Diffusion-controlled reactions in a polydisperse medium of reactive sinks

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We study diffusion-controlled reactions in which a reactive solute diffuses through a medium containing static, reactive, spherical traps of many different sizes. We focus on the cases of impenetrable, i.e., nonoverlapping traps, and of randomly overlapping traps. Bounds for the trapping rate are derived using trial functions of the kind developed by Doi, and by Weissberg and Prager. It is shown that the bounds for trapping rate are relatively insensitive to dispersivity of trap size when they are plotted against the proper scaling variable. The trap volume fraction is the proper scaling variable for randomly overlapping traps. The mean density of traps $\rho(a)$ is shown to be the proper scaling variable for nonoverlapping traps. It is shown that the low-density limits of both the Doi and the Weissberg–Prager bounds fail to reproduce the radius-averaged single-trap solution of Smoluchowski. We give a generalization of these classes of bounds that has the proper behavior. In evaluating trapping bounds for impenetrable traps, the material correlation functions are evaluated for the first time for a nontrivial polydisperse system.

I. INTRODUCTION

Natural processes involving disordered materials will, in general, include particles with a distribution of sizes. Examples of processes in which this polydispersity of size is important include light scattering from colloids, combustion and gasification of coal fragments, and formation of nuclei in models of freezing. Most mathematical models of these processes assume a uniform droplet or particle size; indeed, in many models, such as those based in a lattice geometry, it is impossible to include the important continuum effects of size distribution, e.g., the interaction of particles of widely different sizes.

This paper is part of a long-term effort to calculate the effective or bulk properties of disordered media, using a class of models and techniques derived from the theory of liquids. We briefly review this general project, then describe recent studies that have been made of the influence of polydispersity on bounds for bulk properties. In this paper we focus, in particular, on the influence of dispersity in trap size on bounds for the rate of trapping of diffusing particles, but we indicate the importance of our results in the wider context to be described next.

An important class of two-phase composite materials can be modeled as a continuum of one phase, to be called the matrix or void phase, containing inclusions composed of the other phase. In general, the inclusions can be diverse in size or shape; their positions may be chosen randomly or correlated according to a distribution function. Also, depending on the medium to be modeled, the inclusions may or may not be allowed to overlap. For example, fiber-reinforced composites are typically modeled using nonoverlapping ellipsoidal or cylindrical inclusions; random alloys and porous materials are often modeled using overlapping inclusions. In this paper, the inclusions or trapping sites are taken to be spherical regions with prescribed correlations between their centers. We consider models with various degrees of overlap allowed among the trapping sites.

The trapping problems considered in this paper are, in a sense, the simplest class of diffusion-dominated processes. Whereas the conductivity and elastic properties of random media involve solution for vector and tensor quantities, trapping problems involve only a single scalar quantity, namely the concentration of diffusing particles. We note that, since heat flow in a medium is also described by a diffusion equation, the calculation of cooling rate, e.g., of a liquid containing ice chips, has an identical structure to the problems considered here.

To map this class of models on those used in the theory of liquids, one identifies the centers of inclusions with atoms, and the influences correlating the positions of inclusions with effective potentials between these atoms. The machinery of liquid-state statistical mechanics can then be used to provide integral equations, series expansions, etc., for the physical properties of this class of materials. In particular, Torquato and Stell exploited the fact that the correlation functions for a binary mixture of point particles and molecules are precisely the matrix probability functions which occur in the bounds of Beran for bulk material properties. This correspondence can be extended to give efficient series expansions and estimates for the entire class of material correlation functions which characterize random, two-phase media. These functions give the information about a medium required to evaluate the existing classes of bounds on material properties. Thus, by using such mappings, bounds have been developed for a large class of diffusion-dominated processes, including chemical reactions in porous materials, as well as the electrical conductivity and elastic properties of two-phase media. Fluid dynamic drag and permeability are not obvious members of this class of processes; however, in the limit of creeping flow, the effects of inertia on fluid flow are minor, and a description in terms of the diffusion of fluid elements is then appropriate. In this paper, we study the effect of polydispersity on various bounds on the trapping rate in two-phase media. We focus on the bounds of Weissberg and Prager and Doi. Although the first two authors mentioned developed bounds for fluid permeability, almost identical procedures apply to the trapping problems.

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discussed here, and give bounds for them. A word on terminology is necessary. Following the usage of Doi\textsuperscript{14} we will refer to the trap-free region as the void phase, and to the region which is the union of spherical traps as the trapping, or absorbing phase. This terminology recalls our extended analogy between multiphase chemical systems, and the systems studied here.

Several basic questions need to be addressed:

1. What is the influence of polydispersity on the bulk properties of the class of models described above?

2. What is the influence of polydispersity upon the existing upper and lower bounds, and on the related perturbation expansions\textsuperscript{2,4} for the properties of these models? Do these track the changes in model properties, or simply reflect increased inaccuracy of the bounds involved?

