Diffusion-controlled reactions: Upper bounds on the effective rate constant

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For a diffusion-controlled reaction in a static, reactive bed of nonoverlapping spherical traps, upper bounds on the effective reaction-rate constant have been obtained from a variational principle of Rubinstein and Torquato. The bounds remain finite for all volume fractions and arbitrary distributions of traps. We have obtained two kinds of bounds: one kind depends on the trap volume fraction only; the other includes, in addition, a nearest-neighbor-distance distribution of the traps. The bounds have been explicitly evaluated, in the latter case using the distribution corresponding to the hard-sphere equilibrium ensemble.

I. INTRODUCTION

In recent years, the subject of diffusion-controlled reactions in disordered heterogeneous media has attracted considerable attention. Recent reviews have been presented by Calef and Deutch[1] and by Weiss.[2]

In this note, we address the problem of evaluating the steady-state effective reaction-rate constant for a reactive bed of static traps. We consider a medium composed of identical nonoverlapping spherical traps (sinks) distributed randomly; the reactant diffuses freely in the trap-free region and is instantly absorbed upon contact with a trap. Our method of analysis can be applied for more general geometries than considered in this paper, including polydisperse or nonspherical traps.

The model of spherical traps has been the subject of numerous theoretical investigations. In 1916, Smoluchowski[3] derived an expression for the effective reaction-rate constant for small volume fractions of traps. More recent theoretical approaches include the effective-medium approximations,[4,5] the random-walk analysis of Richards,[6] and cluster-expansion calculations by Mattern and Felderhof.[7] For a system of nonoverlapping spheres at high densities, none of these approaches yields results in a satisfactory agreement with computer-simulation data.[8,9]

Using variational techniques and volume average approach, Reck and Prager[10] derived general expressions for upper and lower bounds on the effective reaction-rate constant k. They evaluated both bounds for a system of overlapping spherical traps. In a slightly more general approach, Rubinstein and Torquato[11] included statistical ensemble averaging. Using an alternative variational principle, Doi[12] derived another expression for a lower bound on k. Subsequently, this bound was evaluated explicitly by Torquato[13] for a system of impenetrable spherical traps.

Using the variational principle of Rubinstein and Torquato,[11] we derive in this paper new variational *upper* bounds on the effective reaction-rate constant for a system of *impenetrable* spherical traps. To obtain the bounds, we consider two classes of trial density fields of reacting particles. One class is obtained by extending the "security-spheres" construction, originally proposed by Keller, Rubenfold, and Molynex[14] in a context of transport coefficients of suspensions. In particular, this construction leads to a bound that is independent of statistical distribution of traps. The bound remains finite for all trap volume fractions. The other class of trial fields considered includes those fields $c(\mathbf{r})$ that are entirely determined by the distance from $\mathbf{r}$ to the center of the nearest trap.[10] The resulting bound is evaluated for the equilibrium hard-sphere ensemble.

II. VARIATIONAL UPPER BOUNDS

We consider reactant particles diffusing independently in a static disordered array of N identical nonoverlapping, spherical traps of radius a, enclosed in a volume V. The disordered state of the array is described by the probability distribution function $\rho(\Gamma)$, where $\Gamma = (1,...,N)$ and $(i) = \mathbf{R}_i$ denotes the position of the center of the ith trap. The distribution $\rho(\Gamma)$ vanishes for overlapping configurations, i.e., if $|\mathbf{R}_i - \mathbf{R}_j| < 2a$ for any pair $i,j \leqslant N$. It is assumed that, in the thermodynamic limit, the reduced distribution functions associated with $\rho(\Gamma)$ are translationally invariant.

Outside the traps, the reactant-particle density $c(\mathbf{r};\Gamma)$ obeys the steady-state diffusion-reaction equation

$$D\nabla^2 c(\mathbf{r};\Gamma) = -\sigma(\mathbf{r}), \qquad (2.1)$$

where D is the diffusion constant and $\sigma(\mathbf{r})$ is the source term independent of the configuration Γ. We assume that the field $c(\mathbf{r};\Gamma)$ vanishes at the surface and inside the traps and obeys the condition corresponding to a nonpermeable wall at the boundary of the volume V. In a steady state, production of the reactant particles σ is compensated by the reaction with the traps.

