I. INTRODUCTION

Diffusion-limited reactions are common to many kinetic systems including suspension polymerization, growth of aerosol or colloidal particles, and the combustion of liquid drops, to name only a few. In these systems, the effective reaction rate is essentially determined by the time scale for the reacting species to diffuse to one another, rather than the time scale for the species to overcome an activation energy barrier. Typically, one of the reacting species is much larger and less mobile than the other reactant, for example, as in the case of the suspended polymer and reactive monomer. In these situations one of the reactants is effectively a static trap, and the time scale is determined by the mobile reactant diffusion coefficient. The concentration of the traps, however, also influences the effective reaction rate because of the competition among them for the mobile reactant. It is our aim to determine the effective reaction rate for spherical traps over a wide range of sphere volume fractions for random and periodic systems.

To determine the effective reaction rate one needs the relationship (ratio) of the average flux into a trap to the average mobile reactant concentration. We have developed a method to directly determine this relationship in the context of electrostatics, which is mathematically analogous to the problem at hand. The method is based upon multipole scattering and properly handling the long-ranged, conditionally convergent interactions among an infinite collection of particles. The method can be used for both random and nonrandom dispersions.

Smoluchowski first computed the infinite dilution or noninteracting traps effective reaction rate by considering a single spherical particle in an unbounded fluid. In the last 15 years a great deal of effort has been devoted to include the effects of interactions among the traps. Lebenhaft and Kapral first used a monopole expansion for spheres on simple and face-centered-cubic lattices. They quantitatively determined the correct $c^{1/3}$ scaling (where $c$ is the trap volume fraction) for the first correction to the rate constant. Their results, however, incorrectly show the effective reaction rate diverging at $c \approx 0.17$, a physically unreasonable result. As we shall show, the divergence is due to the neglect of the average irreducible quadrupole and the source distribution in the fluid phase necessary for a steady-state formulation of the problem. Recently, Venema and Bedeaux have computed the exact effective reaction rate for the cubic lattices using a spherical multipole expansion. At closest packing they found up to 50 moments were required to achieve accuracy to five significant figures.

Felderhof and Deutch used the multipole approach through the dipole level with two-particle ensemble averaging to determine the first correction to Smoluchowski's equation for the random dispersion of spherical particles. Most notably, they found the reaction rate scales as $c^{1/2}$ rather than $c^{1/3}$ as seen in periodic systems. The $c^{1/2}$ correction can also be found by determining the flux into a single reactive sphere in the electrostatic analog of a Brinkman medium. Muthumakar and Cukier extended this work to include higher moments but for penetrable spheres. Muthumakar has also developed an effective medium theory for random systems.

Recently, direct numerical simulations have been used to determine the effective reaction rate for infinite systems of spherical sinks. Lee, Kim, Miller, and Torquato and Zheng and Chiew calculate the reaction rate as the inverse of the average time for tracer particles representing the reactant to randomly walk to one of many randomly placed static traps. The arrival times are averaged over a number of initial starting positions and trap configurations. Both research groups' results compare quite well and are consistent with the lower bounds established by Torquato. Miller and Torquato have performed similar numerical simulations for suspensions of bidisperse traps.

In this paper we shall use our multipole scattering method on infinite random dispersions of spherical traps. Here, we shall only employ up to the quadrupoles in the multipole expansion but shall also directly include the exact near-field two-body interactions to see if this method is as successful for computing the effective reaction rate as it
has been for computing the conductivity. In Sec. II we briefly outline the method and determine explicitly the form of the lower order corrections for cubic lattices. In Sec. III we apply the method to infinite, random dispersions modeled as periodically replicated cells of Monte Carlo generated configurations of a finite number of spheres. We then compare our results to some of the above referred work and to Drinkman-like effective medium theories.

