

Concentration dependence of the rate of diffusion-controlled reactions*

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A theory for the concentration dependence of the rate of diffusion-controlled reactions is formulated. One of the reacting partners is taken to be a collection of static sinks. The steady state situation for a random distribution of these sinks is studied. The rate coefficient is predicted to increase with concentration of sinks and the dependence on concentration is shown to be nonanalytic.

I. INTRODUCTION

The theory of the rate of diffusion-controlled reactions was first formulated by Smoluchowski.¹ The basic idea is that the rate of a reaction can be dominated by the slow diffusive motion required for reacting partners to approach each other, followed by almost instantaneous reaction. Of the many applications of the theory we mention growth of colloidal or aerosol particles, precipitation, catalysis and fluorescence quenching. An application on a more macroscopic scale is combustion, in which the diffusing species is the oxidant and the sink a fuel droplet. Smoluchowski's theory was extended by Debye² to include the effect of potential interactions. The influence of hydrodynamic interactions on the reaction rate has also been studied.³ A quite general mathematical formulation was recently given by Wilemski and Fixman.⁴ They have applied their theory to intrachain reactions of polymers.⁵

An aspect of the theory which so far has received surprisingly little attention is the effect of concentration. In the dilute limit it suffices to consider a single pair of reactants, but at higher concentrations the reaction rate will be affected by the competition between neighboring sinks. The present article is devoted to a study of this effect. The effect has been investigated by Frisch and Collins,⁶ but they predicted a decrease of the reaction rate, rather than an increase as found here.

We make the following simplifying assumptions: One of the reaction partners is assumed much larger than the other, so that these particles can be regarded as stationary and only the diffusive motion of the smaller particles need be considered. We assume a steady-state situation and leave time-dependent effects^{7,8} out of consideration. Further we neglect direct potential² and hydrodynamic interactions.³ Incorporation of some of the above effects can be accomplished if desired.

With the above assumptions our problem reduces to solving Laplace's equation for the density $n(\mathbf{r})$ of the smaller particles with prescribed boundary conditions at the surface of the stationary sinks. Smoluchowski's original boundary condition requires $n(\mathbf{r})$ to vanish at the surface. Accordingly the problem has the obvious electrostatic analogue of finding the potential for a collection of ideally conducting grounded bodies with pre-

scribed potential at infinity. The calculation of the reaction rate then is equivalent to that of the average induced charge. The electrostatic problem for a random collection of spheres was considered in some detail by Kynch.⁹

Variational calculations of the reaction rate for the case where particles are recreated at a constant and uniform rate throughout the solution were made by Reck and Prager.¹⁰ They have derived upper and lower bounds, but unfortunately these widen rather rapidly as a function of concentration. The variational method has been reviewed by Strieder and Aris.¹¹

We derive a hierarchy of equations for a set of correlation functions and decouple by making a superposition approximation. An important aspect of the theory is the effect of screening analogous to Debye screening in a classical plasma or electrolyte solution. Not surprisingly, collective effects dominate the problem.

In Secs. II and III we describe the model and its electrostatic analogue. In Sec. IV we introduce the statistical averaging procedure and discuss the mean field approximation. Of the induced multipole moments only the charges and the dipoles are retained. In Secs. V and VI we discuss the effect of charges only. In Sec. VII we add the effect of dipoles. In the last section we present and discuss the results.

II. DESCRIPTION OF THE MODEL

In an idealized picture the systems under consideration consist of three constituents which will be denoted as fluid, particles, and sinks. The fluid serves merely as an inert solvent in which particles and sinks carry out diffusive motion. A particle and a sink can react and after reaction the particle disappears from the system whereas the change of state of the sink is neglected. The particles are assumed to be much smaller than the sinks, so that they diffuse much faster, since according to Stokes and Einstein the diffusion constant is inversely proportional to radius. As a further approximation we take the sinks to be completely at rest. Thus the particle number density $n(\mathbf{r}, t)$ satisfies the diffusion equation

$$\partial n / \partial t = D_0 \nabla^2 n \quad (2.1)$$

in the part of space occupied by the fluid. The effect of reactions on the particle density must be expressed by a boundary condition at the surface of the sinks, or by an appropriate sink term added to Eq. (2.1).

We recall briefly the Smoluchowski theory¹ for the steady-state reaction rate in a dilute system of spherical sinks. At sufficiently low sink density the competition for particles between sinks can be neglected and one need consider only the effect of a single sink. One assumes that a particle diffusing toward the sink is absorbed instantaneously upon contact and expresses this by requiring the particle density to vanish at the surface. In a steady-state situation one therefore must solve

$$\nabla^2 n = 0, \quad n(\mathbf{r}) = 0 \text{ at } r = R, \quad (2.2)$$

where R is the radius of the sink whose center we have taken to be at the origin. For uniform density n_0 at infinity the solution is

$$n(\mathbf{r}) = n_0 - (n_0 R / r). \quad (2.3)$$

The particle current density is given by $\mathbf{j} = -D_0 \nabla n$ and integrating over the surface of the sink one finds for the number of particles absorbed per second

$$J = 4\pi D_0 R n_0. \quad (2.4)$$

On a macroscopic scale the equation for the average particle density $N = \langle n \rangle$ therefore becomes

$$\partial N / \partial t = D_0 \nabla^2 N - k_0 \rho N, \quad (2.5)$$

with rate constant

$$k_0 = 4\pi D_0 R \quad (2.6)$$

and sink number density ρ .

In a concentrated solution the particle density $n(\mathbf{r}, t)$ varies rapidly on the microscopic length scale, i. e., on a scale of the average distance between sinks. Thus it will no longer be correct to assume that the particle density tends to a constant at a large distance from a single sink. The magnitude of the effect of gradients may be estimated by solving Eq. (2.2) with the condition at infinity $n(\mathbf{r}) \approx n_0 + \mathbf{e}_0 \cdot \mathbf{r}$. The solution is

$$n(\mathbf{r}) = n_0 + \mathbf{e}_0 \cdot \mathbf{r} - n_0 (R/r) - \mathbf{e}_0 \cdot \mathbf{r} (R^3/r^3). \quad (2.7)$$

The particle flux into the sink is still given by Eq. (2.4) and hence it appears that density gradients have no net effect. However, the dipolar disturbance given by the last term makes itself felt at large distances and, when summed over a large number of sinks, contributes significantly to the average local particle density.

