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Concentration Dependence of Diffusion-Controlled Processes Among Stationary Reactive Sinks

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A multiple scattering theory of competition effects in diffusion-controlled reactions are presented. We consider a random array of stationary sinks which react with a density field of another reactant. Using the radiation boundary condition to describe the reaction at the surfaces of the sinks, we treat the modification of the density field due to reaction with sinks exactly. By keeping only the most divergent terms in a given order of scattering and summing them, we obtain the rate constant as a function of the sink concentration in the steady state. We also calculate the concentration-dependent diffusion constant of the density field. Both the rate and diffusion constants have nonanalytic behavior in the sink concentration.

KEY WORDS: Diffusion-controlled reactions; sphere suspensions.

1. INTRODUCTION

The theory of diffusion-controlled reactions presented by Smoluchowski$^{(1)}$ is concerned with the effect on the reaction rate of the slow diffusive motion of the reactants toward each other. When one reactant is stationary (a sink) and the other described by a density field, the steady state density field at **r** is

$$n(\mathbf{r}) = n_0(1 - a/r), \qquad r > a \tag{1.1}$$

for the reactive boundary condition of complete absorption, $n(a) = 0$. In Eq. (1.1), a is the sink radius and n_0 is the density field in the absence of the

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sink. For the one-sink problem, the total flux J into the sink is

$$J = 4\pi D_0 a n_0 \tag{1.2}$$

which defines the rate constant $k_D = 4\pi D_0 a$, where D_0 is the diffusion constant of the density field.

As the sink concentration is increased, this description must be modified.(2) There is a competition among the sinks for the reactive field and a consequent alteration of the rate constant. The long-range diffusive nature of the density field gives rise to divergent integrals reminiscent of those in the Stokes problem.(3) As in the cases of hydrodynamic screening in the Stokes problem(3) and Coulombic screening in Debye–Hückel theory, when all the many-body effects giving rise to the long-range interactions are incorporated, the divergence difficulties are expected to vanish. This competition among the sinks leads to a nonanalytic dependence of the rate constant on the sink concentration. This has been shown to be the case to leading order in the sink concentration for a random array of sinks by Felderhof and Deutch(4) and Lebenhaft and Kapral.(5)

In this work, we obtain an exact expression for the dependence of the rate constant on the sink concentration for a random array of the sinks in the steady state limit, by using a multiple scattering approach.(3,6,7) Our derivation is motivated by the following physical argument: Consider a labeled sink, say α, which reacts with the density field. In addition to the bare density field, α can react with the density field modified by earlier reaction with all the sinks including α. All these contributions to the rate constant are analyzed. By systematically ordering the various reaction (scattering) events and keeping the most divergent term in any order of scattering, we obtain an explicit expression for the rate constant for a random sink array. Using the same multiple scattering formulation we also derive the dependence of the diffusion constant of the density field on the sink concentration.

Our derivation consists of two parts. The first deals with writing a macroscopic equation of motion for the average density field and the definition of the rate and diffusion constants and is contained in Section 2. The second part involves the derivation of the microscopic density field at any space point and averaging it to match with the macroscopic equation of motion. This is presented in Section 3. The details of the calculation of the rate and diffusion constants are given in Sections 4 and 5, respectively. Section 6 contains a discussion of the results.

2. MACROSCOPIC LAW

We consider the system to be composed of a fluid carrying reactive particles described by a density field $n(r)$ and a set of N stationary reactive sinks at concentration $c = N/V$, where V is the total volume of the system. At steady state, the volume rate of production of reactive density due to external sources is just compensated by its removal via the sinks. An auxiliary field $\phi(\mathbf{r})$ is defined such that, in the absence of sinks, the density field satisfies

$$D_0\nabla^2 n(\mathbf{r}) = \phi(\mathbf{r}) \tag{2.1}$$

The solution of Eq. (2.1),

$$n_0(\mathbf{r}) = -\int d\mathbf{r}'\, G(\mathbf{r}-\mathbf{r}')\phi(\mathbf{r}') \tag{2.2a}$$

is given in terms of the diffusive propagator

$$G(r) = (4\pi D_0 r)^{-1} \tag{2.2b}$$

The field $\phi(\mathbf{r})$ can account for external boundary effects, other sources, or fluctuating contributions to the density field. We include it here for generality but will make no use of it in this work. In the presence of the sinks, the diffusive field satisfies

$$D_0\nabla^2 n(\mathbf{r}) = \phi(\mathbf{r}) + \sum_{\alpha=1}^{N}\int d\Omega_\alpha\, \delta(\mathbf{r}-\mathbf{R}_\alpha)\sigma_\alpha(\Omega_\alpha) \tag{2.3}$$

The αth sink absorbs the reactive density field strength $\sigma_\alpha(\Omega_\alpha)$ at any space point on the surface of α, $\mathbf{R}_\alpha = \mathbf{R}_\alpha^0 + \mathbf{r}_\alpha(\Omega_\alpha)$, where $\mathbf{R}_\alpha^0$ is the position vector of the center of mass of α and $\mathbf{r}_\alpha(\Omega_\alpha)$ is the position vector of this surface point from $\mathbf{R}_\alpha^0$; Ω_α denotes the orientation of $\mathbf{r}_\alpha$. For notational convenience, $\mathbf{r}_\alpha$ and Ω_α are used interchangeably in this work. The second term on the right-hand side of Eq. (2.3) gives the net depletion of the reactive density field due to all the sinks.

As we are interested in the macroscopic density field, we average Eq. (2.3) over a distribution of sink centers to obtain

$$\begin{aligned} D_0\nabla^2\langle n(\mathbf{r})\rangle &= \phi(\mathbf{r}) + \left\langle \sum_{\alpha=1}^{N}\int d\Omega_\alpha\, \delta(\mathbf{r}-\mathbf{R}_\alpha)\sigma_\alpha(\Omega_\alpha)\right\rangle \\ &\equiv \phi(\mathbf{r}) + \int d\mathbf{r}'\, \Sigma(\mathbf{r}-\mathbf{r}')\langle n(\mathbf{r}')\rangle \end{aligned} \tag{2.4}$$

Here, the angular bracket denotes the average over the appropriate distribution function. In the last equality of Eq. (2.4) we have defined a (concentration-dependent) macroscopic kernel $\Sigma(\mathbf{r})$ so that Eq. (2.4) has the form of a linear law. Introducing the Fourier space transform of a field $f(\mathbf{r})$ as

$$f(\mathbf{k}) \equiv \int e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r})\, d\mathbf{r} \tag{2.5}$$

Eq. (2.4) is

$$-D_0 k^2\langle n(\mathbf{k})\rangle = \phi(\mathbf{k}) + \Sigma(\mathbf{k})\langle n(\mathbf{k})\rangle \tag{2.6}$$

