

## **Diffusion-Controlled Processes Among Partially Absorbing Stationary Sinks**

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A general linear response theory is presented to calculate the zero-wave-vector and zero-frequency reaction rate coefficient for particles diffusing into absorbing spheres. Allowance is made for possible incomplete particle absorption. A Faxén-like theorem for chemical reactions is derived. The problem is solved completely for a simple regular array of sinks. Exact analytic expressions for the rate coefficient as a function of sink volume fraction are obtained for the sc and fcc lattices. The case of a disordered array of sinks is also considered and the leading order nonanalytic density dependence of the rate coefficient is calculated. In both cases an increase in the rate coefficient with sink density in a local region of the system is found. The general formalism is extended to examine the modification to the particle diffusion coefficient due to the presence of the spheres. For regular arrays of spheres, the mean field result is reproduced.

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**KEY WORDS:** Diffusion-controlled kinetics; diffusion; suspensions of spheres; regular arrays.

### **1. INTRODUCTION**

The description of diffusion-controlled reactions has a long history, dating back to Smoluchowski's pioneering study in 1916.<sup>(1)</sup> The majority of the subsequent investigations have been concerned with the absorption of particles by a single sink, but there have been some studies of competition effects due to the presence of many sinks.<sup>(2)</sup> Our study is most close in spirit to the work of Felderhof and Deutch<sup>(3)</sup> on such competition effects and the resulting concentration dependence of the rate coefficient.

In this study, we present a general formalism enabling us to obtain, in the linear response regime, an exact expression for the reaction rate coefficient

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for particles diffusing among an arbitrary arrangement of stationary spherical sinks. The fluid in which the sinks are suspended and through which the particles diffuse is treated as a continuum. Allowance is made for the possibility of an incomplete absorption of particles. In a separate section, we extend our formal theory to facilitate an examination of the effect that the presence of spheres in the fluid has on the diffusion coefficient of the particles.

In Section 2, starting from the diffusion equation, extended to all space by an appropriate sink term, we derive an expression for the reaction rate coefficient, in the zero-wavevector limit, expressed in terms of an internal response function, relating the sink and density fields, and the diffusion propagator. The dependence of the internal response function on the external one-sink response function is next established by means of a local field analysis.

In Section 3, in the course of investigating the nature of the external one-sink response function, we determine its symmetry properties and then derive its explicit form using two different methods. Both techniques, nevertheless, are based on the multipole expansion of the one-sink response function and use the “radiation” boundary condition. The calculation of the first two moments of the sink field, besides being instructive by itself, allows us to establish a Faxén-like theorem for chemical reactions, similar to the extension of the usual Faxén theorem derived by Mazur and Bedeaux.<sup>(4)</sup> Since the calculation of higher multipoles by this method becomes prohibitively difficult, we present an alternative calculation—valid for *all* terms in the expansion—in the zero-frequency limit.

To demonstrate a numerical calculation utilizing the general theory, we solve completely, in Section 4, the problem for an infinite regular array of sinks, examining in particular the simple cubic and face-centered cubic lattices. These regular array calculations employ techniques used earlier in the study of the dielectric properties of crystals<sup>(5)</sup> and the effective viscosity of regular arrays of spheres.<sup>(6)</sup> For the steady-state situation, we find that only the monopole term of the one-sink response function multipole expansion contributes, due to the highly symmetric nature of the cubic lattices. Our calculation, which is valid for all sink concentrations, predicts the rate coefficient, which measures the rate of disappearance of particles in a locally uniform region of the system, to increase with the sink volume fraction. Moreover, for this system we are able to obtain an analytic expression for the rate coefficient for all concentrations.

In Section 5, we consider the application of the general formalism developed in Section 2 to the case of an irregular array of suspended sinks. Although a complete analysis of this situation is not attempted, the lowest order nonanalytic sink density correction to the rate coefficient is calculated. The calculation closely parallels the Debye–Hückel theory of electrolyte

solutions: First, a formal density expansion of the rate coefficient is carried out, leading to divergent integrals in certain classes of events. The most divergent ring events are next identified and summed to yield a correction to the rate coefficient, which varies as the square root of the sink concentration. Our result to this order agrees with that of Felderhof and Deutch.<sup>(3)</sup>

In Section 6, where we examine the modification to the diffusion coefficient, we reproduce the mean field result for a regular array of spheres. Relative to the diffusion coefficient of the particles in the absence of the sinks, we observe a decrease for the complete reflection boundary condition.

The results are summarized and discussed in Section 7.

## 2. GENERAL THEORY<sup>2</sup>

### 2.1. Formal Results

The equation of motion for particles diffusing among stationary reacting sinks is given by

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) = D_0 \nabla^2 n(\mathbf{r}, t) - \mathcal{S}(\mathbf{r}, t) \quad (1)$$

where  $n(\mathbf{r}, t)$  is the density field of the diffusing particles,  $D_0$  is the diffusion coefficient in the absence of sinks, and  $\mathcal{S}(\mathbf{r}, t)$  is some appropriate sink term. The introduction of this sink term precludes the necessity for specifying the boundary conditions on the surface of the sink at this stage of the calculation.<sup>3</sup>

The formal solution of Eq. (1) is

$$n(\mathbf{r}, t) = n_0(\mathbf{r}, t) - \int d\mathbf{r}' dt' \mathcal{G}_0(\mathbf{r} - \mathbf{r}', t - t') \mathcal{S}(\mathbf{r}', t') \quad (2)$$

where  $n_0(\mathbf{r}, t)$  is a solution of the diffusion equation without sink term present, and the diffusion propagator  $\mathcal{G}_0(\mathbf{r}, t)$  is given by

$$\mathcal{G}_0(\mathbf{r}, t) = (4\pi D_0 t)^{-3/2} \exp(-r^2/D_0 t) \quad (3)$$

<sup>2</sup> A study of the shear viscosity of a suspension of spheres using analogous techniques can be found in Ref. 7.

<sup>3</sup> In this paper we shall primarily be concerned with the structure of the frequency-dependent rate coefficient  $k_f(\omega)$ . In order to obtain an expression for this quantity we do not need to pose a specific initial value problem; rather it is convenient to work with the Fourier components of the density field. For the relation of this type of formalism to the solution of specific initial value problems see, e.g., Ref. 14.

In the linear response regime, the sink field  $\mathcal{S}(\mathbf{r}, t)$  can be related to the density field by the response function  $s(\mathbf{r}, t|\mathbf{r}', t')$ ,

$$\mathcal{S}(\mathbf{r}, t) = \int d\mathbf{r}' dt' s(\mathbf{r}, t|\mathbf{r}', t')n(\mathbf{r}', t') \equiv sn \quad (4)$$

Thus, the internal response function  $s$  formally accounts for the overall perturbing effect that the presence of the suspended spheres has on the density field of the particles diffusing through the solvent. When this expression is used in Eq. (2), we can write the formal relation

$$n = (1 + \mathcal{G}_0 s)^{-1} n_0 \quad (5)$$

and using Eq. (5) in (4), we find

$$\mathcal{S} = s(1 + \mathcal{G}_0 s)^{-1} n_0 \quad (6)$$

Ensemble-averaging Eqs. (5) and (6) over the sink distribution, it is easy to show that

$$\langle \mathcal{S} \rangle = \langle s(1 + \mathcal{G}_0 s)^{-1} \rangle \langle (1 + \mathcal{G}_0 s)^{-1} \rangle^{-1} \langle n \rangle \equiv S \langle n \rangle \quad (7)$$

The average above may be interpreted as an average over regions large compared to the sinks and small compared to the variations in  $n_0$ , or as an ensemble average over sphere configurations, e.g.,

$$\langle \text{----} \rangle = \Xi^{-1} \sum_{N=1}^{\infty} \frac{z^N}{N!} \int d\mathbf{R}_1 \dots d\mathbf{R}_N \exp[-\beta W_N(\mathbf{R}^N)] \text{----}$$

where  $\Xi$  is the grand partition function and  $W_N$  is the effective potential energy for  $N$  sinks in the fluid, which determines the sink distribution.

More explicitly, in  $(\mathbf{k}, \omega)$  representation we can write

$$\langle \mathcal{S} \rangle(\mathbf{k}, \omega) = (2\pi)^{-4} \int d\mathbf{k}' d\omega' S(\mathbf{k}, \omega|\mathbf{k}', \omega') \langle n \rangle(\mathbf{k}', \omega') \quad (8)$$

Due to the stationarity and translational invariance of the system,  $S(\mathbf{k}, \omega|\mathbf{k}', \omega')$  is diagonal:

$$S(\mathbf{k}, \omega|\mathbf{k}', \omega') = S(\mathbf{k}, \omega)(2\pi)^4 \delta(\mathbf{k} - \mathbf{k}') \delta(\omega - \omega') \quad (9)$$

We shall identify the  $\mathbf{k} = 0$  limit of  $S(\mathbf{k}, \omega)$  with the rate coefficient

$$k_f(\omega) = S(\mathbf{k} = 0, \omega) N_s^{-1} \quad (10)$$

where  $N_s$  is the number density of the sinks.

Higher order terms in  $\mathbf{k}$  will yield corrections to the diffusion coefficient because of the presence of sink terms. This division is somewhat arbitrary for the higher order terms. In this article, we shall primarily be concerned with the structure of the rate coefficient  $k_f$ .

## 2.2. Local Field Analysis

In order to obtain the rate coefficient we must first calculate the response function  $s$  in Eq. (4). In this subsection, we show how  $s$  can be related to the external response function for a *single* sink:

$$\mathcal{S}(\mathbf{r}, t) = \int d\mathbf{r}' dt' \sigma(\mathbf{r}, t | \mathbf{r}', t') n_0(\mathbf{r}', t') \quad (11)$$

If there are  $N$  sinks in the fluid, then

$$\mathcal{S}(\mathbf{r}, t) = \sum_{i=1}^N \mathcal{S}_i(\mathbf{r}, t) \quad (12)$$

where  $\mathcal{S}_i(\mathbf{r}, t)$  is the sink field term corresponding to the  $i$ th sink. For this case, we can replace  $n_0$  in Eq. (11) by the effective density field, which *also* contains the density field due to all other sinks,

$$\mathcal{S}_i(\mathbf{r}, t) = \int d\mathbf{r}' dt' \sigma(\mathbf{r} - \mathbf{R}_i, t | \mathbf{r}' - \mathbf{R}_i, t') n_{i,\text{eff}}(\mathbf{r}', t') \quad (13)$$

where [cf. Eq. (2)]

$$n_{i,\text{eff}}(\mathbf{r}, t) = n_0(\mathbf{r}, t) - \sum_{j \neq i} \int d\mathbf{r}' dt' \mathcal{G}_0(\mathbf{r} - \mathbf{r}', t - t') \mathcal{S}_j(\mathbf{r}', t') \quad (14)$$

Assuming that the sinks are nonoverlapping and nontouching spheres of radius  $a$ , and introducing the cutoff function

$$\theta(\mathbf{r}) = \begin{cases} 0 & \text{if } r < l \\ 1 & \text{if } r > l \end{cases}$$

where  $l$  can lie between  $\epsilon$  and  $2a - \epsilon$ , with  $\epsilon$  an infinitesimally small positive number,<sup>4</sup> we find that Eq. (14) becomes

$$\begin{aligned} n_{i,\text{eff}}(\mathbf{r}, t) &= n_0(\mathbf{r}, t) - \sum_{j \neq i} \int d\mathbf{r}' dt' \mathcal{G}_0(\mathbf{r} - \mathbf{r}', t - t') \theta(\mathbf{r}' - \mathbf{R}_i) \mathcal{S}_j(\mathbf{r}', t') \\ &= n_0(\mathbf{r}, t) - \int d\mathbf{r}' dt' \mathcal{G}_0(\mathbf{r} - \mathbf{r}', t - t') \theta(\mathbf{r}' - \mathbf{R}_i) \mathcal{S}(\mathbf{r}', t') \end{aligned} \quad (15)$$

Summing Eq. (13) over  $i$  and using Eq. (15), we have that

$$\begin{aligned} \mathcal{S}(\mathbf{r}, t) &= \int d\mathbf{r}' dt' \sigma_b(\mathbf{r}, t | \mathbf{r}', t') n_0(\mathbf{r}', t') \\ &\quad - \int d\mathbf{r}' dt' H_\sigma(\mathbf{r}, t | \mathbf{r}', t') \mathcal{S}(\mathbf{r}', t') \end{aligned} \quad (16)$$

or, in formal notation,

$$\mathcal{S} = \sigma_b n_0 - H_\sigma \mathcal{S} \quad (17)$$

<sup>4</sup> The flexibility in the choice of  $l$  arises from the use of the multiple expansion (see Ref. 7).