We shall replace Eq. (2.1) by a microscopic equation valid for all space with added sink terms representing the monopole and dipole contributions, namely

$$\begin{aligned} \partial n / \partial t = D_0 \left[\nabla^2 n(\mathbf{r}, t) - 4\pi \sum_{j=1}^{\infty} q_j \delta(\mathbf{r} - \mathbf{r}_j) \right. \\ \left. + 4\pi \sum_{j=1}^{\infty} \mathbf{p}_j \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_j) \right]. \quad (2.8) \end{aligned}$$

The boundary condition $n = 0$ at a sink surface is omitted and the monopole and dipole strengths q_j and \mathbf{p}_j are

chosen appropriately to account for this. One can derive a macroscopic equation for the average density $N(\mathbf{r}, t) = \langle n \rangle$ by averaging Eq. (2.8) over volume elements, or more conveniently, over an ensemble $\Phi(\mathbf{r}_1, \dots, \mathbf{r}_\infty)$ of configurations of the sink centers. Defining

$$Q(\mathbf{r}, t) = \left\langle \sum_{j=1}^{\infty} q_j \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle, \quad \mathbf{P}(\mathbf{r}, t) = \left\langle \sum_{j=1}^{\infty} \mathbf{p}_j \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle, \quad (2.9)$$

one finds the macroscopic equation

$$\partial N / \partial t = D_0 [\nabla^2 N - 4\pi Q + 4\pi \nabla \cdot \mathbf{P}]. \quad (2.10)$$

On the macroscopic level one expects that the competition for particles between sinks will change the rate coefficient to a value $k(\rho)$ dependent on the sink concentration ρ . At the same time the particles will be affected in their diffusive motion and this alters the diffusion coefficient to a new value $D(\rho)$. Thus in a concentrated solution one expects a macroscopic equation of the form

$$\partial N / \partial t = \nabla \cdot [D(\rho) \nabla N] - k(\rho) \rho N. \quad (2.11)$$

This equation is identical with Eq. (2.10) provided we can establish the relations

$$k(\rho) \rho N = 4\pi D_0 Q, \quad (2.12)$$

$$D(\rho) \nabla N = D_0 \nabla N + 4\pi D_0 \mathbf{P}.$$

In the present article we shall be concerned primarily with the concentration dependent rate coefficient $k(\rho)$.

In a stationary situation with a steady supply of particles at infinity, the time derivative on the left of Eqs. (2.8), (2.10), and (2.11) vanishes and the monopole strength q_j and dipole strength \mathbf{p}_j are determined as in Eqs. (2.3) and (2.7), where now n_0 and \mathbf{e}_0 must be replaced by the sum of the density distribution imposed from the outside and the contribution from all the other sinks.

III. ELECTROSTATIC ANALOGY

As long as we restrict ourselves to steady-state situations and neglect time derivatives our problem has a simple electrostatic analogy. We must solve the Laplace equation $\nabla^2 n = 0$ with the boundary condition $n = 0$ at the surface of the sinks. Thus our problem amounts to solving the electrostatic problem of finding the potential due to a collection of ideally conducting grounded spheres in the presence of a given external potential. It is slightly more convenient to define the potential as $\phi(\mathbf{r}) = -n(\mathbf{r})$. If a constant value ϕ_0 is prescribed at infinity then for a finite collection of spheres the potential falls off asymptotically as

$$\phi(\mathbf{r}) \approx \phi_0 + (q_{\text{tot}}/r), \quad \text{as } r \rightarrow \infty, \quad (3.1)$$

where q_{tot} is the total charge induced in the spheres. This is directly related to the total particle flux into the system and we find the simple relation

$$J_{\text{tot}} = 4\pi D_0 C n_0, \quad (3.2)$$

where $C = -q_{\text{tot}}/\phi_0$ is the capacity of the collection of spheres. Henceforth we shall use terminology suggested by this electrostatic analogy.

The solution (2. 7) represents the potential due to a single grounded sphere centered at the origin and placed in the external potential $\phi_0(\mathbf{r}) = \phi_0 - \mathbf{e}_0 \cdot \mathbf{r}$. It can be written in the form

$$\phi(\mathbf{r}) = \phi_0(\mathbf{r}) + (q/r) + (\mathbf{p} \cdot \mathbf{r})/r^3, \tag{3. 3}$$

where q is the induced charge and \mathbf{p} the induced dipole moment, given by

$$q = -\gamma\phi_0, \quad \mathbf{p} = \alpha\mathbf{e}_0, \tag{3. 4}$$

with capacity $\gamma = R$ and polarizability $\alpha = R^3$.

In general higher multipole moments will also be induced but experience in electrostatics leads us to expect that for a large number of spheres their effect is small when the average distance is much larger than the radius. We shall completely neglect higher multipole moments in this article and restrict attention to charges and dipoles. Then the potential due to a collection of sinks centered at positions $(\mathbf{r}_1, \dots, \mathbf{r}_n)$ is given in analogy to Eq. (3. 3) by

$$\phi(\mathbf{r}) = \phi_0(\mathbf{r}) + \sum_{j=1}^n \frac{q_j}{|\mathbf{r} - \mathbf{r}_j|} + \sum_{j=1}^n \frac{\mathbf{p}_j \cdot (\mathbf{r} - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}_j|^3}, \tag{3. 5}$$

where now we consider $\phi_0(\mathbf{r})$ to be any solution of the Laplace equation $\nabla^2\phi_0 = 0$, and where the charges q_j and dipole moments \mathbf{p}_j must be determined self-consistently. They are given by the set of coupled equations

$$\begin{aligned} q_j &= -\gamma \left[\phi_0(\mathbf{r}_j) + \sum_{k \neq j} L_{jk} q_k + \sum_{k \neq j} \mathbf{F}_{jk} \cdot \mathbf{p}_k \right], \\ \mathbf{p}_j &= \alpha \left[-\nabla_j \phi_0(\mathbf{r}_j) + \sum_{k \neq j} \mathbf{F}_{jk} q_k + \sum_{k \neq j} \mathbf{T}_{jk} \cdot \mathbf{p}_k \right], \end{aligned} \tag{3. 6}$$

where we have abbreviated

$$L_{jk} = r_{jk}^{-1}, \quad \mathbf{F}_{jk} = -\nabla_j L_{jk}, \quad \mathbf{T}_{jk} = \nabla_j \nabla_j L_{jk}. \tag{3. 7}$$