Expanding Σ in powers of $\mathbf{k}$ shows that the concentration dependent rate constant, $k_f(c)$, is

$$k_f(c) = \Sigma(\mathbf{k}=0) \equiv \Sigma^{(0)} \tag{2.7a}$$

and the concentration-dependent diffusion constant, $D(c)$ is

$$D(c) - D_0 = \frac{1}{2}\frac{d^2}{dk^2}\Sigma(\mathbf{k})\bigg|_{\mathbf{k}=0} \equiv \Sigma^{(2)} \tag{2.7b}$$

Thus, a calculation of two spatial integrals of $\Sigma(r)$, $\Sigma^{(0)}$ and $\Sigma^{(2)}$ determines $k_f(c)$ and $D(c)$. The formal solution of Eq. (2.4) is

$$\langle n(\mathbf{r})\rangle = n_0(\mathbf{r}) - \int d\mathbf{r}' \int d\mathbf{r}''\, G(\mathbf{r}-\mathbf{r}')\Sigma(\mathbf{r}'-\mathbf{r}'')\langle n(\mathbf{r}'')\rangle \tag{2.8}$$

The form of $\Sigma(\mathbf{r})$ depends on the shape of the sinks and the specification of reaction at the sink surfaces. We assume that the sinks are spheres of common radius a and use the traditional "radiation boundary condition"

$$n(\mathbf{R}_\alpha) = \frac{k_D}{k_0}\mathbf{r}\cdot\nabla n(\mathbf{r})\bigg|_{r\to R_\alpha^+} \equiv \mathcal{G}(\mathbf{R}_\alpha)n(\mathbf{R}_\alpha) \tag{2.9}$$

Here k_0 is a bimolecular rate characterizing the contact reactivity. For $k_0 \to \infty$ one has complete absorption, $n(\mathbf{R}_\alpha) = 0$, and for $k_0 \to 0$ no reaction (no flux across the sink boundary). The R_α^+ limiting procedure ensures that the flux at the sink boundary is evaluated from the outside. The operator $\mathcal{G}(\mathbf{R}_\alpha)$ is defined just for notational convenience.

In the following section we determine Σ by comparing the average solution of the microscopic field equation given in Eq. (2.3), with Eq. (2.8) and using the boundary condition of Eq. (2.9).

3. THE MICROSCOPIC EXPRESSION FOR Σ

The formal solution of Eq. (2.3) is

$$\begin{aligned} n(\mathbf{r}) = n_0(\mathbf{r}) &- \int d\Omega_\alpha\, G(\mathbf{r}-\mathbf{R}_\alpha)\sigma_\alpha(\Omega_\alpha) \\ &- \sum_{\substack{\beta=1\\ \neq\alpha}}^{N} \int d\Omega_\beta\, G(\mathbf{r}-\mathbf{R}_\beta)\sigma_\beta(\Omega_\beta) \end{aligned} \tag{3.1}$$

Thus, the microscopic density field at any space point $\mathbf{r}$ is expressed in terms of the various $\{\sigma_\alpha\}$ and the problem reduces to the determination of these $\{\sigma_\alpha\}$. We obtain a formal expression for these $\{\sigma_\alpha\}$ using the boundary condition given by Eq. (2.9) and a multiple scattering expansion. The procedure is as follows: First, write the density field for a space point on the surface of a sink, say α, from Eq. (3.1). Second, invert this equation to obtain σ_α as a function of $n(R_\alpha)$ and $\{\sigma_{\beta\neq\alpha}\}$. This can be accomplished by defining the *surface* inverse $K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)$ of $G(\mathbf{r}_\alpha,\mathbf{r}'_\alpha)$ via

$$\int d\Omega''_\alpha\, K_\alpha^{-1}(\Omega_\alpha,\Omega''_\alpha)G(\Omega''_\alpha,\Omega'_\alpha)=\delta(\Omega_\alpha-\Omega'_\alpha) \tag{3.2}$$

The surface inverse is obtained by expanding G in spherical harmonics. An explicit expression for K_α^{-1} is presented in Appendix A. Letting $\mathbf{r}=\mathbf{R}'_\alpha$ in Eq. (3.1) and using (3.2) yields

$$\begin{aligned}\sigma_\alpha(\Omega_\alpha)=&-\int d\Omega'_\alpha\, K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)\left[n(\mathbf{R}'_\alpha)-n_0(\mathbf{R}'_\alpha)\right]\\&-\sum_{\substack{\beta=1\\ \neq\alpha}}\int d\Omega'_\alpha\, d\Omega_\beta\, K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)G(\mathbf{R}'_\alpha-\mathbf{R}_\beta)\sigma_\beta(\Omega_\beta)\end{aligned} \tag{3.3}$$

We now express $\sigma_\alpha(\Omega_\alpha)$ in terms of n_0 by using the boundary condition in Eq. (2.9). In this section, only the complete absorption case is considered, $n(\mathbf{R}_\alpha)=0$; the general case is presented in Appendix B. Setting $n(R'_\alpha)=0$ and iterating Eq. (3.3) yields

$$\begin{aligned}\sigma_\alpha(\Omega_\alpha)=&\int d\Omega'_\alpha\, K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)n_0(\mathbf{R}'_\alpha)\\&-\sum_{\substack{\beta=1\\ \beta\neq\alpha}}\int d\Omega'_\alpha\, d\Omega_\beta\, d\Omega'_\beta\, K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)G(\mathbf{R}'_\alpha-\mathbf{R}_\beta)K_\beta^{-1}(\Omega_\beta,\Omega'_\beta)n_0(\mathbf{R}'_\beta)\\&+\sum_{\beta\neq\alpha}\sum_{\gamma\neq\beta}\int d\Omega'_\alpha\, d\Omega_\beta\, d\Omega'_\beta\, d\Omega_\gamma\, d\Omega'_\gamma\, K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)G(\mathbf{R}'_\alpha-\mathbf{R}_\beta)\\&\times K_\beta^{-1}(\Omega_\beta,\Omega'_\beta)G(\mathbf{R}'_\beta-\mathbf{R}_\gamma)K_\gamma^{-1}(\Omega_\gamma,\Omega'_\gamma)n_0(\mathbf{R}'_\gamma)\\&-\sum_{\beta\neq\alpha}\sum_{\gamma\neq\beta}\sum_{\delta\neq\gamma}\int K_\alpha^{-1}GK_\beta^{-1}GK_\gamma^{-1}GK_\delta^{-1}n_0+\cdots\end{aligned} \tag{3.4}$$

Substituting Eq. (3.4) in Eq. (3.1) gives

$$\begin{aligned}n(\mathbf{r})=n_0(\mathbf{r})&-\sum_{\alpha=1}^{N}\int d\mathbf{r}'\, d\mathbf{r}''\, G(\mathbf{r}-\mathbf{r}')T_\alpha(\mathbf{r}'-\mathbf{r}'')n_0(\mathbf{r}'')\\&+\sum_{\alpha=1}^{N}\sum_{\beta\neq\alpha}\int dr'\cdots d\mathbf{r}^{iv}\, G(\mathbf{r}-\mathbf{r}')T_\alpha(\mathbf{r}'-\mathbf{r}'')\\&\times G(\mathbf{r}''-\mathbf{r}''')T_\beta(\mathbf{r}'''-\mathbf{r}^{iv})n_0(\mathbf{r}^{iv})\\&-\sum_{\alpha}\sum_{\beta\neq\alpha}\sum_{\gamma\neq\beta}\int GT_\alpha GT_\beta GT_\gamma n_0+\cdots\end{aligned} \tag{3.5}$$

where

$$T_\alpha(\mathbf{r}-\mathbf{r}')\equiv\int d\Omega_\alpha\, d\Omega'_\alpha\, \delta(\mathbf{r}-R_\alpha)K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)\delta(\mathbf{r}'-\mathbf{R}'_\alpha) \tag{3.6}$$

This result shows that the density field at $\mathbf{r}$ can be written as a series of scatterings from the sinks. The G's propagate the density disturbance from one sink to the next while the T's are the scattering operators at the sphere surfaces. The sink structure is exactly described by Eq. (3.6).