II. METHOD

We formulate the problem as an infinite dispersion of static, nonpenetrable, spherical particles of radius \( a \) immersed in a matrix. A very fast reaction occurs on each sphere surface with a reactant whose concentration at a position \( x \) is denoted by \( \phi(x) \). The reactant has diffusivity \( D \) in the matrix phase and \( D_p \) in the particle phase. Further, to ensure a steady state, there is some reactant source distributed throughout the suspension. The effective reaction rate is then defined as the ratio of the total reactant consumed per unit volume by the traps (or produced per unit volume in the suspension) to the suspension average concentration of the reactant. The average rate of consumption of reactant \( r \) is thus given by \( r = k_{\text{eff}} \langle \phi \rangle n \), where \( k_{\text{eff}} \) is the effective reaction rate, \( \langle \phi \rangle \) is the volume average concentration of the mobile reactant, and \( n \) is the number density of particle traps.

Effectively, we must solve Poisson's equation in the matrix and particle phases with the usual continuity of concentration and flux at the particle surfaces. We need, however, only the average particle flux and the average concentration rather than the detailed concentration field. Because the Poisson equation is linear, there exists the exact relationship

\[
\begin{pmatrix}
Q \\
S
\end{pmatrix} =
\begin{pmatrix}
C_{\phi\phi} & C_{\phi G} \\
C_{G\phi} & C_{GG}
\end{pmatrix}
\begin{pmatrix}
\Phi \\
G
\end{pmatrix}
\]

among \( N \) particles. The vectors \( q, S, \Phi, \) and \( G \) contain the \( N \) particle charges, the \( 3N \) components of the particle dipoles, the \( N \) particle relative concentrations at each particle reference point, \( R_p \), \( \phi(R_p) - \langle \phi(R_p) \rangle \), and \( 3N \) components of the average potential gradient, respectively. The matrix in Eq. (1) is called the capacitance matrix \( C \) in electrostatics and is a geometric quantity dependent only upon the trap configuration, \( D_p/D \), and the form of the source distribution.

Here the particles will be assumed to have a uniform concentration of zero at their surfaces, so if the reactant source is distributed only in the matrix phase the particles are equivalent to electrostatic perfect conductors. If reactant is also distributed in the particle phase, and if \( D_p/D \ll 1 \), the particles are also equivalent to perfect conductors. The capacitance matrix's submatrices relate the charge to the potential \( C_{\phi\phi} \), the charge to the gradient \( C_{G\phi} \), etc. The effective reaction rate is then the suspension average value of the \( C_{\phi\phi} \) coupling when there is no potential gradient. In this case the effective rate constant, nondimensionalized by Smoluchowski's dilute trap rate constant, \( k_s = 4\pi Da \), is

\[
\frac{k_{\text{eff}}}{k_s} = \frac{C_{\phi\phi}}{4\pi Da} 
\]

In our method, which is described elsewhere, we approximate the capacitance matrix by

\[
C \approx C^{-1} + C_{2b} - C_{2b}^{0}
\]

The "potential" matrix \( M^{-1} \) in its exact form is the inverse of the capacitance matrix. Here, we form an approximation to the potential matrix from a moment expansion about each particle derived from the integral representation of Poisson's equation. The moment expansion can be carried out to any level. If the expansion is done up to the quadrupole level, for example, the so-called grand potential matrix \( \hat{\mathbf{M}} \) can be written as

\[
\begin{pmatrix}
\Phi \\
-\mathbf{G}
\end{pmatrix} =
\begin{pmatrix}
\hat{M}_{\phi\phi} & \hat{M}_{\phi G} \\
\hat{M}_{G\phi} & \hat{M}_{GG}
\end{pmatrix}
\begin{pmatrix}
q \\
S
\end{pmatrix}
\]

where \( \mathbf{G} \) is the gradient of the average potential gradient and \( \mathbf{Q} \) is the vector containing the \( N \) particle quadrupoles. For an unbounded statistically homogeneous suspension of particles \( \mathbf{G} = 0 \) because it is inconsistent to have a quadratic concentration field in the absence of boundaries. Since \( \mathbf{G} = 0 \), we can solve for \( \mathbf{Q} \) in terms of \( q \) and \( S \) and form an approximate potential matrix \( M \). If additional moments are included, they can also be solved for in terms of \( q \) and \( S \) since all higher derivatives of the gradient must vanish for an infinite system of particles, and their effects can be included into \( M^{-1} \).