For convenience we assume the sinks to be of equal size. Note that q_j and \mathbf{p}_j depend implicitly on the coordinates of all the sinks and on the external potential $\phi_0(\mathbf{r})$; in the sequel we shall apply statistical averaging to the above equations.

IV. STATISTICAL AVERAGING AND MEAN FIELD APPROXIMATION

The solution given in Eq. (3. 5) is valid for all points of space for which $|\mathbf{r} - \mathbf{r}_j| > R$ (any j), whereas $\phi(\mathbf{r}) = 0$ for $|\mathbf{r} - \mathbf{r}_j| < R$. Like in Eq. (2. 8), it is convenient to summarize the solution in terms of a differential equation valid for all space,

$$\nabla^2 \phi(\mathbf{r}) = -4\pi \sum_{j=1}^n q_j \delta(\mathbf{r} - \mathbf{r}_j) + 4\pi \sum_{j=1}^n \mathbf{p}_j \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_j), \tag{4. 1}$$

which clearly has a solution identical to (3. 5) in the part of space outside the sinks. Averaging over the ensemble of sink positions and using the definitions (2. 9) one finds a differential equation valid on the macroscopic scale

$$\nabla^2 \Phi(\mathbf{r}) = -4\pi Q + 4\pi \nabla \cdot \mathbf{P}. \tag{4. 2}$$

The solution of this equation with the same externally

imposed potential $\phi_0(\mathbf{r})$ defines the macroscopic potential $\Phi(\mathbf{r}) = \langle \phi(\mathbf{r}) \rangle$.

According to definition $\Phi = -N$ and in order to recover the steady-state version of Eq. (2. 11) the charge density $Q(\mathbf{r})$ and polarization $\mathbf{P}(\mathbf{r})$ must be expressed in terms of the average particle density $N(\mathbf{r})$. To this purpose we must apply the averaging procedure to Eqs. (3. 6) relating charges and dipoles.

It is convenient to assume that the sinks are identical and that their labeling is unimportant so that we may work with a probability ensemble $\mathcal{P}(\mathbf{r}_1, \dots, \mathbf{r}_n)$ symmetric in the sink indices. Positional distribution functions are defined by

$$\begin{aligned} \rho(\mathbf{r}) &= \left\langle \sum_{j=1}^n \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle, \\ \rho(\mathbf{r}, \mathbf{r}') &= \left\langle \sum_{j=1}^n \sum_{k=1}^n \delta(\mathbf{r} - \mathbf{r}_j) \delta(\mathbf{r}' - \mathbf{r}_k) \right\rangle, \\ \rho_c(\mathbf{r} | \mathbf{r}') &= \rho(\mathbf{r}, \mathbf{r}') / \rho(\mathbf{r}'), \end{aligned} \tag{4. 3}$$

etc. The conditional average of the charge of a sink, given its position is defined by

$$\bar{q}_1^1 \rho(\mathbf{r}_1) = \mathcal{N} \int q_1 \mathcal{P}(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_2 \dots d\mathbf{r}_n. \tag{4. 4}$$

Similarly one defines

$$\bar{q}_1^{12} \rho(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{N}(\mathcal{N} - 1) \int q_1 \mathcal{P}(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_3 \dots d\mathbf{r}_n \tag{4. 5}$$

when two sink positions are specified, etc. The moments \bar{q}_1^1 and $\bar{\mathbf{p}}_1^1$ are related to the average charge density $Q(\mathbf{r})$ and polarization $\mathbf{P}(\mathbf{r})$ defined in Eq. (2. 9) by

$$\begin{aligned} Q(\mathbf{r}) &= \rho(\mathbf{r}) \int \bar{q}_1^1 \delta(\mathbf{r} - \mathbf{r}_1) d\mathbf{r}_1, \\ \mathbf{P}(\mathbf{r}) &= \rho(\mathbf{r}) \int \bar{\mathbf{p}}_1^1 \delta(\mathbf{r} - \mathbf{r}_1) d\mathbf{r}_1. \end{aligned} \tag{4. 6}$$

Averaging Eqs. (3. 6) under the condition that the position of sink $j=1$ is fixed one obtains, in obvious notation,

$$\begin{aligned} \bar{q}_1^1 &= -\gamma \left[\phi_0(1) + \int L_{12} \bar{q}_2^{12} \rho_c(2 | 1) d(2) \right. \\ &\quad \left. + \int \mathbf{F}_{12} \cdot \bar{\mathbf{p}}_2^{12} \rho_c(2 | 1) d(2) \right], \\ \bar{\mathbf{p}}_1^1 &= \alpha \left[-\nabla_1 \phi_0(1) + \int \mathbf{F}_{12} \bar{q}_2^{12} \rho_c(2 | 1) d(2) \right. \\ &\quad \left. + \int \mathbf{T}_{12} \cdot \bar{\mathbf{p}}_2^{12} \rho_c(2 | 1) d(2) \right]. \end{aligned} \tag{4. 7}$$