The density field given by Eq. (3.5) is a microscopic expression. We average over the distribution of the sinks to obtain the average density field

$$\begin{aligned}\langle n(\mathbf{r})\rangle = n_0(\mathbf{r}) &- \sum_{\alpha} \int d\mathbf{r}'\, d\mathbf{r}''\, G(\mathbf{r}-\mathbf{r}')\langle T_\alpha(\mathbf{r}'-\mathbf{r}'')\rangle n_0(\mathbf{r}'') \\ &+ \sum_{\alpha} \sum_{\beta\neq\alpha} \int d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, G(\mathbf{r}-\mathbf{r}') \\ &\times \big\langle T_\alpha(\mathbf{r}'-\mathbf{r}'')G(\mathbf{r}''-\mathbf{r}''')T_\beta(\mathbf{r}'''-\mathbf{r}^{iv})\big\rangle n_0(\mathbf{r}^{iv}) - \cdots \end{aligned} \qquad (3.7)$$

In order to get an explicit expression for Σ in terms of $\{T_\alpha\}$, we iterate Eq. (2.8) indefinitely:

$$\begin{aligned}\langle n(\mathbf{r})\rangle = n_0(\mathbf{r}) &- \int d\mathbf{r}'\, d\mathbf{r}''\, G(\mathbf{r}-\mathbf{r}')\Sigma(\mathbf{r}'-\mathbf{r}'')n_0(\mathbf{r}'') \\ &+ \int d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, G(\mathbf{r}-\mathbf{r}')\Sigma(\mathbf{r}'-\mathbf{r}'') \\ &\times G(\mathbf{r}''-\mathbf{r}''')\Sigma(\mathbf{r}'''-\mathbf{r}^{iv})n_0(\mathbf{r}^{iv}) \\ &- \int G\Sigma G\Sigma G\Sigma n_0 + \cdots \end{aligned} \qquad (3.8)$$

The Eqs. (3.7) and (3.8) are equivalent. To make a ready comparison of these two equations, write Σ as

$$\Sigma \equiv \sum_{j=1}^{\infty} \Sigma_j \qquad (3.9)$$

where Σ_j corresponds to a sequence of j scatterings (thus containing j "T" operators).

From Eqs. (3.7)–(3.9), it follows that

$$\begin{aligned}\Sigma_1(\mathbf{r}-\mathbf{r}') &= \left\langle \sum_{\alpha=1}^{N} T(\mathbf{r}-\mathbf{r}')\right\rangle \\ \Sigma_2(\mathbf{r}-\mathbf{r}') &= -\int d\mathbf{r}''\, d\mathbf{r}''' \left[\left\langle \sum_{\alpha} \sum_{\beta\neq\alpha} T_\alpha(\mathbf{r}-\mathbf{r}'')G(\mathbf{r}''-\mathbf{r}''')T_\beta(\mathbf{r}'''-\mathbf{r}')\right\rangle \right. \\ &\qquad \left. - \left\langle \sum_{\alpha} T_\alpha(\mathbf{r}-\mathbf{r}'')\right\rangle G(\mathbf{r}''-\mathbf{r}''')\left\langle \sum_{\beta} T_\beta(\mathbf{r}'''-\mathbf{r}')\right\rangle\right] \\ \Sigma_3(\mathbf{r}-\mathbf{r}') &= \int \left\{ \left\langle \sum_{\alpha} \sum_{\beta\neq\alpha} \sum_{\gamma\neq\beta} T_\alpha G T_\beta G T_\gamma \right\rangle - \left\langle \sum_{\alpha} T_\alpha \right\rangle \right. \\ &\qquad \times G\left[\left\langle \sum_{\beta} \sum_{\gamma\neq\beta} T_\beta G T_\gamma \right\rangle - \left\langle \sum_{\beta} T_\beta \right\rangle G \left\langle \sum_{\gamma} T_\gamma \right\rangle\right] \\ &\qquad - \left[\left\langle \sum_{\alpha} \sum_{\beta\neq\alpha} T_\alpha G T_\beta \right\rangle - \left\langle \sum_{\alpha} T_\alpha \right\rangle G \left\langle \sum_{\beta} T_\beta \right\rangle\right] G \left\langle \sum_{\gamma} T_\gamma \right\rangle \\ &\qquad \left. - \left\langle \sum_{\alpha} T_\alpha \right\rangle G \left\langle \sum_{\beta} T_\beta \right\rangle G \left\langle \sum_{\gamma} T_\gamma \right\rangle \right\} \quad \text{etc.} \end{aligned} \qquad (3.10)$$

By evaluating the various Σ_j's given by Eqs. (3.9) and (3.10) and using Eq. (2.7) the concentration dependencies of the reaction rate constant and the diffusion constant can be calculated. The details are presented in the next sections.

4. EVALUATION OF THE RATE CONSTANT

As discussed in Section 2, the rate constant is given by the $k = 0$ part of the Fourier transform of $\Sigma(\mathbf{r})$ defined in Eqs. (3.9) and (3.10). In the explicit evaluation of these Σ_j's, the average is performed over a random distribution of the centers of mass of the N sinks. Since the problem under study is dominated by the long-range diffusive interaction of the sinks, the details of the short-range intersink potential are probably not very important. In view of this, we have employed the sink penetrability assumption in this work. However, the above results for the Σ_j's are exact for sinks with any prescribed interaction potential.

