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# Competitive diffusion into two reactive spheres of different reactivity and size

Heng-Kwong Tsao*
*Department of Chemical and Materials Engineering, National Central University, Chung-li, Taiwan 320, Republic of China*

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Exact series solutions for the reaction rates of two reactive spheres of different reactivity and size are presented. The reaction rates are explicitly expressed in terms of the interparticle distance from reaction- to diffusion-limited conditions. The competitive diffusion favors the larger particle and the reaction rate of the smaller one is significantly reduced as the size ratio increases. For interactions between a diffusion-limited sink and a reaction-limited one, the diffusive interaction favors the reaction rate of the former and hinders that of the latter. Several approximate expressions have been proposed and compared with the exact results. The monopole approximation always underestimates the rate of the smaller sink for diffusion-limited reaction. The asymptotic limit of large size ratio is also analyzed. The asymptotic expression gives a quite accurate result if the smaller particle is regarded as a point sink plus a point dipole.

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## I. INTRODUCTION

Diffusion to the reactive particles is a subject that is relevant to a great number of chemical and physical processes; these include reactions in porous solids and catalysts, crystal growth and coarsening, metabolism rates in cells, etc. [1,2]. The diffusional interaction of a pair of reactive particles is of interest in investigating the effect of the existence of the second particle on the reaction rate. Previous studies on the diffusion-reaction problems have primarily focused on identical sinks [3–9]. In the limit of pure diffusion control, Samson and Deutch [3] have solved the Laplace equation to obtain the reaction rate of two reactive sinks in terms of bispherical coordinate. Zoia and Strieder [4] have accounted for the finite surface reaction rate by following the same approach. Both the exact [4] and asymptotic [5] solutions of the reaction rate are obtained by solving the recurrence relations iteratively. Their solution form is somewhat unhandy. The reaction rate of the diffusion-reaction problem, which is explicitly expressed in terms of interparticle distance has been derived recently by twin spherical expansion [6]. The results obtained by keeping terms up to quadrupole level gives values in excellent agreement with the exact solution.

Since the size distribution of the sinks or traps in many practical systems is not monodisperse, there is a need to understand the competition effects on the reaction rate due to unequal sizes. The effect of polydispersity in trap size on the reaction rate associated with diffusion-controlled reaction among unbounded dispersions of spherical sinks has been examined [10–14]. The reaction rate (relative to the monodisperse case) is found to increase with increasing interfacial-surface area of the sinks [10,11]. Nonetheless, to our knowledge no theoretical expression for two unequal reactive spheres is available. In addition to polydispersity in size, the reactivity of the sinks may be different. For example, in the biological waste-water treatment and cheese manufacture, multiple microbial species are required. As a result, the competition effect may occur for two species with different ability (reactivity) of utilizing the limiting nutrient.

In this paper, the reaction rates for diffusion into two unequal sinks is obtained analytically from reaction- to diffusion-limited conditions. The rate constants of the first-order surface reaction on the two sinks of different size can be different. The outline of the paper is as follows. In Sec. II, on the basis of twin spherical expansion, the exact series solutions are explicitly expressed in terms of the interparticle distance and the size ratio. The rate of diffusion-limited reaction is derived in Sec. III and the reaction rate associated with a first-order surface reaction is obtained in Sec. IV. In Sec. V the asymptotic analysis for large size ratio is presented. By including the first few multipole contributions terms, analytical approximations are proposed and their accuracies are assessed by the exact solution.

## II. THEORETICAL BACKGROUND

Consider a reactant diffusing with a diffusivity $D$ through the inert bulk phase surrounding two reactive spheres of radii $a_1$ and $a_2$. Their center-to-center distance is $R$ apart. The reactant concentration $c(\mathbf{r})$ is described by the Laplace equation

$$D\nabla^2 c(\mathbf{r})=0. \tag{1}$$

At large distance from the reaction pair, the concentration is $c=c_\infty$. By adopting a dimensionless concentration $w=(c_\infty-c)/c_\infty$, this problem is transformed into a dissolved substance diffusing away from the source pair with $w=0$ at infinity. Assume that the reaction on the reactant-impenetrable surface is first order. Since the diffusional rate equals the reaction rate on the surface of the spherical sink, one has the boundary condition

$$D\nabla w\cdot\mathbf{n}_i=k_{s,i}(w-1), \tag{2}$$

where $\mathbf{n}_i$ is the outwardly directed unit normal and $k_{s,i}$ is the surface reaction rate constant of the particle $i$. If the reaction is pure diffusion control, the boundary conditions on the surfaces of the particles become $w=1$, i.e., $c=0$.

The Laplace equation (1) can be solved in spherical coordinates by the method of twin spherical harmonic expan-

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*Email address: hktsao@colloid.che.ncu.edu.tw

sions. Owing to the azimuthal symmetry, the solution is given by

$$w=\sum_{n=0}^{\infty}\left[f_n\left(\frac{a_1}{r_1}\right)^{n+1}P_n(\cos\theta_1)+g_n\left(\frac{a_2}{r_2}\right)^{n+1}P_n(\cos\theta_2)\right]. \tag{3}$$

There are two spherical coordinate systems, $(r_1,\theta_1)$ and $(r_2,\theta_2)$, with origins located in the centers of sphere 1 and 2, respectively. One of the multipole expansions can be transformed into the other set of spherical coordinates through an addition theorem of Legendre functions derived by Hobson [15],

$$\left(\frac{1}{r_k}\right)^{n+1}P_n(\cos\theta_k)=\left(\frac{1}{R}\right)^{n+1}\sum_{q=0}^{\infty}\binom{n+q}{q}\left(\frac{r_{3-k}}{R}\right)^{q}P_q(\cos\theta_{3-k})\quad\text{for } r_{3-k}<R. \tag{4}$$

