Diffusion-controlled reactions. II. Further bounds on the rate constant

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We apply variational principles derived earlier by us to obtain rigorous upper and lower bounds on the rate constant k associated with diffusion-controlled reactions among static, reactive traps. We derive a phase-interchanged interfacial-surface lower bound on k and a new type of lower bound which we term a "void" bound. Among other results, we compute the phase-interchanged interfacial-surface bound on k for a distribution of fully penetrable (i.e., randomly centered) spheres in which the trap region is the space exterior to the spheres (the "holes" between the spheres) and diffusion occurs in the sphere region. We also derive an upper bound on k for identical spherical traps (randomly or periodically arranged), and evaluate it for a simple cubic lattice.

I. INTRODUCTION

Recently we examined the problem of determining the rate constant k associated with diffusion-controlled reactions in two-phase random media composed of two regions: a trap-free region $\mathscr{V}_1$ of volume fraction ϕ_1 containing reactive particles and a trap (or sink) region $\mathscr{V}_2$ of volume fraction ϕ_2.[1] The reactant diffuses in the trap-free region but is instantly absorbed on contact with any trap. At steady state, the rate of production of the diffusing species is exactly compensated by its removal by the traps. Using the method of homogenization, we showed that the rate constant k was the proportionality constant in the relation between the rate of production of the diffusing species and the mean concentration field.[1] We derived rigorous variational upper and lower bounds on k using both ensemble-average and volume-average formulations. Using these general variational principles we obtained three different types of bounds and evaluated them for random and periodic arrays of identical spherical traps.

In this note we shall further apply these variational principles to derive and evaluate bounds on the rate constant for two-phase media of arbitrary microstructure as well as for distributions of spheres. Specifically, we employ the lower and upper bounds on k in the ensemble-average and volume-average formulations, respectively.

II. VARIATIONAL PRINCIPLES

A. Ensemble-average lower bound

Let A be the class of functions u defined by the set

$$A = \{\text{smooth, stationary } u(\mathbf{y},\omega);\ \Delta u = -\gamma \text{ in } \mathscr{V}_1\}. \tag{1}$$

Here $\mathbf{y}$ denotes position, ω represents a realization taken from some probability space Ω, Δ is the Laplacian operator, and γ is a constant. It was shown in Ref. 1 that k is bounded from below by

$$k \geqslant \frac{\gamma^2}{\langle \nabla u \cdot \nabla u I \rangle}, \quad \forall u \in A, \tag{2}$$

where

$$I(\mathbf{y},\omega) = \begin{cases} 1, & \mathbf{y} \in \mathscr{V}_1 \\ 0, & \mathbf{y} \in \mathscr{V}_2 \end{cases} \tag{3}$$

is the characteristic function for the trap-free region and angular brackets denote an ensemble average. Now since $\langle \nabla u \cdot \nabla u \rangle \geqslant \langle \nabla u \cdot \nabla u I \rangle$, we also have the weaker lower bound

$$k \geqslant \frac{\gamma^2}{\langle \nabla u \cdot \nabla u \rangle}, \quad \forall u \in A. \tag{4}$$

B. Volume-average upper bound

Let B be the class of functions u defined by the set

$$B = \{u;\ u = 0 \text{ on } \partial\mathscr{V},\ \bar{u} = \bar{v}\}. \tag{5}$$

Here $\partial\mathscr{V}$ denotes the two-phase interface and a bar over some function f denotes a volume average of that function defined by

$$\bar{f} = \lim_{V \to \mathscr{R}^3} \frac{1}{V} \int_{\mathscr{V}_1} f\, dV, \tag{6}$$

where V is the system volume. The quantity v in Eq. (5) solves the exact problem:

$$\Delta v = -\gamma \quad \text{in } \mathscr{V}_1, \tag{7}$$

$$v = 0 \quad \text{on } \partial\mathscr{V}, \tag{8}$$

$$\frac{\partial v}{\partial n} = 0 \quad \text{on } \partial V. \tag{9}$$

Here ∂V represents the surface of the system volume. The rate constant is bounded from above by

$$k \leqslant \frac{\overline{\nabla u \cdot \nabla u}}{\bar{v}^2}, \quad \forall u \in B. \tag{10}$$

III. LOWER BOUNDS ON THE RATE CONSTANT

A. Phase-interchanged interfacial-surface bound

Consider an "interfacial-surface" admissible field[1] in the set A, Eq. (1):