The right-hand side contains second order averages which in turn are determined by third order averages, thus defining a hierarchy of equations. A simple mean field approximation is obtained by breaking the averages on the right-hand side of Eqs. (4. 7) and writing

$$Q(\mathbf{r}) = -\gamma \rho(\mathbf{r}) \Phi_L(\mathbf{r}), \quad \mathbf{P}(\mathbf{r}) = \alpha \rho(\mathbf{r}) \mathbf{E}_L(\mathbf{r}), \tag{4. 8}$$

with the Lorentz fields $\Phi_L(\mathbf{r})$ and $\mathbf{E}_L(\mathbf{r})$ defined by

$$\Phi_L(\mathbf{r}) = \phi_0(\mathbf{r}) + \lim_{\epsilon \rightarrow 0} \int_{\nu} L(\mathbf{r} - \mathbf{r}') Q(\mathbf{r}') d\mathbf{r}'$$

$$+ \lim_{\delta \rightarrow 0} \int_{\mathcal{V}} \mathbf{F}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}') d\mathbf{r}', \quad (4.9a)$$

$$\mathbf{E}_L(\mathbf{r}) = -\nabla\phi_0(\mathbf{r}) + \lim_{\delta \rightarrow 0} \int_{\mathcal{V}} \mathbf{F}(\mathbf{r} - \mathbf{r}') Q(\mathbf{r}') d\mathbf{r}' \\ + \lim_{\delta \rightarrow 0} \int_{\mathcal{V}} \mathbf{T}(\mathbf{r} - \mathbf{r}') \mathbf{P}(\mathbf{r}') d\mathbf{r}', \quad (4.9b)$$

where the subscript \mathcal{V} indicates that a small sphere of radius δ has been excluded from the region of integration. These fields can be compared with the macroscopic potential $\Phi(\mathbf{r})$ given by the solution of Eq. (4.2)

$$\Phi(\mathbf{r}) = \phi_0(\mathbf{r}) + \int L(\mathbf{r} - \mathbf{r}') Q(\mathbf{r}') d\mathbf{r}' + \int \mathbf{F}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}') d\mathbf{r}'. \quad (4.10)$$

It is easy to see that for the propagators defined in Eq. (3.7) the limits for the potential Φ_L defined in Eq. (4.9a) can be taken without effect so that $\Phi_L(\mathbf{r}) = \Phi(\mathbf{r})$. On the other hand for the macroscopic vector field defined by $\mathbf{E} = -\nabla\Phi$ one has from Eq. (4.9b)

$$\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}) = \mathbf{E}_L(\mathbf{r}) - \frac{4}{3}\pi\mathbf{P}(\mathbf{r}), \quad (4.11)$$

which is the familiar Lorentz local field effect. Combining these results with Eq. (4.8) one finds that in mean field approximation

$$Q = -\gamma\rho\Phi, \quad \mathbf{P} = -\frac{\alpha\rho}{i - \frac{4}{3}\pi\alpha\rho} \nabla\Phi. \quad (4.12)$$

Substituting in Eq. (4.2) and putting $\Phi = -N$ one finds

$$\nabla \cdot [D(\rho)\nabla N] - k(\rho)\rho N = 0 \quad (4.13)$$

with

$$D(\rho) = D_0\sigma(\rho), \\ \frac{\sigma - 1}{\sigma + 2} = \frac{4\pi}{3} \alpha\rho, \quad (4.14)$$

$$k(\rho) = 4\pi D_0\gamma = k_0.$$

Thus in mean field approximation the diffusion coefficient $D(\rho)$ increases beyond its dilute limit value D_0 by a factor $\sigma(\rho)$, which may be called the acceleration factor. This factor is given by a formula identical with the Clausius-Mossotti expression for the dielectric constant of a polarizable medium. In the mean field approximation the rate coefficient has the dilute limit value. In the remainder of this article we shall investigate the effect of correlations on the rate coefficient.

Before proceeding we generalize slightly by modifying the boundary condition at the sink surface to $\phi = R_0(\partial\phi/\partial n)$ at $|\mathbf{r} - \mathbf{r}_j| = R$, corresponding to incomplete absorption of particles.^{6,12} This leads to

$$\gamma = R[1 + (R_0/R)]^{-1}, \quad (4.15)$$

$$\alpha = R^3[1 - (R_0/R)][1 + 2(R_0/R)]^{-1},$$

so that the capacity and polarizability are decreased by effectiveness factors. It is easy to see that the rest of the calculation still applies with these new values of α and γ .

V. THE EFFECT OF CORRELATIONS FOR CHARGES ONLY

In our initial approach to the problem we shall completely neglect the effect of the dipoles and consider charges only. This gives rise to appreciable simplification of the equations. For a dilute sink system the effect of the dipoles is small relative to that of the charges. It will be shown that in the final result for the rate coefficient the dipoles contribute a correction which is of higher order in the sink density.

The first three members of the hierarchy of moment equations for the case of charges only read

$$\bar{q}_1^1 = -\gamma \left[\phi_0(1) + \int L_{12} \bar{q}_2^{12} \rho_c(2 | 1) d(2) \right], \quad (5.1a)$$

$$\bar{q}_1^{12} = -\gamma \left[\phi_0(1) + L_{12} \bar{q}_2^{12} + \int L_{13} \bar{q}_3^{123} \rho_c(3 | 12) d(3) \right], \quad (5.1b)$$

$$\bar{q}_2^{12} = -\gamma \left[\phi_0(2) + L_{21} \bar{q}_1^{12} + \int L_{23} \bar{q}_3^{123} \rho_c(3 | 12) d(3) \right]. \quad (5.1c)$$

Eq. (5.1a) can be rewritten

$$\bar{q}_1^1 = -\gamma \left[\phi_d(1) + \int L_{12} (\bar{q}_2^{12} - \bar{q}_2^{12}) \rho_c(2 | 1) d(2) \right], \quad (5.2)$$

where

$$\phi_d(1) = \phi_0(1) + \int L_{12} \bar{q}_2^2 \rho_c(2 | 1) d(2), \quad (5.3)$$

which we shall call the *direct potential*. Since $\rho_c(2 | 1)$ tends to $\rho(2)$ for large separation of 1 and 2 it is clear from Eq. (4.9a) that the direct potential is a slight modification of the Lorentz potential $\Phi_L(\mathbf{r})$ for the case $\mathbf{P} = 0$. Hence $\phi_d(\mathbf{r})$ will differ only slightly from the macroscopic potential $\Phi(\mathbf{r})$. Since the integrand in Eq. (5.2) will be shown to be short ranged, the right-hand side of this equation contains only local quantities. This is important, because as a consequence one does not have to worry about the shape of the macroscopic sample. The elimination of ϕ_0 by the definition (5.3) and by the proof that $\Phi_L = \Phi$ amount to an application of the extinction theorem to the present case.