For a macroscopically homogeneous system, with the density of traps uniform in the thermodynamic limit and the source term σ independent of the position $\mathbf{r}$, the effective steady-state reaction-rate coefficient k can be defined by the relation

$$k\langle c\rangle = \sigma/D. \qquad (2.2)$$

By $\langle ... \rangle$, we denote the average over the probability distribution $\rho(\Gamma)$ calculated in the thermodynamic limit.

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Upper and lower bounds on the reaction-rate constant can be obtained from variational principles associated with the diffusion-reaction equation (2.1). In this paper, we will use the result derived by Rubinstein and Torquato.[11(a)] Their variational upper bound can be expressed by the following inequality:

$$k \leqslant \frac{\langle \nabla c^* \cdot \nabla c^* \rangle}{\langle c^* \rangle^2}, \tag{2.3}$$

where the trial density field is a continuous function vanishing inside the traps

$$c^*(\mathbf{r};\Gamma) = 0, \quad \text{for } |\mathbf{r} - \mathbf{R}_i| \leqslant a, \quad i = 1,\ldots,N, \tag{2.4}$$

that has the position-independent average

$$\langle c^*(\mathbf{r};\Gamma) \rangle = \text{const.} \tag{2.5}$$

[in the original formulation, Rubinstein and Torquato required that $\langle c^* \rangle = \langle c \rangle$, where c is the solution of Eq. (2.1). Under the conditions specified above Eq. (2.2), $\langle c \rangle$ is spatially uniform in the thermodynamic limit and can be chosen equal to an arbitrary constant.]

III. TRIAL DENSITY FIELDS

To derive from Eq. (2.3) a specific bound on the reaction constant k, one has to construct a trial density field obeying, for all configurations of traps, the conditions specified in the preceding section. The main difficulty is to choose the trial field in such a form that the resulting bound can be evaluated explicitly using limited information about the statistical distribution of traps. We discuss here two classes of trial fields.

A. Security-spheres trial field

A possibility of dealing with the difficulty just mentioned was proposed by Keller, Rubenfold, and Molynex,[14] in a context of transport processes in suspensions. Their idea, adapted to the diffusion-controlled-reaction problem, is as follows: one constructs around each trap a security sphere with a radius not greater than half the distance of the trap to its nearest neighbor. The trial field $c^*(\mathbf{r};\Gamma)$ equals 1 for r outside all security spheres; inside each security sphere, it varies continuously between 0 at the surface of the trap and 1 at the surface of the security sphere. This construction leads to a bound that depends on the distribution of traps through the probability density $p(\rho)$ of finding the center of the nearest trap at a distance ρ from a given trap.

Unfortunately, the bounds resulting from this construction diverge if $p(\rho)$ does not vanish sufficiently fast at contact.[11] This excludes, e.g., the hard-sphere Gibbs distribution. The difficulty stems from the fact that the contribution from a security sphere of radius ν diverges if $\nu \to a$.

We propose here an extension of the security-sphere construction, leading to bounds that are finite for arbitrary distributions of nonoverlapping spherical traps. We consider a trial field in the form of a product of N security-sphere functions centered around all particles. In this way, the boundary condition (2.4) at the surface of each trap is fulfilled for security spheres with arbitrary radii. The source of the divergency can then be removed. Next, we show that the averages on the right-hand side of Eq. (2.3) can be estimated in terms of quantities that are entirely estimated by the density n and the probability distribution $p(\rho)$ alone.

Our trial density field has the following form:

$$c^*(\mathbf{r};\Gamma) = \prod_{i=1}^{N} \{1 + s[r_i;\nu(\rho_i)]\}, \tag{3.1}$$

where $r_i = |\mathbf{r} - \mathbf{R}_i|$ and ρ_i is the distance from the center of the ith trap to the center of its nearest neighbor for a given configuration Γ. Furthermore, $s(r;\nu)$ is a continuous function such that

$$s(r;\nu) = \begin{cases} -1, & \text{if } r < a \\ 0, & \text{if } r > \nu. \end{cases} \tag{3.2}$$

The particular form of the nondecreasing function $\nu(\rho) > a$, describing the radii of the security-sphere functions s, will be specified later. It is easy to check that the trial field (3.1) obeys conditions (2.4) and (2.5).

