Upper and lower bounds for the rate of diffusion-controlled reactions

Peter M. Richards
Sandia National Laboratories, Albuquerque, New Mexico 87185-5800

S. Torquato
Department of Mechanical and Aerospace Engineering, and Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7910

(Received 24 June 1987; accepted 14 July 1987)

Recent upper and lower bounds established by the authors for the rate to diffuse to traps in a random medium are compared in a consistent manner by taking account of how the trap-free volume affects various definitions of the rate constant.

We have independently published[1,2] (referred to as PR and ST, respectively) relatively simple expressions for the average rate at which a diffusing particle is trapped in a medium containing a random distribution of static spherical traps of arbitrary radius and concentration. ST utilized a variational principle[3] which gives a lower bound to the trapping rate k (called R in PR, except where noted otherwise we use the notation of ST) and treated both overlapping (fully penetrable) and nonoverlapping (impenetrable) traps. PR gave a result for k in the case of overlapping traps which, in addition to giving good agreement with simulations, was claimed to be an upper bound. A reader may find it mildly disturbing that PR's upper bound lies below ST's lower bound for overlapping traps when the volume fraction ϕ_2 is appreciable. We show here that the apparent discrepancy is due to different definitions of k in terms of the fraction ϕ_1 of trap-free volume. When this is accounted for, the upper bound of PR happily lies above the lower bound of ST. ST's lower bound for nonoverlapping traps also now falls below the result derived recently by one of us.[4]

The manner in which k is related to ϕ_1 should be clear if k is defined concretely, but this often is not the case and has resulted in some confusion in the past.[5] If the trapping volume acts like a perfect sink in which particles are instantly absorbed, the rate of interest is that which characterizes trapping of particles which initially are outside of traps. In both his simulations and random-walk methods, PR considered only such particles. However, when the problem is treated as a continuum boundary value, one with a continuous distribution of sources, it is sometimes not transparent whether or not the particles generated in the traps are being included. Let the total number of particles created per second outside of traps be N_s and the total number outside of traps at a given time be N_0. Then the average trapping rate per particle k is given by $k = N_s/N_0$. If the numerator and denominator of the right-hand side are divided by the total volume, we have

$$k = s/\bar{c}\,, \qquad (1a)$$

whereas

$$k = \sigma/c_0 \qquad (1b)$$

results if they are divided by the trap-free volume $V\phi_1$. In Eq. (1a) s is the average generation rate over the whole volume and $\bar{c}$ is the average concentration over the whole volume. This volume, however, includes a fraction $1-\phi_1$ over which both the generation rate and concentration are zero. In Eq. (1b) σ and c_0 are average generation rates over the volume for which they are nonzero.

Obviously either Eq. (1a) or (1b) can be used to produce the same k, but confusion can occur if the generation rate and concentration are referred to different volumes, which is what Doi[3] appears to have done. He defines the reaction rate as $k_D = \sigma/\bar{c}$, and it is evident from his Eq. (7) that generation takes place only within the trap-free volume. The proper conversion is thus

$$k = k_D\phi_1 \qquad (2)$$

to convert results of Ref. 3 to the trap rate defined by Eq. (1). Another possibility is to have particles generated at equal rates throughout the entire volume. The average trapping time $\bar{T}$ is then $\bar{T} = 0\times(1-\phi_1) + k^{-1}\phi_1$, the first term indicating instantaneous trapping of particles generated within traps, which[6] leads to a rate $\bar{k} = k/\phi_1$. In attempting to compare Doi's theory with calculations in which particles were apparently generated throughout the volume, ST used this relation but also took $k = k_D$. Consequently,

$$k = k_D^*\phi_1^2 \qquad (3)$$

is the proper relation between the Doi theory and k where k_D^* is what was called k_D in ST.[7] The left-hand side of Eq. (3) is referred to as k(ST) in Figs. 1 and 2. Note that the results reported in Figs. 1 and 2 are based on definition (1).

