

## Diffusion-controlled reactions among spherical traps: Effect of polydispersity in trap size

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We consider determining the steady-state trapping rate  $k$  associated with diffusion-controlled reactions among static, spherical traps with a polydispersity in trap size. Both discrete and continuous size distributions are examined. Theoretical methods, such as rigorous bounds and survival-probability theory, as well as computer-simulation techniques, are employed to address this problem. It is found that the trapping rate for the polydisperse system generally increases or decreases (relative to the monodisperse case) depending upon whether the relative interfacial surface area increases or decreases.

### I. INTRODUCTION

The subject of diffusion-controlled reactions in disordered heterogeneous media is a problem of long-standing interest and has received considerable attention in recent years.<sup>1,2</sup> A diffusion-controlled reaction is one in which the time required for the two reacting species to diffuse into the same neighborhood is the rate-limiting step, the reaction time being negligible in comparison. Diffusion-controlled reactions arise in a host of phenomena in the physical and biological sciences, including radiation damage, heterogeneous catalysis, liquid droplet combustion, colloid or crystal growth, and cell metabolism, to mention but a few examples. In many instances, one of the two reacting species is very large in comparison with the other, and can be considered to be static. It is therefore reasonable to consider a medium of static traps (sinks) which are distributed throughout a region containing reactive particles. The reactant diffuses within the trap-free region but is instantly absorbed upon contact with the surface of any static trap. At steady state, the rate of reactant production exactly equals the rate of removal (trapping) by the sinks.

Smoluchowski<sup>3</sup> derived an expression for the trapping rate (rate constant)  $k$  for a dilute distribution of equisized spherical traps such that trap interactions can be neglected. At higher concentrations, the trapping rate will be affected by a competition between neighboring traps and will depend upon the density of traps.<sup>4</sup> At arbitrary sink concentrations, the rate constant depends upon an infinite set of correlation functions which statistically characterize the microstructure. In general, this set of functions is never known in practice. Thus, there are presently no exact analytical predictions of  $k$  for even simple random-media models (e.g., random distributions of equisized spherical traps) at arbitrary trap concentrations. There are approximate techniques, however,

which enable one to estimate  $k$  for a wide range of sink densities, including effective-medium theories<sup>5-7</sup> and random-walk methods.<sup>8</sup>

If we accept our inability to predict the trapping rate exactly for high trap densities, it follows that any rigorous statement on the subject must be in the form of an inequality, i.e., a rigorous bound. Rigorous bounds on effective properties of random media serve three purposes: (1) they may be utilized to test the validity of a theory or computer experiment,<sup>9</sup> (2) as successively more microstructural information is included, the bounds become progressively narrower,<sup>10</sup> and (3) one of the bounds can typically provide a good estimate of the property for a wide range of volume fractions, even when the reciprocal bound diverges from it.<sup>11</sup> Reck and Prager<sup>12</sup> were the first to obtain variational bounds on  $k$ . Doi found a different lower bound on  $k$ .<sup>13</sup> Talbot and Willis<sup>14</sup> subsequently obtained a Hashin-Shtrikman-like lower bound on  $k$ . More recently, Rubinstein and Torquato<sup>15</sup> developed general variational principles from which they were able to derive four different classes of bounds, both upper and lower bounds.<sup>15,16</sup>

In addition to such analytical methods, computer-simulation "experiments" can be conducted in order to yield "exact" data for the effective trapping rate for systems of arbitrary trap density, penetrability, and distributions of trap shapes and sizes. These data can then be used to test various analytical predictions. Recently, several Monte Carlo studies<sup>8,17,18</sup> have reported results for the trapping rate among equisized spherical traps.

This paper studies the determination of the steady-state trapping rate  $k$  of a system of static, perfectly absorbing, spherical traps with a polydispersity in size. We shall employ both analytical methods (random-walk techniques and rigorous bounds) and computer-simulation techniques to examine the question of what the effect of polydispersity on the trapping rate is.

In Sec. II we discuss our model systems (fully penetrable and totally impenetrable spherical traps with a size distribution) and the normalization for the trapping rate. Section III describes our computer-simulation techniques to obtain the trapping rate for our models. In Sec. IV, we describe the calculation of a two-point lower bound for fully penetrable spheres of two different sizes. Section V presents the extension of Richards's theoretical results<sup>8</sup> for fully penetrable spherical sinks to a distribution of trap sizes, including continuous size distributions. Section VI reports our simulation as well as analytical results, and discusses the effects of polydispersity on the trapping rate  $k$ . Finally, in Sec. VII, we make concluding remarks.