In writing Eq. (16), we have defined the following two operators:

$$\sigma_b(\mathbf{r}, t | \mathbf{r}', t') \equiv \sum_{i=1}^N \sigma(\mathbf{r} - \mathbf{R}_i, t | \mathbf{r}' - \mathbf{R}_i, t') \quad (18)$$

and

$$\begin{aligned} H_\sigma(\mathbf{r}, t | \mathbf{r}', t') \\ \equiv \sum_{i=1}^N \int d\mathbf{r}'' dt'' \sigma(\mathbf{r} - \mathbf{R}_i, t | \mathbf{r}'' - \mathbf{R}_i, t'') \mathcal{G}_0(\mathbf{r}'' - \mathbf{r}', t'' - t') \theta(\mathbf{r}' - \mathbf{R}_i) \end{aligned} \quad (19)$$

If we use Eq. (2) for  $n_0$  in Eq. (17), and solve the resulting equation for  $\mathcal{S}$ , we find

$$\mathcal{S} = (1 + H_\sigma - \sigma_b \mathcal{G}_0)^{-1} \sigma_b n \quad (20)$$

Comparison with Eq. (4) yields

$$s = (1 + H_\sigma - \sigma_b \mathcal{G}_0)^{-1} \sigma_b \quad (21)$$

Equation (21) expresses the response function  $s$  in terms of the one-sink response function  $\sigma$  and the propagator  $\mathcal{G}_0$ . The following section is devoted to the calculation of the response function for a single sink in an arbitrary density field.

### 3. ONE-SINK RESPONSE FUNCTION

The form of the one-sink response function depends on the nature of the boundary conditions that the density field satisfies on the sink's surface. In the calculations which follow, we assume that the sinks are spherical and make use of the ‘‘radiation’’ boundary condition<sup>(8)</sup>:

$$k_D \mathbf{r} \cdot \nabla n(\mathbf{r}, \omega) = k_0 n(\mathbf{r}, \omega) \quad \text{at } r = a \quad (22)$$

where  $k_D = 4\pi D_0 a$  is the Smoluchowski rate coefficient and  $k_0$  is a parameter which can be identified as a specific bimolecular rate constant. When  $k_0 = \infty$ , we have complete absorption of particles on the sink's surface, while if  $k_0 = 0$  there is no reaction.

In order to calculate the response function, we made use of a multipole expansion,

$$\begin{aligned} \sigma(\mathbf{r}, t | \mathbf{r}', t') &= \sigma(\mathbf{r}, t - t' | \mathbf{r}') \\ &= \sum_{m, n=0}^{\infty} (-1)^{m+n} (m! n!)^{-1} \sigma^{mn}(t - t') \odot [\nabla^n \delta(\mathbf{r})][\nabla^m \delta(\mathbf{r}')] \end{aligned} \quad (23)$$

or in  $(k, \omega)$  space,

$$\begin{aligned} \sigma(\mathbf{k}, \omega | \mathbf{k}', \omega') &= \sigma(\mathbf{k}, \omega | \mathbf{k}') 2\pi \delta(\omega - \omega') \\ &= \sum_{m,n=0}^{\infty} (m! n!)^{-1} \sigma^{mn}(\omega) \odot (-i\mathbf{k})^n (i\mathbf{k}')^m 2\pi \delta(\omega - \omega') \end{aligned} \quad (24)$$

In the following subsections, we shall discuss the various properties of  $\sigma$  and derive its explicit form using two different techniques.

### 3.1. Symmetry Properties

By an analysis similar to that in Appendix A of Ref. 7, one may easily establish that the one-sink response function satisfies the following symmetry relations:

$$\sigma(\mathbf{r}, t | \mathbf{r}') = \sigma(\mathbf{r}', t | \mathbf{r}) \quad (25)$$

and

$$\sigma^{mn}(t) = \sigma^{nm}(t) \quad (26)$$

In Fourier space, these relations are

$$\sigma(\mathbf{k}, \omega | \mathbf{k}') = \sigma(-\mathbf{k}', \omega | -\mathbf{k}) \quad (27)$$

and

$$\sigma^{mn}(\omega) = \sigma^{nm}(\omega) \quad (28)$$

### 3.2. Direct Calculation of Moments

Pursuing the strategy outlined in Appendix B of Ref. 7, we shall calculate the first two terms of the response function's multipole expansion. The calculation uses techniques developed by Bedeaux and Mazur in a generalization of Faxén's theorem,<sup>(4)</sup> and will in fact establish a Faxén-like theorem for chemical reactions.<sup>5</sup>

We first write the sink term as a multipole expansion

$$\mathcal{S}(\mathbf{r}, \omega) = \sum_{n=0}^{\infty} (-1)^n (n!)^{-1} \mathbf{S}^n(\omega) \odot [\nabla^n \delta(\mathbf{r})] \quad (29)$$

where the  $n$ th-rank tensor  $\mathbf{S}^n(\omega)$  is given by the  $n$ th moment of  $\mathcal{S}(\mathbf{r}, \omega)$ ,

$$S_{v_1 v_2 \dots v_n}^n = \int_{\mathbf{v}} d\mathbf{r} \mathcal{S}(\mathbf{r}, \omega) r_{v_1} r_{v_2} \dots r_{v_n} \quad (30)$$

<sup>5</sup> The calculation of the moments for the radiation boundary condition is also similar to the partial slip calculation of Faxén's theorem carried out by Albano *et al.*<sup>(9)</sup>

Since these moments can be related to the corresponding terms in the multipole expansion for the response function,<sup>(7)</sup> i.e.,

$$\mathbf{S}^n(\omega) = \sum_{m=0}^{\infty} (m!)^{-1} \sigma^{mn}(\omega) \odot [(\nabla')^m n_0(\mathbf{r}', \omega)]_{\mathbf{r}'=0} \quad (31)$$

we can solve for the  $\sigma^{mn}$  by explicitly calculating the appropriate moments.

Averaging Eq. (22) over the sink's surface, one obtains

$$k_D \overline{a\mathbf{r} \cdot \nabla n(\mathbf{r}, \omega)^S} = k_0 \overline{n(\mathbf{r}, \omega)^S} \quad (32)$$

where

$$\overline{(\dots)^S} = (4\pi a^2)^{-1} \int_V d\mathbf{r} \delta(r - a)(\dots)$$

Applying the divergence theorem to the right side of Eq. (32), one can easily verify that

$$\frac{1}{3} k_D a^2 \overline{\nabla^2 n(\mathbf{r}, \omega)^V} = k_0 \overline{n(\mathbf{r}, \omega)^S} \quad (33)$$

where  $\overline{(\dots)^V}$  denotes a volume average:

$$\overline{(\dots)^V} = (4\pi a^3/3)^{-1} \int_V d\mathbf{r} (\dots)$$

If we take the surface average of the time Fourier transform of Eq. (2), we find

$$\overline{n(\mathbf{r}, \omega)^S} = \overline{n_0(\mathbf{r}, \omega)^S} - A(\omega) \quad (34)$$

where

$$A(\omega) = \mathcal{G}_0(a, \omega) \int d\mathbf{r}' (\alpha r')^{-1} \sinh(\alpha r') \mathcal{S}(\mathbf{r}', \omega) \quad (35)$$

and

$$\mathcal{G}_0(\mathbf{r}, \omega) = (4\pi D_0 r)^{-1} \exp(-\alpha r) \quad (36)$$

with  $\alpha = (-i\omega/D_0)^{1/2}$ . It now readily follows from the Fourier transform of Eq. (1) that

$$\nabla^2 n(\mathbf{r}, \omega) = \alpha^2 n(\mathbf{r}, \omega) + D_0^{-1} \mathcal{S}(\mathbf{r}, \omega) \quad (37)$$

and the radiation boundary condition can be rewritten as

$$\frac{1}{3} k_D (\alpha a)^2 \overline{n(\mathbf{r}, \omega)^V} + \int_V d\mathbf{r} \mathcal{S}(\mathbf{r}, \omega) = k_0 \overline{n(\mathbf{r}, \omega)^S} \quad (38)$$

Since  $\overline{n(\mathbf{r}, \omega)^V} = 0$ , and with the use of Eq. (34), we find that Eq. (38) simplifies to

$$\int_V d\mathbf{r} \mathcal{S}(\mathbf{r}, \omega) = k_0 \overline{n_0(\mathbf{r}, \omega)^S} - k_0 A(\omega) \quad (39)$$



and hence,

$$A(\omega) = \overline{n_0(\mathbf{r}, \omega)^S} - k_0^{-1} \int_V d\mathbf{r} \mathcal{S}(\mathbf{r}, \omega) \quad (40)$$

Next, averaging Eq. (2) over the volume of the sink and noting again that  $\overline{n(\mathbf{r}, \omega)^V} = 0$ , one obtains

$$0 = \overline{n_0(\mathbf{r}, \omega)^V} - \frac{3(\alpha a)^{-2}}{k_D} \int_V d\mathbf{r}' \mathcal{S}(\mathbf{r}', \omega) + 3(\alpha a)^{-2}(1 + \alpha a)A(\omega) \quad (41)$$

Making use of Eq. (40), we finally obtain the expression for the first moment of  $\mathcal{S}(\mathbf{r}, \omega)$ :

$$\int_V d\mathbf{r} \mathcal{S}(\mathbf{r}, \omega) = \frac{k_D k_0}{k_0 + k_D(1 + \alpha a)} \left[ \frac{(\alpha a)^2}{3} \overline{n_0(\mathbf{r}, \omega)^V} + (1 + \alpha a) \overline{n_0(\mathbf{r}, \omega)^S} \right] \quad (42)$$

The flux of particles across the surface of the sink,  $\Phi$ , can be obtained by integrating Eq. (1), for the case of a single sink, over the volume of the sink. The result is

$$\Phi(\omega) = 4\pi a^2 D_0 \left( \frac{\partial n(\mathbf{r}, \omega)}{\partial r} \right)_{r=a} = \int_V d\mathbf{r} \mathcal{S}(\mathbf{r}, \omega) \quad (43)$$

or, using Eq. (42),

$$\Phi(\omega) = \frac{k_D k_0}{k_0 + k_D(1 + \alpha a)} \left[ \frac{(\alpha a)^2}{3} \overline{n_0(\mathbf{r}, \omega)^V} + (1 + \alpha a) \overline{n_0(\mathbf{r}, \omega)^S} \right] \quad (44)$$