The concentration distribution can then be rewritten as

$$w(r_1,\theta_1)=\sum_{n=0}^{\infty}\left[f_n\left(\frac{a_1}{r_1}\right)^{n+1}+\left(\frac{r_1}{R}\right)^{n}\sum_{m=0}^{\infty}g_m\binom{m+n}{n}\left(\frac{a_2}{R}\right)^{m+1}\right]P_n(\cos\theta_1)\quad\text{for } r_1<R \tag{5}$$

or

$$w(r_2,\theta_2)=\sum_{n=0}^{\infty}\left[g_n\left(\frac{a_2}{r_2}\right)^{n+1}+\left(\frac{r_2}{R}\right)^{n}\sum_{m=0}^{\infty}f_m\binom{m+n}{n}\left(\frac{a_1}{R}\right)^{m+1}\right]P_n(\cos\theta_2)\quad\text{for } r_2<R. \tag{6}$$

The coefficients $f_i$ and $g_i$ are to be determined by the boundary condition.

## III. DIFFUSION-LIMITED CONDITION

In the limit of pure diffusion control for both sinks, the boundary conditions are simply

$$w(r_1=a_1)=w(r_2=a_2)=1. \tag{7}$$

Substituting Eqs. (5) and (6) into the boundary condition (7) and using the orthogonality property associated with the Legendre polynomials yields

$$\delta_{n0}=f_n+\left(\frac{a_1}{R}\right)^{n}\sum_{m=0}^{\infty}g_m\binom{m+n}{n}\left(\frac{a_2}{R}\right)^{m+1} \tag{8}$$

and

$$\delta_{n0}=g_n+\left(\frac{a_2}{R}\right)^{n}\sum_{m=0}^{\infty}f_m\binom{m+n}{n}\left(\frac{a_1}{R}\right)^{m+1}, \tag{9}$$

where $\delta_{nm}=1$ for $n=m$, $\delta_{nm}=0$ otherwise.

Equations (8) and (9) can be solved analytically by the iteration method. Let $f_n$ and $g_n$ be expressed in terms of infinite series,

$$f_n=\sum_{i=0}^{\infty}f_n^{(i)}\quad\text{and}\quad g_n=\sum_{i=0}^{\infty}g_n^{(i)}. \tag{10}$$

When $R\to\infty$, the above result should reduce to that associated with an isolated reactive sphere. Consequently, we choose $f_n^{(0)}$ and $g_n^{(0)}$ to satisfy the solutions of a single sphere of radius $a_1$ or $a_2$, respectively,

$$f_n^{(0)}=\delta_{n0}\quad\text{and}\quad g_n^{(0)}=\delta_{n0}. \tag{11}$$

This result can serve as a leading order solution.

Inserting Eq. (10) into Eqs. (8) and (9), one obtains the level $k$ correction, $f_n^{(k)}$ and $g_n^{(k)}$, in terms of the solution at $(k-1)$ level, $f_n^{(k-1)}$ and $g_n^{(k-1)}$, for $k\geqslant 1$,

$$f_n^{(k)}=-\left(\frac{a_1}{R}\right)^{n}\sum_{m=0}^{\infty}g_m^{(k-1)}\binom{m+n}{n}\left(\frac{a_2}{R}\right)^{m+1} \tag{12}$$

and

$$g_n^{(k)}=-\left(\frac{a_2}{R}\right)^{n}\sum_{m=0}^{\infty}f_m^{(k-1)}\binom{m+n}{n}\left(\frac{a_1}{R}\right)^{m+1}. \tag{13}$$

The solutions of $f_n^{(k)}$ and $g_n^{(k)}$ can then be obtained and

$$g_n^{(k)}=(-1)^k\sum_{m_1=0}^{\infty}\cdots\sum_{m_{k-1}=0}^{\infty}\left\{\prod_{i=1}^{k-1}\binom{m_{i-1}+m_i}{m_i}\right\}\left(\frac{a_2}{R}\right)^{n+2(m_1+\cdots+m_{k-1})+k}\left(\frac{1}{s}\right)^{2(m_1+m_3+\cdots)+[(k+1)/2]}. \tag{14}$$

where $s=a_2/a_1$ and $m_0=n$. Note that $[x]$ in the exponent of $s$ denotes the largest integer less than $x$.

The dimensionless reaction rate of the reactive sphere $i$, $\Xi_i$, scaled by that associated with the same isolated particle, is given by

$$\Xi_1(R)=\frac{-\int_A D\nabla w\cdot\mathbf{n}_1 dA}{4\pi D a_1 c_\infty}=\frac{f_0}{f_0^{(0)}}$$

and

$$\Xi_2(R)=\frac{-\int_A D\nabla w\cdot\mathbf{n}_2 dA}{4\pi D a_2 c_\infty}=\frac{g_0}{g_0^{(0)}},\tag{15}$$

where the dimensionless reaction rate $\Xi$ is obtained by using Eqs. (5) and (6) and the orthogonality property. If we keep the series solution up to $(a_2/R)^5$, the reaction rates are

$$\Xi_1(R)=1-\left(\frac{a_2}{R}\right)+\frac{1}{s}\left(\frac{a_2}{R}\right)^2-\frac{1}{s}\left(\frac{a_2}{R}\right)^3+\left(\frac{1}{s}+\frac{1}{s^2}\right)\left(\frac{a_2}{R}\right)^4 -\left(\frac{1}{s}+\frac{1}{s^2}+\frac{1}{s^3}\right)\left(\frac{a_2}{R}\right)^5+O\left(\frac{a_2}{R}\right)^6\tag{16}$$

and

$$\Xi_2(R)=1-\frac{1}{s}\left(\frac{a_2}{R}\right)+\frac{1}{s}\left(\frac{a_2}{R}\right)^2-\frac{1}{s^2}\left(\frac{a_2}{R}\right)^3+\left(\frac{1}{s^2}+\frac{1}{s^3}\right) \times\left(\frac{a_2}{R}\right)^4-\left(\frac{1}{s^2}+\frac{1}{s^3}+\frac{1}{s^4}\right)\left(\frac{a_2}{R}\right)^5+O\left(\frac{a_2}{R}\right)^6.\tag{17}$$

Equations (16) and (17) are accurate for $R\gg(a_1+a_2)$. They reduce to the result of two identical sinks when $s=1$ [6].