3. Which scaling variables are appropriate for combining data on the properties of random materials having different distributions of particle sizes?

We attempt both to collect the existing data on these questions, and to shed new light on them.

This paper is organized as follows: in Sec. II we sketch the variational principles used to derive upper and lower bounds on trapping rate. In Sec. III we generalize to the polydisperse case a series expansion technique that allows one to calculate correlation functions occurring in the bounds in Sec. II. In Sec. IV the lower bound of Doi for trapping rate is applied to diffusion through a system of randomly overlapping traps. In order to apply the Doi bounds to this system, the correlation functions of Sec. III are calculated for this case and discussed in detail. In Sec. V the Doi bounds are evaluated for the trapping rate in a medium containing nonoverlapping traps. The correlation functions for such a medium are calculated by using a numerical Percus–Yevick solution for the standard thermal correlation function of polydisperse hard spheres. In Sec. VI we discuss the scaling properties of the various classes of bounds evaluated and explore their dependence on polydispersity. We establish proper scaling variables, in terms of which the Doi bounds for various levels of dispersity collapse onto a single curve. Finding such variables is a basic goal of this research, in both theoretical and practical terms. Our search for good scaling variables is carried out in the context, of both previous results on polydisperse systems, and of some relevant results in the mathematical theory of diffusion. We also show that in both the randomly overlapping and the impenetrable cases, the standard Doi bound does not achieve the proper low-density limit. The Doi bounds are generalized to correct this problem by the choice of a suitable, radius-dependent one-particle trial function. In Sec. VII we show that the Weissberg–Prager bounds for trapping rate also fail to achieve the correct low-density limit. The solution adopted in Sec. VI to correct this defect works in this case also. Section VIII presents our conclusions. In an appendix, we discuss the radius distribution functions used in this work.

II. DERIVATION OF BOUNDS ON TRAPPING RATE FROM VARIATIONAL PRINCIPLES

In this section, we will discuss some of the main variational arguments that have been used to place bounds on the trapping rate for particles diffusing in random, two-phase media. Specifically, we will review the variational formulation originally used by Doi to provide a lower bound on the trapping rate. We also discuss an alternative formulation of this bound, using the energy formalism, that relates the Doi bound to other classes of bounds on the trapping rate, including that analogous to the Weissberg–Prager bound for fluid permeability.

Some remarks about our choice of units are necessary. Any distribution function used to specify trap sizes will contain a reference length $a_0$, which is the single value of trap radius around which the distribution is peaked in the monodisperse limit. We use this to nondimensionalize all quantities in this paper, including the trap density $\rho$ and the various moments of the radius distribution function, which we write $(a^*)$.

We consider, then, a random, two-phase material in which one phase, to be called the void phase, contains a constant density of particles undergoing Brownian motion. The second phase consists of extended inclusions, or traps, that immediately annihilate the diffusing particles on contact. In the general case, these inclusions may have an arbitrary distribution of sizes and shapes, and may have arbitrary correlations between their centers. The diffusing particles are assumed to be generated in the void phase at a constant rate $\sigma(x)$; this is necessary to allow the establishment of a steady state. The concentration $c(x)$ of the particles then obeys the equations

\begin{equation}
DV^2c(x) + \sigma(x) = 0, \quad x \in \mathcal{V} \tag{2.1}
\end{equation}

\begin{equation}
c(x) = 0, \quad x \in \partial \mathcal{V}. \tag{2.2}
\end{equation}

Here $D$ is the diffusion constant, and $\mathcal{V}$ and $\partial \mathcal{V}$ are, respectively, the void phase, and its interface with the trapping phase. The random media considered here can be specified by fixing the trap density, trap size distribution, and correlation function between trap centers. We will use angle brackets $\langle \rangle$ to denote an average over a random ensemble, keeping these quantities fixed. For such an ensemble, the volume-averaged particle concentration $c(\mathcal{x})$ will be proportional to the rate of particle trapping. In a steady state, this must equal the volume-averaged rate of particle creation. Thus

\begin{equation}
\sigma(\mathcal{x}) = D c(\mathcal{x}) \tag{2.3}
\end{equation}

This defines the trapping rate $k$. We will use the symbol $\xi(x)$ for the rate of particle trapping occurring at the point $x$. This function is defined for a specific realization of the porous medium and is nonzero only at the interface of the void and trapping region. By using the Green's function for the Laplace equation (2.1)

\begin{equation}
G(x, x') = \frac{1}{4\pi} \frac{1}{|x - x'|} \tag{2.4}
\end{equation}

we can write a formal solution to the problem defined by Eqs. (2.2) and (2.3):

\begin{equation}
Dc(x)/\sigma(x) = \int_V d^3 x' G(x, x') - \int_{\partial V} d^3 x' G(x, x') \xi(x'). \tag{2.5}
\end{equation}

Note that this is not yet a full solution because the very difficult problem of satisfying the boundary condition (2.2) has

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not been addressed. Doi approached this problem by recasting the condition (2.2) in a variational form. He proved that a certain functional of $\xi(x)$ is minimized when $c(x)$, as given by Eq. (2.5), satisfies Eq. (2.2). The variational bound thus obtained is one reciprocal to the classical Helmholz principle in that the roles of the Euler–Lagrange equation appropriate to this problem and the boundary condition (2.3) have been interchanged.