Equation (44) constitutes a type of generalized Faxén theorem for reactions, in that the particle flux, being the analog of the force, is related to the surface and volume averages of the density field in the absence of the sink.<sup>(4)</sup>

If we consider the case of a constant external density field  $n_0(\omega)$  and use the fact that  $\nabla^2 n_0(\mathbf{r}, \omega) = \alpha^2 n_0(\mathbf{r}, \omega)$ , then Eq. (44) becomes

$$\Phi(\omega) \equiv k_f(\omega) n_0(\omega) = \frac{k_D k_0 (1 + \alpha a)}{k_0 + k_D (1 + \alpha a)} n_0(\omega) \quad (45)$$

Hence, the rate coefficient for a *dilute* suspension of partially absorbing sinks in a uniform external density field is

$$k_f(\omega) = \frac{k_0 k_D (1 + \alpha a)}{k_0 + k_D (1 + \alpha a)} \quad (46)$$

In Appendix A, we demonstrate that

$$\overline{n_0(\mathbf{r}, \omega)^S} = (\alpha a)^{-1} \sinh(\alpha a) n_0(r = 0, \omega)$$

and

$$\overline{n_0(\mathbf{r}, \omega)^V} = 3(\alpha a)^{-1} [\cosh(\alpha a) - (\alpha a)^{-1} \sinh(\alpha a)] n_0(r = 0, \omega) \quad (47)$$

so that for the more general case of arbitrary external density fields,

$$\int_V d\mathbf{r} \mathcal{S}(\mathbf{r}, \omega) = \frac{k_0 k_D e^{\alpha a}}{k_0 + k_D(1 + \alpha a)} n_0(\mathbf{r} = 0, \omega) \quad (48)$$

Consulting Eqs. (29)–(31) and (48), we single out

$$\begin{aligned} S^0(\omega) &= \int_V d\mathbf{r} \mathcal{S}(\mathbf{r}, \omega) = \frac{k_0 k_D e^{\alpha a}}{k_0 + k_D(1 + \alpha a)} n_0(\mathbf{r} = 0, \omega) \\ &= \sum_{m=0}^{\infty} (m!)^{-1} \sigma^{m0}(\omega) \odot [(\nabla')^m n_0(\mathbf{r}', \omega)]_{\mathbf{r}'=0} \end{aligned} \quad (49)$$

from which we conclude that

$$\sigma^{00}(\omega) \equiv \sigma^{00}(\omega) \equiv k_j^{(0)}(\omega) = \frac{k_0 k_D e^{\alpha a}}{k_0 + k_D(1 + \alpha a)} \quad (50)$$

and

$$\sigma^{m0}(\omega) = 0 \quad \text{for } m \neq 0 \quad (51)$$

The calculation of the second moment follows a similar strategy. Only the result is presented below, and some details are given in Appendix B. We find

$$\begin{aligned} \sigma^{11}(\omega) = \sigma^{11} \mathbf{1} &= \left[ 1 - \frac{3k_D[1 + \alpha a + \frac{1}{3}(\alpha a)^2]}{(1 + \alpha a)(k_D - k_0)} \right]^{-1} \left[ \frac{3k_D[1 + \alpha a + \frac{1}{3}(\alpha a)^2]}{1 + \alpha a} \right. \\ &\quad \left. \times a^2 \sum_{j=0}^{\infty} \frac{2(j+1)(\alpha a)^{2j}}{(2j+3)!} + \frac{k_D}{3} (\alpha a)^2 a^2 \sum_{j=0}^{\infty} \frac{6(j+1)(\alpha a)^{2j}}{(2j+5)!} \right] \mathbf{1} \end{aligned} \quad (52)$$

and

$$\sigma^{m1}(\omega) = 0 \quad \text{for } m \neq 1 \quad (53)$$

### 3.3. Calculation Employing Explicit Solutions for Density Fields

We shall present in this subsection an alternative calculation of the external one-sink response function. Moreover, we shall demonstrate that for vanishing frequency, *all* the multipoles are explicitly known.

In view of Eqs. (29) and (31), Eq. (2) may be rewritten as

$$n(\mathbf{r}) = n_0(\mathbf{r}) - \sum_{m,n=0}^{\infty} (-1)^n \sigma^{mn} (m! n!)^{-1} \odot [\nabla^n \mathcal{G}_0(\mathbf{r})][(\nabla')^m n_0(\mathbf{r}')]_{\mathbf{r}'=0} \quad (54)$$

Since the density field  $n_0(\mathbf{r})$  appearing above is arbitrary, we shall require it, for reasons which will shortly become clear, to assume the form

$$n_0(\mathbf{r}) = \mathbf{a}_l \odot \mathbf{r}^l \quad (l = 0, 1, 2, \dots) \quad (55)$$

for some spatially independent  $l$ -tensor  $\mathbf{a}_l$ .

In a steady-state situation, solutions to the diffusion equation

$$\nabla^2 n(\mathbf{r}) = 0 \quad (56)$$

for the radiation boundary condition at the sink's surface, and given the form in Eq. (55) far from the sink, are readily constructed. Indeed, the general solution takes the form

$$n^{(l)}(\mathbf{r}) = \mathbf{a}_l \odot \left( \mathbf{r}^l + c_l \nabla^l \frac{1}{r} \right) \quad (57)$$

where

$$c_l = (-1)^l \frac{2l+1}{(2l+1)!!} a^{2l+1} \frac{l - (k_0/k_D)}{l+1 + (k_0/k_D)} \quad (58)$$

Using this general solution, for  $l = 0, 1, 2, \dots$ , along with Eq. (54), we can derive the tensorial properties of  $\sigma^{ln}$ , and furthermore, generate its general expression.

Equating Eqs. (54) and (57), we obtain

$$c_l \mathbf{a}_l \odot \nabla^l \frac{1}{r} = - \sum_{n=0}^{\infty} (-1)^n \sigma^{ln} \odot (l! n!)^{-1} \left( \nabla^n \frac{1}{4\pi D_0 r} \right) \mathbf{a}_l \quad (59)$$

from which we conclude:

$$(i) \quad \sigma^{ln} = \begin{cases} \sigma^{ll} & \text{if } n = l \\ 0 & \text{otherwise} \end{cases} \quad (60)$$

$$(ii) \quad \sigma_{\mu_1 \mu_2 \dots \mu_l \nu_1 \nu_2 \dots \nu_l}^{ll} = \sigma^{ll} \delta_{\mu_1 \nu_1} \delta_{\mu_2 \nu_2} \dots \delta_{\mu_l \nu_l} \quad (61)$$

$$(iii) \quad \sigma^{ll} = -4\pi D_0 (-1)^l c_l (l!)^2 \quad (62)$$

We note that these results are in complete agreement with those of the previous subsection when  $\alpha$  vanishes.

#### 4. REGULAR ARRAY OF SINKS

Having developed the formal theory for diffusion-controlled processes for a uniform distribution of spherical sinks, we shall now specialize to the case when the sinks form an infinite, three-dimensional perfect array suspended in the fluid. Both the simple and face-centered cubic lattices will be examined. Although this is a highly idealized situation, the calculations can be carried out for arbitrary sink densities, and hence, much information about the concentration dependence of the rate coefficient can be obtained.

For a regular array of suspended spheres, the averaging procedure used in Section 2 is not necessary. Instead, we utilize the periodic nature of the array in order to derive results which are valid for small wave vectors.

#### 4.1. Monopole Approximation

As we have already seen [cf. Eq. (6)] the effect that the presence of the sinks has on the density profile of diffusing particles can be described by the external response function  $s_{\text{ext}}$ ,

$$\mathcal{S} = s_{\text{ext}}n_0 \quad (63)$$

with

$$s_{\text{ext}} = s(1 + \mathcal{G}_0s)^{-1} \quad (64)$$

or, using Eq. (21),

$$s_{\text{ext}} = (1 + H_\sigma)^{-1}\sigma_b \quad (65)$$

It is clear from the definitions of the operators  $H_\sigma$  and  $\sigma_b$  [cf. Eqs. (18) and (19)] that  $s_{\text{ext}}$  is a periodic operator, and Eq. (63) can now be rewritten in  $(k, \omega)$  space as<sup>(5)</sup>

$$\mathcal{S}(\mathbf{k}, \omega) = \sum_{\mu} s_{\text{ext}}^{\mu}(\mathbf{k}, \omega)n_0(\mathbf{k} - \mathbf{k}_{\mu}, \omega) \quad (66)$$

where  $s_{\text{ext}}^{\mu}$  is the discrete operator representation of  $s_{\text{ext}}$ , and the  $\mathbf{k}_{\mu}$  are the reciprocal lattice vectors. Before obtaining an explicit expression for  $s_{\text{ext}}^{\mu}$ , we observe that in Fourier space the operator  $\sigma_b$  becomes

$$\sigma_b(\mathbf{k}, \omega|\mathbf{k}') = (2\pi)^3 \sum_{\lambda} \sigma_b^{\lambda}(\mathbf{k}, \omega)\delta(\mathbf{k} - \mathbf{k}' - \mathbf{k}_{\lambda}) \quad (67)$$

where

$$\sigma_b^{\lambda}(\mathbf{k}, \omega) = k_j^{(0)}(\omega)N_s \quad (68)$$

In the derivation of the above identity, use was also made of the relation<sup>(5)</sup>

$$N_s \sum_{\lambda} \exp(i\mathbf{k}\cdot\mathbf{r}) = \sum_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{R}_i)$$

where  $N_s$  is the number density of the sinks.

A straightforward algebraic manipulation, which we defer to Appendix C, of Eqs. (65) and (68), together with the observation of the periodicity of the operators  $(1 - H_\sigma)^{-1}$  and  $\sigma_b$ , yields

$$s_{\text{ext}}^{\mu}(\mathbf{k}, \omega) = k_j^{(0)}(\omega)N_s[1 + k_j^{(0)}(\omega)N_s\mathcal{H}(k, \omega)]^{-1} \quad (69)$$

where

$$\mathcal{H}(\mathbf{k}, \omega) = \sum_{\lambda} H(\mathbf{k} - \mathbf{k}_{\lambda}, \omega) = \sum'_{\lambda} \mathcal{G}_0(\mathbf{k} - \mathbf{k}_{\lambda}, \omega) \quad (70)$$

The last equality follows directly from the definition of the cutoff operator

$H(\mathbf{r}, t) = \mathcal{G}_0(\mathbf{r}, t)$  if  $r > l$ , and 0 if  $r < l$ ;  $0 < l < 2a$ . The prime on the last lattice sum denotes the exclusion of the origin.