### IV. FIRST-ORDER REACTION

When the rate of surface reaction is comparable to the diffusional rate for both sinks, the boundary condition, Eq. (2), must be employed. Inserting Eqs. (5) and (6) into Eq. (2) leads to

$$f_n=\frac{\lambda_1^{-1}}{(n+1)+\lambda_1^{-1}}\,\delta_{n0}-\frac{\lambda_1^{-1}-n}{\lambda_1^{-1}+(n+1)}\left(\frac{a_1}{R}\right)^n \times\sum_{m=0}^{\infty} g_m\binom{m+n}{n}\left(\frac{a_2}{R}\right)^{m+1}\tag{18}$$

and

$$g_n=\frac{\lambda_2^{-1}}{\lambda_2^{-1}+(n+1)}\,\delta_{n0}-\frac{\lambda_2^{-1}-n}{\lambda_2^{-1}+(n+1)}\left(\frac{a_2}{R}\right)^n \times\sum_{m=0}^{\infty} f_m\binom{m+n}{n}\left(\frac{a_1}{R}\right)^{m+1}.\tag{19}$$

The parameter $\lambda_i^{-1}=k_{s,i}a_i/D$ denotes the ratio of the reaction rate to the diffusional rate associated with the particle $i$. The process of the reaction on the particle $i$ is diffusion limited for $\lambda_i^{-1}\gg 1$ and reaction control if $\lambda_i^{-1}\ll 1$.

Again, we adopt the series solution, Eq. (10), to solve the foregoing equations. The leading order solution is chosen to be that associated with the corresponding isolated sphere,

$$f_n^{(0)}=\frac{\lambda_1^{-1}}{\lambda_1^{-1}+(n+1)}\,\delta_{n0}$$

and

$$g_n^{(0)}=\frac{\lambda_2^{-1}}{\lambda_2^{-1}+(n+1)}\,\delta_{n0}.\tag{20}$$

In terms of the solution at $(k-1)$ level, $f_n^{(k-1)}$ and $g_n^{(k-1)}$, for $k\geq 1$, one obtains

$$f_n^{(k)}=-\Lambda_{1,n}\left(\frac{a_1}{R}\right)^n\sum_{m=0}^{\infty} g_m^{(k-1)}\binom{m+n}{n}\left(\frac{a_2}{R}\right)^{m+1}\tag{21}$$

and

$$g_n^{(k)}=-\Lambda_{2,n}\left(\frac{a_2}{R}\right)^n\sum_{m=0}^{\infty} f_m^{(k-1)}\binom{m+n}{n}\left(\frac{a_1}{R}\right)^{m+1},\tag{22}$$

where

$$\Lambda_{1,n}=\left[\frac{\lambda_1^{-1}-n}{\lambda_1^{-1}+(n+1)}\right]\quad\text{and}\quad\Lambda_{2,n}=\left[\frac{\lambda_2^{-1}-n}{\lambda_2^{-1}+(n+1)}\right],\tag{23}$$

for $n\geq 0$.

The general solution can then be expressed as

$$f_n^{(k)}=(-1)^k\Lambda_{1,n}\big(\Lambda_{1,0}^{(k+1)-2[(k+1)/2]}\Lambda_{2,0}^{k-2[(k/2)]}\big)\sum_{m_1=0}^{\infty}\cdots\sum_{m_{k-1}=0}^{\infty}\left\{\prod_{i=1}^{k-1}\binom{m_{i-1}+m_i}{m_i}\Lambda_{i+1-2[i/2],m_i}\right\}\times\left(\frac{a_1}{R}\right)^{n+2(m_1+\cdots+m_{k-1})+k}s^{2(m_1+m_3+\cdots)+[(k+1)/2]} \tag{24}$$

and

$$g_n^{(k)}=(-1)^k\Lambda_{2,n}\big(\Lambda_{1,0}^{k-2[k/2]}\Lambda_{2,0}^{(k+1)-2[(k+1)/2]}\big)\sum_{m_1=0}^{\infty}\cdots\sum_{m_{k-1}=0}^{\infty}\left\{\prod_{i=1}^{k-1}\binom{m_{i-1}+m_i}{m_i}\Lambda_{i-2[(i-1)/2],m_i}\right\}\times\left(\frac{a_2}{R}\right)^{n+2(m_1+\cdots+m_{k-1})+k}\left(\frac{1}{s}\right)^{2(m_1+m_3+\cdots)+[(k+1)/2]}. \tag{25}$$

The dimensionless reaction rate $\Xi_i$ associated with the sphere $i$, scaled by that of the isolated particle, is given by

$$\Xi_1(R)=\frac{-\int_A D\boldsymbol{\nabla}w\cdot\mathbf{n}_1 dA}{4\pi D a_1 c_\infty\dfrac{\lambda_1^{-1}}{\lambda_1^{-1}+1}}=\frac{f_0}{f_0^{(0)}}$$

and

$$\Xi_2(R)=\frac{-\int_A D\boldsymbol{\nabla}w\cdot\mathbf{n}_2 dA}{4\pi D a_2 c_\infty\dfrac{\lambda_2^{-1}}{\lambda_2^{-1}+1}}=\frac{g_0}{g_0^{(0)}}. \tag{26}$$