We obtain a set of equations for the integrand in Eq. (5.2) by subtracting Eq. (5.1a) from (5.1b), and changing indices

$$\bar{q}_1^{12} - \bar{q}_1^1 \\ = -\gamma \left\{ L_{12} \bar{q}_2^{12} + \int L_{13} [\bar{q}_3^{123} \rho_c(3 | 12) - \bar{q}_3^{13} \rho_c(3 | 1)] d(3) \right\}, \quad (5.4)$$

$$\bar{q}_2^{12} - \bar{q}_2^2 \\ = -\gamma \left\{ L_{21} \bar{q}_1^{12} + \int L_{23} [\bar{q}_3^{123} \rho_c(3 | 12) - \bar{q}_3^{23} \rho_c(3 | 2)] d(3) \right\}.$$

At this point we break the hierarchy by making a superposition approximation which we expect to be exact in the limit of low sink density. Explicitly the *superposition approximation* is

$$\bar{q}_3^{123} \rho_c(3 | 12) \approx \bar{q}_3^3 \rho(3) + [\bar{q}_3^{13} \rho_c(3 | 1) - \bar{q}_3^3 \rho(3)]$$

$$\begin{aligned}
 & + [\bar{q}_3^{23} \rho_c(3|2) - \bar{q}_3^3 \rho(3)] \\
 & = \bar{q}_3^{13} \rho_c(3|1) + \bar{q}_3^{23} \rho_c(3|2) - \bar{q}_3^3 \rho(3). \quad (5.5)
 \end{aligned}$$

Upon substitution in Eqs. (5.4) one obtains the closed set of equations

$$\bar{q}_1^{12} - \bar{q}_1^1 = -\gamma \left\{ L_{12} \bar{q}_2^{12} + \int L_{13} [\bar{q}_3^{23} \rho_c(3|2) - \bar{q}_3^3 \rho(3)] d(3) \right\}, \quad (5.6)$$

$$\bar{q}_2^{12} - \bar{q}_2^2 = -\gamma \left\{ L_{21} \bar{q}_1^{12} + \int L_{23} [\bar{q}_3^{13} \rho_c(3|1) - \bar{q}_3^3 \rho(3)] d(3) \right\}.$$

These equations describe two important effects. First, the direct interaction between a pair is taken into account to all orders of "reflections." Secondly, the influence of the other sinks leads to the effect of screening. That screening occurs is clear from a macroscopic consideration. If we place an additional external charge in our system then the sinks in the immediate neighborhood will acquire induced charges to a total amount exactly equal and opposite to the external charge. As a result the Coulomb potential of the external charge is modified to a potential of the Yukawa form. The effect is completely analogous to Debye screening in a plasma or an electrolyte solution. Mathematically the screening leads to a relation between moments which we shall call the *screening relation*. From Eq. (5.6) it follows that if $\bar{q}_1^{12} - \bar{q}_1^1$ is to fall off faster with distance than the Coulomb potential L_{12} , then one must have

$$\bar{q}_1^1 = \int [\bar{q}_2^2 \rho(2) - \bar{q}_2^{12} \rho_c(2|1)] d(2). \quad (5.7)$$

This relation will be verified from the explicit solution.

Henceforth we restrict attention to a region which is spatially uniform, where the density ρ and the charge density Q are constant and pair correlation functions depend on spatial distances only. Thus we can write

$$\begin{aligned}
 \bar{q}_1^1 &= \bar{q}_2^2 = Q/\rho, \\
 \bar{q}_1^{12} &= \bar{q}_2^{12} = (Q/\rho) [1 + f(r_{12})].
 \end{aligned} \quad (5.8)$$

The pair of Eqs. (5.6) reduces to a single equation for the correlation function $f(r_{12})$, which can be written

$$(1 + \gamma L_{12}) f(r_{12}) = -\gamma \left[I(r_{12}) + \int L_{13} f(r_{32}) \rho_c(3|2) d(3) \right], \quad (5.9)$$

where

$$I(r_{12}) = L_{12} + \int L_{13} (\rho_c(3|2) - \rho) d(3). \quad (5.10)$$

In relative coordinates $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{r}' = \mathbf{r}_3 - \mathbf{r}_2$ these equations become

$$\begin{aligned}
 [1 + (\gamma/r)] f(r) &= -\gamma I(r) - \gamma F(r), \\
 I(r) &= r^{-1} + \Psi(r),
 \end{aligned} \quad (5.11)$$

where we have introduced the functions

$$F(r) = \int \frac{f(r') \rho_c(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad \Psi(r) = \int \frac{\rho_c(r') - \rho}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (5.12)$$

Because of the spherical symmetry of the functions $f(r')$ and $\rho_c(r')$, the functions $F(r)$ and $\Psi(r)$ clearly depend on the radial distance r only.