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$$u(\mathbf{y},\omega) = \gamma \int G(\mathbf{y}-\mathbf{x})\left[I(\mathbf{x}) - \frac{\phi_1}{s} M(\mathbf{x})\right] d\mathbf{x}, \quad (11)$$

where

$$G(\mathbf{x},\mathbf{y}) = \frac{1}{4\pi} \frac{1}{|\mathbf{x}-\mathbf{y}|} \quad (12)$$

is the Green's function of Δ,

$$M(\mathbf{x},\omega) = |\nabla I(\mathbf{x},\omega)| \quad (13)$$

is the characteristic function of the interface $\partial\mathscr{V}$, and

$$s = \langle M(\mathbf{x}) \rangle \quad (14)$$

is the specific surface (i.e., expected interfacial surface area per unit volume). In Ref. 1 it was shown

$$\langle \nabla u \cdot \nabla u \rangle_1 = \gamma^2 \int G(\mathbf{r})\left[F_{vv}(\mathbf{r}) - \frac{2\phi_1}{s} F_{sv}(\mathbf{r}) + \left(\frac{\phi_1}{s}\right)^2 F_{ss}(\mathbf{r})\right] d\mathbf{r}, \quad (15)$$

where

$$F_{vv}(\mathbf{r}) = \langle I(\mathbf{x}) I(\mathbf{x}+\mathbf{r}) \rangle, \quad (16)$$

$$F_{sv}(\mathbf{r}) = \langle M(\mathbf{x}) I(\mathbf{x}+\mathbf{r}) \rangle, \quad (17)$$

$$F_{ss}(\mathbf{r}) = \langle M(\mathbf{x}) M(\mathbf{x}+\mathbf{r}) \rangle. \quad (18)$$

The functions (16)–(18) are referred to as void–void, surface–void, and surface–surface correlation functions, respectively. These statistical functions and their generalizations have been studied by Torquato.[2] The subscript 1 after the angular brackets of Eq. (15) emphasizes the fact that diffusion is occurring in phase 1. Substitution of Eq. (15) into Eq. (4) leads to the interfacial-surface lower bound

$$k^{(1)} \geqslant \left\{ \int_0^\infty r\left[F_{vv}^{(1)}(r) - \frac{2\phi_1}{s} F_{sv}^{(1)}(r) + \left(\frac{\phi_1}{s}\right)^2 F_{ss}^{(1)}(r)\right] dr \right\}^{-1}, \quad (19)$$

for statistically isotropic media, where $r = |\mathbf{r}|$. The superscript 1 in bound (19) underscores the fact that diffusion is occurring in phase 1, i.e., that the void phase is phase 1. Bound (19) was first derived by Doi[3] and later rederived in Ref. 1 using a different approach. Note that for a dilute distribution of identical spherical traps of radius a ($\phi_2 \ll 1$), bound (19) yields the exact Smoluchowski result $k = 3\phi_2/a^2$.

Now suppose that diffusion is occurring in phase 2, i.e., let phase 1 represent the trap region. Consider computing an interfacial-surface lower bound for this case using the phase-interchanged version of bound (4) and the trial field

$$\mathbf{u}(\mathbf{y},\omega) = \gamma \int G(\mathbf{y}-\mathbf{x})\left[J(\mathbf{x}) - \frac{\phi_2}{s} M(\mathbf{x})\right] d\mathbf{x}, \quad (20)$$

where

$$J(\mathbf{x},\omega) = 1 - I(\mathbf{x},\omega). \quad (21)$$

Therefore,

$$\langle \nabla u \cdot \nabla u \rangle_2 = \langle \nabla u \cdot \nabla u \rangle_1 + \gamma^2 \int_0^\infty r\left[\frac{2F_{sv}^{(1)}(r)}{s} - 1 + \frac{(1-2\phi_1}{s^2} F_{ss}^{(1)}(r)\right] dr. \quad (22)$$

Equation (22) states we can write the energy functional for phase 2 in terms of the energy functional for phase 1 plus an integral involving F_{sv} and F_{ss}. Substitution of Eq. (22) into bound (4) then gives

$$k^{(2)} \geqslant \left\{ \int_0^\infty r\left[F_{vv}^{(1)}(r) - \frac{2\phi_1}{s} F_{sv}^{(1)}(r) + \left(\frac{\phi_1}{s}\right)^2 F_{ss}^{(1)}(r)\right] dr + \int_0^\infty r\left[\frac{2F_{sv}^{(1)}(r)}{s} - 1 + \frac{(1-2\phi_1)}{s^2} F_{ss}^{(1)}(r)\right] dr \right\}^{-1}. \quad (23)$$