With the above-mentioned averaging procedure, we proceed to evaluate the Σ_j's. From Eqs. (3.6) and (3.10), $\Sigma_1(\mathbf{r}-\mathbf{r}')$ becomes

$$\Sigma_1(\mathbf{r}-\mathbf{r}') = \frac{1}{V}\sum_{\alpha}\int d\mathbf{R}_\alpha^0\, d\Omega_\alpha\, d\Omega'_\alpha \times \delta(\mathbf{r}-\mathbf{R}_\alpha^0-\mathbf{r}_\alpha)K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)\delta(\mathbf{r}'-\mathbf{R}_\alpha^0-\mathbf{r}'_\alpha) \tag{4.1}$$

Performing the Fourier transform as given by Eq. (2.5), Eq. (4.1) readily yields

$$\Sigma_1(\mathbf{k}) = c\int d\Omega_\alpha\, d\Omega'_\alpha\, K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)\exp\left[-i\mathbf{k}\cdot(\mathbf{r}_\alpha-\mathbf{r}'_\alpha)\right] \tag{4.2}$$

By expanding K_α^{-1} in spherical harmonics, as in Appendix A, one has

$$K_\alpha^{-1}(\Omega,\Omega') = \sum_{l=0}^{\infty}\sum_{l'=0}^{\infty}\sum_{m=-l}^{l}\sum_{m'=-l'}^{l'} K_{lm,l'm'}^{-1}Y_{lm}(\Omega)\,Y_{l'm'}^{*}(\Omega') \tag{4.3a}$$

where

$$K_{lm,l'm'}^{-1} = K_l^{-1}\delta_{ll'}\delta_{mm'} \tag{4.3b}$$

by symmetry. Explicit evaluation of K_l^{-1} yields (see Appendix A)

$$K_l^{-1} = D_0a(2l+1) \tag{4.4}$$

Use of Eqs. (4.3) and (4.4) in Eq. (4.2) gives

$$\Sigma_1(k=0) = ck_D \tag{4.5}$$

When the averaging in the Σ_2 term is performed, the integrand in Σ_2 contains a factor of (g_2-1), where g_2 is the radial distribution function. Since we consider here a penetrable sink system, Σ_2 vanishes.

We now proceed to evaluate Σ_3. Equation (3.10) shows that there are two possible scattering sequences, viz., $\langle T_\alpha G T_{\beta\neq\alpha} G T_{\gamma\neq\beta,\alpha}\rangle$ and $\langle T_\alpha G T_{\beta\neq\alpha} G T_\alpha\rangle$. The first term, $\gamma \neq \alpha$, involves a factor of $(g_3 - 1)$ in the integrand, where g_3 is the three-particle distribution function. For penetrating spheres, $\langle T_\alpha G T_{\beta\neq\alpha} G T_{\gamma\neq\beta,\alpha}\rangle$ thus vanishes. The second term in Σ_3 is

$$\begin{aligned}\Sigma_{3,\gamma=\alpha}(\mathbf{r}-\mathbf{r}') = \int & d\Omega_\alpha\, d\Omega'_\alpha\, d\Omega''_\alpha\, d\Omega'''_\alpha\, d\Omega_\beta\, d\Omega'_\beta \\ & \times \Big\langle \sum_\alpha \sum_{\beta\neq\alpha} \delta(\mathbf{r}-\mathbf{R}^0_\alpha-\mathbf{r}_\alpha) K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha) \\ & \times G\big(\mathbf{R}^0_\alpha+\mathbf{r}'_\alpha-\mathbf{R}^0_\beta-\mathbf{r}_\beta\big) K_\beta^{-1}(\Omega_\beta,\Omega'_\beta) \\ & \times G\big(\mathbf{R}^0_\beta+\mathbf{r}'_\beta-\mathbf{R}^0_\alpha-\mathbf{r}''_\alpha\big) K_\alpha^{-1}(\Omega''_\alpha,\Omega'''_\alpha) \\ & \times \delta\big(\mathbf{r}'-\mathbf{R}^0_\alpha-\mathbf{r}'''_\alpha\big)\Big\rangle + o(1/V) \end{aligned} \tag{4.6}$$

The Fourier transform of Eq. (4.6) is

$$\begin{aligned}\Sigma_3(\mathbf{k}) = c^2 \int & d\Omega_\alpha\, d\Omega'_\alpha\, d\Omega''_\alpha\, d\Omega'''_\alpha\, d\Omega_\beta\, d\Omega'_\beta \int \frac{d^3k'}{(2\pi)^3}\, G^2(k') \\ & \times \exp\big[-i\mathbf{k}\cdot(\mathbf{r}_\alpha-\mathbf{r}'''_\alpha) + i\mathbf{k}'\cdot(\mathbf{r}'_\alpha-\mathbf{r}_\beta+\mathbf{r}'_\beta-\mathbf{r}''_\alpha)\big] \\ & \times K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha) K_\beta^{-1}(\Omega_\beta,\Omega'_\beta) K_\alpha^{-1}(\Omega''_\alpha,\Omega'''_\alpha) \end{aligned} \tag{4.7}$$

where $G(k) = 1/D_0k^2$ is the Fourier transform of the diffusive propagator $G(\mathbf{r})$. By expanding the K^{-1}'s in spherical harmonics as in Eq. (4.3), and performing the angular integrations, Eq. (4.7) reduces to, for the $k = 0$ part,

$$\Sigma_3(k=0) = 4\pi c^2 k_D^2 \int_0^\infty \frac{dk'\,k'^2}{(2\pi)^3}\, j_0^2(k'a)\, G^2(k')\, T(k') \tag{4.8}$$

Here,

$$\begin{aligned} T(k) &= \int d\Omega_\beta\, d\Omega'_\beta\, K_\beta^{-1}(\Omega_\beta,\Omega'_\beta) \exp\big[-i\mathbf{k}\cdot(\mathbf{r}_\beta-\mathbf{r}'_\beta)\big] \\ &= k_D \sum_l (2l+1)^2 j_l^2(ka) \end{aligned} \tag{4.9}$$

with j_l the spherical Bessel function of the first kind of order l. The integral in Eq. (4.8) diverges since the integrand $\sim 1/k^{2'}$ as $k' \to 0$. As shown in the following paragraphs, all Σ_j's, $j \geqslant 4$, also contain divergent terms. Since all the integrals of these terms diverge individually, we sum the integrand first and then perform the integration.

For the system of penetrating spheres, the only scattering sequences in Σ_4 that do not vanish upon averaging are $\langle T_\alpha G T_{\beta\neq\alpha} G T_{\gamma\neq\beta} G T_\alpha \rangle$ and $\langle T_\alpha G T_{\beta\neq\alpha} G T_\alpha G T_{\beta\neq\alpha} \rangle$. Both these sequences lead to divergent integrals. In Appendix C, it is shown that the latter term is less divergent than the former. We keep only those scattering sequences which are the most divergent in any given order of scatterings. (These are the ring terms). Therefore, for Σ_4, the leading divergent term is, after Fourier transformation,

$$\begin{aligned}\Sigma_4(\mathbf{k}) = -c^3 \int d\Omega_\alpha\, d\Omega'_\alpha\, d\Omega''_\alpha\, d\Omega'''_\alpha\, d\Omega_\beta\, d\Omega'_\beta\, d\Omega_\gamma\, d\Omega'_\gamma \int \frac{d^3k'}{(2\pi)^3} G^3(k') \\ \times \exp\left[-i\mathbf{k}\cdot(\mathbf{r}_\alpha - \mathbf{r}'''_\alpha) + i\mathbf{k}'\cdot(\mathbf{r}'_\alpha - \mathbf{r}''_\alpha - \mathbf{r}_\beta + \mathbf{r}'_\beta - \mathbf{r}_\gamma + \mathbf{r}'_\gamma)\right] \\ \times K_\alpha^{-1}(\Omega_\alpha, \Omega'_\alpha) K_\beta^{-1}(\Omega_\beta, \Omega'_\beta) K_\gamma^{-1}(\Omega_\gamma, \Omega'_\gamma) K_\alpha^{-1}(\Omega''_\alpha, \Omega'''_\alpha) \qquad (4.10)\end{aligned}$$