One of the difficulties in deciding whether and how an incompletely specified result should be modified to have the proper dependence on ϕ_1 is that $0.5 < \phi_1 < 1$ for almost all published results, so there is no order-of-magnitude effect. An exception is the case of fully overlapping spheres where ϕ_1 can be made arbitrarily small. We show in the Appendix that in the limit $\phi_1 \to 0$, a simple physical argument predicts $k \propto f^2$ where $f = 4\pi\rho R^3/3$ is the reduced density and ρ is the sphere number density ($f = -\ln\phi_1$ in the continuum limit and is the same as Doi's γ). Both PR's rate constant and Eq. (2) are shown to have this dependence, which confirms that Eq. (2) is the proper way to modify the Doi result. We also show that $k(\mathrm{PR})/k_D\phi_1 = 12/\pi$ in this limit, where k(PR) is the PR rate constant.

A less important point is that although both PR and ST normalized rate constants to $k_S = 3D\phi_2/R^2$, the $\phi_2 = 1-\phi_1 \to 0$ limit, PR replaced ϕ_2 with the above f, which is ϕ_2 only with the neglect of overlap. For overlapping

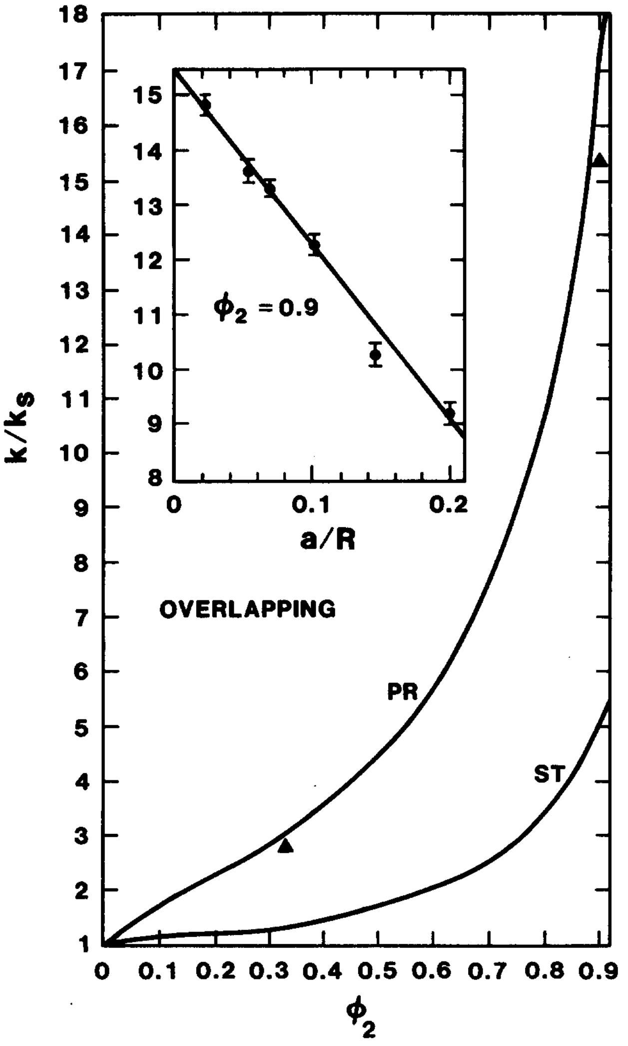

FIG. 1. Upper (PR) and lower (ST) bounds on k/k_S as a function of trap volume fraction ϕ_2 for overlapping traps. Triangles are from simulations obtained by methods similar to described in Ref. 1 and extrapolated to $R/a \to \infty$. Inset shows extrapolation for $\phi_2 = 0.9$.