In Ref. 1 we computed bound (19) for, among other model microstructures, the "Swiss cheese" model, i.e., a distribution of fully penetrable (spatially uncorrelated) spherical traps of radius a. Here we shall compute bound (23) for the same model except that diffusion will take place in the space interior to the spheres (i.e., we consider the inverted Swiss cheese model). For this microgeometry, the number density of spheres ρ is related to ϕ_1 (the volume fraction of the trap region) by the simple expression $\phi_1 = \exp(-\eta)$, where $\eta = 4\pi a^3 \rho/3$ is a reduced density.[2] For $\phi_1 < 0.03$, the trap region is disconnected and the traps are the oddly shaped "holes" between the spheres (cf. Fig. 1). At $\phi_1 \cong 0.03$ the trap phase percolates, i.e., the trap region becomes continuous.[4] The rate constant is expected to increase as ϕ_1 is increased. At $\phi_1 \cong 0.7$, the sphere phase (i.e., the phase in which transport takes place) ceases to percolate[5]; at this transition, the rate constant becomes very large (but finite) compared to its dilute limit (cf. Fig. 2). This is in contrast to the related problem of flow in porous media in which the inverse fluid permeability becomes infinite whenever the flu-

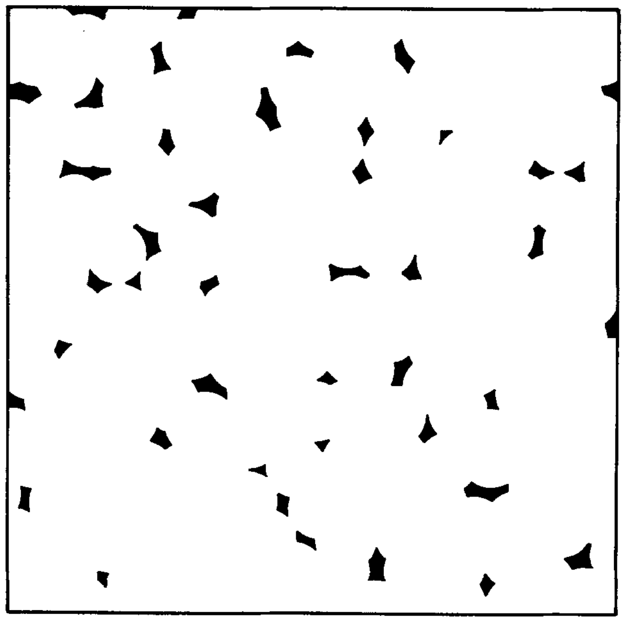

FIG. 1. Distribution of fully penetrable disks at a very high volume fraction of disks. The trap region (black area) is composed of the "holes" between the disks. Diffusion takes place in the disk region (white area). This is termed the "inverted Swiss cheese" model.

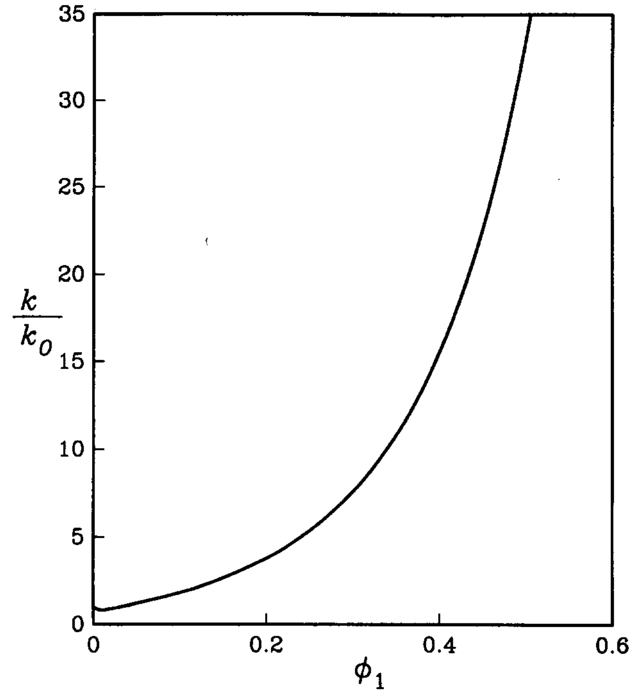

FIG. 2. The scaled rate constant k/k_0 (where $k_0 = 3\eta^2\phi_1/2a^2$) as a function of the trap volume fraction ϕ_1 for the inverted Swiss cheese model in which the spheres have radius a. Diffusion occurs in the sphere phase. The space exterior to the spheres is the trap region.

id phase ceases to percolate. The two problems have long been known to be mathematically related to one another, however (see Refs. 1, 3, 6, and references therein). To be sure, we have recently derived bounds on the fluid permeability[6] which are the analogs of the bounds obtained on the rate constant given in the first paper of this series and in the present one (i.e., interfacial-surface, multiple-scattering, security-spheres, and void bounds). However, the important difference between the two problems described above (namely, that the rate constant remains finite while the inverse permeability becomes infinite for a disconnected transport phase) has heretofore not been pointed out.