If the series solution is truncated after $(a_2/R)^5$, the reaction rate is written as

$$\Xi_1(R)=1-\Lambda_{2,0}\left(\frac{a_2}{R}\right)+\frac{\Lambda_{1,0}\Lambda_{2,0}}{s}\left(\frac{a_2}{R}\right)^2-\frac{\Lambda_{1,0}\Lambda_{2,0}^2}{s}\left(\frac{a_2}{R}\right)^3+\left[\frac{\Lambda_{1,0}\Lambda_{2,1}}{s}+\frac{(\Lambda_{1,0}\Lambda_{2,0})^2}{s^2}\right]\left(\frac{a_2}{R}\right)^4-\left[\frac{\Lambda_{1,0}\Lambda_{2,0}\Lambda_{2,1}}{s}+\frac{\Lambda_{1,0}^2\Lambda_{2,0}^3}{s^2}+\frac{\Lambda_{1,1}\Lambda_{2,0}^2}{s^3}\right]\left(\frac{a_2}{R}\right)^5+O\left(\frac{a_2}{R}\right)^6 \tag{27}$$

and

$$\Xi_2(R)=1-\frac{\Lambda_{1,0}}{s}\left(\frac{a_2}{R}\right)+\frac{\Lambda_{1,0}\Lambda_{2,0}}{s}\left(\frac{a_2}{R}\right)^2-\frac{\Lambda_{1,0}^2\Lambda_{2,0}}{s^2}\left(\frac{a_2}{R}\right)^3+\left[\frac{(\Lambda_{1,0}\Lambda_{2,0})^2}{s^2}+\frac{\Lambda_{1,1}\Lambda_{2,0}}{s^3}\right]\left(\frac{a_2}{R}\right)^4-\left[\frac{\Lambda_{1,0}^2\Lambda_{2,1}}{s^2}+\frac{\Lambda_{1,0}^3\Lambda_{2,0}^2}{s^3}+\frac{\Lambda_{1,0}\Lambda_{1,1}\Lambda_{2,0}}{s^4}\right]\left(\frac{a_2}{R}\right)^5+O\left(\frac{a_2}{R}\right)^6. \tag{28}$$

When $\Lambda_{1,0}=\Lambda_{2,0}=1$, Eqs. (27) and (28) reduce to Eqs. (16) and (17) for diffusion-limited condition. On the other hand, for $s=1$ and $\Lambda_{1,n}=\Lambda_{2,n}$, we recover the results for two identical sinks [6].

## V. RESULTS AND DISCUSSION

The reaction rates of two unequal spherical sinks immersed in an infinite domain are calculated for different size $a_i$ and reactivity $k_i$. Using the method of twin spherical expansion, the reaction rate can be explicitly expressed in terms of the interparticle distance from reaction-limited to diffusion-limited conditions. Different from identical sinks, there are three independent dimensionless parameters in determining the reaction rate, $\lambda_1^{-1}$, $\lambda_2^{-1}$, and $s$. $\lambda_i^{-1}$ represents the resistance ratio of diffusion to surface reaction associated with the sink $i$ and $s$ is the size ratio. There exist three asymptotic limits: (1) diffusion limited, $\lambda_1^{-1}\gg 1$ and $\lambda_2^{-1}\gg 1$; (2) $\lambda_1^{-1}\ll 1$ and $\lambda_2^{-1}\gg 1$; (3) reaction limited, $\lambda_1^{-1}\ll 1$ and $\lambda_2^{-1}\ll 1$. The second regime corresponds to the diffusive interaction between a reaction-limited sink and a diffusion-limited one.

Figure 1 shows the variation of the dimensionless reaction rates $\Xi$ with the center-to-center distance $R$ for the size ratio $s=2$. The cases considered are: (1) diffusion-limited condition, $\lambda_s^{-1}=\lambda_l^{-1}=\infty$; (2) two sinks of the same reactivity, $\lambda_s^{-1}=2$ and $\lambda_l^{-1}=4$. As anticipated, the dimensionless reaction rates rise and approach unity as the separation increases. Moreover, the diffusional interaction is more significant for the fast surface reaction than for the slow one. For diffusion-limited condition, the rates of the two particles at contact are $\Xi_l=0.852$ for the larger sink and $\Xi_s=0.494$ for the smaller one. Note that the reaction rate for a pair of identical sinks at contact (relative to that of an isolated sink) is $\ln 2$. As a consequence, one important feature revealed in Fig. 1 is that the competitive diffusion favors the larger particle and the reaction rate of the smaller sink is substantially reduced.

To further demonstrate the effect of size differences on the rate, Fig. 2 depicts the variation of the reaction rate of two contact sinks with the size ratio. It clearly shows that the existence of a larger sink nearby leads to a significant reduc-

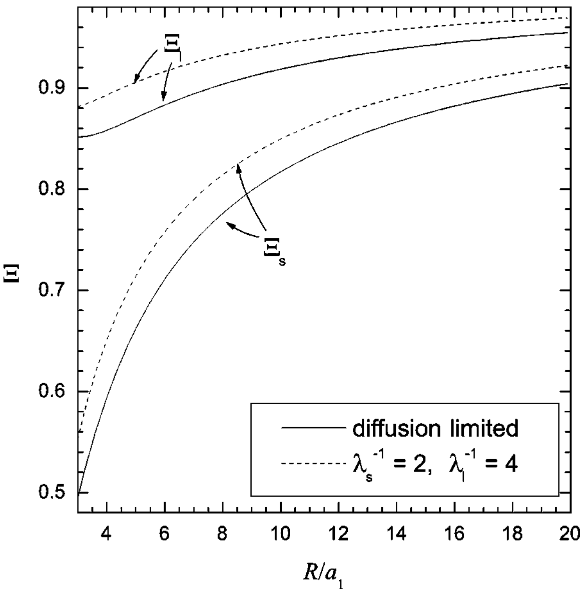

FIG. 1. The variation of the dimensionless reaction rate with the center-to-center distance for the size ratio $s=2$.