## II. MODEL SYSTEMS AND TRAPPING RATE NORMALIZATION

We shall consider the trapping of reactants among static, spherical traps with a discrete or continuous distribution in size. Although all subsequent theoretical results will be presented for fully penetrable (spatially uncorrelated) traps (see Fig. 1), we shall present some simulation results for the case of totally impenetrable (spatially correlated) traps. These two models are the extreme limits of the general penetrable-concentric-shell model<sup>19</sup> in which the impenetrability parameter  $\lambda$  varies continuously between zero (in the case of fully penetrable particles) and unity (in the case of totally impenetrable particles). Thus, we will be examining the effect of penetrability as well as polydispersity on the trapping rate.

Consider a system of  $N$  spheres consisting of  $p$  different sizes. Let  $N_i$  and  $R_i$  be the number and radius of type- $i$

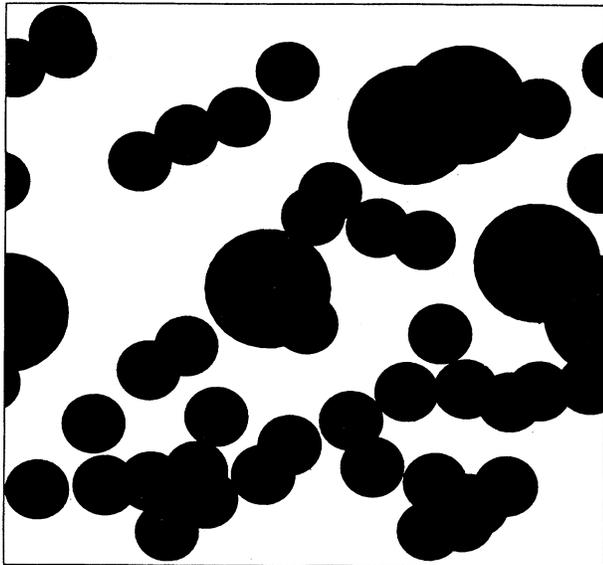


FIG. 1. Realization of a system of fully penetrable disks of two different radii  $R_1$  and  $R_2$ . Here the volume fraction  $\phi_2$  is about 0.3,  $R_2/R_1=0.5$ , and  $\rho_2/\rho_1=8.0$ .  $\rho_i$  is the number density of the type- $i$  particles.

particles, respectively. As mentioned in Sec. I, the bulk properties of a random medium depend upon an infinite set of statistical correlation functions. The simplest and most basic of these functions are the volume fraction of one of the phases, say, phase 2 (the particle phase), which we denote by  $\phi_2$ , and the specific surface  $s$ , the interface area per unit volume. It is useful to explicitly state these functions for our model systems. For totally impenetrable spheres, we have the simple results

$$\phi_2 = \sum_{i=1}^p \rho_i \frac{4\pi}{3} R_i^3, \quad (1)$$

$$s = \sum_{i=1}^p \rho_i 4\pi R_i^2, \quad (2)$$

where  $\rho_i$  is the number density of type- $i$  particles. For fully penetrable spheres,<sup>20</sup>

$$\phi_2 = 1 - \exp \left[ - \sum_{i=1}^p \rho_i \frac{4\pi}{3} R_i^3 \right], \quad (3)$$

$$s = \left[ \sum_{i=1}^p \rho_i 4\pi R_i^2 \right] \exp \left[ - \sum_{i=1}^p \rho_i \frac{4\pi}{3} R_i^3 \right], \quad (4)$$

All of these results are readily extended to the case of a continuous distribution in size characterized by a probability density function  $f(R)$ . For totally impenetrable spheres,

$$\phi_2 = \rho \frac{4\pi}{3} \langle R^3 \rangle, \quad (5)$$

$$s = \rho 4\pi \langle R^2 \rangle, \quad (6)$$

and for fully penetrable spheres<sup>20</sup>

$$\phi_2 = 1 - \exp \left[ - \rho \frac{4\pi}{3} \langle R^3 \rangle \right], \quad (7)$$

$$s = \rho 4\pi \langle R^2 \rangle \exp \left[ - \rho \frac{4\pi}{3} \langle R^3 \rangle \right], \quad (8)$$

where  $\rho$  is the total number density and

$$\langle R^n \rangle = \int_0^\infty R^n f(R) dR. \quad (9)$$

From the equations above, it is seen that both  $\phi_2$  and  $s$  are larger for totally impenetrable particles than for fully penetrable particles at fixed density  $\rho$ .

A particularly useful probability density function (and one we employ in Sec. V) is the Schulz distribution<sup>21</sup>

$$f(R) = \frac{1}{(m-1)!} \left[ \frac{m}{\langle R \rangle} \right]^m R^{m-1} \times \exp(-mR/\langle R \rangle), \quad m \geq 2, \quad (10)$$

which normalizes to unity. The moments of the Schulz function are

$$\langle R^n \rangle = \frac{(n+m-1)!}{(m-1)!m^n} \langle R \rangle^n. \quad (11)$$

Therefore, by increasing  $m$ , the variance decreases, i.e., the distribution becomes sharper.  $f(R)$  is unimodal and peaks at

$$R_{\text{mode}} = \frac{m-1}{m} \langle R \rangle. \quad (12)$$

For small  $m$ ,  $R_{\text{mode}} < \langle R \rangle$ ; but for  $m \rightarrow \infty$ ,  $R_{\text{mode}} \rightarrow \langle R \rangle$  and  $f(R) \rightarrow \delta(R - \langle R \rangle)$ . Figure 2 shows the distribution (10) for various values of  $m$ . Chiew and Glandt<sup>20</sup> for a Schulz distribution found the interesting result that narrower distributions result in larger specific surfaces.