Upon performing the angular integrations, Eq. (4.10) simplifies to

$$\Sigma_4(k=0) = -4\pi c^3 k_D^2 \int_0^\infty \frac{dk}{(2\pi)^3} k^2 j_0^2(ka) G^3(k) T^2(k) \qquad (4.11)$$

This also diverges as noted above. Note that this divergence goes like $-1/k^4$ as $k \to 0$. Similarly, it can be shown that the ring term of Σ_j diverges like $(-k^2)^{2-j}$ as $k \to 0$, for $j \geqslant 3$. Collecting all these ring terms, we obtain

$$\begin{aligned}\sum_{j=3} \Sigma_j(k=0) &= 4\pi c^2 k_D^2 \int_0^\infty \frac{dk\, k^2}{(2\pi)^3} T(k) j_0^2(ka) G^2(k) \\ &\quad \times \left[1 - cT(k)G(k) + c^2T^2(k)G^2(k) - \cdots\right] \\ &= \frac{c^2 k_D^2}{2\pi^2 D_0^2} \int_0^\infty dk\, \frac{T(k) j_0^2(ka)}{\left[k^2 + cT(k)/D_0\right]} \qquad (4.12)\end{aligned}$$

The integral now is convergent. Therefore, within the approximation of keeping only the most divergent terms, the rings, in a given order of scatterings, the rate constant is exactly

$$k_f(c) = k_D + \frac{c k_D^3}{2\pi^2 D_0^2} \int_0^\infty dk\, \frac{j_0^2(ka) \sum_l (2l+1)^2 j_l^2(ka)}{k^2 + 4\pi c a \sum_l (2l+1)^2 j_l^2(ka)} \qquad (4.13)$$

A plot of Eq. (4.13) is given in Fig. 1. If we use the approximation of taking the scattering operator $T(k)$ as being determined only by the $k \to 0$ limit

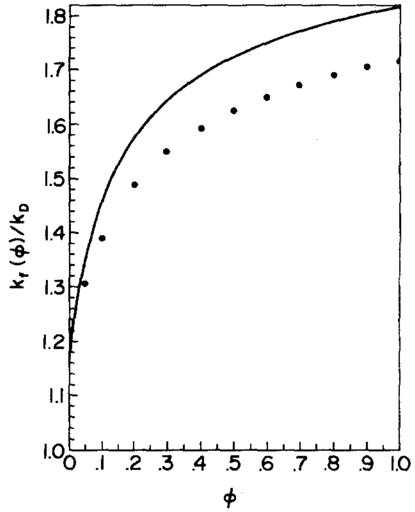

Fig. 1. Rate coefficient $k_f(\phi)/k_D$ as a function of volume fraction ϕ. Solid line: Full result of Eq. (4.13). Dotted line: Monopole approximation of Eq. (4.14).

(the monopole approximation), then $T(k=0)=k_D$. Then k_f reduces to

$$k_f = k_D\left\{2-\left(1/2\sqrt{3\phi}\right)\left[1-\exp\left(-2\sqrt{3\phi}\right)\right]\right\} \tag{4.14}$$

where $\phi = 4\pi a^3 c/3$ is the volume fraction of the sinks. For sufficiently low volume fractions, we recover the result of Felderhof and Deutch,$^{(5)}$

$$k_f = k_D\left[1+(3\phi)^{1/2}+\cdots\right] \tag{4.15}$$

5. EVALUATION OF THE DIFFUSION CONSTANT

As defined in Section 2, $D(c)-D_0$ is given by $\Sigma^{(2)}$. We present some details of the calculation of $\Sigma^{(2)}$ from Eq. (3.10) in this section.

The k^2 coefficient of Σ_1 is, from Eqs. (4.2),

$$\begin{aligned}\Sigma_1^{(2)} &= -c\frac{\hat{k}\hat{k}}{2} : \int d\Omega_\alpha\, d\Omega'_\alpha\, (\mathbf{r}_\alpha-\mathbf{r}'_\alpha)(\mathbf{r}_\alpha-\mathbf{r}'_\alpha)K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)\\ &= -c\hat{k}\hat{k} : \int d\Omega_\alpha\, d\Omega'_\alpha\, (\mathbf{r}_\alpha\mathbf{r}_\alpha-\mathbf{r}_\alpha\mathbf{r}'_\alpha)K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha)\end{aligned} \tag{5.1}$$

where $\hat{k}=\mathbf{k}/k$. Using Eqs. (4.3) and (4.4) to perform the angular integrals in Eq. (5.1) leads to

$$\Sigma_1^{(2)} = -\frac{4\pi}{3}ca^2\left(K_0^{-1}-K_1^{-1}\right)=2D_0\phi \tag{5.2}$$

The next nonvanishing term for $\Sigma^{(2)}$ is $\Sigma_3^{(2)}$ and is given, from Eqs. (4.7) and (4.9), as

$$\Sigma_3^{(2)} = -c^2\frac{\hat{k}\hat{k}}{2} : \int d\Omega_\alpha\, d\Omega'_\alpha\, d\Omega''_\alpha\, d\Omega'''_\alpha \int \frac{d^3k'}{(2\pi)^3}(\mathbf{r}_\alpha - \mathbf{r}'''_\alpha)(\mathbf{r}_\alpha - \mathbf{r}'''_\alpha)$$
$$\times G^2(k')T(k')\exp\left[i\mathbf{k}'\cdot(\mathbf{r}'_\alpha - \mathbf{r}''_\alpha)\right]K_\alpha^{-1}(\Omega_\alpha, \Omega'_\alpha)K_\alpha^{-1}(\Omega''_\alpha, \Omega'''_\alpha) \quad (5.3)$$

The terms with $\mathbf{r}_\alpha\mathbf{r}_\alpha$ and $\mathbf{r}'''_\alpha\mathbf{r}'''_\alpha$ are divergent and we label their sum as $\Sigma_3^{(2)}(a)$. The terms with $\mathbf{r}_\alpha\mathbf{r}'''_\alpha$ are nondivergent and we label their sum as $\Sigma_3^{(2)}(b)$. They can be expressed as

$$\Sigma_3^{(2)}(a) = -\frac{8}{3}a^4D_0^2c^2\int_0^\infty dk\, k^2T(k)G^2(k)j_0^2(ka) \quad (5.4a)$$

and

$$\Sigma_3^{(2)}(b) = 24a^4D_0^2c^2\int_0^\infty dk\, k^2T(k)G^2(k)j_1^2(ka) \quad (5.4b)$$