By applying the Laplace operator in Eq. (5.12) one finds for $F(r)$ the ordinary differential equation

$$\frac{d^2 F}{dr^2} + \frac{2}{r} \frac{dF}{dr} = -4\pi f(r) \rho_c(r), \quad (5.13)$$

with solution

$$F(r) = (F_0/r) + \tilde{F}(r), \quad (5.14)$$

where

$$\begin{aligned}
 F_0 &= \int_0^\infty 4\pi f(r') \rho_c(r') r'^2 dr', \\
 \tilde{F}(r) &= \int_r^\infty 4\pi f(r') \rho_c(r') r' dr' \\
 &\quad - r^{-1} \int_r^\infty 4\pi f(r') \rho_c(r') r'^2 dr'.
 \end{aligned} \quad (5.15)$$

Similarly one has

$$\Psi(r) = (\Psi_0/r) + \tilde{\Psi}(r), \quad (5.16)$$

with

$$\begin{aligned}
 \Psi_0 &= \int_0^\infty 4\pi (\rho_c(r') - \rho) r'^2 dr', \\
 \tilde{\Psi}(r) &= \int_r^\infty 4\pi (\rho_c(r') - \rho) r' dr' \\
 &\quad - r^{-1} \int_r^\infty 4\pi (\rho_c(r') - \rho) r'^2 dr'.
 \end{aligned} \quad (5.17)$$

The screening relation (5.7) can now be written

$$F_0 + \Psi_0 + 1 = 0, \quad (5.18)$$

and Eq. (5.11) becomes

$$[1 + (\gamma/r)] f(r) = -\gamma [\tilde{\Psi}(r) + \tilde{F}(r)]. \quad (5.19)$$

We must show that this equation has a solution $f(r)$ which vanishes sufficiently rapidly at infinity. By differentiating Eq. (5.19) twice with respect to r one finds

$$(r + \gamma) \left(\frac{d^2 f}{dr^2} \right) + 2 \left(\frac{df}{dr} \right) - 4\pi \gamma r \rho_c(r) f = 4\pi \gamma r [\rho_c(r) - \rho]. \quad (5.20)$$

Since $\rho_c(r)$ rapidly tends to the constant ρ it follows that Eq. (5.20) has a solution which is exponentially damped $f \sim \exp(-\kappa r)$ with a screening length κ^{-1} given by

$$\kappa^2 = 4\pi \gamma \rho. \quad (5.21)$$

At low density the screening length is large, and in this case we can expect the superposition approximation (5.5) to be valid. Because of the long range of the interaction collective effects predominate.

The integral which we need in Eq. (5.2) reduces in the uniform case to

$$4\pi(Q/\rho) \int_0^\infty f(r) \rho_c(r) r dr. \quad (5.22)$$

For this we must solve Eq. (5.20) for $f(r)$, but unfortunately the explicit solution can not be obtained in gen-

eral. Therefore we now specialize to a particular choice for the conditional pair correlation function $\rho_c(r)$.

VI. EXPLICIT SOLUTION FOR THE CHARGE CORRELATION FUNCTION

In order to make further progress we assume that the sink system is dilute so that the pair correlation function $\rho_c(r)$ can be replaced by

$$\begin{aligned} \rho_c(r) &= \rho \quad \text{for } r \geq d, \\ &= 0 \quad \text{for } r < d, \end{aligned} \quad (6.1)$$

where $d = 2R$ is the sphere diameter. Then Eq. (5.20) reduces to a homogeneous equation. Introducing

$$x = \kappa r, \quad \hat{f}(x) = f(r), \quad (6.2)$$

one can write it in the dimensionless form

$$(x + \epsilon)\hat{f}'' + 2\hat{f}' - x\hat{f} = 0, \quad (6.3)$$

where a prime denotes differentiation with respect to x and $\epsilon = \kappa\gamma$. Equation (6.3) is related to the equation for the confluent hypergeometric function¹³ and the solution with desired behavior at infinity can be written

$$\bar{f}(x) = 2\Gamma(a)U(a, 2, 2(x + \epsilon))e^{-x\epsilon}, \quad a = 1 - \frac{1}{2}\epsilon, \quad (6.4)$$

where the overbar denotes that we have chosen a convenient normalization. In fact, in our problem the normalization of the solution $\hat{f}(x)$ is prescribed by the screening relation (5.18) which presently reads

$$\hat{F}_2(\kappa d) = (8c - 1)\epsilon, \quad (6.5)$$

where

$$\hat{F}_2(x) = \int_x^\infty \hat{f}(x')x'^2 dx' \quad (6.6)$$

and

$$c = \frac{4}{3}\pi\rho R^3, \quad \epsilon = \kappa\gamma. \quad (6.7)$$

Here c is the volume fraction occupied by sinks and ϵ is related to c via Eq. (5.21) by

$$\epsilon^2 = 3\tau^3 c, \quad (6.8)$$

where τ is the effectiveness factor defined by $\gamma = \tau^{-1}R$ and given by Eq. (4.15). The parameter ϵ is therefore at most equal to κR , where κ^{-1} is the screening length, and is small for small volume fraction.

The integral we need in Eq. (5.22) can be written

$$4\pi Q \int_d^\infty f(r)r dr = (Q/\rho\gamma)\hat{F}_1(\kappa d), \quad (6.9)$$

where

$$\hat{F}_1(x) = \int_x^\infty \hat{f}(x')x' dx'. \quad (6.10)$$

If we work with a function $\bar{f}(x)$ with normalization different from Eq. (6.5), and with corresponding integrals $\bar{F}_1(x)$ and $\bar{F}_2(x)$, then we have

$$\hat{F}_1(\kappa d) = [\bar{F}_1(\kappa d)/\bar{F}_2(\kappa d)](8c - 1)\epsilon. \quad (6.11)$$

We wish to evaluate this expression for small ϵ , which implies small $\kappa d = 2\tau\epsilon$.

From the known series expansion of the confluent hypergeometric function¹³ one finds for the behavior for small $x + \epsilon$ of the function $\bar{f}(x)$ defined in Eq. (6.4)

$$\begin{aligned} \bar{f}(x) &= (x + \epsilon)^{-1} - \epsilon \ln(x + \epsilon) - 1 \\ &\quad - \epsilon(\gamma_E + \ln 2) + \frac{1}{2}\epsilon^2(x + \epsilon) \ln(x + \epsilon) + O(x + \epsilon), \end{aligned} \quad (6.12)$$

where $\gamma_E = 0.57721\dots$ is Euler's constant. The asymptotic behavior of the solution for large x is given by

$$\bar{f}(x) = 2^{6/2}\Gamma\left(1 - \frac{\epsilon}{2}\right)\frac{e^{-(x+\epsilon)}}{x^{1-\epsilon/2}} [1 + O(x^{-1})] \quad \text{as } x \rightarrow \infty. \quad (6.13)$$

This confirms the exponential behavior previously stated but provides a more accurate estimate. The result (6.13) shows that the characteristic decay length of the function $f(r)$ is indeed given by the screening length κ^{-1} .