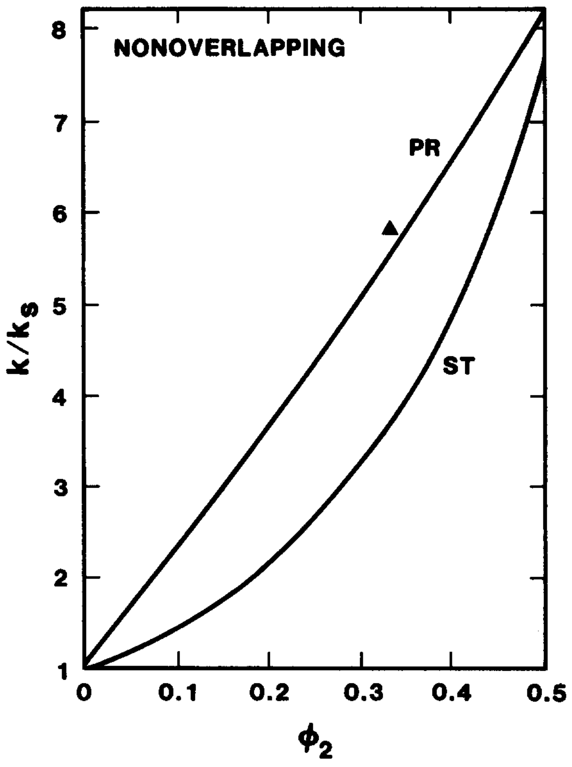

FIG. 2. Similar to Fig. 1 for nonoverlapping traps, where k(PR) and data point are from Ref. 4.

spheres with randomly distributed centers in a continuum, $\phi_2 = 1 - e^{-f} = f$ for $f \to 0$; with no overlap of course $\phi_2 = f$ always. Here we follow ST and therefore use ϕ_2 in k_S.

Figures 1 and 2 give, for overlapping and nonoverlapping traps respectively, the proper comparison of $k(\mathrm{PR})/k_S$ and $k(\mathrm{ST})/k_S$. Also shown are some of the simulation data of Refs. 1 and 4 together with some new results for overlapping traps for $\phi_1 \approx 0.1$. A final comment is that the ST result for nonoverlapping traps may be shown to give $k(\mathrm{ST})/k_S - 1$ proportional to ϕ_2 as $\phi_2 \to 0$, whereas the exact result[8] is $k/k_S - 1 = (3\phi_2)^{1/2}$ for $\phi_2 \to 0$, which is obeyed by k(PR).

Work performed at Sandia National Laboratories was supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789. S.T. acknowledges the support of the National Science Foundation under Grant No. CBT-8514841.

APPENDIX: LIMIT OF $\phi_1 \to 0$ (SMALL VOID FRACTION)

When the spherical traps overlap to the extent that only a small fraction of the volume is trap free, the system may be viewed as one with a number of small voids which are not connected to each other by diffusion paths. A particle then diffuses only in the void of radius r in which it was generated and has a lifetime $T \sim r^2/D$ with D the diffusion coefficient. The probability of a particle being generated inside a given void is proportional to its volume if the generation rate is uniform throughout the trap free region; so the average lifetime or inverse trapping rate is

$$k^{-1} \propto D^{-1} \int_0^\infty dr\, r^5 p(r) \Big/ \int_0^\infty dr\, r^3 p(r)\,, \qquad \text{(A1)}$$

where $p(r)$ is the probability of finding of void of radius r. $p(r)$ is estimated for a system of overlapping spheres of radius R on a lattice with a^{-3} sites per volume ($R/a \gg 1$ in the continuum limit used) as follows. To have a void of radius r requires there be no trap centers within a radius $r + R$ centered at the origin, the probability for which is $(1-c)^{N_{r+R}}$ where c is the probability a site is a trap center and $N_{r+R} = 4\pi(r+R)^3/3a^3$ is the number of sites within the sphere. Termination of the void region at r requires there to be at least one center in the shell between $r + R$ and $r + R + a$, the probability for which is $4\pi(R+r)^2 ac$ in the limit $a \to 0$. For $c \ll 1$, $(1-c)^x \approx e^{-cx}$, and we note that $4\pi R^3 c/3a^3$ is just the nonoverlapping volume fraction f. These enable us to write