The accuracy of the potential matrix, and hence, the accuracy of the potential invert depend upon the number of moments retained in its formulation. The inversion of the potential matrix captures the many-body far-field particle interactions since the inversion is equivalent to a many-body method of reflections solution. Note, care must be taken in forming the potential matrix for an infinite suspension because the particle interactions are long-ranged, giving rise to convergence difficulties (see Ref. 1 for details).

Recall we are considering particles analogous to perfect conductors in the electrostatic problem. If two nearby particles have different concentrations the flux between them is logarithmically singular in gap width. To include these near-field effects all the moments would have to be included in the potential formulation. Rather than do this, the near-field interactions are included directly by addition of the exact two-body capacitance matrix, \( C_{2b} \), less the far-field two-body capacitance matrix, \( C_{2b}^{0} \), already included in the potential invert. The two-body capacitance matrices contain all the interactions between two particles alone in the matrix. The method proves very accurate for computing effective conductivities, which are determined by the average particle dipoles, and we wish to discover how helpful this approach is for the present problem.
Ignoring for the moment the addition of two-body interactions and using the moment scattering only, we may derive analytically the effective reaction rate for cubic arrays up to the quadrupole level. From Bonnecaze and Brady's equation (37), the relative concentration of a sphere at its reference point is given by

\[ \phi(R_a) = \frac{q_a}{4\pi Da} \left( 1 + \frac{c}{r} + \sum_{\beta \neq a} \frac{q_{\beta}}{r} \right) \]

\[ + \frac{1}{2} \frac{Q_{\beta}}{r} \nabla_{\beta} \nabla_{\beta} \frac{1}{r} - \frac{1}{4\pi D_\beta} \left( \int_{V_R} \nabla_{\beta} \frac{1}{r} n(\mathbf{q}) \nabla_{\beta} \frac{1}{r} dV \right) + \frac{n(S)}{2} \nabla_{\beta} \nabla_{\beta} \frac{1}{r} \]

The first term on the right-hand side contains the sphere self-term and the second term includes both the constant dipole and quadrupole. It is these integrals that insure an absolutely convergent concentration difference since the diverging sums exactly cancel with growing integrals for large r. Similar equations can be written for G and VG for any particle a. Now for cubic lattices, the sphere quadrupole is zero due to the lattice symmetry, and further, there is no coupling between the concentration and dipoles, again because of cubic symmetry. So up to the quadrupole level the relative potential for a sphere in a cubic lattice is given by

\[ \phi(R_a) = \frac{q_a}{4\pi Da} \left( 1 + \frac{c}{r} + \sum_{\beta \neq a} \frac{q_{\beta}}{r} \right) \]

\[ + \frac{1}{2} \frac{Q_{\beta}}{r} \nabla_{\beta} \nabla_{\beta} \frac{1}{r} - \frac{1}{4\pi D_\beta} \left( \int_{V_R} \nabla_{\beta} \frac{1}{r} n(\mathbf{q}) \nabla_{\beta} \frac{1}{r} dV \right) + \frac{n(S)}{2} \nabla_{\beta} \nabla_{\beta} \frac{1}{r} \]