All $\Sigma_j^{(2)}, j \geqslant 4$, have divergent terms. In the spirit of the last section, we keep only the most divergent term in a given order of scattering for the a and b series. Collecting these ring terms, we obtain

$$\sum_{j=3}^{\infty}\Sigma_j^{(2)}(a) = -c^2\hat{k}\hat{k} : \int d\Omega_\alpha\, d\Omega'_\alpha\, d\Omega''_\alpha\, d\Omega'''_\alpha\, \mathbf{r}_\alpha\mathbf{r}_\alpha \int \frac{d^3k'}{(2\pi)^3}$$
$$\times \exp\left[i\mathbf{k}'\cdot(\mathbf{r}'_\alpha - \mathbf{r}''_\alpha)\right]K_\alpha^{-1}(\Omega_\alpha\Omega'_\alpha)K_\alpha^{-1}(\Omega''_\alpha, \Omega'''_\alpha)$$
$$\times G^2(k')T(k')\left\{1 - cT(k')G(k') + \left[cT(k')G(k')\right]^2 - \cdots\right\}$$
$$= -\frac{6}{\pi}\phi^2D_0\int_0^\infty dx\, \frac{\overline{T}(x)j_0^2(x)}{x^2 + 3\phi\overline{T}(x)} \quad (5.5a)$$

In the last equality we have introduced dimensionless terms $x = ka$ and $T(k) = k_D\overline{T}(x)$. For the b series we have

$$\sum_{j=4}^{\infty}\Sigma_j^{(2)}(b) = -c^2\hat{k}\hat{k} : \int d\Omega_\alpha\, d\Omega'_\alpha\, d\Omega''_\alpha\, d\Omega'''_\alpha\, \mathbf{r}_\alpha\mathbf{r}'''_\alpha \int \frac{d^3k'}{(2\pi)^3}$$
$$\times \exp\left[i\mathbf{k}'\cdot(\mathbf{r}'_\alpha - \mathbf{r}''_\alpha)\right]K_\alpha^{-1}(\Omega_\alpha\Omega'_\alpha)K_\alpha^{-1}(\Omega''_\alpha, \Omega'''_\alpha)$$
$$\times G^3(k')T^2(k')\left\{1 - cT(k')G(k') + \left[cT(k')G(k')\right]^2 - \cdots\right\}$$
$$= -\frac{162}{\pi}\phi^3D_0\int_0^\infty dx\, \frac{\overline{T}(x)j_1^2(x)}{x^2\left[x^2 + 3\phi\overline{T}(x)\right]} \quad (5.5b)$$

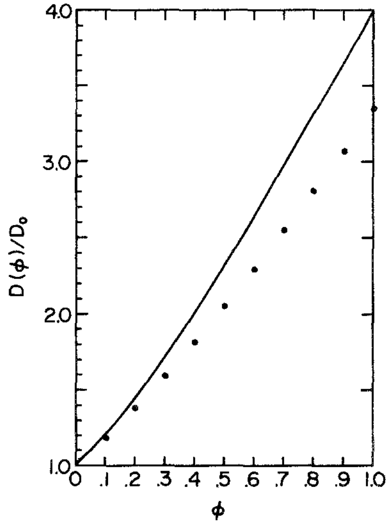

Fig. 2. Diffusion coefficient $D(\phi)/D_0$. Solid line: Full result of Eq. (5.6). Dotted line: Monopole approximation of Eq. (5.7).

Combining Eqs. (5.2)–(5.5) yields

$$\frac{D(\phi)}{D_0} = 1 + 2\phi + \frac{6}{\pi}\phi^2 \int_0^\infty dx\, \frac{\left[9j_1^2(x) - j_0^2(x)\right]\bar{T}(x)}{x^2 + 3\phi \bar{T}(x)} \tag{5.6}$$

This exact result, within the approximation of keeping only the ring terms, is plotted as a function of volume fraction in Fig. 2.

The use of the monopole approximation, $T(k) = k_D$, in Eq. (5.6) yields

$$\frac{D(\phi)}{D_0} = 1 + 2\phi + \frac{18}{5}\phi^2 - \phi\left\{1 - \left(1/2\sqrt{3\phi}\right)\left[1 - \exp\left(-2\sqrt{3\phi}\right)\right]\right\} - 9\phi\left[I_{3/2}\left(\sqrt{3\phi}\right)K_{3/2}\left(\sqrt{3\phi}\right) - 1/3 + 2\phi/15\right] \tag{5.7}$$

where $I_{3/2}$ and $K_{3/2}$ are modified Bessel functions. This approximation is also plotted in Fig. 2.

Expanding Eq. (5.7) in powers of ϕ yields

$$D(\phi)/D_0 = 1 + 2\phi - \sqrt{3}\,\phi^{3/2} + (8/5)\phi^2 - 3\sqrt{3}\,\phi^{5/2} + o(\phi^3) \tag{5.8}$$

6. DISCUSSION

We have presented a multiple scattering approach to the diffusion-controlled reaction between a uniform reactant density field and a random array of stationary reactive sinks. This treatment leads to an exact formulation of the response function, Σ, for the system. Σ contains all the information regarding the concentration dependencies of the rate constant for the reaction and the diffusion constant of the density field. The reaction at any surface point on any sink is described by a scattering operator, T, and we have derived an expression for Σ in terms of any general structure for T. In addition, the many-body effects arising from all the scatterings involving the various sinks are formally incorporated.

When any single sequence of scatterings is considered, divergent integrals can occur. By keeping only the most divergent terms (ring terms) in any given order of scattering operators, we obtain a divergence-free theory for the rate constant and the diffusion constant as given by Eqs. (4.13) and (5.4). We recover the earlier result Eq. (4.15) of Felderhof and Deutch(4) and Lebenhaft and Kapral(5) to the leading order in sink concentration for the rate constant by neglecting the wave vector dependence of T. The Deutch–Felderhof procedure involves a hierarchy of correlation functions which is closed by a superposition approximation. Thus, beyond the leading term ($c^{1/2}$), the two approaches are not directly comparable. Recently, Bixon and Zwanzig(8) calculated D to $o(\phi)$ and we agree with their result as well as with the corrected calculation of Deutch *et al.*(9) This result is analytic since it describes the modification of the diffusion constant by independent spheres. The nonanalytic behavior occurs when multisink correlations are accounted for.

It should be pointed out that at high sink concentration, the macroscopic law, Eq. (3.1), is not correct. The nonlocal effects which are contained in Σ should become important, and the macroscopic equation should be appropriately modified.