In Appendix A, we show that if $s(r;\nu)$ is bounded between -1 and 0, the following inequality holds for all r and Γ:

$$c^*(\mathbf{r};\Gamma) \geqslant 1 + \sum_{i=1}^{N} s[r_i;\nu(\rho_i)]. \tag{3.3}$$

If, in addition, we set

$$\nu(\rho) \leqslant \rho/\sqrt{2} \tag{3.4}$$

for all $\rho \geqslant 2a$, then we get the inequality

$$[\nabla c^*(\mathbf{r};\Gamma)]^2 \leqslant \sum_{i=1}^{N} \{\nabla s[r_i;\nu(\rho_i)]\}^2, \tag{3.5}$$

also proven in Appendix A, provided that $s(r;\nu)$ is a monotonic function of r. [We note that for monotonic s, Eq. (3.2) implies that s is bounded between -1 and 0].

The inequalities (3.3) and (3.5) can be used to obtain bounds that depend on the distribution of traps through n and $p(\rho)$. Namely, by inserting Eqs. (3.3) and (3.5) into relation (2.3), after evaluation of the averages, we get

$$k \leqslant \frac{n \int_{2a}^{\infty} d\rho\, p(\rho) \int d\mathbf{r} \{\nabla s[r;\nu(\rho)]\}^2}{\{1 + n \int_{2a}^{\infty} d\rho\, p(\rho) \int d\mathbf{r}\, s[r;\nu(\rho)]\}^2}, \tag{3.6}$$

provided that

$$1 + n \int_{2a}^{\infty} d\rho\, p(\rho) \int d\mathbf{r}\, s[r;\nu(\rho)] > 0. \tag{3.7}$$

In order to obtain the best upper bound for a given $\nu(\rho)$, we minimize the right-hand side of Eq. (3.6) with respect to the security-sphere function s. In Appendix B, we show that the optimal security-sphere function satisfies the Poisson equation with a uniform charge density. By substituting the optimal function s at the right-hand side of Eq. (3.6), we get

$$k \leqslant k_S \frac{2I_1}{(1 - \phi I_2)^2 + \phi^2 I_1 I_3}, \tag{3.8}$$

where

$$I_1 = \frac{1}{2} \int_{2a}^{\infty} d\rho\, p(\rho) \frac{\tilde{\nu}(\rho)}{\tilde{\nu}(\rho) - 1}, \tag{3.9}$$

$$I_2 = \frac{1}{2} \int_{2a}^{\infty} d\rho\, p(\rho) \tilde{\nu}(\rho)[\tilde{\nu}(\rho) + 1], \tag{3.10}$$

$$I_3 = \frac{1}{10}\int_{2a}^{\infty} d\rho\, p(\rho)[4\tilde{v}^5(\rho) - 5\tilde{v}^4(\rho) - 5\tilde{v}^3(\rho) + 5\tilde{v}^2(\rho) + 5\tilde{v}(\rho) - 4]. \quad (3.11)$$

Here $k_S = 3\phi a^{-2}$ is the low-density limit of k, $\phi = 4\pi n a^3/3$ denotes the volume fraction of the traps, and $\tilde{v} = v/a$.

According to our derivation, the inequality (3.8) is always satisfied if the relations (3.4) and (3.7) hold, and $s[r;v(\rho)]$ is monotonic for all ρ. As we argue in Appendix B, we can assure that the function s minimizing the right-hand side of Eq. (3.6) under the boundary condition (3.2) is monotonic and satisfies Eq. (3.7) by setting

$$v_{\min} \leqslant v(\rho) \leqslant v_{\max}, \quad (3.12)$$

where

$$v_{\max}^3 = v_{\min}^3 + \frac{2(v_{\min} - a)^2}{(2v_{\min} - a)} v_{\min}^{-1}[a^3\phi^{-1} - v_{\min}^3]. \quad (3.13)$$

