Concentration dependence of diffusion-controlled reactions among static reactive sinks

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We evaluate a rigorous lower bound on the rate constant k associated with diffusion-controlled reactions in a porous medium composed of impenetrable spherical sinks, for a wide range of sink volume fractions. The results are compared to an effective-medium approximation for k. It is found that the lower bound gives a useful estimate of the rate constant for virtually all sink concentrations.

Diffusion-controlled reactions play a critical role in heterogeneous catalysis, combustion, growth of colloidal particles, and of polymer chains, precipitation, fluorescence quenching, and cell metabolism. We consider a system composed of N static and reactive spherical sinks statistically distributed throughout a solvent containing reactive particles. For such a porous material, we denote by ϕ_1 and ϕ_2 the volume fraction of the void (solvent) region and of the region of space occupied by the sinks, respectively. The reactant diffuses in the solvent but is instantly absorbed on contact with any sink. At steady state, the rate of production σ of the diffusing species is exactly compensated by its removal by the sinks. For a particular volume fraction ϕ_2, σ is proportional to the mean concentration $\langle C \rangle$ of the diffusing species, i.e., $\sigma = k \langle C \rangle$, where k is the effective rate constant.

At sufficiently low sink concentrations such that interactions between sinks of radius R can be neglected, it is well known that the rate constant is given by $k_S = 3D\phi_2/R^2$, where D is the diffusion coefficient of the particles in the solvent.[1] At higher sink densities, the reaction rate will be affected by the competition between neighboring sinks. For small ϕ_2, asymptotic expansions of k for random arrays of nonoverlapping sinks (which correct the Smoluchowski result) have been derived[2,3] and are found to predict that the rate of reaction increases with increasing sink density. The low-density expansion of k recently derived by Mattern and Felderhof[3] is given by

$$\frac{k_{\rm MF}}{k_S} = 1 + \epsilon - \epsilon^2 E_1(6\epsilon) + 1.9107\epsilon^2 - \frac{41}{60}\epsilon^3 + \cdots, \tag{1}$$

where $\epsilon = \sqrt{3\phi_2}$ and E_1 is the exponential integral. Muthukumar[4] has developed an effective-medium approximation (EMA), for nonoverlapping sinks, that enables one to study the behavior of k over the entire concentration range. He found that

$$\frac{k_{\rm M}}{k_S} = \frac{x^2}{3\phi_2(1 - A\phi_2)}, \tag{2}$$

where

$$x[1 - \exp(-2x)] = 6\phi_2$$

and

$$A = 2x \left\{ \frac{1}{[1 + (1/x)][(1 + e^{-2x}) - (1/x)(1 - e^{-2x})]} - \frac{1}{(1 - e^{-2x})} \right\}.$$

Note that Eq. (2) was derived by evaluating the exact EMA expression obtained in Ref. 4 in the hydrodynamic (i.e., small wave number) approximation.

In this paper we compute the lower bound on k due to Doi[5] for a random distribution of impenetrable spherical sinks. Rigorous upper and lower bounds on the effective property of disordered media are useful because: (i) they enable one to test the merits of a theory, (ii) one of the bounds (the lower bound in the case of the rate constant) can typically provide a relatively useful estimate of the property[6], and (iii) as successively more microstructural information is included, the bounds become progressively tighter.[7]

The Doi lower bound k is given by

$$k_{\rm D} \geqslant \frac{D}{\phi_1 \int_0^\infty dx\, x[F_{\rm VV}(x) - 2(\phi_1/s)F_{\rm SV}(x) + (\phi_1^2/s^2)F_{\rm SS}(x)]}. \tag{3}$$

Here s is the specific surface (expected interface area per unit volume) and $F_{\rm VV}$, $F_{\rm SV}$, and $F_{\rm SS}$, are the void–void, surface–void, and surface–surface correlation functions, respectively. For example, $F_{\rm SV}(x)$ gives the correlation associated with finding a point on the two-phase interface and another point in the void region separated by a distance x. Doi noted

TABLE I. The reduced rate constant k/k_S vs sink volume fraction ϕ_2. Included in the table are results for the EMA (Ref. 4) and the Doi lower bound (Ref. 5) for the case of impenetrable sinks (as computed here) and fully penetrable sinks (as computed in Ref. 5).