tion of the reaction rate, which declines as the size ratio is increased. On the other hand, with a smaller sink in the neighborhood, the reaction rate is disturbed only to some extent. The minimum reaction rate of the larger sink always occurs as $s\rightarrow 1$ and depends on $\lambda_s^{-1}$ for the same reactivity, i.e., $k_l=k_s$. As $s=1$ with $\lambda_s^{-1}=2$, the reaction rate is $\Xi_s=\Xi_l=0.755$. Nevertheless, the qualitative behavior of the reaction rate is similar to that associated with diffusion-limited reaction whatever the value of $\lambda_s^{-1}$ is.

The variation of the reaction rate at contact with $\lambda_s^{-1}$ is shown in Fig. 3 for $s=1$ and 2 with $\lambda_l^{-1}=s\lambda_s^{-1}$. When $\lambda_s^{-1}\ll 1$ ($\lesssim 0.01$), the reaction reaches the reaction-limited regime and the rate is essentially $\Xi\simeq 1$. On the other hand, as $\lambda_s^{-1}\gg 1$ ($\gtrsim 10$), the reaction rates are basically the same as those of diffusion-limited reaction, which are determined by the size ratio $s$. The rate calculated for a pair of identical sinks ($s=1$) provides the upper bound of $\Xi_s$ for the smaller sink and the lower bound of $\Xi_l$ for the larger one.

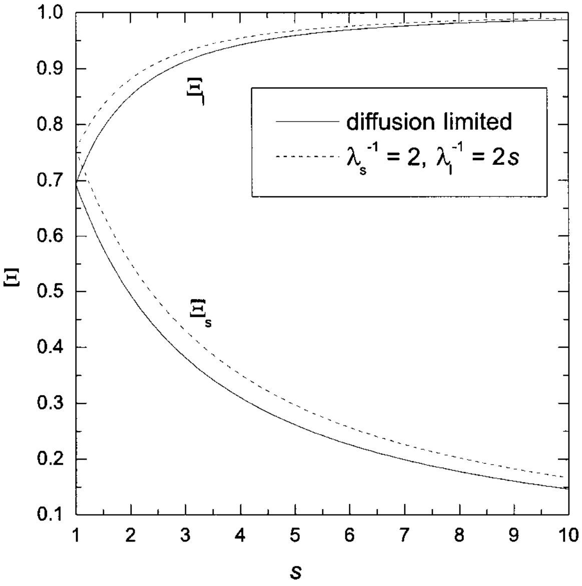

FIG. 2. The variation of the dimensionless reaction rate of two contact sinks with the size ratio.

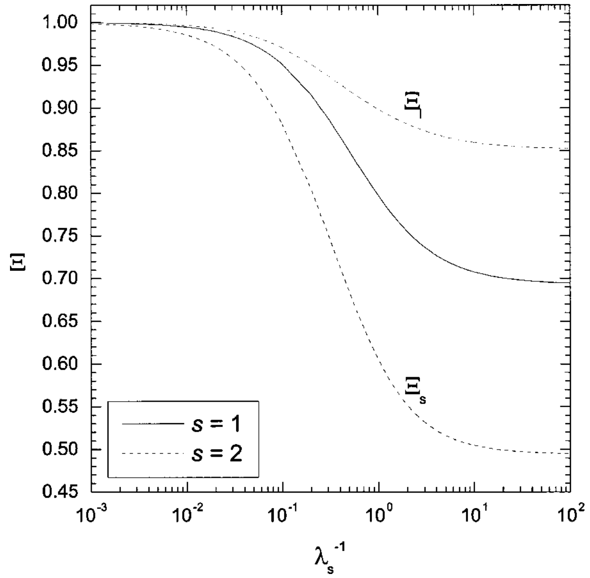

FIG. 3. The variation of the dimensionless reaction rate of two contact sinks with the parameter $\lambda_s^{-1}$ for different size ratios, $s=1$ and 2.

The diffusive interaction of a reaction-limited sink with a diffusion-limited one takes place when $\lambda_d^{-1}\rightarrow\infty$ and $\lambda_r^{-1}\rightarrow 0$. This condition may correspond to a large ratio of the size or of the rate constant when one of the sink has $k_r a_r/D\ll 1$. In this asymptotic limit, the reaction rates at contact are solely decided by the size ratio. The effect of diffusional competition for such a pair is depicted in Fig. 4. For two sinks of the same size, the diffusive interaction favors the diffusion-limited sink, of which the rate is slighted reduced, $\Xi_d=0.963$. However, the rate of the reaction-limited sink is substantially lowered to $\Xi_r=0.537$. To compensate this effect due to different reactivities, one can reduce the size of the diffusion-limited sink. As illustrated in Fig. 4, when $a_d/a_r=0.218$, the size effect cancels out the reactivity effect and the net result of the diffusive interaction yields an equal reaction rate $\Xi_r=\Xi_d=0.851$.

For a polydisperse dispersion of diffusion-limited sinks, it is found that a higher reaction rate is associated with a larger surface area for a given volume fraction [10,11]. If the total volume of the two sinks are fixed, the reaction rate of this system is given by $\Xi_t(R)=\frac{1}{2}[2/(1+s^3)]^{1/3}[\Xi_s+s\Xi_l]$, which is scaled by $8\pi Dac_\infty$ with $a$ being the sink radius for $s=1$. Obviously, the surface area is maximum as $s=1$. When $s\rightarrow\infty$, $\Xi_l\rightarrow 1$ whatever the interparticle separation $R$ is. Therefore, one has a lower bound $\Xi_t=2^{-2/3}$. As shown in Fig. 5, the reaction rate $\Xi_t$ declines and reaches the lower bound as the size ratio (surface area) is increased (decreased). The size polydispersity leads to a reduction of the total reaction rate, varying from 0.693 to 0.630 maximally. Nonetheless, it is only 10% reduction.