To optimize the resulting bounds on the reaction constant, we chose for each ϕ the maximal value of $v_{\min}$ that satisfies Eq. (3.4) for all $\rho \geqslant 2a$ and does not exceed $v_{\max}$ [see Eq. (3.13)]; i.e., we set

$$v_{\min} = \min(a\sqrt{2}, a\phi^{-1/3}). \quad (3.14)$$

It is easy to notice that by considering security spheres all with the same radius v, independent of ρ, we obtain from Eq. (3.8) a bound that does not depend on the distribution $p(\rho)$. To obtain such a bound, we simply set

$$v(\rho) = v_{\min}, \quad (3.15)$$

which is sufficient to fulfill the required conditions (3.4) and (3.12). For a fixed radius v, the integrals (3.9)–(3.11) can be evaluated trivially with the aid of the normalization condition for $p(\rho)$ and an analytical expression for the bound can be easily obtained. The resulting bound is entirely determined by the density of the traps n and their radius a.

The bound on k can be improved by including information on the nearest-neighbor distribution $p(\rho)$. In this case, to optimize the bound, we chose

$$v(\rho) = \min(\rho/\sqrt{2}, v_{\max}). \quad (3.16)$$

Note that in this way, for low densities, we include contributions from very large security spheres, so that the correct low density limit is obtained.

The numerical results for the bounds derived in this section are presented in Sec. IV.

B. Voronoi-polyhedrons trial field

The second class of trial density fields considered includes all $c^*(\mathbf{r};\Gamma)$ of the following form:

$$c^*(\mathbf{r};\Gamma) = w[\min(|\mathbf{r} - \mathbf{R}_i|)], \quad (3.17)$$

where w is a continuous function such that

$$w(x) = 0, \quad \text{if } x < a \quad (3.18)$$

and $\min(|\mathbf{r} - \mathbf{R}_i|)$ is the distance from point $\mathbf{r}$ to the center of the nearest trap. The trial field (3.17) obviously fulfills condition (2.4) and is continuous inside each Voronoi polyhedron; it is also continuous at the boundaries of Voronoi polyhedrons since then, by definition, the distances to all nearest neighbors are equal. A trial field of the form (3.17) was previously used by Reck and Prager[10] to calculate the upper bound on k for a system of overlapping traps.

By inserting the trial density field (3.17) into the inequality (2.3), we get the relation

$$k \leqslant \frac{\int_a^\infty q(r)[dw(r)/dr]^2 dr}{[\int_a^\infty q(r)w(r)dr]^2}, \quad (3.19)$$

where $q(r)$ is the probability density for finding the center of the nearest trap at a distance r from a given point.

To obtain the best upper bound on k within the class of trial fields considered, we minimize the right-hand side of Eq. (3.19) with respect to $w(r)$. As we show in Appendix C, the result of the minimization is the following:

$$k \leqslant \left[\int_a^\infty \frac{\exp[-\beta(r)]}{d\beta(r)/dr} dr\right]^{-1}, \quad (3.20)$$

where $\beta(r)$ is given by

$$\beta(r) = -\ln\left[\int_r^\infty q(r')dt'\right]. \quad (3.21)$$

We will now discuss the numerical results for the bounds derived in the present section.

IV. RESULTS AND CONCLUSIONS

We have evaluated numerically the security-spheres upper bounds (3.8)–(3.11) and the Voronoi-polyhedrons upper bound (3.20). The bounds (3.8)–(3.11) were evaluated for the choices (3.15) and (3.16) of the function $v(\rho)$. We recall that the bound with the choice (3.15) does not depend on the statistical distribution of the traps. For the choice (3.16), we used a very accurate analytical expression for the distribution $p(\rho)$ resulting from the hard-sphere equilibrium ensemble, derived recently by Torquato, Lu, and Rubinstein.[15] For the Voronoi-polyhedrons bound (3.20), we used the expression for the distribution $q(r)$, also derived by Torquato and his collaborators.[15] (In all our calculations, we used the expressions of Torquato *et al.* derived from the Carnahan–Starling approximation for the contact value of the pair distribution function.)

Our numerical results for the reduced rate constant k/k_S are presented in Fig. 1, along with computer simulation data of Lee and collaborators.[9] We also include in the figure the Doi lower bound, as evaluated by Torquato.[13] [For volume fractions above the equilibrium hard-sphere fluid–solid phase transition, the densities $p(\rho)$ and $q(r)$ we use, the simulation results, and the Doi lower bound correspond to the undercooled-liquid or glassy states.]