For monodisperse systems of spherical sinks, the trapping rate  $k$  is typically normalized by the dilute Smoluchowski<sup>3</sup> result

$$k_s = \frac{3D\phi_2}{R^2}, \quad (13)$$

where  $D$  is the diffusion coefficient. For polydisperse systems of spherical traps, there are a variety of ways to normalize  $k$ . One natural normalization is the appropriately generalized dilute-limit result

$$k_s = \frac{3D\phi_2}{\langle R \rangle^2 \mu_3}, \quad (14)$$

where for the discrete case

$$\langle R^n \rangle = \sum_{i=1}^p \frac{\rho_i}{\rho} R_i^n. \quad (15)$$

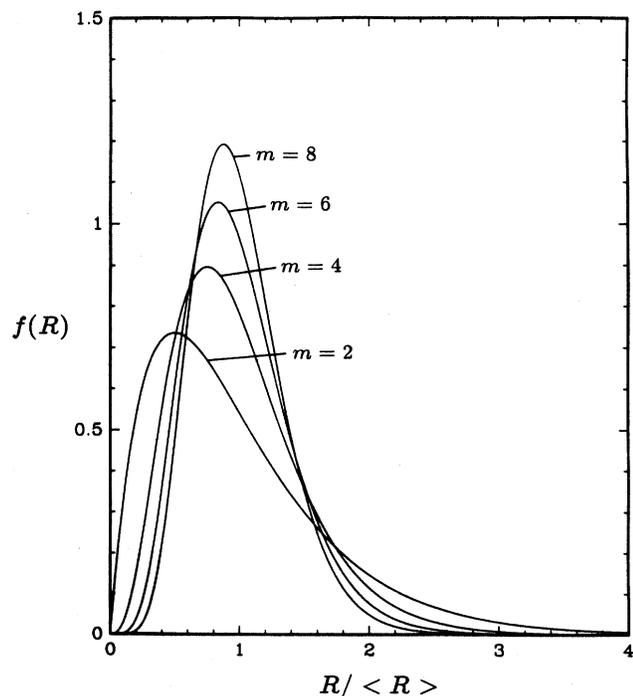


FIG. 2. Schulz distribution  $f(R)$  as a function of  $R/\langle R \rangle$  for  $m=2, 4, 6$ , and  $8$ .

For the discrete or continuous cases

$$\mu_n = \frac{\langle R^n \rangle}{\langle R \rangle^n}. \quad (16)$$

### III. SIMULATION PROCEDURE

Recent studies have demonstrated the success of using continuum-random-walk simulations in studies of the trapping rate in random arrays of equisized spherical sinks. The comprehensive study by Lee *et al.*,<sup>17</sup> in particular, provided a large amount of simulation data on the effective rate constant for random distributions in the penetrable-concentric-shell model<sup>19</sup> for various impenetrability parameters and volume fractions. Additionally, Zheng and Chiew<sup>18</sup> independently reported similar results for the extreme cases of fully penetrable and totally impenetrable spheres using a different algorithm. Data from both studies compare very well to each other, as well as to the theory of Richards for fully penetrable sinks.

Here we extend the method of Lee *et al.*<sup>17</sup> to a polydisperse system of spherical traps consisting of  $p$  different-sized particles of variable penetrability. First, we generate realizations of random distributions of spheres using a Metropolis<sup>22</sup> algorithm and periodic boundary conditions. Second, we employ a Pearson random-walk<sup>23</sup> algorithm to ascertain the trapping rate per realization and then average over a sufficiently large number of realizations to obtain  $k$ . In a Pearson ("continuum") random walk the step size  $a$  is fixed and successive directions are random and uncorrelated. The trapping rate  $k$  is simply the inverse of the average time taken for the random walkers to get trapped,  $\bar{\tau}$ . If the mean numbers of steps  $\bar{n}$  taken by the walker is large ( $\bar{n} \gg 1$ ), then the random walk becomes simple Brownian motion and we have

$$k = (\bar{\tau})^{-1} = \frac{6D}{\bar{n}a^2}, \quad (17)$$

where again  $D$  is the diffusion coefficient. In order to simulate Brownian motion, the step size  $a$  must be small compared to the smallest of the  $p$  radii,  $R_{\text{min}}$ . Hence, we compute  $k$  for fixed trap volume fraction  $\phi_2$  by varying the step size  $a$  and then extrapolating to the  $a/R_{\text{min}} \rightarrow 0$  limit. As  $\phi_2$  increases, the need for such extrapolation becomes increasingly important. Scaling the relation (17) by the Smolchowski result (14) yields the dimensionless rate constant

$$\frac{k}{k_s} = \frac{2(\langle R \rangle/a)^2 \mu_3}{\bar{n} \phi_2}. \quad (18)$$