It is of interest to study the asymptotic behavior of bound (23) for the inverted swiss cheese model in the limit $\phi_1 \ll 1$. Denoting the right-hand side of bound (23) by $k_L^{(2)}$, and carrying out the asymptotic expansion, we find

$$k_L^{(2)} \sim \frac{3}{2a^2} (\ln \phi_1)^2 \phi_1 \quad (\phi_1 \ll 1). \tag{24}$$

Since the holes are not spherically symmetric, result (24) can not be expected to be the exact dilute limit. This is in contrast to the other extreme case $\phi_2 \ll 1$ where the bound (19) captures the Smoluchowski result. We do conjecture, however, that the dilute limit of $k^{(2)}$ is of the form $c(\ln \phi_1)^2 \phi_1/a^2$ with $c \geqslant 3/2$. The correlation functions of bound (23) are known analytically for this model[3] and bound (23) can be evaluated for all ϕ_1. In Fig. 2 we plot the scaled rate constant $k^{(2)}/k_0$ (where $k_0 = 3\eta^2\phi_1/2a^2$) as a function of the volume fraction of the traps ϕ_1.

B. Weaker "void" bound

Consider the following admissible field in the set A:

$$u(\mathbf{y},\omega) = \frac{\gamma}{\phi_2} \int G(\mathbf{y}-\mathbf{x})[I(\mathbf{x}) - \phi]. \tag{25}$$

This is to be contrasted with the interfacial-surface field (11). Consider the terms within the brackets of each of these expressions. Although the first terms are the same to within a factor of ϕ_2, the second term of Eq. (25), unlike Eq. (11), does not involve interfacial information. From bound (2) and Eq. (25), we find for a statistically isotropic medium that

$$k^{(1)} \geqslant \left\{ \frac{1}{\phi_2^2} \int_0^\infty r\,[F_{vv}^{(1)}(r) - \phi_1^2]\,dr \right\}^{-1}. \tag{26}$$

We refer to bound (26) as a *void* lower bound. The phase-interchanged version of bound (26) is easily shown to be

$$k^{(2)} \geqslant \left\{ \frac{1}{\phi_1^2} \int_0^\infty r\,[F_{vv}^{(1)}(r) - \phi_1^2]\,dr \right\}^{-1}. \tag{27}$$

It is noteworthy that the void lower bound (26) is the diffusion-controlled analog of a fluid permeability upper bound derived by Prager and by Berryman and Milton.[7] The latter authors employed an approach to obtain such an upper bound which is not the analog of the procedure described here, however. (Elsewhere[6] we shall derive this permeability upper bound using a methodology analogous to the one employed in this study.)

Using the low-density expansion of F_{vv} for a distribution of identical spheres[8] of radius a, one can compute Eq. (26) through order ϕ_2 for such a model of spherical traps:

$$k^{(1)} \geqslant \frac{5\phi_2}{2a^2}, \quad (\phi_2 \ll 1). \tag{28}$$

Therefore, the void bound (26), unlike the interfacial-surface bound (19), does not yield the exact Smoluchowski result $k = 3\phi_2/a^2$ in the dilute limit. (The analogous fluid permeability upper bound[7] does not yield the correct dilute-limit Stokes result.) The reason for this is that interfacial-surface trial field, unlike trial field (25), is exact for a dilute distribution of spherical traps. From a microstructural standpoint, this is reflected in the appearance of correlation functions in bound (19) which contain information about the interfacial surface.

Suppose now we consider a distribution of fully penetrable spheres and let the trap region (phase 1) be the space exterior to the spheres. Then for small concentrations of traps ($\phi_1 \ll 1$), void bound (27) yields

$$k^{(2)} \geqslant \frac{9}{16a^2} (\ln \phi_1)^2 \phi_1 \tag{29}$$

which is not as sharp as the interfacial-surface counterpart (24).