The above results for periodic arrays show the known \( O(c^{1/3}) \) scaling of the first correction to the Smoluchowski result for small c. For a random medium the first correction to the rate is \( O(c^{1/2}) \) as can be shown by solving the electrostatic analog of the Brinkman equation for a single sphere with reactant concentration \( \phi \) vanishing at its surface and \( \phi = (\phi) \) far from the sphere. The Brinkman-like equation is motivated physically as follows: The steady-state reaction-diffusion equation is given by

\[ D \nabla^2 \phi + r = 0, \]

where \( r \) is the rate of production per unit volume of the species. The total flux into an isolated sphere in a matrix is given by \( q = 4\pi Da(\phi - \langle \phi \rangle) \), where here \( \phi \) is the concentration of the diffusing species at the sphere's surface. If we imagine our Brinkman-like effective medium as a collection of spheres distributed randomly in space, the rate of production per unit volume is \( -n4\pi Da(\phi - \langle \phi \rangle) \). Therefore, the Brinkman-like equation is

\[ \nabla^2 \phi - n4\pi a(\phi - \langle \phi \rangle) = 0. \]

Solving Eq. (10) with the aforementioned boundary conditions, we find the effective reaction rate is given by

\[ \frac{k_{eff}}{k_a} = 1 + \sqrt{3c}, \]

which is precisely Felderhof and Deutch's first correction, showing the \( O(c^{1/2}) \) scaling.

This Brinkman-like effective medium theory can be modified further to be "self-consistent" and include the effective diffusivity of the diffusing species in the dispersion. In this case we write the Brinkman-like equation as

\[ D_{eff} \nabla^2 \phi - k_{eff} n(\phi - \langle \phi \rangle) = 0, \]

where \( D_{eff} \) is the effective diffusivity for a random array of perfect spherical conductors and is a function of the trap volume fraction, and \( k_{eff} \) is the sought after reaction rate. Solving Eq. (12) we find the implicit relation for the reaction rate.

\[ \frac{k_{eff}}{k_a} = \frac{1}{\sqrt{3c k_{eff} D_{eff}}} + \frac{D_{eff}}{D}. \]

Lebenhaft and Kapral's result does not include the c term in the denominator of Eq. (8) since they did not include the \( (q) \) term due to the irreducible quadrupole and the source distribution in the matrix phase in their analysis. Neglecting this term results in an aphysical divergence at \( c \approx 0.17 \). Venema and Bedeaux have continued the expansion in spherical harmonics to include in Eq. (8) additional terms of increasing powers of c in the denominator. Also, many investigators have considered the problem with the source distribution in the matrix phase only, in which case Eq. (8) is multiplied by \( (1 - c) \). Within the context of our method, this can be shown explicitly after some tedious manipulations and is physically reasonable since the problem is linear and must scale with the source strength; hence, if the source strength is reduced by \( (1 - c) \), so must the effective reaction rate.

The above results for periodic arrays show the known \( O(c^{1/3}) \) scaling of the first correction to the Smoluchowski result for small c. For a random medium the first correction to the rate is \( O(c^{1/2}) \) as can be shown by solving the electrostatic analog of the Brinkman equation for a single sphere with reactant concentration \( \phi \) vanishing at its surface and \( \phi = (\phi) \) far from the sphere. The Brinkman-like equation is motivated physically as follows: The steady-state reaction-diffusion equation is given by

\[ D \nabla^2 \phi + r = 0, \]

where \( r \) is the rate of production per unit volume of the species. The total flux into an isolated sphere in a matrix is given by \( q = 4\pi Da(\phi - \langle \phi \rangle) \), where here \( \phi \) is the concentration of the diffusing species at the sphere's surface. If we imagine our Brinkman-like effective medium as a collection of spheres distributed randomly in space, the rate of production per unit volume is \( -n4\pi Da(\phi - \langle \phi \rangle) \). Therefore, the Brinkman-like equation is

\[ \nabla^2 \phi - n4\pi a(\phi - \langle \phi \rangle) = 0. \]

Solving Eq. (10) with the aforementioned boundary conditions, we find the effective reaction rate is given by

\[ \frac{k_{eff}}{k_a} = 1 + \sqrt{3c}, \]

which is precisely Felderhof and Deutch's first correction, showing the \( O(c^{1/2}) \) scaling.