We now use the procedure described above to compute  $k$  for *bidisperse* systems of both fully penetrable and totally impenetrable distributions of spherical traps. At fixed  $\phi_2$ , the central cell contains 490 particles. For each realization at constant volume fraction  $\phi_2$ , we perform 500 random walks per step size  $a$ . The number of steps taken by each walker before encountering a trap is recorded. (As was done in Ref. 17, we use the GRID method<sup>24</sup> to

significantly reduce the computing time required to test for trapping.) We consider up to five different step sizes. This is carried out for 50 different configurations. For each step size, the number of steps taken before being trapped is averaged over all walks and configurations and the scaled trapping rate is determined from (18). The value of  $k$  reported in Sec. VI is obtained by extrapolating the data to the limit  $a/R_{\min} \rightarrow 0$ . On a VAX 3200 the CPU time required for each volume fraction varied from 3–6 hours, depending on the volume fraction and the step sizes used. Table I lists the step sizes employed in our simulations.

#### IV. RIGOROUS LOWER BOUND ON $k$

Doi,<sup>13</sup> and later Rubinstein and Torquato<sup>15</sup> using a different approach, found that the trapping rate  $k$  for statistically homogeneous media of general topology was bounded from below by

$$k \geq D\phi_1 \left[ \int \frac{1}{4\pi r} \left[ F_{vv}(\mathbf{r}) - \frac{2\phi_1}{s} F_{sv}(\mathbf{r}) + \frac{\phi_1^2}{s^2} F_{ss}(\mathbf{r}) \right] d\mathbf{r} \right]^{-1}. \quad (19)$$

The functions  $F_{vv}(\mathbf{r})$ ,  $F_{sv}(\mathbf{r})$ , and  $F_{ss}(\mathbf{r})$  are the void-void, surface-void, and surface-surface correlation functions, respectively. The asymptotic behavior as  $|\mathbf{r}| \rightarrow \infty$  of these correlation functions is given by

$$F_{vv}(\mathbf{r}) \rightarrow \phi_1^2, \quad F_{sv}(\mathbf{r}) \rightarrow s\phi_1, \quad F_{ss}(\mathbf{r}) \rightarrow s^2, \quad (20)$$

where  $\phi_1$  is the volume fraction of the void phase (trap-free region) and  $s$  is the specific surface (i.e., the area of

TABLE I. Computer-simulation results for the scaled trapping rate  $k/k_s$  for bidispersed systems of fully penetrable ( $\lambda=0$ ) and totally impenetrable ( $\lambda=1$ ) traps with  $R_2/R_1=0.5$  and  $\rho_2/\rho_1=8$ . Here  $\phi_2$  is the trap volume fraction, and  $R_i$  and  $\rho_i$  denote the radius and density of type- $i$  particles.

$\phi_2$	$\lambda=0$	$\lambda=1$
0.2		3.15
0.3	2.61	4.76
0.4	3.16	
0.5	3.97	
0.6	4.96	
0.7	6.52	

the interface per unit volume). Following Rubinstein and Torquato,<sup>15</sup> we refer to (19) as a two-point “interfacial-surface” lower bound. Note that for statistical isotropic media (which is what is considered below), the correlation functions depend only upon the distance  $r=|\mathbf{r}|$ .

Application of bounds of the type (19) in the recent past has been virtually nonexistent because of the difficulty involved in ascertaining the associated correlation functions. Torquato<sup>25</sup> has recently developed a formalism to obtain and compute  $F_{vv}$ ,  $F_{sv}$ ,  $F_{ss}$  (and their higher-order generalizations) for distributions of identical particles from a general  $n$ -point distribution function  $H_n$ . The extension of this methodology to particles with a size distribution is quite straightforward and details will be omitted here.

Consider evaluating (19) for a bidisperse system of fully penetrable spheres. Then using the formalism of Ref. 25, it can be shown that

$$F_{vv}(r) = \exp[-(\rho_1 V_2^{(1)} + \rho_2 V_2^{(2)})], \quad (21)$$

$$F_{sv}(r) = \exp \left\{ -\frac{4\pi}{3} \left[ \rho_1 R_1^3 \left[ 1 + \frac{3r}{4R_1} - \frac{r^3}{16R_1^3} \right] + \rho_2 R_2^3 \left[ 1 + \frac{3r}{4R_2} - \frac{r^3}{16R_2^3} \right] \right] \right\} \\ \times 4\pi \left[ \rho_1 R_1 \left[ \frac{R_1}{2} + \frac{r}{4} \right] + \rho_2 R_2 \left[ \frac{R_2}{2} + \frac{r}{4} \right] \right], \quad 0 < r < 2R_2 \quad (22)$$