Rubenstein and Torquato showed that one can also derive Doi's bound for trapping by minimizing a standard energy-like functional very closely related to that used by Doi. This formulation is convenient in that it allows a unified derivation of two bounds on trapping rate, the Doi bound and another bound directly analogous to the Weissberg–Prager bound for the permeability of fluid in porous media. We will follow this derivation here. For this purpose, we define the rescaled concentration $w(x)$ by the relation

$$w(x) = \frac{Dc(x)}{\sigma(x)}. \tag{2.6}$$

If we assume that the medium is locally stationary, so that variations in $\sigma(\tilde{x})$ occur only on length scales large compared to the trap size, we can then derive the approximate equation

$$\nabla^2 w(x) = -1, \quad x \in V \tag{2.7}$$

$$w(x) = 0, \quad x \in \partial V. \tag{2.8}$$

Here we have extended the definition of $w(x)$ to be zero outside the void region, i.e., inside the traps. In terms of $w(x)$, the trapping rate is given by

$$k^{-1} = w(x) = \langle w(x)I_v(x) \rangle. \tag{2.9}$$

We note that the quantity $k^{-1}$ has dimensions of (length)$^2$.

Here we have introduced $I_v(x)$, the indicator function for the void phase

$$I_v(x) = \begin{cases} 1 & x \in V \\ 0 & x \in \partial V \end{cases}. \tag{2.10}$$

One can easily rewrite Eq. (2.9) for the trapping rate as

$$k^{-1} = \langle \nabla w(x) \cdot \nabla w(x) I_v(x) \rangle. \tag{2.11}$$

To see this, replace the right-hand side of Eq. (2.11) by a volume average of the quantity in brackets, integrate by parts, and use Eqs. (2.7) and (2.8). Furthermore, one can show that, in the class of functions $w(x)$ satisfying Eq. (2.7), the quadratic functional in Eq. (2.11) is minimized by the function $u(x)$ also satisfying Eq. (2.8). That is

$$1 = \frac{1}{\langle \nabla u(x) \cdot \nabla u(x) \rangle}. \tag{2.12}$$

for $u(x)$ any solution of Eq. (2.7).

Equation (2.12) is then a general starting point for the derivation of bounds on the trapping rate $k$. For example, to derive the Doi bound on trapping rate, one substitutes into Eq. (2.12) the form on the right-hand side of Eq. (2.5) for the rescaled concentration $u(x)$, and carries out the ensemble average implied by the angular brackets. In Sec. VII we will find it useful to assume a very general form for the derivative of the surface trapping rate $\xi(x)$. We first assume the form for $\xi(x)$,

$$\xi(x) = \prod_{i} \xi_i(x_i, a_i) \{1 - I_v(x_i, a_i)\}. \tag{2.13}$$

Here the product is over inclusions, or traps. The functions $I_v$, are indicator functions for the interior volume of the individual traps. Note that if the one-particle functions $\xi_i$ were absent, Eq. (2.13) would be the indicator function for the void phase. We note that, in general, the gradient of an indicator function for any volume is a delta function which is zero except at its surface. Specifically,

$$|\nabla I_v(x)| = I_{\bar{v}}(x). \tag{2.14}$$

Here, the function $I_{\bar{v}}(x)$ will be termed the indicator function for the surface of the $i$th trap even though it is actually singular on that surface rather than taking the value unity. The derivative of the trial function in Eq. (2.13) is then

$$\nabla \xi(x) = \sum_{i} \xi_i(x, a_i) I_{\bar{v}}(x) I_v(x). \tag{2.15}$$

The frequently used symbol $I_{\bar{v}}(x)$ is often written simply as $m(x, a_i)$. The simplest choice for $\xi_i$ is to assume it a constant, independent of both $x$ and $a_i$. We will make this choice here and discuss it further in Sec. VI. With this choice, the lower bound (2.12) is

$$k > A^{-1} \tag{2.16}$$

with

$$A = \int_0^\infty \int_0^\infty d^3x_{12} d^3x_{13} \nabla G(x_{12}) \cdot G(x_{13}) \times \left[ \xi_i^2 F_{sw}(x_1, x_2, x_{13}) - 2 \xi_i F_{sw}(x_1, x_2, x_{13}) \right. \right.$$\left.$$+ F_{sw}(x_1, x_2, x_{13}) \right]. \tag{2.17}$$