One can see from the figure that the security-spheres upper bound (3.8)–(3.11), evaluated using the fixed security-sphere radius (3.15), systematically overestimates the simulation data by a factor of 2, or so. The bound remains finite for all densities, up to the hard-sphere close-packing volume fraction $\phi_{cp} = \pi/(3\sqrt{2})$. The choice (3.16) of the security sphere radii improves the bound for low densities and yields the exact low-density limit. This is, however, at the expense of including additional information about the nearest-neighbor probability distribution $p(\rho)$.

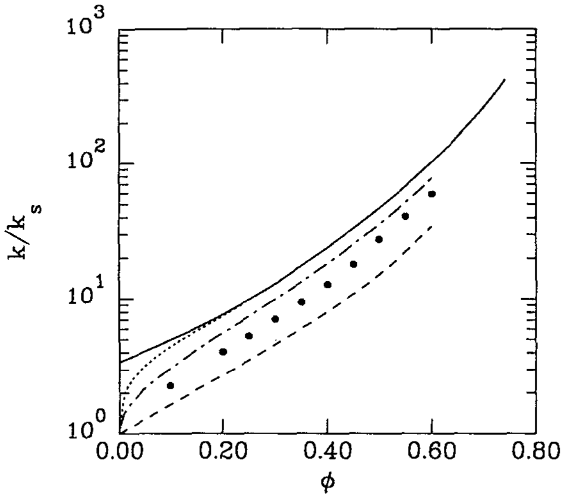

FIG. 1. Reduced effective reaction-rate constant k/k_S for a random array of impenetrable spherical traps, as a function of the volume fraction ϕ of traps. The security-spheres upper bound (3.8) with the choice (3.15) of the function ν, solid line; with the choice (3.16) of ν, dotted line; the Voronoi-polyhedrons upper bound (3.20), dot–dashed line; the simulation results of Lee *et al.* (Ref. 9), circles; the Doi lower bound, as evaluated by Torquato (Ref. 13), dashed line. Note that the bound given by the solid line does not depend on the statistical distribution of traps.

The Voronoi-polyhedron bound (3.20) improves substantially over the bounds discussed above. It gives the exact low-density limit and for intermediate and high densities overestimates the simulation results by 30%–50%. This bound depends on the probability distribution $q(r)$; the probability distributions $p(\rho)$ and $q(\rho)$ are related to each other and include equivalent information about the statistical state of the system.[15]

The ideas presented in this paper can also be applied to analyze other linear transport processes in random media. We are currently working on evaluating a lower bound on the collective mobility for a suspension of spherical particles.

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APPENDIX A

Let us consider a trial function (3.1). One can rewrite it in the following form:

$$c^*(\mathbf{r}:\Gamma) = 1 + \sum_{i=1}^{N} s[r_i;\nu(\rho_i)] \times \prod_{j=i+1}^{N} \{1 + s[r_j;\nu(\rho_j)]\}, \tag{A1}$$

where $\Pi_{j=N+1}^{N} \equiv 1$. From the above equation, for $s(r;\nu)$ satisfying Eq. (3.2) and bounded between -1 and 0, Eq. (3.3) immediately follows.

To get the estimate (3.5), we start from the identity

$$\begin{aligned}[\nabla c^*(\mathbf{r};\Gamma)]^2 &= \sum_{i=1}^{N} \{\nabla s[r_i;\nu(\rho_i)]\}^2 \times \prod_{k\neq i}^{N} \{1 + s[r_k;\nu(\rho_k)]\}^2 + \sum_{i\neq j}^{N} \nabla s[r_i;\nu(\rho_i)] \\ &\cdot \nabla s[r_j;\nu(\rho_j)] \prod_{k\neq i}^{N} \{1 + s[r_k;\nu(\rho_k)]\} \times \prod_{k\neq j}^{N} \{1 + s[r_k;\nu(\rho_k)]\}.\end{aligned} \tag{A2}$$

If $\nu(\rho) \leqslant \rho/\sqrt{2}$ and $s(r;\nu)$ is a monotonic function of r, then the scalar product $\mathbf{r}_i \cdot \mathbf{r}_j$ resulting from derivatives in the second term is negative for all $\mathbf{r}_i$ and $\mathbf{r}_j$ for which this term does not vanish. Therefore, using a similar argument as before, we get Eq. (3.5).