$$= \exp \left\{ -\frac{4\pi}{3} \left[ \rho_1 R_1^3 \left[ 1 + \frac{3r}{4R_1} - \frac{r^3}{16R_1^3} \right] + 2\rho_2 R_2^3 \right] \right\} 4\pi \left[ \rho_1 R_1 \left[ \frac{R_1}{2} + \frac{r}{4} \right] + \rho_2 R_2^2 \right], \quad 2R_2 < r < 2R_1 \quad (23)$$

$$= \exp \left\{ -\frac{8\pi}{3} (\rho_1 R_1^3 + \rho_2 R_2^3) \right\} [4\pi (\rho_1 R_1^2 + \rho_2 R_2^2)], \quad r > 2R_1, \quad (24)$$

$$F_{ss}(r) = \exp[-(\rho_1 V_2^{(1)} + \rho_2 V_2^{(2)})] \left\{ 16\pi^2 \left[ \rho_1 R_1 \left[ \frac{R_1}{2} + \frac{r}{4} \right] + \rho_2 R_2 \left[ \frac{R_2}{2} + \frac{r}{4} \right] \right]^2 + \frac{2\pi}{r} (\rho_1 R_1^2 + \rho_2 R_2^2) \right\}, \quad 0 < r < 2R_2 \quad (25)$$

$$= \exp[-(\rho_1 V_2^{(1)} + \rho_2 V_2^{(2)})] \left\{ 16\pi^2 \left[ \rho_1 R_1 \left[ \frac{R_1}{2} + \frac{r}{4} \right] + \rho_2 R_2^2 \right]^2 + \frac{2\pi}{r} \rho_1 R_1^2 \right\}, \quad 2R_2 < r < 2R_1 \quad (26)$$

$$= \exp[-(\rho_1 V_1^{(1)} + \rho_2 V_2^{(2)})] [16\pi^2 (\rho_1 R_1^2 + \rho_2 R_2^2)^2], \quad r > 2R_2, \quad (27)$$

where

$$V_2^{(i)}(r) = \frac{4\pi}{3} R_i^3 \left[ 1 + \frac{3r}{4R_i} - \frac{r^3}{16R_i^3} \right], \quad 0 < r < 2R_i \quad (28)$$

$$= \frac{8\pi}{3} R_i^3, \quad r > 2R_i \quad (29)$$

is the union volume of two spheres of radius  $R_i$  separated by a distance  $r$ .<sup>26</sup> The result (21) for  $F_{vv}$  (or more precisely, its continuous distribution analog) was first given by Stell and Rikvold.<sup>27</sup> Results (22)–(27) are new, however. With the above forms of the correlation functions, it is a simple matter then to insert them into integral (19), and numerically integrate it to determine the value of the bound for a given value of  $\phi_2$ . These results are summarized in Sec. VI.

## V. SURVIVAL-PROBABILITY THEORY

Richards<sup>8</sup> derived a theoretical expression for the trapping rate  $k$  for a distribution of equisized fully penetrable spheres by obtaining the survival probability for a random walker. The resulting relation for  $k$  has been shown to agree quite well with simulation results.<sup>17,18</sup> In the same paper, Richards also derives an expression for the trapping rate for a system of fully penetrable spheres with a *discrete* size distribution, namely, he found

$$k = \frac{\Gamma}{1 - \sqrt{\pi} \gamma e^{\gamma^2} \operatorname{erfc}(\gamma)}, \quad (30)$$

where

$$\Gamma = 4\pi D \sum_{i=1}^p \rho_i R_i, \quad (31)$$

$$\gamma = 8(\pi D)^{1/2} \sum_{i=1}^p \rho_i R_i^2, \quad (32)$$

and

$$y = \frac{\gamma}{2\sqrt{\Gamma}}. \quad (33)$$

Here  $\operatorname{erfc}(y)$  denotes the complimentary error function of argument  $y$ . Now using the notation of Sec. II and the dilute Smoluchowski result (14), we can recast the above equation for the trapping rate as

$$\frac{k}{k_s} = \frac{\eta}{\phi_2} \frac{1}{1 - \sqrt{\pi} \gamma e^{\gamma^2} \operatorname{erfc}(\gamma)}, \quad (34)$$

where

$$\eta = \rho \frac{4\pi}{3} \langle R^3 \rangle, \quad (35)$$

and  $\langle R^3 \rangle$  is given by Eq. (15). Note that for small trap densities, expression (34) for the scaled trapping rate gives

$$\frac{k}{k_s} = 1 + \sqrt{3\phi_2} + \dots,$$

which to the same order is identical to the corresponding nonanalytic expansion for equisized traps,<sup>4</sup> i.e., po-

lydispersity effects are contained in higher-order terms, represented by the ellipsis. We should note here that bound (19) gives an order  $\phi_2$  correction to  $k/k_s$ . As is now known,<sup>15,16</sup> it is difficult to construct variational trial fields for bounds which incorporate nonanalytic terms due to screening.