This Brinkman-like effective medium theory can be modified further to be "self-consistent" and include the effective diffusivity of the diffusing species in the dispersion. In this case we write the Brinkman-like equation as

\[ D_{eff} \nabla^2 \phi - k_{eff} n(\phi - \langle \phi \rangle) = 0, \]

where \( D_{eff} \) is the effective diffusivity for a random array of perfect spherical conductors and is a function of the trap volume fraction, and \( k_{eff} \) is the sought after reaction rate. Solving Eq. (12) we find the implicit relation for the reaction rate.

\[ \frac{k_{eff}}{k_a} = \frac{1}{\sqrt{3c k_{eff} D_{eff}}} + \frac{D_{eff}}{D}. \]
in the effective reaction rate constant; the two sets of results are indistinguishable.

In addition to our simulation results, we also plot the results of the random walker simulations of Lee et al., the lower bound of Torquato, and the theoretical results of Felderhof and Deutch. Our limited multipole expansion matches Lee et al.'s simulations up to \( c = 0.3 \), after which it grossly underpredicts the effective reaction rate, indeed dropping below the lower bound for \( c \approx 0.45 \). Our simulation results compare quite well to the results of Felderhof and Deutch up to about \( c = 0.08 \), again indicating that the \( c^{1/2} \) dependence is properly captured at low volume fractions with our method. Even at modest volume fractions Felderhof and Deutch’s result seem to over predict the reaction constant predicted by both our and Lee et al.’s results.

The reaction rate computed from the Brinkman-like effective medium equation (13) using known results for \( D_{eff} \) is also shown in Fig. 1. These results compare quite well to those of Lee et al. for small and large volume fractions, although they are off by as much as 25% at intermediate values. The use of such an effective medium equation can perhaps provide a reasonable estimate of the reaction rate for nonspherical particles if effective conductivity data is available.

Based upon the results presented here and Venema and Bedeaux’s work, it would appear that a very large number of many-body multipoles must be included to accurately compute the effective reaction rate. As mentioned earlier, Venema and Bedeaux reported 50 spherical moments were needed to compute the reaction rate for an fcc lattice accurate to five significant figures. Venema also found that when calculating the reaction rate for a regular array of cylinders, the rate would alternately exhibit a maximum or no maximum depending upon if an odd or even number of moments were used in the multipole scattering; this is consistent with our results. Unfortunately, adding exact near-field two-body interactions, which is very effective for approximating the neglected higher order moments for the effective conductivity problem, does not help in this case. Since there is no relative potential or concentration difference between particles, there is no near-field singular behavior dominating the effect of the neglected higher moments. It appears, therefore, that if a multipole scattering method is used to compute the effective reaction rate, many moments must be included in the formulation.

---

III. RESULTS FOR RANDOM DISPERSIONS OF SPHERICAL TRAPS

Several simulations were performed to determine the effective reaction rate for a random suspension of spherical traps. To simulate an infinite collection of traps, a finite number of spheres were randomly placed in a cubic box via Monte Carlo methods, and the box was periodically replicated throughout all space. Previous work has found that 32 particles per cell is sufficient to obtain results independent of cell size. The mobility matrix was formed as described earlier and elsewhere taking advantage of the periodicity. Simulations were performed with and without the addition of the near-field two-body interactions. The results are illustrated in Fig. 1 for a constant source distribution in the matrix phase only. Recall for a constant source distribution in both the particle and matrix phases, these effective reaction rates must be divided by \((1 - c)\).

The nonanalytic \( c^{1/2} \) dependence at low volume fractions of the effective reaction rate constant is apparent in our results as observed in the decreasing slope up to 10 vol%. The computed rate constant, however, exhibits a maximum at around \( c = 0.4 \), which is not a physically reasonable result. The rate constant should increase with the volume fraction of traps because the reactant will have less distance to diffuse in order to react with the one of the traps. A maximum also occurs in our analytic result for the cubic lattices. Evidently many multipoles are necessary to compute the reaction rate constant accurately. The addition of two-body interactions produced negligible changes to the effective reaction rate constant; the two sets of results are indistinguishable.