The integral equation (5.19) from which Eq. (6.3) has been obtained can be written in the present case

$$(x + \epsilon)\bar{f}(x) = \bar{F}_2(x) - x\bar{F}_1(x). \quad (6.14)$$

Differentiating with respect to x one finds that $\bar{F}_1(x)$ can be expressed in terms of $\bar{f}(x)$ and $f'(x)$ by

$$\bar{F}_1(x) = -\bar{f}(x) - (x + \epsilon)\bar{f}'(x). \quad (6.15)$$

The functions $\bar{F}_1(x)$ and $\bar{F}_2(x)$ are needed for a value $x = \nu\epsilon$, where ν is of order unity ($= 2\tau$) and ϵ is small. From the known series expansion one finds for such values of x

$$\begin{aligned} \bar{F}_1(x) &= 1 + \epsilon \ln(x + \epsilon) - x + \epsilon(\gamma_E + \ln 2) + O(\epsilon^2 \ln \epsilon), \\ \bar{F}_2(x) &= 1 - \epsilon + O(\epsilon^2 \ln \epsilon), \quad \epsilon \text{ small, } x = \nu\epsilon. \end{aligned} \quad (6.16)$$

The ratio of these expressions can be used in Eq. (6.11). Before deriving the final result for the rate coefficient we study the effect of the dipoles.

VII. CHARGES AND DIPOLES

We now consider the additional effect of the induced dipoles. In many respects the calculation is similar to that of the preceding sections. As a starting point one uses Eqs. (4.7) for the induced charge and dipole moment of a sink 1, given its position \mathbf{r}_1 . One then proceeds as in Sec. V and derives a hierarchy of equations which is decoupled by making the superposition approximation (5.5) for the charges and analogously for the dipole moments.

In a spatially uniform region the sink density ρ , the charge density Q , and the macroscopic potential Φ are constant, whereas the macroscopic electric field \mathbf{E} and polarization \mathbf{p} vanish. For the first order moments one has $\bar{q}_1^1 = (Q/\rho)$ and $\bar{\mathbf{p}}_1^1 = 0$. Moreover, the pair correlation functions depend only on the vector distance $\mathbf{r}_1 - \mathbf{r}_2$. One defines the radial correlation functions $f(r_{12})$ and $g(r_{12})$ by

$$\begin{aligned} \bar{q}_1^{12} &= \bar{q}_2^{12} = (Q/\rho)[1 + f(r_{12})], \\ \bar{\mathbf{p}}_1^{12} &= -\bar{\mathbf{p}}_2^{12} = (Q/\rho)(\mathbf{r}_1 - \mathbf{r}_2)g(r_{12}). \end{aligned} \quad (7.1)$$

The correlation functions $f(r)$ and $g(r)$ satisfy the coupled equations

$$\begin{aligned}
 [1 + (\gamma/r)]f(r) &= -\gamma[I(r) + F(r) - r^{-1}g(r) \\
 &\quad - G(r) - r(dG/dr)], \\
 [1 + (2\alpha/r^3)]g(r) &= \alpha[-r^{-1}(dI/dr) - \frac{2}{3}\pi\rho_c(r)g(r) \\
 &\quad + r^{-3}f(r) - r^{-1}(dF/dr)], \quad (7.2)
 \end{aligned}$$

where $I(r)$ and $F(r)$ are defined in Eqs. (5.10) and (5.12) and $G(r)$ is defined by

$$G(r) = \int \frac{g(r')\rho_c(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (7.3)$$

The integral which is needed in Eq. (4.7a), reduces in the spatially uniform case to

$$4\pi(Q/\rho) \int_0^\infty [f(r) - g(r)]\rho_c(r)r dr. \quad (7.4)$$

Specializing to a dilute sink system one replaces the pair correlation function $\rho_c(r)$ by the expression given in Eq. (6.1). Introducing

$$x = \kappa r, \quad \hat{f}(x) = f(r), \quad \hat{g}(x) = g(r), \quad (7.5)$$

one can now write the integral equations (7.2) in the dimensionless form

$$\begin{aligned}
 (x + \epsilon)\hat{f}(x) - \epsilon\hat{g}(x) &= \hat{F}_2(x) - x\hat{F}_1(x) + x\hat{G}_1(x), \\
 -\epsilon^3\hat{f}(x) + [(\theta + \frac{2}{3}\epsilon^2)x^3 + 2\epsilon^3]\hat{g}(x) &= -\epsilon^2\hat{F}_2(x)
 \end{aligned} \quad (7.6)$$

with the definitions

$$\begin{aligned}
 \hat{F}_1(x) &= \int_x^\infty x' \hat{f}(x') dx', \quad \hat{F}_2(x) = \int_x^\infty x'^2 \hat{f}(x') dx', \\
 \hat{G}_1(x) &= \int_x^\infty x' \hat{g}(x') dx'. \quad (7.7)
 \end{aligned}$$

Furthermore $\epsilon = \kappa\gamma$ is the previously introduced small parameter, and $\theta = (\gamma^3/\alpha)$ is equal to unity for complete absorption, and otherwise is given by Eqs. (4.15). It is easily shown that $\theta \geq 1$. In deriving Eqs. (7.6) we have made use of the screening relation (5.18) which is again valid. This provides the normalization condition

$$\hat{F}_2(\kappa d) = (8c - 1)\epsilon, \quad (7.8)$$

identical to Eq. (6.5). The required integral (7.4) can be written

$$4\pi Q \int_0^\infty [f(r) - g(r)]r dr = (Q/\rho\gamma)[\hat{F}_1(\kappa d) - \hat{G}_1(\kappa d)]. \quad (7.9)$$

It is again more convenient to work with functions with arbitrary normalization and we shall denote these by an overbar. From Eq. (7.8) we find the relation

$$\hat{F}_1(\kappa d) - \hat{G}_1(\kappa d) = [(\bar{F}_1(\kappa d) - \bar{G}_1(\kappa d))/\bar{F}_2(\kappa d)](8c - 1)\epsilon. \quad (7.10)$$