Here the $F$ functions are the material distribution functions. These functions are the reduced distribution functions associated with finding, at particular spatial locations, elements of trap surface and trap volume. For example, $F_{sw}(x_1, x_2, x_{13})$ is the reduced distribution function associated with finding, in a sample of random material, the points $x_1$ and $x_2$ both on the surface of traps, and the point $x_{13}$ in the void phase. These functions have already been characterized in detail. It will suffice here to define the necessary material distribution functions in terms of the indicator function $I_v(x)$ for the void phase. This will be done below. Note that the subscripts "s" and "w" on a material distribution function stand for "surface" and "void," respectively. The subscripts correspond, one to one, to the restrictions on the corresponding position arguments. Equation (2.16) is easily derived by inserting Eq. (2.5) into Eq. (2.11) and noting that, e.g.,

$$F_{sw}(x_1, x_2, x_{13}) = \langle \nabla I_v(x_1) \nabla I_v(x_2) I_v(x_{13}) \rangle. \tag{2.18}$$

A lower quality Doi bound that depends only on functions of two variables can be provided by noting that

$$\langle \nabla u(x) \cdot \nabla u(x) I_v(x) \rangle < \langle \nabla u(x) \cdot \nabla u(x) \rangle. \tag{2.19}$$

This gives a lower bound of the form (2.16), but with $A$ now given by

$$A = \int_0^\infty dx_{12} x_{12} \left[ \xi_i^2 F_{sw}(x_{13}) - 2 \xi_i F_{sw}(x_{12}) \right.$$\left.$$+ F_{sw}(x_{12}) \right]. \tag{2.20}$$
The function $F_{\omega}(x_1,x_2)$ is the distribution function associated with finding the point $x_1$ on the surface of an inclusion and the point $x_2$ is the void phase. The function $F_{\omega}(x_1,x_2)$ is the distribution function associated with finding the points $x_1$ and $x_2$ both in the void phase of a two-phase medium. Similarly, $F_{\omega}(x_1,x_2)$ is the distribution function associated with finding the points $x_1$ and $x_2$ both on the interface between void and trapping phases.

We can characterize these functions in terms of an ensemble average over the void phase indicator function and its derivative: $I_\omega(x)$:

\begin{align}
F_{\omega}(x_1,x_2) &= \langle I_\omega(x_1)I_\omega(x_2) \rangle, \\
F_{\omega}(x_1,x_2) &= \langle \nabla I_\omega(x_1)I_\omega(x_2) \rangle, \\
F_{\omega}(x_1,x_2) &= \langle \nabla I_\omega(x_1)\nabla I_\omega(x_2) \rangle.
\end{align}

One can obtain bounds on the trapping rate analogous to those developed by Weissberg and Prager\textsuperscript{15,16} for the fluid permeability by the use of a trial function $u(x)$ analogous to that used in kinetic theory.\textsuperscript{30} Such multiple-scattering trial functions are written as the sum of a function accounting for single-particle scattering, a function corresponding to scattering of pairs of particles, etc. We retain only the first term in such an expansion, and write the trial function

\begin{equation}

u(x) = \int G(x,y) - \sum \xi_j(x,x_i,\alpha_i)G(x,x_i) \\
\times [1 - m(x,x_i,\alpha_i)]
\end{equation}

Here the terminology is the same as in Eqs. (2.13) and (2.15). Substituting this form into the functional on the right-hand side of Eq. (2.19) gives the lower bound

\begin{equation}
k > \bar{A}^{-1}
\end{equation}

with

\begin{equation}
\bar{A} = \frac{1}{\rho^2} \int F_{\omega}(x_1,x_2) |\nabla G(x_1)|^2 dx_{12} \\
+ \frac{1}{\rho^2} \int Q_3(x_{12},x_{23}) \nabla G(x_{12}) \cdot \nabla G(x_{23}) dx_{12} dx_{23},
\end{equation}

where

\begin{equation}
Q_3(x_{12},x_{23}) = F_{\omega}(x_1,x_2,x_3) - \rho F_{\omega}(x_1,x_2) \\
- \rho F_{\omega}(x_1,x_3) + \rho^2 \phi_0.
\end{equation}

Here the $F$ functions are material distribution functions, with the subscript “$\rho$” for “particle” here denoting the center of a trap. The function $F_{\omega}(x_1,x_2)$ is the probability distribution associated with finding, in a random sample of a two-phase medium, the point $x_1$ in the void phase, and the point $x_2$ at the center of a trap. The function $F_{\omega}(x_1,x_2)$ is defined similarly.

In Sec. III, we will derive general formulas for the material distribution functions $F_{\omega}, F_{\omega}, F_{\omega}$ in a polydispersity medium of the type discussed in this paper. Similar formulas are available\textsuperscript{25} for the evaluation of the other functions introduced in this section. However, these will not be needed here, as we will discuss the Weissberg–Prager bound in Sec. VII only for a system of randomly placed traps, in which case evaluation of these functions is straightforward.