APPENDIX B

In order to obtain the optimal upper bound on k resulting from Eq. (3.6), we minimize the right-hand side of this relation. This is equivalent to minimizing the functional

$$J(s,\lambda) = \frac{1}{2}\lambda^2 n \int d\rho\, p(\rho) \int d\mathbf{r} \{\nabla s[r;\nu(\rho)]\}^2 \tag{B1}$$

with the constraint

$$\lambda \left\{1 + n \int d\rho\, p(\rho) \int d\mathbf{r}\, s[r;\nu(\rho)]\right\} = 1 \tag{B2}$$

over all λ and all continuous functions s that satisfy the boundary conditions (3.2).

The Euler–Lagrange equations corresponding to this variational problem have the form

$$\lambda \nabla^2 s[r;\nu(\rho)] = -\Lambda, \tag{B3}$$

$$n\lambda \int d\rho\, p(\rho) \int d\mathbf{r} \{\nabla s[r;\nu(\rho)]\}^2 = \Lambda\left\{1 + n \int d\rho\, p(\rho) \times \int d\mathbf{r}\, s[r;\nu(\rho)]\right\}, \tag{B4}$$

where Λ is the Lagrange multiplier. The solution to Eq. (B3) has the form

$$s(r;\nu) = \frac{\alpha(\nu)}{r} + \beta(\nu) - \frac{\Lambda}{6\lambda} r^2. \tag{B5}$$

Using the boundary conditions (3.2) and Eq. (B4), one can find explicit expressions for the coefficients α, β, and Λ/λ:

$$\frac{\alpha(\nu)}{a} = \frac{\tilde{\nu}}{1-\tilde{\nu}} - \frac{\Lambda a^2}{6\lambda} \tilde{\nu}(1+\tilde{\nu}), \tag{B6}$$

$$\beta(\nu) = \frac{1}{\tilde{\nu}-1} + \frac{\Lambda a^2}{6\lambda} (1 + \tilde{\nu} + \tilde{\nu}^2), \tag{B7}$$

$$\frac{\Lambda a^2}{\lambda} = \frac{6\phi I_1}{1-\phi I_2}. \tag{B8}$$

Here $\tilde{\nu} = \nu/a$, and I_1 and I_2 are given by Eqs. (3.9) and (3.10), respectively.

One can then easily check that for a given ν, $s(r;\nu)$ is monotonic for all $r \leqslant r_0 = [-3\lambda\alpha(\nu)/\Lambda]^{1/3}$, where it has the maximum. For ν satisfying Eq. (3.12), the integrals I_1 and I_2 can be easily estimated in terms of $\nu_{\min}$ and $\nu_{\max}$. Then it can be shown that Eq. (3.13) implies the inequality $\nu \leqslant r_0$. A straightforward calculation involving Eq. (3.13) shows that $\nu_{\max} \leqslant \phi^{-1/3}$. For $\nu \leqslant \phi^{-1/3}$ and $s(r;\nu)$ bounded between -1 and 0, condition (3.7) can be checked by a simple calculation involving Eq. (3.2) and the normalization of $p(\rho)$.

APPENDIX C

In the same way as in Appendix B, we obtain the Euler–Lagrange equations associated with the variational problem (3.19)

$$\frac{d}{dr} q(r) \frac{d}{dr} w(r) = -\frac{\Lambda}{\lambda} q(r) \tag{C1}$$

and

$$\lambda \int_a^\infty q(r)[dw(r)/dr]^2 dr = \Lambda \int_a^\infty q(r) w(r) dr. \tag{C2}$$

The solution of Eq. (C1) has the form

$$w(r) = \frac{\Lambda}{\lambda} \int_a^r \frac{dr}{d\beta(r)/dr}, \tag{C3}$$

where $\beta(r)$ is defined by Eq. (3.21). By substituting Eq. (C3) at the right-hand side of Eq. (3.19), using Eq. (C2), and integrating by parts we arrive at Eq. (3.20).

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