$$p(r) \propto f(1+z)^2 e^{-f(1+z)^3} \qquad \text{(A2)}$$

with $z = r/R$. In the small void fraction limit $\phi_1 = e^{-f} \ll 1$, the integrals in Eq. (A1) are dominated by the $z \ll 1$ behavior of the integrands whereby use of Eqs. (A2) in Eq. (A1) gives

$$k \propto Df^2/R^2 \quad (\phi_1 \to 0)\,. \qquad \text{(A3)}$$

The proportionality constant depends on the precise relation between T and R and precise $p(r)$, both of which are influenced by the fact that the actual voids are not spherical. However, as long as the basic physical argument is correct, the constant is of no concern here.

To compare PR with Eq. (A3) we use the $y \gg 1$ limit of his expression [Eq. (7) of PR]

$$k(\mathrm{PR})^{-1} = [1 - \sqrt{\pi} y e^{y^2} \mathrm{erfc}(y)]/[3Df/R^2], \tag{A4}$$

where $3Df/R^2$ is the $f \ll 1$ limit defined as Γ in PR and $y = (3f/\pi)^{1/2}$. For $y \gg 1$, $\mathrm{erfc}(y) = e^{-y^2}\pi^{-1/2}(y^{-1} - y^{-3}/2)$, whereby Eq. (A4) gives

$$k(\mathrm{PR}) = (18/\pi)Df^2/R^2 \quad (f \gg 1, \text{ equivalent to } \phi_1 \ll 1). \tag{A5}$$

The Doi result for overlapping traps is [Eqs. (21) and (48) of Ref. 3 combined]

$$k = (R^2\phi_1/D)\int_0^1 dx[(3f)^{-1} + x(1-x)^2] \times \exp[-f(3x/2 - x^3/2)], \tag{A6}$$

where we have noted that his γ is the same as our f and $\phi_1 = e^{-f}$. For large f, the integral, defined as I, is dominated by the $x \ll 1$ behavior of the integrand. It is therefore $I = 2/3f^2$, whereby

$$k_D\phi_1 = (3/2)(Df^2/R^2) \quad (f \gg 1). \tag{A7}$$

Equations (A5) and (A7) have the functional dependence predicted by the physical reasoning which led to Eq. (A3), but note that it was accomplished in Eq. (A7) only by scaling k by the factor ϕ_1. The upper (PR) and lower (Doi) bounds of Eqs. (A5) and (A7) are seen to be in the ratio $12/\pi$.

[1]P. M. Richards, J. Chem. Phys. **85**, 3520 (1986).
[2]S. Torquato, J. Chem. Phys. **85**, 7178 (1986).
[3]M. Doi, J. Phys. Soc. Jpn. **40**, 567 (1976).
[4]P. M. Richards, Phys. Rev. B **35**, 248 (1987).
[5]See, for example, the comments by C. W. J. Beenakker and J. Ross [J. Chem. Phys. **84**, 3857 (1986)] on the work of Ref. 8 and subsequent rebuttal by K. Mattern and B. U. Felderhof [J. Chem. Phys. **85**, 5382 (1986)].
[6]Note that $\bar{k} = k_D$.
[7]This implies that the original Doi bound on k should not be divided by ϕ_1 in order to compare it to the result of M. Muthukumar, J. Chem. Phys. **76**, 2667 (1982). However, Muthukumar's result still violates the Doi lower bound on k for nonoverlapping traps (which was calculated in Ref. 2 and is shown in Fig. 2 here), albeit for $\phi_2 > 0.37$ instead of for $\phi_2 > 0.24$.
[8]B. U. Felderhof and J. M. Deutch, J. Chem. Phys. **64**, 4551 (1976).