Given the discussion of Sec. II, the extension of (34) to the continuous case is quite straightforward. One simply employs the continuous formula for the moments of  $R$  [i.e., Eq. (9)], which arise in (34), instead of the discrete version, Eq. (15). The dimensionless quantity  $y$  is explicitly given by

$$y = \frac{2\rho^{1/2} \int_0^\infty R^2 f(R) dR}{\left( \int_0^\infty R f(R) dR \right)^{1/2}}, \quad (36)$$

where  $f(R)$  is the continuous probability density function described above Eq. (5). In Sec. VI, we shall evaluate (34) for both bidispersed and continuous polydispersed media.

## VI. RESULTS AND DISCUSSION

Here we present computer-simulation results, calculations of the interfacial-surface bound (19), and evaluations of Richards's expression (34) for polydispersed systems of spherical traps. We examine both bidispersed and continuous polydispersed cases.

### A. Bidispersed media

Figure 3 compares our simulation results for the scaled trapping rate  $k/k_s$  with the lower bound (19) and expression (34) for a bidispersed distribution of *fully penetrable* spheres in which  $R_2/R_1=0.5$  and  $\rho_2/\rho_1=8$ . If the spheres were *totally impenetrable*, then this case could be interpreted as corresponding to one in which exactly half of the spheres of a monodispersed system (and thus half the volume of the spheres) are broken down into spheres of half the radius but eight times as dense as the larger species (or, alternatively, half of the spheres are consolidated to form an equal volume of spheres of twice the original radius). Now since the spheres are actually taken to be fully penetrable to one another, such an interpretation is correct only at dilute conditions since for such microstructures the reduced density for type- $i$  particles  $\rho_i 4\pi R_i^3/3$  is not generally equal to the volume fraction for type- $i$  particles [see Eqs. (1) and (3)]. From Fig. 3 it is seen that the prediction (34) happily lies above the rigorous two-point lower bound. Three-point lower bounds, such as multiple-scattering bounds,<sup>15</sup> should provide significant improvement over the two-point interfacial-surface lower bound computed here. The exact Monte Carlo data for fully penetrable traps are slightly below the prediction of (34). Thus, relation (34) provides a good estimate for the trapping rate for this bidispersed system, as was the case for the monodispersed system.<sup>17,18</sup>

Also included in Fig. 3 are two Monte Carlo simulation points for a distribution of totally impenetrable spherical traps of two different sizes. As for the fully pe-

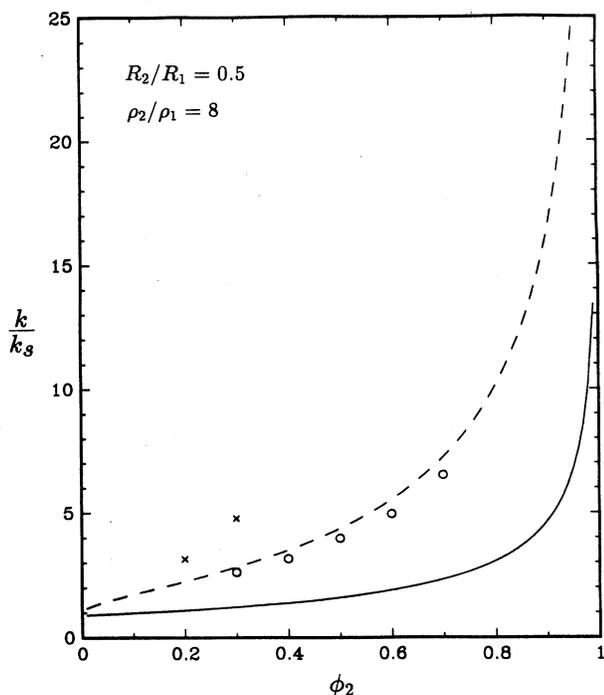


FIG. 3. Scaled trapping rate  $k/k_s$  for a bidispersed system of spherical traps with  $R_2/R_1=0.5$  and  $\rho_2/\rho_1=8.0$ . Solid line is the rigorous lower bound [Eq. (19)] for fully penetrable traps, dashed line is Richard's theory [Eq. (22)] for fully penetrable traps, circles are simulation results for fully penetrable traps, and the crosses are simulation results for totally impenetrable traps.  $k_s$  is given by Eq. (14).

netrable case, the ratio of sphere radii is  $R_2/R_1=0.5$  and  $\rho_2/\rho_1=8$ . As expected, the trapping rate is higher for the totally impenetrable ( $\lambda=1$ ) case than for the instance  $\lambda=0$  because of the larger interfacial-surface area available for reaction in the former model (see discussion of Sec. III). Numerical values for the trapping rates  $k/k_s$  are tabulated in Table I for both fully penetrable and totally impenetrable traps. It is important to note that there is presently no available theory to predict  $k$  accurately for impenetrable-trap systems for arbitrary trap volume fractions, even for the simpler case of equisized traps. To be sure, Richard's theory for equisized impenetrable traps<sup>28</sup> provides a good estimate of  $k$  up to moderate values of  $\phi_2$ , but underestimates  $k$  for moderate to high  $\phi_2$ . In fact, for  $\phi_2 > 0.52$ , his theory violates the two-point lower bound computed by Torquato,<sup>9</sup> and thus the latter is the more reliable in such instances.