Due to the obvious periodic nature of the internal response function  $s$ , one may recast Eq. (4) in  $(\mathbf{k}, \omega)$  space into

$$\mathcal{S}(\mathbf{k}, \omega) = \sum_{\mu} s^{\mu}(\mathbf{k}, \omega) n(\mathbf{k} - \mathbf{k}_{\mu}) \quad (71)$$

Furthermore, one may verify that

$$s^{\mu}(\mathbf{k}, \omega) = k_f^{(0)}(\omega) N_s \left\{ 1 + k_f^{(0)}(\omega) N_s \times \sum_{\lambda} [H(\mathbf{k} - \mathbf{k}_{\lambda}, \omega) - \mathcal{G}_0(\mathbf{k} - \mathbf{k}_{\lambda}, \omega)] \right\}^{-1} \quad (72)$$

Since our aim is to obtain a macroscopic expression for the reaction rate coefficient, we restrict ourselves to small wave vectors in the first Brillouin zone. Hence, retaining terms corresponding to  $\mu = 0$  in each of Eqs. (66) and (71), and using Eq. (2), we obtain

$$\begin{aligned} \mathcal{S}(\mathbf{k}, \omega) &= [1 - s_{\text{ext}}^0(\mathbf{k}, \omega) \mathcal{G}_0(\mathbf{k}, \omega)]^{-1} s_{\text{ext}}^0(\mathbf{k}, \omega) n(\mathbf{k}, \omega) \\ &= s^0(\mathbf{k}, \omega) n(\mathbf{k}, \omega) \end{aligned} \quad (73)$$

from which we identify

$$s^0(\mathbf{k}, \omega) = [1 - s_{\text{ext}}^0(\mathbf{k}, \omega) \mathcal{G}_0(\mathbf{k}, \omega)]^{-1} s_{\text{ext}}^0(\mathbf{k}, \omega) \quad (74)$$

Substituting into the above equation the explicit expression for  $s_{\text{ext}}^0(\mathbf{k}, \omega)$ , Eq. (69), we obtain the desired form of the internal response function:

$$s^0(\mathbf{k}, \omega) = \{1 + k_f^{(0)}(\omega) N_s [\mathcal{H}(\mathbf{k}, \omega) - \mathcal{G}_0(\mathbf{k}, \omega)]\}^{-1} k_f^{(0)}(\omega) N_s \quad (75)$$

The  $\mathbf{k} = 0$  limit of  $s^0(\mathbf{k}, \omega)$  can be identified as the macroscopic rate coefficient  $k_f(\omega) N_s = s^0(\mathbf{k} = 0, \omega)$ , i.e.,

$$k_f(\omega) = k_f^{(0)}(\omega) [1 + k_f^{(0)}(\omega) N_s M(0, \omega)]^{-1} \quad (76)$$

where we have introduced the nonsingular lattice sum

$$M(0, \omega) = \mathcal{H}(0, \omega) - \mathcal{G}_0(0, \omega) \quad (77)$$

## 4.2. Contributions from Higher Order Multipoles

When  $\mathbf{k} = 0$ , one may readily verify that the operator  $\sigma_b^{\lambda-\mu}$  appearing in Eq. (C1) assumes the general form

$$\sigma_b^{\lambda-\mu}(-\mathbf{k}_{\mu}, \omega) = \sum_{n=0}^{\infty} A_n(\omega) (\mathbf{k}_{\mu} \cdot \mathbf{k}_{\lambda})^n \quad (78)$$

where the  $A_n(\omega)$  are some appropriate frequency-dependent coefficients, for example,  $A_0(\omega) = k_f^{(0)}(\omega)N_s$ . Furthermore, Eq. (C5) generalizes to

$$\delta_{\lambda,0} = f^\lambda + \sum_{n=0}^{\infty} A_n(\omega) f^{(n)} \odot \mathbf{k}_\lambda^n H(-\mathbf{k}_\lambda, \omega) \quad (79)$$

where

$$f^{(n)} = \sum_{\mu} f^\mu \mathbf{k}_\mu^n \quad (80)$$

Successive multiplication of Eq. (79) by  $\mathbf{k}_\lambda^i$  followed by summation gives the identity

$$\delta_{i,0} = f^{(i)} + \sum_{n=0}^{\infty} A_n(\omega) f^{(n)} \odot \mathcal{H}^{(n+i)} \quad (81)$$

where we have defined the tensorial lattice sum

$$\mathcal{H}^{(n)} = \sum_{\lambda} \mathbf{k}_\lambda^n H(-\mathbf{k}_\lambda, \omega) \quad (82)$$

For a cubic lattice, symmetry considerations simplify the form of these sums considerably. First, only lattice sums  $\mathcal{H}^{(n)}$  with  $n$  even assume non-vanishing values. Second, the tensorial nature of these sums can be exactly specified:

$$\mathcal{H}_{\mu_1\nu_1\mu_2\nu_2\cdots\mu_{n/2}\nu_{n/2}}^{(n)} = \mathcal{H}_n P_{\mu_1\nu_1\mu_2\nu_2\cdots\mu_{n/2}\nu_{n/2}} \delta_{\mu_1\nu_1} \delta_{\mu_2\nu_2} \cdots \delta_{\mu_{n/2}\nu_{n/2}} \quad (83)$$

Here,  $\mathcal{H}_n$  is a scalar lattice sum defined by

$$\mathcal{H}_n = \frac{1}{3^{n/2}} \sum_{\lambda} k_\lambda^n H(-\mathbf{k}_\lambda, \omega) \quad (84)$$

and  $P_{\mu_1\nu_1\cdots\mu_{n/2}\nu_{n/2}}$  denotes the summation of all possible permutations of  $\delta_{\mu_1\nu_1} \cdots \delta_{\mu_{n/2}\nu_{n/2}}$ .

Following the scheme outlined in Appendix C, it can be demonstrated that

$$s_{\text{ext}}^0(0, \omega) = A_0(\omega) \left[ 1 - \sum_{n=0}^{\infty} A_n(\omega) f^{(n)} \odot \mathcal{H}^{(n)} \right] \quad (85)$$

Since the tensors  $\mathcal{H}_{\mu_1\nu_1\cdots\mu_{n/2}\nu_{n/2}}^{(n)}$  and  $f_{\mu_1\nu_1\cdots\mu_{n/2}\nu_{n/2}}^{(n)}$  are symmetric with respect to the interchange of any two indices, and furthermore,  $\mathcal{H}_n = \alpha^n \mathcal{H}_0$ , an examination of the matrix of coefficients for the  $n$  simultaneous equations in  $f^{(0)}$ ,  $f^{(2)}$ , ...,  $f^{(n)}$  allows one to conclude that, in the zero-frequency limit, Eq. (85) simplifies to the monopole result.

### 4.3. Calculation of Lattice Sums

The techniques employed in transforming slowly converging sc and fcc lattice sums into rapidly converging ones via the Nijboer–de Wette modification of the Ewald method<sup>(10)</sup> have already been described in Ref. 5 and the Appendix of Ref. 6. By the same procedure, the lattice sum  $M(0, \omega)$  [cf. Eq. (77)] may be shown to be

$$N_s M(0, \omega) = -(4\pi D_0)^{-1} \sum_i R_i^{-1} \operatorname{erfc}\left(\frac{\sqrt{\pi} R_i}{b}\right) e^{-\alpha R_i} - \frac{N_s}{D_0} \sum_\lambda \kappa^{-2} e^{-(b/4\pi)\kappa^2} + \frac{b^2 N_s}{4\pi D_0} + (2\pi D_0 b)^{-1} - \frac{N_s}{i\omega} \quad (86)$$

where

$$\kappa = |\boldsymbol{\kappa}| = |\alpha \hat{\mathbf{r}} - i \mathbf{k}_\lambda|$$

The explicit expressions for the lattice vector  $\mathbf{R}_i$  and the reciprocal lattice vector  $\mathbf{k}_\lambda$  can also be found in the Appendix of Ref. 6;  $b$  is a cutoff parameter of the order of the lattice spacing.

For zero frequency, Eq. (86) simplifies to give

$$N_s M(0, 0) = -(4\pi D_0)^{-1} \sum_i R_i^{-1} \operatorname{erfc}\left(\frac{\sqrt{\pi} R_i}{b}\right) - \frac{N_s}{D_0} \sum_\lambda k_\lambda^{-2} \exp\left(-\frac{b^2}{4\pi} k_\lambda^2\right) + (2\pi D_0 b)^{-1} + \frac{b^2 N_s}{4\pi D_0} \equiv -\frac{m}{k_D} \phi^{1/3} \quad (87)$$

where  $\phi$  is the volume fraction,

$$\phi = \frac{4}{3} \pi a^3 N_s = \frac{4\pi a^3}{3 d^3}$$

and  $d$  is the length of the unit cell, and the prime on the summation sign excludes the origin.

Having performed the summations in Eq. (87), we obtained the following results:

$$\text{sc lattice} \quad m = 1.760 \quad (88)$$

$$\text{fcc lattice} \quad m = 1.792 \quad (89)$$

Thus, the zero-frequency rate coefficient takes the form [cf. Eq. (76)]

$$k_f = k_f^{(0)} \left[ 1 - \left( 1 + \frac{k_D}{k_0} \right)^{-1} m \phi^{1/3} \right]^{-1} \quad (90)$$

The graphs of the rate coefficient as a function of  $\phi^{1/3}$  for various values of  $k_D/k_0$  are given in Fig. 1 for both the sc and fcc lattices. Several important

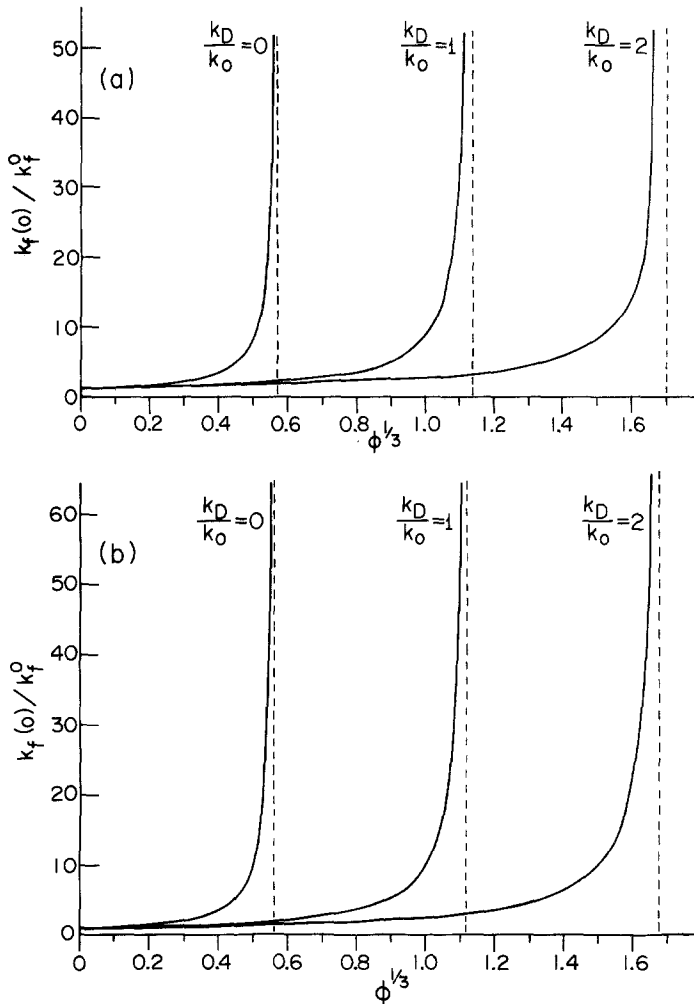


Fig. 1. Rate coefficient  $k_f(0)/k_f^0$  as a function of  $\phi^{1/3}$  for various values of  $k_D/k_0$  for (a) simple cubic and (b) face-centered cubic lattices. The closest packing for (a) and (b) occurs at  $\phi^{1/3} = 0.806$  and  $\phi^{1/3} = 0.904$ , respectively.

observations can be made: First, we note the characteristic increase and eventual divergence of the rate coefficient as the sink volume fraction increases. Second, as the ratio  $k_D/k_0$  increases from the initial value of zero, corresponding to complete absorption, the pole shifts to higher values of volume fraction; eventually, the singularity appears for unphysical values of  $\phi$  only, i.e., values greater than closest packing.



The increase of the reaction rate coefficient with the sink density has already been discussed in some detail by Felderhof and Deutch<sup>(3)</sup> for a disordered array of sinks, and was attributed to a screening phenomenon.