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APPENDIX A

The expansion of $G(\mathbf{r}_\alpha, \mathbf{r}'_\alpha)$ in spherical harmonics is

$$G(\mathbf{r}_\alpha, \mathbf{r}'_\alpha) = \sum_{lml'm'} G_{lm;\,l'm'} Y_{lm}(\Omega_\alpha) Y^*_{l'm'}(\Omega'_\alpha) \tag{A.1}$$

where $G_{lm;\,l'm'} = G_l \delta_{ll'} \delta_{mm'} = [D_0 a(2l+1)]^{-1}$. Similarly expanding K_α^{-1} as

$$K_\alpha^{-1}(\Omega_\alpha, \Omega'_\alpha) = \sum_{lml'm'} K^{-1}_{lm;\,l'm'} Y_{lm}(\Omega_\alpha) Y^*_{l'm'}(\Omega'_\alpha) \tag{A.2}$$

we obtain from Eq. (3.2)

$$K^{-1}_{lm;\,l'm'} = \left(G_{lm;\,l'm'}\right)^{-1} = K_l^{-1}\delta_{ll'}\delta_{mm'} \tag{A.3}$$

where

$$K_l^{-1} = D_0 a(2l+1) \tag{A.4}$$

The one-sink rate constant is given by Eq. (4.2) to be

$$k_D = \int d\Omega_\alpha \, d\Omega'_\alpha \, K_\alpha^{-1}(\Omega_\alpha, \Omega'_\alpha) \tag{A.5}$$

Substituting Eqs. (A.2)–(A.4) into Eq. (A.5) and performing the angular integrations yields

$$k_D = 4\pi D_0 a \tag{A.6}$$

Now, we derive Eq. (4.9). Expanding $K_\beta^{-1}(\Omega_\beta, \Omega'_\beta)$ in spherical harmonics, and doing the angular integrations leads to

$$\begin{aligned} T(\mathbf{k}) &= \int d\Omega_\beta \, d\Omega'_\beta \exp\left[-i\mathbf{k}\cdot(\mathbf{r}_\beta - \mathbf{r}'_\beta)\right] K_\beta^{-1}(\Omega_\beta, \Omega'_\beta) \\ &= (4\pi)^2 \sum_l j_l^2(ka) K_l^{-1} \sum_{m=-l}^{l} Y_{lm}(\Omega_k) Y^*_{lm}(\Omega_k) \\ &= k_D \sum_l (2l+1)^2 j_l^2(ka) \end{aligned} \tag{A.7}$$

where we have utilized Eq. (A.4).

APPENDIX B

In this appendix, we present a derivation of the microscopic density field of the reactant for the general reaction boundary condition, Eq. (2.9), instead of the simpler complete absorption condition treated in the text.

Substituting Eq. (3.1) for $n(\mathbf{r})$ on the right-hand side of Eq. (2.9), we obtain

$$n(\mathbf{R}_\alpha) = -\sum_{\beta=1}^{N} \int d\Omega_\beta \, \mathcal{G}_\alpha(\mathbf{R}_\alpha) G(\mathbf{R}_\alpha - \mathbf{R}_\beta) \sigma_\beta(\Omega_\beta) \tag{B.1}$$

since $n_0(\mathbf{r})$ is assumed to be uniform everywhere. Use of Eq. (B.1) in Eq. (3.3) yields

$$\begin{aligned} \sigma_\alpha(\Omega_\alpha) &- \int d\Omega'_\alpha \, d\Omega''_\alpha \, K_\alpha^{-1}(\Omega_\alpha, \Omega'_\alpha) \mathcal{G}_\alpha(R'_\alpha) G(R'_\alpha - R''_\alpha) \sigma_\alpha(\Omega''_\alpha) \\ &= \int d\Omega'_\alpha \, K_\alpha^{-1}(\Omega_\alpha, \Omega'_\alpha) n_0(R'_\alpha) - \sum_{\beta\neq\alpha} \int d\Omega'_\alpha \, d\Omega_\beta \, K_\alpha^{-1}(\Omega_\alpha, \Omega'_\alpha) \\ &\quad \times \left[1 - \mathcal{G}_\alpha(R'_\alpha)\right] G(R'_\alpha - R_\beta) \sigma_\beta(\Omega_\beta) \end{aligned} \tag{B.2}$$

Iterating Eq. (B.2) we get

$$\begin{aligned}\sigma_\alpha(\Omega_\alpha) = &\int d\Omega'_\alpha\, d\Omega''_\alpha\; g(\Omega_\alpha,\Omega'_\alpha)K_\alpha^{-1}(\Omega'_\alpha,\Omega''_\alpha)n_0(R''_\alpha)\\ &-\sum_{\beta\neq\alpha}\int d\Omega'_\alpha\, d\Omega''_\alpha\, d\Omega_\beta\, d\Omega'_\beta\, d\Omega''_\beta\\ &\times g(\Omega_\alpha,\Omega'_\alpha)K_\alpha^{-1}(\Omega'_\alpha,\Omega''_\alpha)\left[1-\mathcal{G}_\alpha(R''_\alpha)\right]G(R''_\alpha-R_\beta)\\ &\times g(\Omega_\beta,\Omega'_\beta)K_\beta^{-1}(\Omega'_\beta,\Omega''_\beta)n_0(R''_\beta)\\ &+\sum_{\beta\neq\alpha}\sum_{\gamma\neq\beta}\int\cdots gK_\alpha^{-1}(1-\mathcal{G}_\alpha)GgK_\beta^{-1}(1-\mathcal{G}_\beta)GgK_\gamma^{-1}n_0 \qquad \text{(B.3)}\end{aligned}$$

where g is defined by

$$\begin{aligned}&\int d\Omega''_\alpha\left[\delta(\Omega_\alpha-\Omega''_\alpha)-\int d\Omega'''_\alpha K^{-1}(\Omega_\alpha,\Omega'''_\alpha)\right.\\ &\qquad\left.\times\mathcal{G}_\alpha(R'''_\alpha)G(R'''_\alpha-R''_\alpha)\right]g(\Omega''_\alpha,\Omega'_\alpha)=\delta(\Omega_\alpha-\Omega'_\alpha) \qquad \text{(B.4)}\end{aligned}$$

Representing G as its Fourier transform and explicitly using the operator from Eq. (2.9) we obtain

$$\begin{aligned}&\int d\Omega'_\alpha\, d\Omega''_\alpha\, K_\alpha^{-1}(\Omega''_\alpha,\Omega'_\alpha)\mathcal{G}_\alpha(R'_\alpha)G(R'_\alpha-R_\alpha)\\ &\quad=\frac{ik_D}{D_0k_0}\int d\Omega'_\alpha\, d\Omega''_\alpha\int\frac{d^3k}{(2\pi)^3}K_\alpha^{-1}(\Omega''_\alpha,\Omega'_\alpha)\\ &\qquad\times\mathbf{r}'_\alpha\cdot\mathbf{k}k^{-2}\exp\left[i\mathbf{k}\cdot(\mathbf{r}'_\alpha-\mathbf{r}_\alpha)\right]\\ &\quad=\frac{(4\pi)^2k_DK_0^{-1}}{(2\pi)^3D_0k_0}\sum_{\lambda'\mu'}\sum_{m=-1}^{+1}\int_0^\infty dk\, j_1(ka^+)j_{\lambda'}(ka)(-i)^{\lambda'}Y_{\lambda'\mu'}(\Omega_\alpha)\\ &\qquad\times\left[\int d\Omega'_\alpha\,\mathbf{r}'_\alpha Y^*_{1m}(\Omega'_\alpha)\right]\left[\int d\Omega_k\,\mathbf{k}Y_{1m}(\Omega_k)Y^*_{\lambda'\mu'}(\Omega_k)\right]\\ &\quad=-k_D/k_0 \qquad \text{(B.5)}\end{aligned}$$