The presentation adopted here allows us to show readily that, for a system of nonoverlapping traps, the Doi bound given by Eqs. (2.16) and (2.20) is the optimal two-point bound. To see this, note that an extended formal analogy exists\textsuperscript{30} between the scalar diffusion problem discussed in this paper and an electrostatic problem on the same geometry. Specifically, we interpret the functional on the right-hand side of Eq. (2.19) as the electrostatic energy of a system of conducting spherical inclusions, with the functions $u(x)$ and $\xi(x)$ being, respectively, the electrical potential and the charge density. It follows from this analogy that the optimal trial function is of the form (2.5) used by Doi. To see this, note that the electrostatic energy of a system of charged spherical conductors is always minimized by distributing the charges on the surfaces of the conductors. The trial function (2.5) corresponds to such a distribution.

III. POLYDISPERSE MATERIAL DISTRIBUTION FUNCTIONS

In this section, we derive expressions for the void–void, surface–void, and surface–surface material distribution functions, to be called $F_{\omega}(x), F_{\omega}(x), F_{\omega}(x)$ for a medium in which the nonvoid phase is formed by the overlap of spheres with radii chosen from a random distribution. These are the material distribution functions, as defined in Sec. II, for the centers and surfaces of spherical traps. In this section, we solve the mathematical problem of obtaining general expressions for these functions, considered as an exercise in geometric probability theory. We sometimes use the terms “sphere” and “inclusion” to refer to the traps. The derivation will be general enough to allow arbitrary correlation between trap centers. Series representations, in the monodisperse case, for the distribution functions studied here have been given before.\textsuperscript{12} However, the extension to the case of polydisperse media performed here is entirely new. These formula will be applied to the cases of randomly overlapping and impenetrable inclusions in Secs. IV and V, respectively. In the derivations of Sec. II, the indicator function $I_\omega(x)$ was used to restrict integration to the void phase, i.e., to the region free of traps. Similarly, $\nabla I_\omega(x)$ will be zero except on the boundary of this phase, in which case it is proportional to the normal vector to the interface. When the volume averages of Sec. II are replaced with ensemble averages over the position and size of the inclusions that make up the solid phase, the property bounds of that section will then depend on ensemble-averaged products of $I_\omega(x), \nabla I_\omega(x)$, and the distribution functions for the centers of inclusions. The low-order functions of this kind were defined in Ref. 16. Their study was systematized in Torquato and Stell\textsuperscript{11} and Torquato.\textsuperscript{12}

In Sec. II, we defined the ensemble average indicated by $\langle \rangle$ as an average over trap positions and sizes. Actually, in a large system, it is sufficient simply to average over trap positions; the average over sizes becomes redundant. This is true because the average over positions of traps provides that a particular position can be occupied by any one of them. Since the radii of these traps are chosen from the distribution $f(a)$.
and, because the number of traps is assumed extremely large, this permutation of the traps is equivalent to an average over their radii. This fact will be exploited in this section. It allows us to consider a system of traps, each having a fixed size chosen from a radius distribution function $f(r)$. This allows the derivation of formulas for the material distribution functions by a direct extension of the arguments used in the monodisperse case.

From their definitions, one can immediately write down the behavior, for large argument, of these functions. In the limit of large separation $x_{12} \to \infty$, one has

$$ F_{\text{av}}(x_{12}) \to \phi_{x}^4, \quad (3.1) $$

$$ F_{\text{av}}(x_{12}) \to \phi_{x} s, \quad (3.2) $$

$$ F_{\text{av}}(x_{12}) \to s^2, \quad (3.3) $$

where $\phi_s$ and $s$ are the void fraction and specific surface, defined, respectively, as the fraction of the system volume outside the traps, and the trap–void interface area per unit volume.

We first develop a series representation for the void–void distribution function as the others will be derived from it. In a system of freely overlapping, equal-sized spherical inclusions of radius $a$, the configurations in which the points $x_1$ and $x_2$ lie outside of all the spheres are precisely those configurations in which a particular volume is empty of sphere centers, namely the union volume of the exclusion spheres (of radius $a$) around each of the two points $x_1$ and $x_2$. The probability that this volume is empty in a system with arbitrary correlations between the sphere centers is given for equal-sized inclusions by the second equation of the Mayer–Montroll hierarchy$^{31}$:

$$ F_{\text{av}}(x_{12};a) = 1 - \frac{1}{N} \sum_{n=1}^{N} \int dx_3 D(x_{12},x_2,a_{n}) \rho(x_3) + \frac{1}{2!} \frac{1}{N} \sum_{m=1}^{N} \left[ \frac{1}{N} \sum_{k=1}^{N} \int dx_3 \int dx_4 D(x_{12},x_3,a_{m}) D(x_{12},x_4,a_{k}) \rho(x_3) \rho(x_4) \right] $$