The effect of bidispersity can most clearly be seen by examining the ratio of the bidispersed trapping rate  $k_B$  to that of the corresponding trapping rate for a monodispersed case  $k_M$  at the same value of  $\phi_2$ . Since the survival-probability theory provides a simple means of closely approximating exact data for the case of spatially uncorrelated traps ( $\lambda=0$ ), Eq. (30) can be used to calculate this ratio. The sphere radius in the bidispersed case  $R_1$  is taken to be equal to the radius of the traps in the monodispersed system. Using Eq. (30) it is found that

$$\frac{k_B}{k_M} = \left\{ \left[ 1 + \frac{\rho_2}{\rho_1} \frac{R_2}{R_1} \right] \left/ \left[ 1 + \frac{\rho_2}{\rho_1} \left( \frac{R_2}{R_1} \right)^3 \right] \right\} \times \frac{1 - \sqrt{\pi} y_M e^{y_M^2} \operatorname{erfc}(y_M)}{1 - \sqrt{\pi} y_B e^{y_B^2} \operatorname{erfc}(y_B)}, \quad (37)$$

where  $y_B$  and  $y_M$  are obtained from Eq. (33) for the bidispersed and monodispersed cases, respectively. It is interesting to note that at  $\phi_2=1$ ,

$$\frac{k_B}{k_M} = S^2,$$

where

$$S = \left[ 1 + \frac{\rho_2}{\rho_1} \left( \frac{R_2}{R_1} \right)^2 \right] \left/ \left[ 1 + \frac{\rho_2}{\rho_1} \left( \frac{R_2}{R_1} \right)^3 \right] \right. \quad (38)$$

is the ratio of the specific surface of the bidispersed system to that of the monodispersed system at fixed  $\phi_2$ . In Fig. 4 we plot the ratio  $k_B/k_M$  versus the trap volume fraction  $\phi_2$  for several values of  $R_2/R_1 (<1)$  and  $\rho_2/\rho_1 (>1)$ , including  $R_2/R_1=0.5$  and  $\rho_2/\rho_1=8$ , which correspond to the values used in Fig. 3. As expected, the trapping rate ratio  $k_B/k_M$ , at a given value of  $\phi_2$ , increases due to the relative increase in the interfacial-surface area. Interestingly, the ratio  $k_B/k_M$  is a weakly linear function of  $\phi_2$  for a large range of  $\phi_2$  and in some cases is almost a constant over the range of  $\phi_2$ .

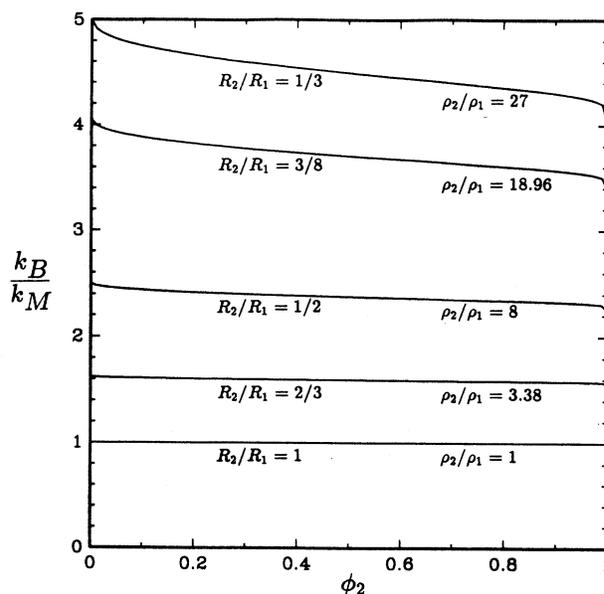


FIG. 4. Ratio of the bidispersed trapping rate  $k_B$  to that of the monodispersed case  $k_M$  at the same value of the trap volume fraction  $\phi_2$ . Curves are for selected values of the ratio of the number densities  $\rho_2/\rho_1$  and radii  $R_2/R_1$  ( $R_1 > R_2$ ) which satisfy the constraint relation  $(\rho_2/\rho_1)(R_2/R_1)^3=1$ . Both  $k_B$  and  $k_M$  are calculated from Eq. (30). Note that Eq. (43) for  $K$  gives a good approximation to  $k_B/k_M$  for a wide range of parameters.