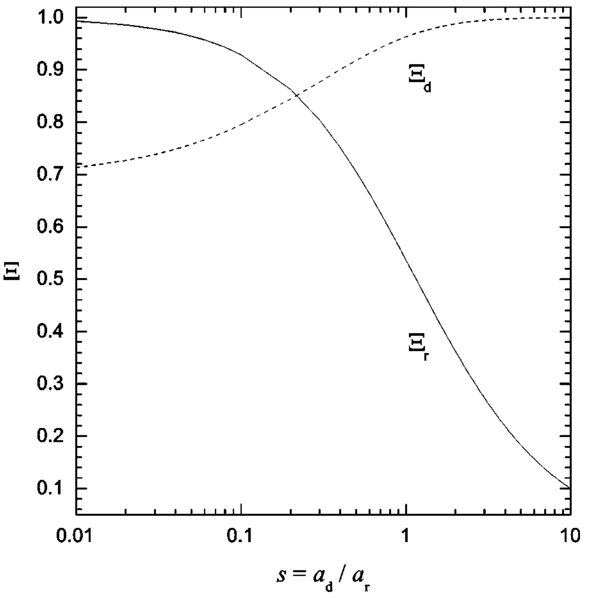

FIG. 4. A plot of the reaction rate (at contact) associated with the diffusive interaction between a diffusion-limited sink and a reaction-limited one against the size ratio.

### A. Approximate solutions

The method of twin spherical expansion is based on a multipole expansion and the exact solution is obtained by keeping infinite multipole contributions. The approximate solutions can be obtained by considering the first few multipoles. The monopole approximation has been widely used in studying the diffusion-reaction problems [2,13,14,16]. If we keep the monopole only, i.e., $f_0$ and $g_0$ in Eq. (6), the reaction rates for diffusion-limited condition are simply

$$\Xi_{0,s}(x,y) = \frac{1-y}{1-xy} \tag{29}$$

and

$$\Xi_{0,l}(x,y) = \frac{1-x}{1-xy}, \tag{30}$$

where $x = a_1/R$ and $y = a_2/R$. If the dipole terms, i.e., $f_1$ and $g_1$ are also kept in Eq. (6), then the dimensionless reaction rates become

$$\Xi_{1,s}(x,y) = \frac{1-y-x^3y-4x^3y^3+2x^3y^4}{1-xy-x^3y-xy^3-4x^3y^3+x^4y^4} \tag{31}$$

and

$$\Xi_{1,l}(x,y) = \frac{1-x-xy^3-4x^3y^3+2x^4y^3}{1-xy-x^3y-xy^3-4x^3y^3+x^4y^4}. \tag{32}$$

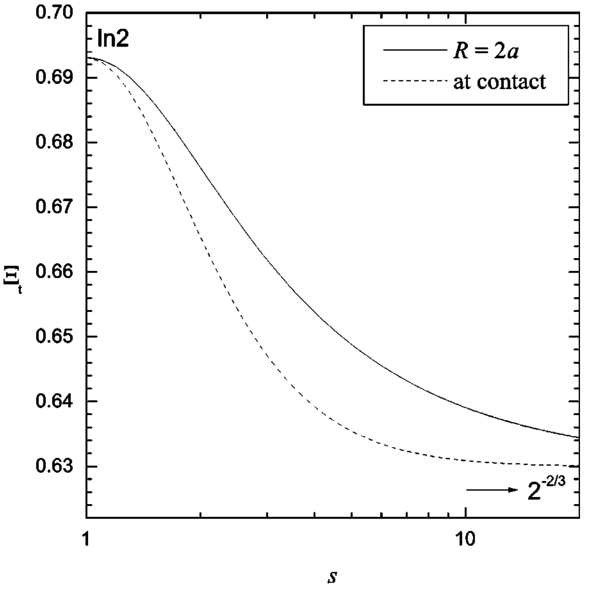

FIG. 5. The variation of the total diffusion-limited reaction rate with the size ratio for $R = 2a$ and at contact.

The exact series expressions in Eqs. (16) and (17) converge slowly for $R \to (a_1 + a_2)$. However, with the exact series solution in hand, we can always use the Shank transform or the Padé approximation to obtain an accurate, analytical approximation. The convergence rate of Eqs. (16) and (17) can be greatly improved by the Shank transform,

$$\Xi_{s,s} = \frac{x+y+x^2-y^3+yx^3+x^2y^3}{x+y+x^2+xy+y^2}, \tag{33}$$

$$\Xi_{s,l} = \frac{x+y+y^2-x^3+xy^3+x^3y^2}{x+y+x^2+xy+y^2}. \tag{34}$$

### B. Asymptotic analysis for large size ratio ($s \gg 1$)

When the size ratio is large, the simplest model is a point source and a planar surface. Unfortunately, such approach would lead to a singular perturbation because the leading order concentration due to the planar surface is uniform everywhere, which cannot satisfy the boundary conditions on the planar surface and at infinity simultaneously. Consequently, the planar surface has to be replaced by a sphere.