ϕ_2	Impenetrable spherical sinks $\frac{k_M}{k_S}$	Impenetrable spherical sinks $\frac{k_D}{k_S}$	Fully penetrable spherical sinks $\frac{k_D}{k_S}$
0.10	2.30	1.82	1.36
0.20	3.74	3.39	1.89
0.30	5.49	6.53	2.76
0.40	7.39	13.37	4.25
0.50	9.28	30.4	7.06
0.60	11.12	86.2	13.05
0.64	11.84		17.42
0.70			28.57
0.80			84.30
0.90			515.4

that to improve upon bound (3), higher-order correlation functions (i.e., three-point and higher-order correlations) must be incorporated. For the case of impenetrable sinks, we compute (3), for $0 \leqslant \phi_2 \leqslant 0.6$, using a trapezoidal rule and the results for $s(= 4\pi R^2 \rho$, where ρ is the sink number density), F_{VV},[8] and the surface correlation functions, F_{SV} and F_{SS}.[9] (Note that the maximum sink volume fraction reported here $\phi_2 = 0.6$ corresponds to about 94% of the random close-packing value.[10]) In Table I and Fig. 1 we compare the Doi lower bound on k/k_S for impenetrable sinks to the EMA, Eq. (2).[11] Included in Table I and Fig. 1 is the Doi lower bound on k/k_S for the case of fully penetrable (i.e., randomly centered) spherical sinks calculated in Ref. 5.

A major conclusion drawn from these results is that the Doi lower bound for impenetrable sinks can provide a relatively useful estimate of k for virtually the entire volume fraction range. This conclusion is based on three observations. Firstly, for $\phi_2 > 0.24$ the EMA, Eq. (2), violates the Doi lower bound for an array of impenetrable sinks. For example, at $\phi_2 = 0.6$, k_D/k_S is 7.75 times larger than k_M/k_S. This is to be contrasted with the fact that for $\phi_2 < 0.24$, k_M/k_S is at most 1.27 times larger than k_D/k_S. Secondly, in the vicinity of $\phi_2 = 0.1$, bound (3) is in better agreement with the low-density expansion of Mattern and Felderhof Eq. (1), than is relation (2), e.g., at $\phi_2 = 0.1$, $k_{MF}/k_S = 2.01$, $k_M/k_S = 2.30$, and $k_D/k_S = 1.82$. (For very small ϕ_2, the converse is true.) Thirdly, it has been shown that the Doi bound on the fluid permeability of an array of impenetrable spheres [which involves the same integral as in (3)] is in relatively good agreement with the empirical Kozeny–Carman relation.[12] In light of the fact that flow and diffusion problems are closely related, this indicates that k_D/k_S can provide useful estimates of k/k_S for the case of impenetrable sinks for a wide range of ϕ_2. This offers hope that bounds which include higher-order correlation functions[13] will lead to even more accurate estimates of k.

Comparison of the Doi lower bound on k/k_S for impenetrable and fully penetrable sinks reveals that increasing the degree of penetrability decreases the effective rate constant at the same ϕ_2. This is not unexpected since the specific surface for fully penetrable spheres $(4\pi R^2 \rho \phi_1)$ is always smaller than the specific surface for impenetrable spheres $(4\pi R^2 \rho)$ at the same ϕ_2.

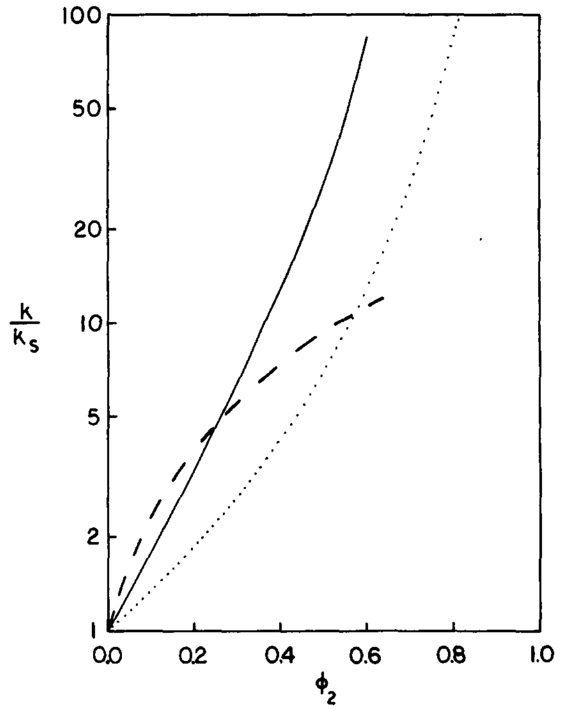

FIG. 1. The reduced rate constant k/k_S vs ϕ_2. Solid (—) and dashed (– – –) lines are, respectively, the Doi lower bound and EMA relation for impenetrable spherical sinks. Dotted (···) line is the Doi lower bound for fully penetrable spherical sinks.

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