The integral equations (7.6) can not be solved exactly. For the asymptotic behavior of the functions $\bar{f}(x)$ and $\bar{g}(x)$ for large values of x one finds

$$\bar{f}(x) \approx Ae^{-\lambda x} x^{-\beta}, \quad \bar{g}(x) \approx -A(\epsilon^2/\mu\lambda) e^{-\lambda x} x^{-\beta-1}, \quad \text{as } x \rightarrow \infty, \quad (7.11)$$

where A is a normalization constant and

$$\begin{aligned}
 \lambda &= [1 - (\epsilon^2/\mu)]^{1/2}, \\
 \beta &= 1 - \frac{1}{2}\epsilon\lambda,
 \end{aligned}$$

$$\mu = \theta + \frac{2}{3}\epsilon^2. \quad (7.12)$$

The behavior of the functions $\bar{F}_1(x)$, $\bar{F}_2(x)$, and $\bar{G}_1(x)$ for small values of ϵ can be found by a perturbation expansion. The calculation is lengthy and we shall omit the details. Choosing a normalization corresponding to that of the preceding section one finds for values $x = \nu\epsilon$, where ν is of order unity and ϵ is small,

$$\begin{aligned}
 \bar{F}_1(x) - \bar{G}_1(x) &= 1 + \epsilon \ln(x + \epsilon) - x + \epsilon(\gamma_E + \ln 2) \\
 &\quad + \epsilon J(\nu, \theta) + O(\epsilon^2 \ln \epsilon), \quad (7.13)
 \end{aligned}$$

$$\bar{F}_2(x) = 1 - \epsilon + O(\epsilon^2 \ln \epsilon), \quad \epsilon \text{ small, } x = \nu\epsilon,$$

where

$$J(\nu, \theta) = \int_\nu^\infty \frac{u^3 du}{(u+1)^2(\theta u^2 + 2)}. \quad (7.14)$$

Thus the ratio needed in Eq. (7.10) has a value only slightly different from that given by Eq. (6.17).

VIII. RESULTS AND DISCUSSION

We now summarize our results. The generalization of Eq. (5.2) to the case including dipoles is given by

$$\begin{aligned}
 \bar{q}_1^1 &= -\gamma \left[\phi_d(1) + \int L_{12}(\bar{q}_2^{12} - \bar{q}_2^2) \rho_c(2|1) d(2) \right. \\
 &\quad \left. + \int \mathbf{F}_{12} \cdot (\bar{\mathbf{p}}_2^{12} - \bar{\mathbf{p}}_2^2) \rho_c(2|1) d(2) \right]. \quad (8.1)
 \end{aligned}$$

In a spatially uniform region this can be written with the aid of Eqs. (7.1)

$$Q = -\gamma\rho\phi_d - 4\pi\gamma Q \int_0^\infty [f(r_{12}) - g(r_{12})]\rho_c(2|1)r_{12} dr_{12}. \quad (8.2)$$

With the density correlation function given by Eq. (6.1) one finds for the direct potential

$$\phi_d = \Phi - 2\pi d^2 Q. \quad (8.3)$$

Substituting in Eq. (8.2) one finds the constitutive equation

$$Q = -a(\rho)\rho\Phi, \quad (8.4)$$

where $a(\rho)$ has the dimension of length and is given by

$$a(\rho) = \gamma[1 - 2\tau^2\epsilon^2 + \hat{F}_1(\kappa d) - \hat{G}_1(\kappa d)]^{-1}. \quad (8.5)$$

The corresponding reaction rate coefficient is given by

$$k(\rho) = 4\pi D_0 a(\rho). \quad (8.6)$$

Inserting Eqs. (7.10) and (7.13) one finds

$$\begin{aligned}
 a(\rho) &= \gamma \{ 1 + \epsilon + \epsilon^2 \ln \epsilon + \epsilon^2 [1 - 2\tau + 2\tau^2 + \gamma_E \\
 &\quad + \ln(2 + 4\tau) + J(2\tau, \theta)] + O(\epsilon^3 \ln \epsilon) \}, \quad (8.7)
 \end{aligned}$$

where $\tau = (R/\gamma)$, $\theta = (\gamma^3/\alpha)$, and $\gamma_E = 0.57721\dots$ is Euler's constant. In the fully absorbing case one has $\tau = 1$, $\theta = 1$, and $\epsilon = \kappa\gamma$ can be expressed in terms of the volume fraction $c = \frac{4}{3}\pi\rho R^3$ by $\epsilon = (3c)^{1/2}$. In this case the result (8.7) can be written

$$a(\rho) = \gamma \left\{ 1 + (3c)^{1/2} + \frac{3}{2} c \ln c \right. \\ \left. + 3c \left[1 + \gamma_E + \ln 2 + \frac{3}{2} \ln 3 + J(2, 1) \right] + O(c^{3/2} \ln c) \right\}. \quad (8.8)$$

From Eq (7.14) one finds that the correction term $J(2, 1)$ due to the dipole moments is given by $J(2, 1) = 0.31907\dots$

From Eqs. (8.6) and (8.8) it follows that the rate of reaction increases with increasing density of absorbers. This result is confirmed by a simple cell model calculation, which however leads to a $c^{1/3}$ - rather than a $c^{1/2}$ -correction term. A variational calculation¹⁴ applied to the cell model also leads to a $c^{1/3}$ correction term.

Finally, we note again the approximations made in the present calculation. First, we have assumed that induced multipole moments higher than the dipole can be neglected. Since the major contribution to the integrals comes from the screening range this assumption seems well justified. Moreover, we have shown that the dipole moments contribute an order higher in the density compared with the monopoles and it seems likely that a multipole expansion is directly coupled to a density expansion. Secondly, we have made the superposition approximation embodied in Eq. (5.5). We expect this to be valid for low density, but a systematic parameter expansion analogous to the theory of the classical plasma would be desirable.

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