#### *1. A point sink and a reactive sphere*

When the size ratio is large, i.e., $s \gg 1$, the smaller sink can be regarded as a point sink with the reaction rate $q_1$. With the origin located at the center of the larger sphere 2, the concentration profile is then given by

$$w(r_2,\theta_2) = \sum_{n=0}^{\infty} [A_n r_2^n + B_n r_2^{-(n+1)}] P_n(\cos\theta_2) \quad \text{for } a_2 \leq r_2 < R. \tag{35}$$

where the coefficients $A_n$ and $B_n$ can be determined by the boundary condition at $r_2 = a_2$,

$$A_n = \left(\frac{q_1}{4\pi D}\right)\frac{1}{R^{n+1}}$$

and

$$B_n = a_2\delta_{n0} - \frac{q_1}{4\pi D}\frac{a^{2n+1}}{R^{n+1}}.$$

The reaction rate of the larger sphere, $q_2$, can then be obtained in terms of $q_1$,

$$q_2 = -\int_{A_2} D\boldsymbol{\nabla} w\cdot\mathbf{n}_2 dA = 4\pi D a_2\left(1-\frac{q_1}{4\pi DR}\right). \quad (36)$$

Note that $q_1$ is still unknown and must to be determined by the condition associated with the smaller particle. The concentration at any point can be described by the integral form of the Laplace equation,

$$w(\mathbf{x}) = \frac{q_1}{4\pi D a_1} + \int_{A_2}\left[-(D\boldsymbol{\nabla} w\cdot\mathbf{n}_2)\frac{1}{r_y} + \boldsymbol{\nabla}_y\frac{1}{r_y}\cdot\mathbf{n}_2\right]dA, \quad (37)$$

where $r_y = |\mathbf{x}-\mathbf{y}|$ and $\boldsymbol{\nabla}_y = \partial/\partial(\mathbf{y}-\mathbf{x})$. At the point sink, the concentration is set to $w(R)=1$. In addition, one has

$$\int_{A_2}\boldsymbol{\nabla}_y\frac{1}{r_y}\cdot\mathbf{n}_2 dA = 0, \quad (38)$$

and

$$\int_{A_2}\left[(D\boldsymbol{\nabla} w\cdot\mathbf{n}_2)\frac{1}{r_y}\right]dA = \frac{q_1}{D}\sum_{n=1}^{\infty}\frac{a_2^{n+1}}{R^{2n+2}} - 4\pi\left(1-\frac{q_1}{4\pi DR}\right)\frac{a_2}{R}. \quad (39)$$

Inserting Eqs. (38) and (39) into Eq. (37), the reaction rates can be determined:

$$\Xi_{0+\infty,s} = \frac{1-\dfrac{a_2}{R}}{1-\left(\dfrac{a_1}{R}\dfrac{a_2}{R}\right)\left[1-\left(\dfrac{a_2}{R}\right)^2\right]^{-1}}, \quad (40)$$

and

$$\Xi_{0+\infty,l} = 1-\frac{\dfrac{a_1}{R}\left(1-\dfrac{a_2}{R}\right)}{1-\left(\dfrac{a_1}{R}\dfrac{a_2}{R}\right)\left[1-\left(\dfrac{a_2}{R}\right)^2\right]^{-1}}. \quad (41)$$

The above results can also be easily obtained by truncating terms in the twin spherical expansion unevenly. The assumption that the smaller particle is considered as a point means only monopole contribution, $f_0$, is kept in Eq. (8). On the other hand, we keep all the multipole contributions for the larger particle. Therefore, Eqs. (8) and (9) reduce to

$$f_0 = 1-\sum_{m=0}^{\infty} g_m\left(\frac{a_2}{R}\right)^{m+1} \quad (42)$$

and

$$g_n = \delta_{n0} - \left(\frac{a_1}{R}\right)\left(\frac{a_2}{R}\right)^n f_0 \quad \text{for } n\geqslant 0. \quad (43)$$

Substituting Eq. (43) into Eq. (42) recovers Eq. (40).

### *2. Next order correction*

Now we assume the smaller particle can be represented by a point sink plus a point dipole. The next order correction can be readily made by following the approach of uneven truncation of the twin spherical expansion. As a result, the coefficients $f_0$ and $f_1$ are retained. According to Eqs. (8) and (9), the equations to be solved include Eq. (42) for $f_0$,

$$f_1 = -\left(\frac{a_1}{R}\right)\sum_{m=0}^{\infty}(m+1)g_m\left(\frac{a_2}{R}\right)^{m+1} \quad (44)$$

and

$$g_n = \delta_{n0} - \left(\frac{a_1}{R}\right)\left(\frac{a_2}{R}\right)^n\left[f_0 + (n+1)\left(\frac{a_1}{R}\right)f_1\right] \quad \text{for } n\geqslant 0. \quad (45)$$

Using the relations

$$\sum_{n=0}^{\infty}(n+1)x^n = \frac{1}{(1-x)^2}$$

and

$$\sum_{n=0}^{\infty}(n+1)^2 x^n = \frac{1+x}{(1-x)^3},$$

one has

$$\Xi_{1+\infty,s} = f_0 = \frac{\beta(x,y)}{\alpha(x,y)}, \quad (46)$$

where

$$\alpha = 1-\frac{xy}{1-y^2} - \frac{x^4y^2}{(1-y^2)^4-(1-y^4)x^3y}$$

and

$$\beta = 1-y-\frac{x^3y^2(1-y^2)}{(1-y^2)^3 - x^3y(1+y^2)}.$$

Here $x=a_1/R$ and $y=a_2/R$. The reaction rate for the larger particle is given by

$$\Xi_{1+\infty,l} = g_0 = 1-x(f_0+xf_1), \quad (47)$$

with

$$f_1 = \left[1 - \frac{x^3 y(1+y^2)}{(1-y^2)^3}\right]^{-1}\left[\frac{x^2 y}{(1-y^2)^2}\frac{\beta}{\alpha} - xy\right].$$

Note that if those asymptotic results are expanded in Taylor series, one recovers Eq. (16) fully from Eq. (46). However, using Eq. (40) obtained from a point sink can only give Eq. (16) accurately up to $O(y^4)$.