The second equality in Eq. (B.5) is obtained by expanding K_α^{-1} in spherical harmonics and performing the Ω'_α integration. The superscript on a in the argument of j_1 in Eq. (B.5) indicates that the limit of a is approached from outside the sink in the use of $\mathcal{G}$. If we keep only the monopole term in the expansion of σ, we get from Eqs. (B.5) and (B.4)

$$g(\Omega_\alpha,\Omega'_\alpha)=\left(1+\frac{k_D}{k_0}\right)^{-1}\delta(\Omega_\alpha,\Omega'_\alpha)\equiv g\delta(\Omega_\alpha,\Omega'_\alpha) \qquad \text{(B.6)}$$

Utilizing Eq. (B.3) in Eq. (3.1), the average density field becomes

$$\begin{aligned}\langle n(\mathbf{r})\rangle = n_0(\mathbf{r}) &- \sum_{\alpha} \int d\mathbf{r}'\, d\mathbf{r}''\, G(\mathbf{r}-\mathbf{r}')\langle \tilde{T}_\alpha(r'-\mathbf{r}'')\rangle n_0(\mathbf{r}'') \\ &+ \sum_{\alpha} \sum_{\beta\neq\alpha} \int d\mathbf{r}'\, d\mathbf{r}''\, d\mathbf{r}'''\, d\mathbf{r}^{iv}\, G(\mathbf{r}-\mathbf{r}')\langle T_\alpha(\mathbf{r}'-\mathbf{r}'') \\ &\times \tilde{G}(\mathbf{r}''-\mathbf{r}''')\tilde{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv})\rangle n_0(\mathbf{r}^{iv}) \\ &- \sum_{\alpha} \sum_{\beta\neq\alpha} \sum_{\gamma\neq\beta} \int \cdots G\langle \tilde{T}_\alpha \tilde{G} \tilde{T}_\beta \tilde{G} \tilde{T}_\gamma \rangle n_0 + \cdots \end{aligned} \tag{B.7}$$

where $\tilde{T}_\alpha(\mathbf{r}) = gT_\alpha(\mathbf{r})$ and

$$\tilde{T}_\alpha(\mathbf{r}-\mathbf{r}')\tilde{G}(\mathbf{r}'-\mathbf{r}'') = \tilde{T}_\alpha(\mathbf{r}-\mathbf{r}')[1-\mathcal{G}_\alpha(r')]G(\mathbf{r}'-\mathbf{r}'') \tag{B.8}$$

Combination of Eqs. (B.7) and (3.8) gives an expression for Σ which is then used to obtain k_f and $D(c)$ for the general radiation boundary condition. The leading term for k_f is, from Eqs. (B.6)–(B.8) and (3.8)

$$\Sigma(k=0) = g\int d\Omega_\alpha\, d\Omega'_\alpha\, K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha) = \left(\frac{k_0 k_D}{k_0+k_D}\right) \tag{B.9}$$

It is natural to consider the radiation boundary condition with the further stipulation that the density at $r=a$ is angle independent. Then $\sigma(\Omega_\alpha)$ is also angle independent to leading order in concentration, and Eqs. (B.5), (B.6), and (B.9) are exact. Within this context it is straightforward to calculate the concentration dependencies of $k_f(c)$ and $D(c)$. For the rate constant, the result presented in Eq. (4.13) is modified merely by a scaling of k_D to gk_D. The factors of $\mathcal{G}$ in Eq. (B.7) lead to less divergent terms in a given order of scattering.

APPENDIX C

We show here that the term $S(\mathbf{r}-\mathbf{r}') \equiv \langle T_\alpha G T_{\beta\neq\alpha} G T_\alpha G T_{\beta\neq\alpha}\rangle$ is less divergent than the ring term $\langle T_\alpha G T_{\beta\neq\alpha} G T_{\gamma\neq\beta} G T_\alpha\rangle$. The Fourier transform of S satisfies

$$|S(\mathbf{k})| \leqslant S(\mathbf{k}=0) \tag{C.1}$$

so that we need only consider this limit. Explicitly,

$$\begin{aligned} S(\mathbf{k}=0) \sim \int (\pi d\Omega) \int d^3k'\, d^3k'' \\ &\times \exp[i\mathbf{k}'\cdot(\mathbf{r}'_\alpha - \mathbf{r}'''_\alpha - \mathbf{r}_\beta + \mathbf{r}''_\beta)] \\ &\times \exp[i\mathbf{k}''\cdot(-\mathbf{r}''_\alpha + \mathbf{r}'''_\alpha + \mathbf{r}'_\beta - \mathbf{r}''_\beta)] \\ &\times K_\alpha^{-1}(\Omega_\alpha,\Omega'_\alpha) K_\alpha^{-1}(\Omega''_\alpha\Omega'''_\alpha) K_\beta^{-1}(\Omega_\beta,\Omega'_\beta) K_\beta^{-1}(\Omega''_\beta,\Omega'''_\beta) \\ &\times \frac{1}{k'^2 k''^2}\, \frac{1}{|\mathbf{k}''-\mathbf{k}'|^2} \end{aligned} \tag{C.2}$$

In Eq. (C.2) we suppress numerical factors and use $\sim$ to indicate proportionately. The symbol $\pi d\Omega$ denotes integration over all the appropriate orientations. The divergence comes from $\mathbf{k}', \mathbf{k}'' \rightarrow 0$, so we set the exponential factors to unity, and integrate over the K^{-1} angular dependencies to obtain

$$S(\mathbf{k}=0) \sim \int d^3k' \int d^3k'' \frac{1}{k'^2} \frac{1}{k''^2} \frac{1}{|k''-k'|^2} \sim \int_0^\infty dk' \int_0^\infty dk'' \frac{1}{|k''-k'|^2} \tag{C.3}$$

If we replace $1/k^2$ by $1/(k^2+\epsilon^2)$ in Eq. (C.3), which corresponds to the **r**-space propagator $e^{-\epsilon r}/4\pi r$, then the nature of the large r divergence is manifested as $\epsilon \rightarrow 0$. Using this propagator in Eq. (C.3) and transforming to **r** space yields

$$S(\mathbf{k}=0,\epsilon) \sim \int_0^\infty dr\, \frac{e^{-\epsilon r}}{r} \tag{C.4}$$

With regard to large r, this diverges as $ln\epsilon$. By contrast, the ring term of the same number of scatterings given in Eq. (4.11) goes as

$$\Sigma_4(\mathbf{k}=0) \sim \int_0^\infty dk\, k^2 G^3(k) \tag{C.5}$$

and using $G(k) = 1/(k^2+\epsilon^2)$ shows that Σ_4 diverges as $\Sigma_4(\mathbf{k}=0,\epsilon) \sim 1/\epsilon^3$.

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