The main merit of the preceding calculation is that it can be carried out exactly for an arbitrary value of  $\phi$ , thus allowing one to compute the rate coefficient for *all* values of the volume fraction.

Finally, we wish to point out the similarity of the above results to those for the effective shear viscosity of a regular array of suspended spheres.<sup>(6)</sup> In fact, since the particle diffusion coefficient will be affected by the shear viscosity, we expect that an increase in the viscosity will lead to a corresponding decrease in  $D_0$ . Hence, a complete description of the rate coefficient in this rapidly increasing region also requires a consideration of such viscosity effects.

## 5. DISORDERED ARRAYS OF SINKS

In this section, we shall progress one step further and consider a more commonly encountered physical system, namely, randomly distributed stationary sinks. To greatly simplify the computation, we shall restrict ourselves to the lowest multipole calculation; physically, this amounts to regarding the sinks as being point particles.

The calculation of the general sink concentration dependence of the rate coefficient is a difficult problem, even with the monopole approximation to the response functions. This should be contrasted with the regular array calculations presented above, where the rate coefficient could be calculated to all orders in  $N_s$ . We shall not attempt a complete solution to this problem here, but rather, simply illustrate how the general formalism in Section 2 can be applied to disordered arrays of sinks, and calculate the leading order sink density contribution. In the following subsections, we shall assume that the complete absorption boundary condition applies.

### 5.1. Formal Relation for the Rate Coefficient

In Section 2, we derived the following formal expression, whose zero-wavevector limit was *previously* identified with the reaction rate coefficient [cf. Eq. (7)]:

$$S = \langle s(1 + \mathcal{G}_0 s)^{-1} \rangle \langle (1 + \mathcal{G}_0 s)^{-1} \rangle^{-1} \quad (91)$$

Substituting into this equation the actual form of the *internal* response function [cf. Eq. (21)], one finds that

$$S = \langle \sigma_b(1 + H_\sigma)^{-1} \rangle \langle [1 + \mathcal{G}_0(1 + \sigma_b K)^{-1} \sigma_b]^{-1} \rangle^{-1} \quad (92)$$

where we have also defined a new operator  $K$  by

$$K(\mathbf{r}, t | \mathbf{r}', t') = K(\mathbf{r} - \mathbf{r}', t - t') \equiv \mathcal{G}_0(\mathbf{r} - \mathbf{r}', t - t')[1 - \theta(\mathbf{r} - \mathbf{r}')] \quad (93)$$

which vanishes if  $|\mathbf{r} - \mathbf{r}'| > l$ .

Following a procedure originally used in the study of dielectrics<sup>(5)</sup> and later of the shear viscosity of sphere suspensions,<sup>(7)</sup> we next introduce a convenient operator  $\Lambda$  by the following definition:

$$S \equiv (1 - \Lambda K)^{-1} \Lambda \quad (94)$$

where  $\Lambda$  is given explicitly by

$$\Lambda = \langle \sigma_b (1 + H_\sigma)^{-1} \rangle \langle (1 + H_\sigma)^{-1} \rangle^{-1} \quad (95)$$

In Fourier transform space, the zero-frequency limit of the rate coefficient is now easily attainable by explicitly computing  $K$  and using the diagonality of the operators  $S$ ,  $\Lambda$ , and  $K$ . The latter statement follows directly from the translational invariance and stationarity of the system under consideration.

Thus, one obtains

$$S(\mathbf{k}, \omega = 0) = \left[ 1 - \frac{1 - \cos kl}{D_0 k^2} \Lambda(\mathbf{k}, \omega = 0) \right]^{-1} \Lambda(\mathbf{k}, \omega = 0) \quad (96)$$

where  $\epsilon \leq l \leq 2a - \epsilon$  (cf. Section 2.2).

Expressions analogous to the ones above proved to be extremely useful, for both dielectrics and sphere suspensions, in mean field theoretical investigations, as well as in considering the effect of correlations.

We may now take the  $l \rightarrow 0$  limit of Eq. (96) to obtain

$$k_f(\omega = 0) N_s = S(\mathbf{k} = 0, \omega = 0) = \Lambda(k = 0, \omega = 0) \quad (97)$$

The calculation of the rate coefficient is thus reduced to an evaluation of  $\Lambda$ .

## 5.2. Correlation Contributions to the Rate Coefficient

The strategy of this calculation is straightforward<sup>(7)</sup>: The operator  $\Lambda$  is first expanded in powers of the sink number density  $N_s$ . This, in turn, facilitates the identification of various classes of events—some of which are represented by infinite series of divergent diagrams—which may then be analyzed using techniques familiar from ionic solution theory.<sup>(11)</sup>

Before proceeding with our program, however, we must first review the external one-sink response function<sup>6</sup>  $\sigma_b^N$  in view of the previously stated

<sup>6</sup> The index  $N$  serves to emphasize dependence on the number of sinks under investigation.

approximations which are to be made. Thus, referring to Eqs. (23), (24), and (50), it is clear that

$$\begin{aligned}\sigma_b^N(\mathbf{r}, \omega | \mathbf{r}', \omega') &= k_D [N_s(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')] 2\pi \delta(\omega - \omega') \\ &\equiv \sigma_b^N(\mathbf{r}, \omega | \mathbf{r}') 2\pi \delta(\omega - \omega')\end{aligned}\quad (98)$$

Here, the sink density is denoted by

$$N_s(\mathbf{r}, \omega) = 2\pi \delta(\omega) \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{R}_i) \equiv 2\pi \delta(\omega) N_s(\mathbf{r}) \quad (99)$$

In writing Eqs. (98) and (99), use was made of the fact that only equal time correlation functions ought to be used in the linear regime.

In order to cast Eq. (95) into a more suitable form, we define yet another operator:

$$\mathcal{F}_N \equiv \sigma_b^N (1 + H \sigma_b^N)^{-1} \quad (100)$$

where the cutoff operator  $H \equiv \mathcal{G}_0 \theta$  has already been introduced in Section 4.1. Clearly, Eq. (95) is now given by

$$\Lambda = \langle \mathcal{F}_N \rangle [1 - H \langle \mathcal{F}_N \rangle]^{-1} \quad (101)$$

To obtain a density expansion of  $\Lambda$  in Eq. (101), we first carry out a standard density expansion of the grand canonical ensemble average of  $\mathcal{F}_N$ . To second order in  $N_s$  we find

$$\begin{aligned}\langle \mathcal{F}_N \rangle &= N_s \int d\mathbf{R}_1 \mathcal{F}_1(\mathbf{r}_1) + \frac{1}{2} N_s^2 \int d\mathbf{R}_1 d\mathbf{R}_2 e^{-\beta W_2(\mathbf{R}_{12})} \\ &\quad \times [\mathcal{F}_2(\mathbf{R}_1, \mathbf{R}_2) - \mathcal{F}_1(\mathbf{R}_1) - \mathcal{F}_1(\mathbf{R}_2)] + O(N_s^3)\end{aligned}\quad (102)$$

Substituting this result into Eq. (101) and collecting terms of equal order in  $N_s$ , we find that the operator  $\Lambda$  now becomes

$$\Lambda = N_s \Lambda_1 + N_s^2 \Lambda_2 + O(N_s^3) \quad (103)$$

where the  $\Lambda_i$  are given by

$$\Lambda_1 = \int d\mathbf{R}_1 \mathcal{F}_1(\mathbf{R}_1) \quad (104a)$$

and

$$\begin{aligned}\Lambda_2 &= \frac{1}{2} \int d\mathbf{R}_1 d\mathbf{R}_2 e^{-\beta W_2(\mathbf{R}_{12})} [\mathcal{F}_2(\mathbf{R}_1, \mathbf{R}_2) - \mathcal{F}_1(\mathbf{R}_1) - \mathcal{F}_1(\mathbf{R}_2)] \\ &\quad + \int d\mathbf{R}_1 d\mathbf{R}_2 \mathcal{F}_1(\mathbf{R}_1) H \mathcal{F}_1(\mathbf{R}_2)\end{aligned}\quad (104b)$$

with analogous expressions for higher order  $\Lambda_i$ .

Each one of these  $\Lambda_i$  must be analyzed utilizing the definition of the operator  $\mathcal{F}_N$  [cf. Eq. (100)]. Deferring all technical details to Appendix D, we briefly summarize below the results, which yield the rate coefficient up to the first sink density correction:

(a) To *all* orders in the cutoff propagator,

$$\Lambda_1 = \int d\mathbf{R}_1 \sigma_b^{-1}(\mathbf{R}_1) = k_D \quad (105)$$

which by itself yields, upon substitution into Eqs. (103) and (97), the value of the reaction rate coefficient in the absence of correlations:

$$k_f(\omega = 0) = k_D \quad (106)$$

(b) Divergent integrals are encountered when the higher order  $\Lambda_i$  are calculated. For example, a two-vertex ring event is obtained when terms to *second* order in  $H$  are retained:

$$\begin{aligned} \Lambda_2^R &= \int d\mathbf{R}_1 d\mathbf{R}_2 \sigma_b^{-1}(\mathbf{R}_1) H \sigma_b^{-1}(\mathbf{R}_2) H \sigma_b^{-1}(\mathbf{R}_1) \\ &= \frac{k_D^3}{2\pi^2 D_0^2} \int_0^\infty \frac{dk}{k^2} \end{aligned} \quad (107)$$

The superscript  $R$  on  $\Lambda_2$  refers to the ring nature of the contribution. The two vertex  $[O(N_s^2)]$  term, which is third order in  $H$ , also diverges, though not as strongly as  $\Lambda_2^R$  above. All terms of higher order than third in  $H$  are well behaved.

(c) To each order in  $N_s$ , a similar type of ring event can be identified. For example, the three-vertex term, which is third order in  $H$ , is such a contribution:

$$\begin{aligned} \Lambda_3^R &= - \int d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{R}_3 \sigma_b^{-1}(\mathbf{R}_1) H \sigma_b^{-1}(\mathbf{R}_2) H \sigma_b^{-1}(\mathbf{R}_3) H \sigma_b^{-1}(\mathbf{R}_1) \\ &= \frac{-k_D^4}{2\pi^2 D_0^3} \int_0^\infty \frac{dk}{k^4} \end{aligned} \quad (108)$$

Several remarks can be made: First, it is clear that there are different classes of events, viz. “multiple scattering” processes. The various “multiple scattering” events encountered in this problem, including the cyclic one seen above, have the following interpretation: They describe the cooperative effect of various sink configurations in perturbing the density field of the diffusing particles. This, indeed, is the basis for the correlation contribution to the rate coefficient. Second, as is evident from the discussion in Appendix D, only “closed” events occur, i.e., each vertex, represented by  $\sigma_b^{-1}(\mathbf{R})$ , has at least two “bonds,” each denoting the propagator  $H$ , emanating from it.