$$ + \sum_{k=3}^{\infty} \frac{(-1)^{k-1}}{k!} \frac{1}{N} \sum_{m=1}^{N} \left[ \frac{1}{N} \sum_{k=1}^{N} \int dx_3 \int dx_4 \int dx_5 \int dx_6 \cdots \int dx_{k-1} \int dx_k D(x_{12},x_3,a_{n}) D(x_{12},x_{k-1},a_{n}) D(x_{12},x_{k},a_{n}) \rho(x_3) \rho(x_4) \cdots \rho(x_{k-1}) \rho(x_k) \right] $$

$$ \quad \equiv \sum_{i=3}^{\infty} \frac{(-1)^{k-1}}{k!} \frac{1}{N} \sum_{m=1}^{N} \left[ \frac{1}{N} \sum_{k=1}^{N} \int dx_3 \int dx_4 \int dx_5 \int dx_6 \cdots \int dx_{k-1} \int dx_k D(x_{12},x_3,a_{n}) D(x_{12},x_{k-1},a_{n}) D(x_{12},x_{k},a_{n}) \rho(x_3) \rho(x_4) \cdots \rho(x_{k-1}) \rho(x_k) \right] $$

(3.4)

Here

$$ D(x_{12},x_3,a_{n}) = 1 - \frac{2}{N} \left[ 1 - m(x_3,x_{12},a_{n}) \right] $$

(3.5)

is the indicator function for the union volume of the two spheres of radius $a$ centered at $x_1$ and $x_2$. The function $m(x_3,x_{12},a_{n})$, given by

$$ m(x_3,x_{12},a_{n}) = \begin{cases} 1, & \text{if } |x_3 - x_{12}| < a \\ 0, & \text{otherwise} \end{cases} $$

(3.6)

is the indicator function for a sphere of radius $a$. This implies that the integral over $x_k$ of $D(x_{12},x_1,a_{n})$ is equal to the union volume of two such spheres, which we write $V(x_{12},x_1,a_{n})$.

The series on the right-hand side of Eq. (3.4) arises from a standard inclusion–exclusion argument.$^{27}$ The second term gives the average number of single spheres whose centers are located in the volume $V(x_{12},x_1,a_{n})$; the third term gives the average number of pairs of such spheres, etc. In order to generalize Eq. (3.4) to a polydisperse system, we must replace each radius $a$ in a function $D(x_{12},x_1,a_{n})$ by the radius $a_k$ of the corresponding particle. The result is

$$ F_{\text{av}}(x_{12};\{a_i\}) = 1 - \frac{1}{N} \sum_{n=1}^{N} \int dx_3 D(x_{12},x_2,a_{n}) \rho(x_3) + \frac{1}{2!} \frac{1}{N} \sum_{m=1}^{N} \left[ \frac{1}{N} \sum_{k=1}^{N} \int dx_3 \int dx_4 D(x_{12},x_3,a_{m}) D(x_{12},x_4,a_{k}) \rho(x_3) \rho(x_4) \right] $$

$$ + \sum_{k=3}^{\infty} \frac{(-1)^{k-1}}{k!} \frac{1}{N} \sum_{m=1}^{N} \left[ \frac{1}{N} \sum_{k=1}^{N} \int dx_3 \int dx_4 \int dx_5 \int dx_6 \cdots \int dx_{k-1} \int dx_k D(x_{12},x_3,a_{n}) D(x_{12},x_{k-1},a_{n}) D(x_{12},x_{k},a_{n}) \rho(x_3) \rho(x_4) \cdots \rho(x_{k-1}) \rho(x_k) \right] $$

(3.7)

To understand this expression, consider first the second term on the right-hand side of Eq. (3.7). It is a sum of contributions of which the $n$th gives the probability that the $n$th spherical inclusion, of radius $a_{n}$, overlaps one of the two points $x_1$ and $x_2$. Since all the inclusions are equivalent, we replace the probability density for finding the inclusion at $x_3$ by $\rho(x_3)$ and divide by a factor of $N$, where $N$ is the number of inclusions in the system. Since we ultimately take the thermodynamic limit, $N \to \infty$, we freely replace factors of $1/(N - k)$ by $1/N$, where $k$ is any fixed integer. In this section, we give material distribution functions the argument $\{a_i\}$ to indicate that they describe a polydisperse system. The assumed equality of volume and ensemble averages then allows us to replace each average over sphere radii by an integral over the radius distribution function. This final step must be taken to give computationally useful results; we do this in the next section. We have left the $\{a_i\}$ unaveraged here to facilitate derivations and to allow a direct interpretation of the resulting formulas. Because this series results from a geometric inclusion–exclusion argument,${}^{31}$ successive truncations give monotonically converging series of upper and lower bounds for $F_{\text{av}}(x_{12},x_1,a_{n})$.$^{7}$ If the sphere centers in Eq. (3.4) are uncorrelated, the distribution functions in that series are identically unity. In this case, the series can be immediately summed to give

$$ F_{\text{av}}(x_{12};\{a_i\}) = \exp \left[ - \frac{1}{N} \sum_{i=1}^{N} V(x_{12},a_i) \right]. $$