IV. UPPER BOUNDS ON THE RATE CONSTANT

Here we derive an upper bound on k using "security-spheres" type trial fields which improve upon an upper bound obtained in Ref. 1. Consider constructing a trial field for a distribution of N identical spherical traps of radius a. Let the distance between the ith sphere and its nearest neighbor be $2b_i$. We assume $b_i > a$ for all i. A trial field $\psi \in B$ [where B is given by Eq. (8)] is chosen as follows: for every sphere i we consider the domain defined by itself and a concentric security sphere of radius b_i. In that domain, we solve

$$\nabla \psi_i(\mathbf{x}) = -\alpha \quad \text{in } a < |\mathbf{x} - \mathbf{r}_i| < b_i,$$
$$\psi_i = 0 \quad \text{on } |\mathbf{x} - \mathbf{r}_i| = a,$$
$$\psi_i = \zeta \quad \text{on } |\mathbf{x} - \mathbf{r}_i| = b_i, \tag{30}$$

where $\mathbf{r}_i$ denotes the position of the ith sphere. The trial field ψ is chosen to be equal to ψ_i in the ith security shell and to be ζ elsewhere. We choose ζ such that $\bar{\psi} = \bar{v}$. Finally, the constant α is optimized to obtain the best possible upper bound on k. The trial field used in Ref. 1 is the same as Eq. (30) except that in the former $\alpha = 0$. The trial field (30) should lead to an improved bound since it solves Poisson's (not Laplace's) equation in the security shell.

Substitution of the optimized field (30) into Eq. (8) yields

$$\frac{k}{k_s} \leqslant \frac{c_1 c_2 + 9\phi_2^2 c_1^2 c_3}{c_2^2 + 18\phi_2^2 c_1 c_2 c_3 + 81\phi_2^4 c_1^2 c_3^2}, \tag{31}$$

$$c_1(\beta) = \frac{1}{N}\sum_{i=1}^{N} d(\beta_i), \tag{32}$$

$$c_2(\beta) = \left[1 - \frac{\phi_2}{2}\frac{1}{N}\sum_{i=1}^{N} f(\beta_i)\right]^2, \tag{33}$$

$$c_3(\beta) = \frac{1}{180}\frac{1}{N}\sum_{i=1}^{N} g(\beta_i), \tag{34}$$

$$d(x) = \frac{x}{x-1}, \tag{35}$$

$$f(x) = x(x+1), \tag{36}$$

$$g(x) = 4x^5 - 5x^4 - 5x^3 + 5x^2 + 5x - 4, \tag{37}$$

$$\beta_i = \frac{b_i}{a}, \tag{38}$$

$$\phi_2 = 4\pi a^3 \rho / 3. \tag{39}$$

In bound (31), $k_s = 3\phi_2/a^2$ is the Smoluchowski result and the thermodynamic limit has been taken, i.e., $N \to \infty$, $V \to \infty$, such that $\rho = N/V$ is fixed. Using the law of large numbers, we can replace the sums in bound (31) by integrals. Specifically, for an arbitrary function $F(x)$ we have

$$\frac{1}{N}\sum_{i=1}^{N} F(\beta_i) \to a \int_1^\infty F(\beta) H(a\beta) d\beta, \tag{40}$$

where $H(a\beta)$ is the probability density of spheres with nearest neighbor at the distance $2a\beta$. The integral form of bound (31) is convenient when studying random distribution of spheres.

Consider evaluating bound (31) for a simple cubic lattice with a lattice spacing of $2a\beta$. Then $\phi_2 = \pi/(6\beta)^3$ and

$$c_1 = d(\beta), \tag{41}$$

$$c_2 = \left[1 - \frac{\phi_2}{2} f(\beta)\right]^2, \tag{42}$$

$$c_3 = \frac{1}{180} g(\beta). \tag{43}$$

For small trap concentrations, bound (31) yields

$$\frac{k}{k_s} \leqslant 1 + 1.82\phi_2^{1/3} + O(\phi_2^{2/3}). \tag{44}$$

The coefficient 1.82 is to be contrasted with 1.89, the corresponding coefficient obtained in the upper bound (4.38) of Ref. 1. This represents a 54% improvement relative to the exact coefficient of 1.76.[9] The relative improvement of bound (31) over the corresponding bound (4.38) of Ref. 1 diminishes as ϕ_2 increases. For example, for $\beta = 1.4$ ($\phi_2 \cong 0.1908$), Eq. (30) gives $k/k_s \leqslant 7.44$, whereas (4.38) yields $k/k_s \leqslant 7.58$. We are currently in the process of computing the integral form of bound (31) for a *random* distribution of spherical sinks using a nearest-neighbor distribution function $H(a\beta)$ which is applicable for all volume fractions.

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