In order to calculate the first sink density correction to the rate coefficient, we may make use of techniques which are reminiscent of the Debye–Hückel

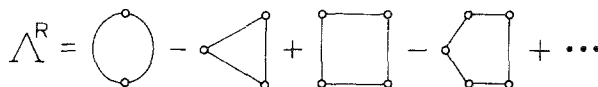


Fig. 2. Ring contributions to the operator  $\Lambda$ . The open circle represents the external one-sink response function  $\sigma_s^1(\mathbf{R})$ ; the bond (—) denotes the propagator  $H$ .

theory of electrolytes. We already noted above that, to each order in the sink density, a ring event which is most divergent can be identified. By a graphical analysis (cf. Fig. 2), one may show that these form a geometric series, which can be summed to yield a finite result. More explicitly, the required series is given by

$$\begin{aligned} \Lambda^R(\mathbf{k} = 0, \omega = 0) &= \frac{k_D^3 N_s^2}{2\pi^2 D_0^2} \int_0^\infty \frac{dk}{k^2} \left[ 1 - \frac{k_D N_s}{D_0 k^2} + \left( \frac{k_D N_s}{D_0 k^2} \right)^2 \dots \right] \\ &= \frac{k_D^3 N_s^2}{2\pi^2 D_0^2} \int_0^\infty \frac{dk}{k^2 + \kappa_s^2} = \frac{k_D}{4\pi} \kappa_s^3 \end{aligned} \quad (109)$$

where the inverse screening length  $\kappa_s$  is given by  $\kappa_s = (k_D N_s / D_0)^{1/2} = (4\pi a N_s)^{1/2}$ . When the above sum is used in conjunction with Eqs. (105) and (97), we finally obtain the following expression for the reaction rate coefficient:

$$k_f = k_D [1 + (3\phi)^{1/2} + O(\phi)] \quad (110)$$

where  $\phi$  is, as before, the sink volume fraction. This result is in agreement with that of Felderhof and Deutch, which was computed by another method.

A systematic computation of higher order sink density corrections to the rate coefficient requires a careful analysis of the other classes of multiple scattering events. Again, the calculation will be similar to the electrolyte problem, but additional complications arise in the higher order density terms due to the direct interaction between the sinks. Nevertheless, as long as the sink distribution is determined by short-range forces, the precise nature of these forces will not affect the  $N_s^{1/2}$  correction term. This is due to the fact that this arises from the long-distance behavior of the diffusive propagator.

Probably a more tractable way of extending such calculations into the high-density regime is by making use of effective field methods. Such methods have proved useful in the study of the friction and viscosity of concentrated sphere suspensions.<sup>(12)</sup>

## 6. DIFFUSION OF PARTICLES AMONG STATIONARY SPHERES

In the previous sections we were concerned with the calculation of the rate coefficient, and made no reference to the modification of the diffusion

coefficient of the particles due to reaction. Indeed, even for completely reflecting spheres, the diffusion coefficient is modified by the sphere distribution. To illustrate this, we shall examine in detail the purely diffusive situation. We do so for two reasons: First, the calculation is considerably simplified, allowing us to extend the previously discussed formalism. Second, the problem by itself is an interesting one, since it may have an application to diffusion in solids.

### 6.1. General Results

In order to derive an expression for the diffusion coefficient, we exploit the fact that the “sink” term can be written as the divergence of an induced diffusion flux field  $\mathbf{J}(\mathbf{r}, t)$ , when no particles are absorbed by the spheres. The equation of motion then takes the form

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D_0 \nabla^2 n(\mathbf{r}, t) - \nabla \cdot \mathbf{J}(\mathbf{r}, t) \quad (111)$$

The analysis now follows standard lines. We define a response function  $\mathcal{D}$  by

$$\mathbf{J}(\mathbf{r}, t) = - \int d\mathbf{r}' dt' \mathcal{D}(\mathbf{r}, t | \mathbf{r}', t') \cdot \nabla' n(\mathbf{r}', t') \equiv \mathcal{D} \cdot \nabla n \quad (112)$$

The configurational average of  $\mathbf{J}$  can be used to define a correction to the macroscopic diffusion coefficient

$$\langle \mathbf{J} \rangle = -\Delta \mathbf{D} \cdot \nabla \langle n \rangle \quad (113)$$

where, by an analysis similar to that of Section 2, we find

$$\Delta \mathbf{D} = \langle \mathcal{D} \cdot (1 - \nabla \nabla \mathcal{G}_0 \cdot \mathcal{D})^{-1} \rangle \cdot \langle (1 - \nabla \nabla \mathcal{G}_0 \cdot \mathcal{D}) \rangle^{-1} \quad (114)$$

In order to use this equation, the internal response function must be related to an external one-sphere response function, via a local field analysis similar to that in Section 2.2. If we define the external one-sphere response function  $\mathcal{D}_{\text{ext}}$  by

$$\mathbf{J}(\mathbf{r}, t) = - \int d\mathbf{r}' dt' \mathcal{D}_{\text{ext}}(\mathbf{r}, t | \mathbf{r}', t') \cdot \nabla' n_0(\mathbf{r}', t') \quad (115)$$

then we find that

$$\mathcal{D} = (1 + \xi \cdot \nabla \nabla \mathcal{G}_0 - H_{\xi})^{-1} \cdot \xi \quad (116)$$

where

$$\xi(\mathbf{r}, t | \mathbf{r}', t') = \sum_{i=1}^N \mathcal{D}_{\text{ext}}(\mathbf{r} - \mathbf{R}_i, t | \mathbf{r}' - \mathbf{R}_i, t') \quad (117)$$

and

$$\begin{aligned}
 H_2(\mathbf{r}, t | \mathbf{r}', t') &= \sum_{i=1}^N \int d\mathbf{r}'' dt'' \\
 &\times \mathcal{D}_{\text{ext}}(\mathbf{r} - \mathbf{R}_i, t | \mathbf{r}'' - \mathbf{R}_i, t'') \cdot \nabla'' \nabla'' \mathcal{G}_0(\mathbf{r}'' - \mathbf{r}', t'' - t') \theta(\mathbf{r}' - \mathbf{R}_i) \quad (118)
 \end{aligned}$$

The one-sphere external response function  $\mathcal{D}_{\text{ext}}$  can be identified with the dipole contribution to the multipole expansion of the previously encountered response function  $\sigma$  [cf. Eq. (23)], which, for vanishing frequency, becomes  $\sigma^{11} = -2\pi D_0 a^3$ .

Finally, we observe that in the mean field approximation, i.e., when the density operator is replaced by its ensemble average, Eq. (114) becomes

$$\begin{aligned}
 \Delta D(\mathbf{r}, t | \mathbf{r}', t') &= \langle \mathcal{D} \rangle (\mathbf{r}', t | \mathbf{r}', t') \\
 &= [-\frac{3}{2}\phi D_0 / (1 + \frac{1}{2}\phi)] \mathbf{1} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \\
 &= \Delta D_0 \mathbf{1} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (119)
 \end{aligned}$$

where we referred to Eq. (116). Substituting Eqs. (112) and (119) into the Fourier transform of the equation of motion [cf. Eq. (111)], we find that

$$(-i\omega + k^2 D) \langle n(\mathbf{k}, \omega) \rangle = n_0(\mathbf{k}, \omega) \quad (120)$$

where we defined the mean field diffusion coefficient

$$D \equiv D_0 + \Delta D_0 = \frac{1 - \phi}{1 + \frac{1}{2}\phi} D_0 \quad (121)$$

## 6.2. Regular Array of Spheres

The specialization of the diffusion problem to an infinite, regular arrangement of spheres is analogous to the analysis appearing in Section 4.1, and we shall therefore only present below the pertinent results.

The periodic operator can be written as

$$\xi(\mathbf{k} | \mathbf{k}') = (2\pi)^3 \sum_{\lambda} \xi^{\lambda}(\mathbf{k}) \delta(\mathbf{k} - \mathbf{k}' - \mathbf{k}_{\lambda}) \quad (122)$$

where

$$\xi^{\lambda}(\mathbf{k}) = -2\pi D_0 N_s a^3 \mathbf{1} \equiv \xi^0 \mathbf{1} \quad (123)$$

Defining a new cutoff operator  $H$  by

$$H(\mathbf{r}, t) = \begin{cases} \nabla \nabla \mathcal{G}_0(\mathbf{r}, t) & \text{if } r > l \quad (0 < l < 2a) \\ 0 & \text{otherwise} \end{cases} \quad (124)$$

it is straightforward to show that, in  $(\mathbf{k}, \omega)$  space, the expression for the induced diffusion flux is given by

$$\mathbf{J}(\mathbf{k}, 0) = - \sum_{\lambda} \mathcal{D}_{\text{ext}}^{\lambda}(\mathbf{k}, 0) \cdot i(\mathbf{k} - \mathbf{k}_{\lambda}) n_0(\mathbf{k} - \mathbf{k}_{\lambda}, 0) \quad (125)$$

where the discrete representation of the periodic operator  $\mathcal{D}_{\text{ext}}$  is

$$\mathcal{D}_{\text{ext}}^{\mu}(\mathbf{k}, 0) = \xi^0 [1 - \xi^0 \mathbf{Q}(\mathbf{k}, 0)]^{-1} \quad (126)$$

and

$$\mathbf{Q}(\mathbf{k}, 0) = \sum_{\lambda} \mathbf{H}(\mathbf{k} - \mathbf{k}_{\lambda}, 0) \quad (127)$$

is a newly defined lattice sum.

As before, restricting our considerations to the first Brillouin zone, we can identify the following relation for the internal response function  $\mathcal{D}$ , expressed in terms of  $\xi^0$  and the elementary lattice sum  $\mathbf{Q}$ :

$$\mathcal{D}(\mathbf{k}, 0) = \xi^0 [1 - \xi^0 \mathbf{K}(\mathbf{k}, 0)]^{-1} \quad (128)$$

with

$$\mathbf{K}(\mathbf{k}, 0) = \mathbf{Q}(\mathbf{k}, 0) + \mathbf{k} \mathbf{k} \mathcal{G}_0(\mathbf{k}, 0) \quad (129)$$

In view of our results for the reactive problem, clearly the lattice sum  $N_s \mathbf{Q}(0, 0)$  vanishes, thus allowing us to write Eq. (128) as follows:

$$\mathcal{D}(0, 0) = \frac{-\frac{3}{2}\phi D_0}{1 + \frac{1}{2}\phi} \mathbf{1} = \Delta D_0 \mathbf{1} \quad (130)$$

where we utilized Eq. (123). We recognize this as the mean field result [cf. Eq. (119)].

## 7. DISCUSSION AND SUMMARY

An important feature in any investigation of diffusion-limited reactions, via the diffusion equation approach, is the manner by which Fick's law of diffusion is extended to account for the presence of other stationary bodies suspended in the fluid; the very existence of this suspension perturbs the density field of the diffusing particles.

Traditionally, this problem has been approached in one of two ways. First, by the specification of precise initial and boundary conditions to be satisfied by the equation of motion. While this procedure may be carried out effectively for one, several, or, perhaps, a regular array of sinks, it rapidly becomes prohibitively difficult whenever an examination of an arbitrary suspension of sinks is required.

To this end, a second approach exists: namely, the addition of some



appropriate sink term to the starting diffusion equation. The issue of stipulating the exact boundary conditions is thus temporarily evaded, and a formal theoretical development may be initiated. Nevertheless, new complications arise; the newly inserted sink field must be expressed in terms of the density field, so that useful solutions for the modified equation of motion may be obtained.

This, indeed, was the motivation behind the development of the formal theory outlined in this article, whose essence is encompassed in its usage of standard linear response theory; the perturbation to the diffusing particles' density caused by the presence of the stationary sinks in the fluid was taken into account by the introduction of the *internal* response function  $s$ , which in turn was written, via the so-called local field analysis, as a function of the diffusion propagator  $\mathcal{G}_0$  and the *external one-sink* response function  $\sigma$ . This latter response function governs the reaction of the density field to the introduction of a *single* sink into the fluid. Having related the sink and density fields, the ensemble average of the equation of motion yielded a simple macroscopic law [cf. Eq. (7)], permitting the identification of the zero-wave-vector rate coefficient for the absorption of diffusing particles by the suspended stationary sinks.