For bidispersions in which  $k_B/k_M$  is approximately a constant over the range of  $\phi_2$ , one can estimate  $k_B/k_M$  by evaluating it at  $\phi_2=0$ ,

$$K \equiv \lim_{\phi_2 \rightarrow 0} \frac{k_B}{k_M} = \left[ 1 + \frac{\rho_2}{\rho_1} \frac{R_2}{R_1} \right] / \left[ 1 + \frac{\rho_2}{\rho_1} \left( \frac{R_2}{R_1} \right)^3 \right]. \quad (39)$$

Expression (39) is obtained from Eqs. (13) and (14). Note that if  $R_1 > R_2$ , the ratio  $K > 1$  and is a monotonically increasing function of both  $\rho_2/\rho_1$  and  $R_2/R_1$ , and if  $R_1 < R_2$ , the ratio  $K < 1$  and is a monotonically decreasing function of both  $\rho_2/\rho_1$  and  $R_2/R_1$ . It is of interest to relate  $K$  to the ratio  $S$ . Observe that  $S$  has the same general properties as  $K$ , i.e.,  $S$  is a monotonically increasing function of its variables with the minimum  $S=1$  located at  $\rho_2/\rho_1=R_2/R_1=1$  when  $R_1 > R_2$ , and is a monotonically decreasing function of its variables when  $R_1 < R_2$ . Combining (38) and (39) yields

$$K = f \left( \frac{\rho_2}{\rho_1}, \frac{R_2}{R_1} \right) S, \quad (40)$$

where

$$f = \left[ 1 + \frac{\rho_2}{\rho_1} \frac{R_2}{R_1} \right] / \left[ 1 + \frac{\rho_2}{\rho_1} \left( \frac{R_2}{R_1} \right)^2 \right]. \quad (41)$$

Now (40) is *not* an explicit relation in terms of  $S$ , since  $S$  itself changes as a function of  $\rho_2/\rho_1$  and  $R_2/R_1$ . However, such an explicit expression can be obtained by imposing a reasonable constraint relation between the ratios  $\rho_2/\rho_1$  and  $R_2/R_1$ . For example, a meaningful constraint is to require that if  $\rho_2/\rho_1$  increases, then  $R_2/R_1$  must decrease and vice versa. (If both variables decreased simultaneously, for example, then the effect of polydispersity would be minimum, i.e., the deviation of  $K$  and  $S$  from unity would be small.) Hence, suppose one imposes the constraint  $(\rho_2/\rho_1)(R_2/R_1)^3 = \text{const}$ , then using the above relations one can obtain  $K$  explicitly in terms of  $S$ . For simplicity, if we take the aforementioned constant to be unity [i.e.,  $(\rho_2/\rho_1)(R_2/R_1)^3=1$ ], which states that the reduced densities of each type particle are equal, i.e.,  $4\pi\rho_1R_1^3/3=4\pi\rho_2R_2^3/3$ , then

$$f = \frac{1+(1-2S)^2}{2S} \quad (42)$$

and (40) yields

$$K = 1 + 2S(S-1). \quad (43)$$

The second term of (43) gives the contribution to  $K$  due to polydispersity effects. Note the monotonic dependence of  $K$  on  $S$ . The constraint  $(\rho_2/\rho_1)(R_2/R_1)^3=1$  was also used to generate the curves of Fig. 4. It is seen that for a wide range of parameters, Eq. (43) gives a good approximation to  $k_B/k_M$ .

### B. Continuous polydispersed media

The trapping rate of continuous distributions of trap sizes for fully penetrable spherical traps can be evaluated using expressions (30) or (34) and (36). The trapping rate for several cases of the Schulz distribution (10) was calculated for different values of  $m$ . The trapping rate for each case was lower than the monodispersed case, and increased with increasing  $m$ . This again confirmed expected behavior, i.e., the trapping rate increases or decreases as the relative specific surface increases or decreases, respectively.

## VII. CONCLUSIONS

We have generated exact computer-simulation results and calculated rigorous two-point lower bounds and theoretical results for the trapping rate of a system of fully penetrable and totally impenetrable spherical traps, polydispersed in size. Simulation and survival-probability results<sup>8</sup> satisfy the rigorous two-point interfacial-surface lower bound for a distribution of fully penetrable spherical traps of two different sizes. The survival-probability expression only slightly overestimates the trapping rate for fully penetrable traps as determined from simulations, verifying the validity of the theory for polydispersed media. We have extended Richard's survival-probability theory<sup>8</sup> to accommodate continuous size distributions of fully penetrable spherical traps. It is noted that there are still no theories capable of predicting the trapping rate for totally impenetrable traps at moderate to high densities. In each of the cases examined in this study, it was seen that the trapping rate (relative to the monodispersed case) increased or decreased according to whether the relative interfacial-surface area increased or decreased, respectively.

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