Until now we have proposed five approximate solutions, including monopole $\Xi_0$, dipole $\Xi_1$, shank transform $\Xi_s$, a point sink $\Xi_{0+\infty}$, and a point sink plus dipole $\Xi_{1+\infty}$. These approximate results for diffusion-limited reaction can be accessed by the exact solutions. Since the multipole expansion is good for large separations, one would anticipate that the most significant deviation from the exact solution takes place at two sinks in touch. As a result, we compare those approximate reaction rates with the exact solutions at $R/a_1=(s+1)$. Figure 6(a) shows the variation of the reaction rate of the smaller sink with the size ratio. One can see that the monopole and dipole approximations always underestimate the rates. On the other hand, regarding the smaller sphere as a point sink yields results that always overestimate the rates. Both the shank transform and the approximation of a point sink plus a dipole representing the smaller particle give results that agree quite well with the exact solutions. The variation of the reaction rate of the larger sink with the size ratio is depicted in Fig. 6(b). Similar results are obtained. The shank transform gives better results for small $s$ and the error is less than 6% for $s \leqslant 10$. On the other hand, the approximation of a point sink plus a point dipole yields excellent results for large $s$ and the error is within 3% for $s \leqslant 10$. The success of this approximation is attributed to the following fact. The coefficients associated with the large particle, i.e., $g_n$, decline slowly when $s \gg 1$. On the contrary, the coefficients associated with the smaller particles, i.e., $f_n$, decay very fast after $n \geqslant 2$. Nevertheless, at $s=1$, this approximation gives two different rates. $\Xi_{1+\infty,s}=0.713$ and $\Xi_{1+\infty,s}=0.672$. This is not surprising because only two terms are kept for one sink while infinite terms are kept for the other sink.

The monopole and dipole approximations do not yield satisfactory results for two sinks at contact when $s$ deviates from unity. In addition, the approximate expression Eq. (30) for monopole level clearly shows the existence of a local minima at $R/a_1=(1-\sqrt{1-s^{-1}})^{-1}$ for $s=a_2/a_1 \geqslant \frac{1}{2}(1+\sqrt{5})$. Similarly, Eq. (32) for dipole level also shows a local minima. They are not observed in exact solutions, e.g., Fig. 1 for $s=2$. This consequence points out the inaccuracy of the approximations associated with the first few truncated moments. However, it must be noted that the dipole approximation does give an excellent agreement with the exact solution at $s=1$ and this fact is also shown in Fig. 6 [6,17].

Our analysis indicates that the diffusive interactions can be significantly influenced by the size and reactivity effects. The competitive diffusion favors the larger particle and the reaction rate of the smaller one is substantially reduced as the size ratio increases. When a particle subject to a slow reaction is in the neighborhood of another particle with a fast reaction, the reaction rate of the former can also be significantly hindered by the latter due to diffusive interactions. Finally, several approximate expressions with theoretical backgrounds have been proposed and compared with the exact results. The shank transform and the approximation regarding the smaller particle as a point sink plus a point dipole give values in reasonable agreement with the exact solutions. These approaches for obtaining approximate solutions of diffusion-limited condition can also be applied to reactive spheres with first-order surface reaction [6].

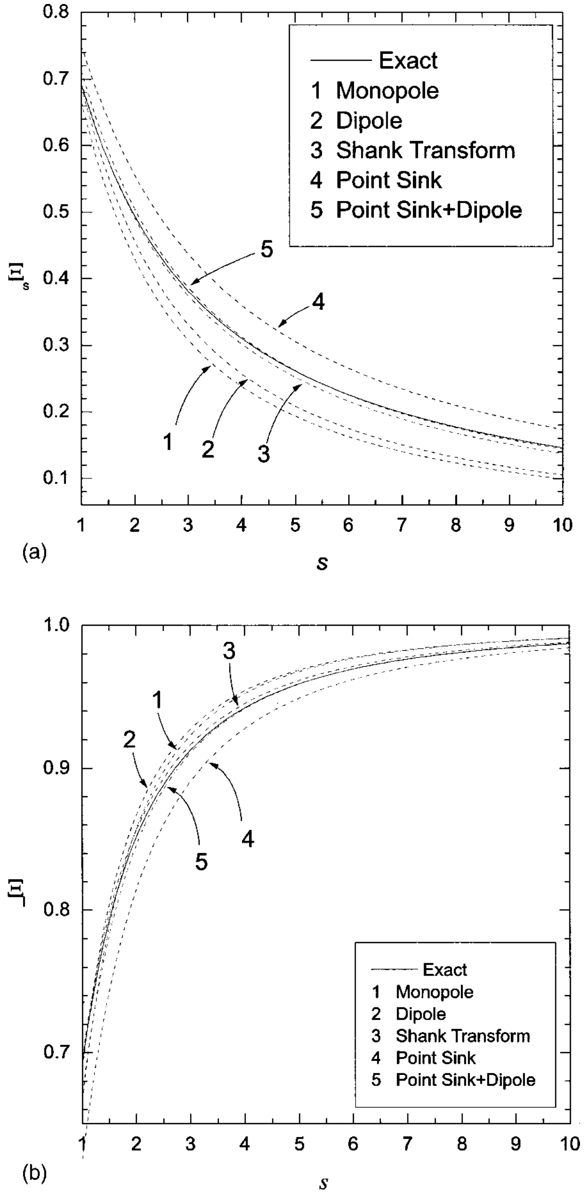

FIG. 6. The comparison of the exact solution with the approximate expressions. The diffusion-limited reaction rate is plotted against the size ratio for (a) the smaller sink and (b) the larger sink.

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