In the course of this study, a generalized Faxén-like theorem for chemical reactions was derived. This theorem relates the flux of particles across the sink's surface to the averages over the sink's volume and surface of the diffusing particles' number density field, in the *absence* of sinks. This theorem provides a compact representation of the flux for arbitrary density fields far from the sink. In special limits, conventional results are obtained. For example, if we consider a homogeneous external density field, Eq. (45) is obtained. This is the commonly quoted Fick's law result for the flux using the radiation boundary condition.<sup>(8)</sup> If we consider the case where the external density field  $n_0$  is inhomogeneous (but satisfies the diffusion equation), then

$$\Phi(\omega) = \frac{k_0 k_D e^{\alpha a}}{k_0 + k_D(1 + \alpha a)} n_0(\mathbf{r} = 0, \omega)$$

The formal expressions for the rate coefficients derived in Section 2 were exact and valid for all frequencies and sink densities. In order to illustrate the use of this formalism, several explicit calculations were carried out.

For the case of a regular array of sinks, treated in Section 4, the procedure of averaging over the sink configurations is not necessary and lattice sums can be calculated to yield expressions valid for all sink densities.

Although the model is highly idealized, several important conclusions can be drawn:

(a) The rate coefficient increases and eventually diverges as the sink volume increases.

(b) The position of the singularity in the relation for the rate coefficient depends upon the actual value of the ratio  $k_D/k_0$ . Furthermore, this pole shifts to higher values of sink volume fraction, eventually disappearing from the physical regime, which ends at closest packing. In fact, one readily notices that the singularity in the rate coefficient appears in this physical region only for the complete or nearly complete absorption boundary condition (cf. Fig. 1). This behavior can be attributed to a screening phenomenon. We further note that regular array suspensions of spheres have been prepared,<sup>(13)</sup> and possibly diffusion-controlled reactions can be studied in such systems.

The case of a disordered array is treated in Section 5. Here, one must deal with the configuration averaging which was avoided in the regular array case. After showing that the standard density expansion leads to divergent integrals, the most divergent class of terms—the ring events—were summed to yield the lowest order nonanalytic sink density correction to the rate coefficient. The result agrees with an earlier calculation by Felderhof and Deutch, obtained by a different method.

Finally, recognizing that for particles diffusing among completely reflecting stationary suspended spheres the “sink” field may be given by the divergence of an induced diffusion flux field, the present formalism was readily extended to allow for the calculation of the *effective* diffusion coefficient, in the linear response regime. The procedure used proceeded along standard lines, requiring only minor modifications. For a regular cubic array of *spheres*, the effective diffusion coefficient is the same as the mean field result.

## APPENDIX A

In order to derive the surface and volume averages of  $n_0(\mathbf{r}, \omega)$  and  $\mathbf{r}n_0(\mathbf{r}, \omega)$ , we refer to Appendix B of Ref. 7; employing the techniques therein, one can establish that

$$\overline{n_0(\mathbf{r}, \omega)^S} = \sum_{j=0}^{\infty} \frac{a^{2j}}{(2j+1)!} [\nabla^{2j} n_0(\mathbf{r}, \omega)]_{\mathbf{r}=0} \quad (\text{A1})$$

and

$$\overline{n_0(\mathbf{r}, \omega)^V} = \sum_{j=1}^{\infty} \frac{6ja^{2(j-1)}}{(2j+1)!} [\nabla^{2(j-1)} n_0(\mathbf{r}, \omega)]_{\mathbf{r}=0} \quad (\text{A2})$$

Since  $n_0(\mathbf{r}, \omega)$  satisfies the diffusion equation  $\alpha^2 n_0(\mathbf{r}, \omega) = \nabla^2 n_0(\mathbf{r}, \omega)$ , therefore

$$\nabla^{2j} n_0(\mathbf{r}, \omega) = \alpha^{2j} n_0(\mathbf{r}, \omega) \quad (\text{A3})$$

for  $j = 0, 1, 2, 3, \dots$

Equations (A1) and (A2) can now be written as

$$\overline{n_0(\mathbf{r}, \omega)^S} = \sum_{j=0}^{\infty} \frac{(\alpha a)^{2j}}{(2j+1)!} n_0(0, \omega) = (\alpha a)^{-1} \sinh(\alpha a) n_0(0, \omega) \quad (\text{A4})$$

and

$$\begin{aligned} \overline{n_0(\mathbf{r}, \omega)^V} &= \sum_{j=1}^{\infty} \frac{6j(\alpha a)^{2(j-1)}}{(2j+1)!} n_0(0, \omega) \\ &= 3(\alpha a)^{-1} [\cosh(\alpha a) - (\alpha a)^{-1} \sinh(\alpha a)] n_0(0, \omega) \end{aligned} \quad (\text{A5})$$

In the same manner, one can readily show that

$$\overline{\mathbf{r}n_0(\mathbf{r}, \omega)^S} = a^2 \sum_{j=0}^{\infty} \frac{2(j+1)(\alpha a)^{2j}}{(2j+3)!} [\nabla n_0(\mathbf{r}, \omega)]_{\mathbf{r}=0} \quad (\text{A6})$$

and

$$\overline{\mathbf{r}n_0(\mathbf{r}, \omega)^V} = a^2 \sum_{j=0}^{\infty} \frac{6(j+1)(\alpha a)^{2j}}{(2j+5)!} [\nabla n_0(\mathbf{r}, \omega)]_{\mathbf{r}=0} \quad (\text{A7})$$

## APPENDIX B

In this appendix we determine the expression for the dipole contribution to the multipole expansion of the response function  $\sigma$ . To achieve this, we first consider the second moment of  $\mathcal{S}(\mathbf{r}, \omega)$ .

From the radiation boundary condition, Eq. (22), we get

$$k_D \overline{\mathbf{r} \cdot \nabla n(\mathbf{r}, \omega)^S} = k_0 \overline{\mathbf{r} n(\mathbf{r}, \omega)^S} \quad (\text{B1})$$

Calculating  $\overline{\mathbf{r} \cdot \nabla n(\mathbf{r}, \omega)^S}$  explicitly and substituting the result into the above equation, we find

$$\int_V d\mathbf{r} \mathbf{r} \mathcal{S}(\mathbf{r}, \omega) = (k_0 - k_D) \overline{\mathbf{r} n(\mathbf{r}, \omega)^S} - \frac{1}{3} k_D (\alpha a)^2 \overline{\mathbf{r} n(\mathbf{r}, \omega)^V} \quad (\text{B2})$$

Expressions for  $\overline{\mathbf{r} n(\mathbf{r}, \omega)^S}$  and  $\overline{\mathbf{r} n(\mathbf{r}, \omega)^V}$  can be easily derived by multiplying the time Fourier transform of Eq. (2) through by  $\mathbf{r}$  and then averaging over the surface and volume of the spherical sink, respectively. Thus,

$$\overline{\mathbf{r} n(\mathbf{r}, \omega)^S} = \overline{\mathbf{r} n_0(\mathbf{r}, \omega)^S} - \mathbf{B}(\omega) \quad (\text{B3})$$

and

$$\begin{aligned} \overline{\mathbf{r} n(\mathbf{r}, \omega)^V} &= \overline{\mathbf{r} n_0(\mathbf{r}, \omega)^V} - \frac{3(\alpha a)^{-2}}{k_D} \int_V d\mathbf{r} \mathbf{r} \mathcal{S}(\mathbf{r}, \omega) \\ &\quad + \frac{9[1 + \alpha a + \frac{1}{3}(\alpha a)^2]}{(\alpha a)^2(1 + \alpha a)} \mathbf{B}(\omega) \end{aligned} \quad (\text{B4})$$

where

$$\begin{aligned} \mathbf{B}(\omega) &= \mathcal{G}_0(a, \omega)(1 + \alpha a) \int_V d\mathbf{r}' \mathbf{r}' (\alpha r')^{-3} \\ &\quad \times [\alpha r' \cosh(\alpha r') - \sinh(\alpha r')] \mathcal{S}(\mathbf{r}', \omega) \end{aligned} \quad (\text{B5})$$

We can derive another expression for  $\mathbf{B}(\omega)$ , in terms of the second moment of  $\mathcal{S}(\mathbf{r}, \omega)$ , by observing that  $\overline{\mathbf{r}n(\mathbf{r}, \omega)^V} = 0$  and using Eqs. (B2) and (B3):

$$\mathbf{B}(\omega) = \overline{\mathbf{r}n_0(\mathbf{r}, \omega)^S} - (k_D - k_0)^{-1} \int_V d\mathbf{r} \mathbf{r} \mathcal{S}(\mathbf{r}, \omega) \quad (\text{B6})$$

which upon substitution into Eq. (B4) yields

$$\begin{aligned} &\int_V d\mathbf{r} \mathbf{r} \mathcal{S}(\mathbf{r}, \omega) \\ &= \left\{ 1 - \frac{3k_D[1 + \alpha a + \frac{1}{3}(\alpha a)^2]}{(1 + \alpha a)(k_D - k_0)} \right\}^{-1} \left\{ \frac{3k_D[1 + \alpha a + \frac{1}{3}(\alpha a)^2]}{1 + \alpha a} \overline{\mathbf{r}n_0(\mathbf{r}, \omega)^S} \right. \\ &\quad \left. + \frac{k_D}{3} (\alpha a)^2 \overline{\mathbf{r}n_0(\mathbf{r}, \omega)^V} \right\} \end{aligned} \quad (\text{B7})$$

or, using the results of Appendix A [cf. Eqs. (A6) and (A7)],

$$\begin{aligned} &\int_V d\mathbf{r} \mathbf{r} \mathcal{S}(\mathbf{r}, \omega) \\ &= \left\{ 1 - \frac{3k_D[1 + \alpha a + \frac{1}{3}(\alpha a)^2]}{(1 + \alpha a)(k_D - k_0)} \right\}^{-1} \left\{ \frac{3k_D[1 + \alpha a + \frac{1}{3}(\alpha a)^2]}{1 + \alpha a} \right. \\ &\quad \times a^2 \sum_{j=0}^{\infty} \frac{2(j+1)(\alpha a)^{2j}}{(2j+3)!} \\ &\quad \left. + \frac{k_D}{3} (\alpha a)^2 a^2 \sum_{j=0}^{\infty} \frac{6(j+1)(\alpha a)^{2j}}{(2j+5)!} \right\} [\nabla n_0(\mathbf{r}, \omega)]_{\mathbf{r}=0} \end{aligned} \quad (\text{B8})$$

Now, relating the multipole expansion of the sink term to that of the response function [cf. Eqs. (29)–(31)], we see that

$$\begin{aligned} S^1(\omega) &= \sum_{m=0}^{\infty} (m!)^{-1} \sigma^{m1}(\omega) \odot [\nabla^m n_0(\mathbf{r}, \omega)]_{\mathbf{r}=0} \\ &= \int_V d\mathbf{r} \mathbf{r} \mathcal{S}(\mathbf{r}, \omega) \end{aligned} \quad (\text{B9})$$

Comparing this expression with Eq. (B8), we finally conclude that the only nonvanishing coefficient is

$$\begin{aligned} \sigma^{11}(\omega) = \sigma^{11} \mathbf{1} &= \left\{ 1 - \frac{3k_D[1 + \alpha a + \frac{1}{3}(\alpha a)^2]}{(1 + \alpha a)(k_D - k_0)} \right\}^{-1} \\ &\times \left\{ \frac{3k_D[1 + \alpha a + \frac{1}{3}(\alpha a)^2]}{1 + \alpha a} a^2 \sum_{j=0}^{\infty} \frac{2(j+1)(\alpha j)^{2j}}{(2j+3)!} \right. \\ &\left. + \frac{k_D}{3} (\alpha a)^2 a^2 \sum_{j=0}^{\infty} \frac{6(j+1)(\alpha a)^{2j}}{(2j+5)!} \right\} \mathbf{1} \end{aligned} \quad (\text{B10})$$

## APPENDIX C

Referring to Eq. (65), we find that

$$\begin{aligned} j_{\text{ext}}^{\mu}(\mathbf{k}, \omega) &= [(1 - H_{\sigma})^{-1} \sigma_b]^{\mu}(\mathbf{k}, \omega) \\ &= \sum_{\lambda} [(1 - H_{\sigma})^{-1}]^{\lambda}(\mathbf{k}, \omega) \sigma_b^{\mu-\lambda}(\mathbf{k} - \mathbf{k}_{\lambda}, \omega) \\ &= \sum_{\lambda} [(1 - \sigma_b H)^{-1}]^{\lambda}(\mathbf{k}, \omega) k_f^{(0)}(\omega) N_s \end{aligned} \quad (\text{C1})$$

where we first used the properties of periodic operators, then Eq. (68), and finally recognized that  $H_{\sigma} = \sigma_b H$ .

