ is subsequently obtained from Eq. (8b) by use of S_1 of Eq. (11) and replacement of S_2 by $S_2^{\pm}$. Finally, $f_2 = f_2^{+} + f_2^{-}$.

One may solve Eq. (12) for noninteracting point traps by transforming it into a 2D diffusion in a wedge of angle θ_0, $\cos\theta_0 = \pm\mu$, and absorbing sides.[5] Integration of the Green's function for this problem[15] in radial coordinates gives

$$f_2^{\pm} = 8\sin\theta_0 \int_0^{\infty} r\,dr \int_0^{\theta_0} d\theta \left\{ \left(\frac{8}{\pi}\right)^{1/2} \sum_{n=0}^{\infty} \frac{\sin[(2n+1)\pi\theta/\theta_0]}{2n+1} r e^{-r^2} [I_{\nu^+}(r^2) + I_{\nu^-}(r^2)] - \mathrm{erf}(\sqrt{2}r\sin\theta)\,\mathrm{erf}[\sqrt{2}r\sin(\theta_0-\theta)] \right\}, \tag{13}$$

where $\nu^{\pm} \equiv [(2n+1)\pi/\theta_0 \pm 1]/2$, $I_\nu(r)$ are the modified Bessel functions of the first kind and order ν, and $\theta_0 = \cos^{-1}(\pm\mu)$ is the wedge angle for the $\pm$ configuration.

We were able to obtain f_2^{-} analytically for several special values of μ. For $\mu=1$ we get $f_2 = 4\ln 2 - 8/\pi$, in agreement with the short-time expansion of the survival probability for static traps. To obtain the general solution for noninteracting traps we have integrated Eq. (13) numerically and fitted it to $f_2 \approx 0.197\mu^2 + 0.0285\mu^4$, with an (absolute) error ≤ 0.001. This correction term is relatively small because the terms $f_2^{\pm}$ have opposite signs.

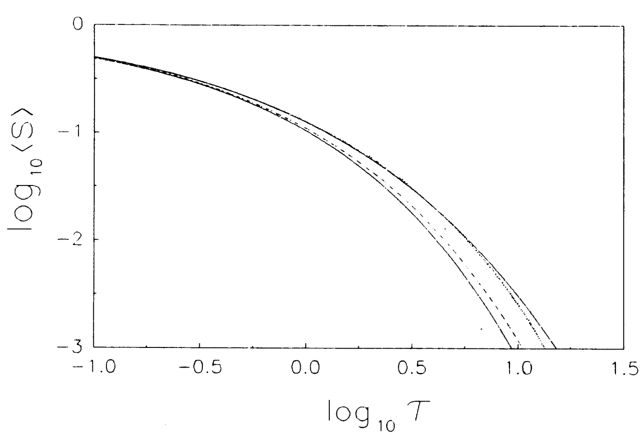

FIG. 1. The time dependence $[\tau = c^2(D_w+D_t)t]$ of the survival probability for one-dimensional diffusion with mobile, noninteracting traps for various values of μ: Lower solid curve is exact for static particles ($\mu=0$) and identical to the Smoluchowski result; upper solid curve is exact for static traps ($\mu=1$); dashed curve for equal diffusion coefficients ($\mu=\frac{1}{2}$) and dotted curve for $\mu=1$ are obtained from density expansion.

Figure 1 shows the survival probability for three different values of μ. The two full lines are the exact results for static particles ($\mu=0$, the Smoluchowski result) and static traps[9] ($\mu=1$). The $\mu=1$ curve is higher because reaction takes place only with the two neighboring static traps, not with traps that were initially further away.[8] Survival probabilities for other values of μ are expected to fall in the narrow region between these two limits.

The utility of Eq. (10) is illustrated for two μ values: $\mu=\frac{1}{2}$ (dashed) and $\mu=1$ (dotted). $\mu=1$ is the worst case for the theory, yet the dotted curve agrees remarkably well with the exact solution for static traps, except at very long times. The exact survival probability obtained from accurate simulations for $\mu=\frac{1}{2}$ is expected to be almost indistinguishable from the dashed curve calculated in the time range shown.

As can be seen in Fig. 1, the Smoluchowski result remains accurate for longer times as μ decreases. For example, for equal diffusion coefficients the error is $\leq 10\%$ when $\langle S(t)\rangle \geq 0.5$. Since 1D is most unfavorable for a mean-field-like theory, one expects the accuracy of the Smoluchowski theory to improve even more dramatically in higher dimensions. The density expansion introduced in this work can be used to verify this expectation.

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[a]Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases.

[b]Department of Computer Research and Technology, Building 12A, Room 2007. On leave from the Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel.

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