(3.8)

In order to define the surface–void and surface–surface distribution functions, and make contact with their deriva-
tion in the case of a monodisperse system, we now sketch the
derivation of these functions for that case. In Sec. II we de-
define \(I_0(x,a)\) to be the indicator function for the void or ma-
trix region. It is convenient to redefine this function as fol-
lows: \(I_0(x,a)\) is equal to unity if the point \(x\) is further from
every trap center than \(a\); otherwise it is zero. We can then
define the following generalization of the void–void distribu-
tion function

\[
F_v(x_1, x_2, a_1, a_2) = \langle I(x_1, a_1) I(x_2, a_2) \rangle,
\]

(3.9)

where the brackets denote an ensemble average. Note that
this function serves merely to allow us to write down formal
expressions for the material distribution functions being
studied; \(a_1\) and \(a_2\) are not the radius of anything in particu-
lar. By retracing the argument that leads to Eq. (3.4), we see
that the generalized function defined in Eq. (3.9) obeys a
similar equation given by replacing \(m(x_1,a)\) by \(m(x_1,a_1)\)
and \(m(x_2,a)\) by \(m(x_2,a_2)\). Note that we here consider
\(I_0(x,a)\) to be a function of particle radius because the void
phase decreases in volume if we increase the radius of each
inclusion keeping the position of its center constant. For a
fixed value of \(x\), the indicator function \(I_0(x,a)\) will change
with an infinitesimal increase in \(a\) only if \(x\) is on the surface of
the region occupied by the inclusions. Thus, we define the
surface–volume and surface–surface distribution functions,
respectively, for a monodisperse system

\[
F_{sv}(x_1, x_2) = -\frac{d}{da_1}_{a_1 = a_2 = a} F_v(x_1, x_2, a_1, a_2),
\]

(3.10)

\[
F_{ss}(x_1, x_2) = \frac{d^2}{da_1 da_2}_{a_1 = a_2 = a} F_v(x_1, x_2, a_1, a_2).
\]

(3.11)

These distribution functions can be calculated for a polydis-
perse system by generalizing the method that leads to Eqs.
(3.10) and (3.11). To do this we alter the function defined by
Eq. (3.7) as follows: replace, in each occurrence of the
function \(D(x_1, x_2, x_3, a_3)\), the factor \(m(x_1, x_2, a_3)\) by
\(m(x_1, x_2, a_{31})\) and \(m(x_2, x_3, a_3)\) by \(m(x_2, x_3, a_{32})\). This is
again a formal recipe: the subscript “3” is chosen arbitrarily,
and the quantities “a_{31}” and “a_{32}” are dummy variables. We
write this object as \(F_{w}(x_1, x_2, a_{31}, a_{32}, a_{3j})\). The surface-
volume and surface–surface distribution functions are then
given by the operations

\[
F_{w}(x_1, x_2, a_{3j}) = -\frac{d}{da_{3j}}_{a_{31} = a_{32} = a} F_{v}(x_1, x_2, a_{31}, a_{32}, a_{3j}),
\]

(3.12)

\[
F_{w}(x_1, x_2, a_{3j}) = \frac{d^2}{da_{31} da_{32}}_{a_{31} = a_{32} = a} F_{v}(x_1, x_2, a_{31}, a_{32}, a_{3j}),
\]

(3.13)

The purpose of these labeling tricks is to give an explicit
analytic formula for the necessary distribution functions,
with all the ensemble averages to be performed carefully de-
\[
F_{w}(x_1, x_2) = \sum_{k=0}^{\infty} \frac{(-\rho)^k}{k!} \frac{1}{N} \sum_{n_1=1}^{N} \cdots \frac{1}{N} \sum_{n_k=1}^{N} \int dy_1 \cdots dy_k \Delta \prod_{i=1}^{k} D(x_1, x_2, y_i, a_{n_i}) \times \prod_{i=1}^{k} \frac{1}{N} \sum_{m=1}^{N} \int dx_i \delta(x_{13} - a_{m}) \times \left[ 1 - \rho(x_{13}, y_1, \ldots, y_k) \right].
\]

(3.14)

The probabilistic interpretation of this formula is as follows:
in order that the point \(x_1\) be on the external surface of the
trapping phase (i.e., that it be on the surface of a trap, or
inclusion) and that the point \(x_2\) be located in the void phase,
three events must all occur. First, an inclusion with radius
\(a_{m}\) must have its center separated from \(x_1\), by a distance
\(a_{m}\). Second, this inclusion must not overlap the point \(x_2\). The
joint probability of these two events is given by the quantity
in curly brackets in Eq. (3.14). Third, no other inclusion
may overlap either \(x_1\) or \(x_2\). To account for this, we write an
inclusion–inclusion series similar to Eq. (3.7). Here the \(k\) th
term gives the joint probability of \(k\) inclusions each over-
lapping one of the two points \(x_1, x_2\).