Due to its periodic character, the operator  $(1 - \sigma_b H)^{-1}(\mathbf{k}, \omega)$  can be written as

$$(1 - \sigma_b H)^{-1}(\mathbf{k}, \omega | \mathbf{k}') = (2\pi)^3 \sum_{\lambda} f^{\lambda}(\mathbf{k}, \omega) \delta(\mathbf{k} - \mathbf{k}' - \mathbf{k}_{\lambda}) \quad (\text{C2})$$

where

$$f^{\lambda}(\mathbf{k}, \omega) = [(1 - \sigma_b H)^{-1}]^{\lambda}(\mathbf{k}, \omega) \quad (\text{C3})$$

From the definition of the inverse of a periodic operator, we have

$$[f \cdot (1 - \sigma_b H)]^{\lambda}(\mathbf{k}, \omega) = \delta_{\lambda,0} = \begin{cases} 1 & \text{if } \mathbf{k}_{\lambda} = 0 \\ 0 & \text{otherwise} \end{cases} \quad (\text{C4})$$

Using Eq. (68) and noting that the cutoff operator  $H$  is diagonal in  $\mathbf{k}$ , we see that

$$\begin{aligned} \delta_{\lambda,0} &= \sum_{\mu} f^{\mu}(\mathbf{k}, \omega) (1 - \sigma_b H)^{\lambda-\mu}(\mathbf{k} - \mathbf{k}_{\mu}, \omega) \\ &= f^{\lambda}(\mathbf{k}, \omega) - k_f^{(0)} N_s \sum_{\mu} f^{\mu}(\mathbf{k}, \omega) H(\mathbf{k} - \mathbf{k}_{\lambda}, \omega) \end{aligned} \quad (\text{C5})$$

Summing Eq. (C5) over all  $\lambda$ , one obtains

$$\sum_{\mu} f^{\mu}(\mathbf{k}, \omega) = \left[ 1 - k_f^{(0)} N_s \sum_{\lambda} H(\mathbf{k} - \mathbf{k}_{\lambda}, \omega) \right]^{-1} \quad (\text{C6})$$

Clearly, Eq. (C5) can now be rearranged to yield

$$f^\wedge(\mathbf{k}, \omega) = \delta_{\lambda,0} + k_f^{(0)} N_s \left[ 1 - k_f^{(0)} N_s \sum_{\alpha} H(\mathbf{k} - \mathbf{k}_{\alpha}, \omega) \right]^{-1} H(\mathbf{k} - \mathbf{k}_{\lambda}, \omega) \quad (\text{C7})$$

using which allows us to express Eq. (C1) as follows:

$$s_{\text{ext}}^{\mu}(\mathbf{k}, \omega) = k_f^{(0)} N_s [1 - k_f^{(0)} N_s \mathcal{H}(\mathbf{k}, \omega)]^{-1} \quad (\text{C8})$$

## APPENDIX D

We give below some details concerning the calculation of the first sink density correction to the rate coefficient, which was outlined in Section 5.

### D1. Multiple Scattering Contributions

Equations (105), (107), and (108) were derived by using the explicit form of the operator  $\mathcal{F}_N$  [cf. Eq. (100)] in Eqs. (104). This was further simplified by noticing that terms involving  $\sigma_b^{-1}(\mathbf{R})H\sigma_b^{-1}(\mathbf{R})$  vanish identically; this follows directly from the presence of the Dirac delta functions  $\delta(\mathbf{r} - \mathbf{R}_1)\delta(\mathbf{r}' - \mathbf{R}_1)$  in  $\sigma_b^{-1}(\mathbf{r}, \omega|\mathbf{r}')$  [cf. Eq. (98)].

In analyzing the various operators  $\Lambda_i$  of Eq. (103), one may use the following formulas for the  $\mathcal{F}_N$  (we write explicit results for  $N = 1, 2, 3$ ):

$$\begin{aligned} \mathcal{F}_1(\mathbf{R}_1) &= \sigma_b^{-1}(\mathbf{R}_1) \sum_{i=0}^{\infty} (-1)^i [H\sigma_b(\mathbf{R}_1)]^i \\ &= \sigma_b(\mathbf{R}_1) \end{aligned} \quad (\text{D1})$$

$$\begin{aligned} \mathcal{F}_2(\mathbf{R}_1, \mathbf{R}_2) &= [1 - \sigma_b^{-1}(\mathbf{R}_1)H]\sigma_b^{-1}(\mathbf{R}_2) \sum_{i=0}^{\infty} (-1)^i [H\sigma_b^{-1}(\mathbf{R}_1)H\sigma_b^{-1}(\mathbf{R}_2)]^i \\ &\quad + [1 - \sigma_b^{-1}(\mathbf{R}_2)H]\sigma_b^{-1}(\mathbf{R}_1) \sum_{i=0}^{\infty} (-1)^i [H\sigma_b^{-1}(\mathbf{R}_2)H\sigma_b^{-1}(\mathbf{R}_1)]^i \end{aligned} \quad (\text{D2})$$

and

$$\begin{aligned} \mathcal{F}_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) &= [1 - \sigma_b^{-1}(\mathbf{R}_2)H - \sigma_b^{-1}(\mathbf{R}_3)H]\sigma_b^{-1}(\mathbf{R}_1) \sum_{i=0}^{\infty} (-1)^i \\ &\quad \times \{ [H\sigma_b^{-1}(\mathbf{R}_2)H\sigma_b^{-1}(\mathbf{R}_1)]^i + [H\sigma_b^{-1}(\mathbf{R}_2)H\sigma_b^{-1}(\mathbf{R}_3)]^i \\ &\quad + [H\sigma_b^{-1}(\mathbf{R}_3)H\sigma_b^{-1}(\mathbf{R}_1)]^i + [H\sigma_b^{-1}(\mathbf{R}_3)H\sigma_b^{-1}(\mathbf{R}_2)]^i \} \\ &\quad + \text{all possible permutations} \end{aligned} \quad (\text{D3})$$

In order to identify the ring terms, these general relations, which clearly introduce numerous *classes* of closed diagrams, need not be used in full.

Instead, one may merely retain terms to the desired order in  $H$ . Pursuing this strategy, one finally obtains the desired results.

## D2. Ring Diagrams

To illustrate the procedure used in computing such diagrams (cf. Fig. 2), we shall consider in detail the simplest case, viz.  $\sigma_b^{-1}(\mathbf{R}_1)H\sigma_b^{-1}(\mathbf{R}_2)H\sigma_b^{-1}(\mathbf{R}_1)$ . Using Eqs. (D1) and (D2), we note that

$$\begin{aligned}\Lambda_2^R &= \int d\mathbf{R}_1 d\mathbf{R}_2 e^{-\beta W_2(R_{12})} \sigma_b^{-1}(\mathbf{R}_1)H\sigma_b^{-1}(\mathbf{R}_2)H\sigma_b^{-1}(\mathbf{R}_1) \\ &= \int d\mathbf{R}_1 d\mathbf{R}_2 \sigma_b^{-1}(\mathbf{R}_1)H\sigma_b^{-1}(\mathbf{R}_2)H\sigma_b^{-1}(\mathbf{R}_1) \\ &\quad + \int d\mathbf{R}_1 d\mathbf{R}_2 [e^{-\beta W_2(R_{12})} - 1] \sigma_b^{-1}(\mathbf{R}_1)H\sigma_b^{-1}(\mathbf{R}_2)H\sigma_b^{-1}(\mathbf{R}_1) \quad (D4)\end{aligned}$$

Provided the interaction potential between the sinks has a short range, the second integral in Eq. (D4) is well behaved, and the singularity resides in the first term. This is what was referred to as  $\Lambda_2^R$  in Eq. (107). In analyzing the singular ring contributions, we may then neglect the direct interaction between the sinks.

We may write the first term in Eq. (D4) explicitly in  $(k, \omega)$  space for  $\omega = 0$  as

$$\begin{aligned}\Lambda_2^R(\mathbf{k}, 0|\mathbf{k}') &= \Lambda_2^R(\mathbf{k}, 0)(2\pi)^3 \delta(\mathbf{k} - \mathbf{k}') \\ &= (2\pi)^{-6} \int d\mathbf{R}_1 d\mathbf{R}_2 \int d\mathbf{k}_1 d\mathbf{k}_2 \sigma_b^{-1}(\mathbf{k}|\mathbf{k}_1; \mathbf{R}_1) \\ &\quad \times H(\mathbf{k}_1)\sigma_b^{-1}(\mathbf{k}_1|\mathbf{k}_2; \mathbf{R}_2)H(\mathbf{k}_2)\sigma_b^{-1}(\mathbf{k}_2|\mathbf{k}'; \mathbf{R}_1) \\ &= \frac{k_D^3}{(2\pi)^6} \int d\mathbf{R}_1 d\mathbf{R}_2 \int d\mathbf{k}_1 d\mathbf{k}_2 H(\mathbf{k}_1)H(\mathbf{k}_2) \\ &\quad \times \exp[i(\mathbf{k}_1 - \mathbf{k}) \cdot \mathbf{R}_1] \exp[i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{R}_2] \\ &\quad \times \exp[i(\mathbf{k}' - \mathbf{k}_2) \cdot \mathbf{R}_1] \quad (D5)\end{aligned}$$

Combining exponential terms and performing the substitution  $\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$  and a subsequent integration over  $\mathbf{R}_2$  yields for  $\Lambda_2^R(\mathbf{k}, 0)$

$$\begin{aligned}\Lambda_2^R(\mathbf{k}, 0) &= \Lambda_2^R(0, 0) = \frac{k_D^3}{(2\pi)^6} \int d\mathbf{R}_{12} \int d\mathbf{k}_1 d\mathbf{k}_2 H(\mathbf{k}_1)H(\mathbf{k}_2) \\ &\quad \times \exp[i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{R}_{12}] \quad (D6)\end{aligned}$$

Finally, integrating over  $R_{12}$ , we find that Eq. (D6) simplifies to

$$\Lambda_2^R = \left(\frac{k_D}{2\pi}\right)^3 \int d\mathbf{k} [H(\mathbf{k})]^2 = \left(\frac{k_D}{2\pi}\right)^3 \int \frac{d\mathbf{k}}{D_0^2 k^2} \quad (D7)$$

which is identical to Eq. (107). The higher order calculations follow in a parallel fashion.

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