For a system of overlapping spheres with general corre-
lations between the sphere centers, a formula for the sur-
face–surface distribution function is provided by the follow-
ing inclusion–inclusion argument: there are two distinct
situations in which the points \(x_1\) and \(x_2\) are both found on
the external surface of a system of overlapping spheres. First,
both points may be on the surface of the same sphere. Sec-
ond, the points \(x_1\) and \(x_2\) may be on the surface of two differ-
ent spheres, such that neither point is contained inside either
sphere. In order that both points be on the boundary between
void and inclusion phases, one further requires that the
points \(x_1\) and \(x_2\) also be external to the remaining spheres.
As in Eq. (3.14), this requires subtracting for each case just
mentioned, the probability that one extra particle is present
and includes one or both of the points, adding the probability
that two extra particles are present, each of which includes
one or both of the points, etc. The result is

\[
F_{w}(x_1, x_2) = \sum_{k=0}^{\infty} \frac{(-\rho)^k}{k!} \frac{1}{N} \sum_{n_1=1}^{N} \cdots \frac{1}{N} \sum_{n_k=1}^{N} \int dy_1 \cdots dy_k \Delta \prod_{i=1}^{k} D(x_1, x_2, y_i, a_{n_i}) \times \prod_{i=1}^{k} \frac{1}{N} \sum_{m=1}^{N} \int dx_i \delta(x_{13} - a_{m}) \times \left[ 1 - \rho(x_{13}, y_1, \ldots, y_k) \right].
\]

(3.15)
Here we have averaged over the positions, but not the radii, of the inclusions. As mentioned above, the average over individual trap radii is redundant in the thermodynamic limit. For applications of the formulas (3.7), (3.14), and (3.15), we replace each sum over particle radii by an average as follows:

$$
\frac{1}{N} \sum_{n=1}^{N} h(a_m) \to \int f(a) h(a) \, da.
$$

(3.16)

The structure of Eq. (3.15) is easily understood as follows: in order for the points $x_1$ and $x_2$ to lie on the void–trap interface, they must not be interior to any trap. The first sum on the right-hand side of Eq. (3.15) is the inclusion–exclusion sum that accounts for the possibility that the points $x_1$ and $x_2$ may be contained in one or more inclusions. Thus the $k$th term in this sum gives the probability that there are $k$ different inclusions, at positions $y_1, \ldots, y_k$, respectively, each of which contains either the point $x_1$ or the point $x_2$. The product of $D$ functions is just the indicator function for this event. The quantity in curly brackets is the probability density for finding points $x_1$ and $x_2$ on the surface, either of the same inclusion, or of two different inclusions. This expression contains two terms, corresponding, respectively, to these two occurrences. In the case of arbitrary correlations between the centers of inclusions, successive truncations of the series (3.15) will give upper and lower bounds for $F_{sw}(x_{12})$ as described above. We will not pursue this here.

IV. DOI BOUNDS FOR RANDOMLY CENTERED INCLUSIONS

In this section, we evaluate the distribution functions of Sec. III in the case of a medium whose trapping phase is composed of randomly overlapping polydisperse inclusions. Specifically, we work with spherical inclusions whose radius is chosen either from the gamma or lognormal distribution. We discuss the variation of the distribution functions in these two cases as the polydispersity increases. We also calculate the Doi bound of Sec. II and discuss its variation with density and polydispersity.

We first use the formulas of Sec. III to develop expressions for the material distribution functions in the case of randomly centered traps.

In this case, the formulas (3.12) and (3.13) can be directly used to evaluate the distribution functions. The function $\mathcal{V}(x_1,x_2,a_1,a_2)$ is useful for this purpose. It is

$$
\mathcal{V}(x_{12},a_1,a_2) = \begin{cases} 
\pi \left[ x_{12} + a_1 + a_2 \right]^2 \left[ \frac{(a_1 - a_2)^2}{4x_{12}} + \frac{1}{2}(a_1 + a_2 - \frac{1}{2}x_{12}) \right], & x_{12} < (a_1 + a_2) \\
\frac{4\pi}{3} \left( a_1^3 + a_2^3 \right), & x_{12} > (a_1 + a_2)
\end{cases}.
$$

(4.1)

When $a_1 = a_2 = a$, this reduces to

$$
\mathcal{V}(x_{12},a) = \begin{cases} 
\pi \left[ a^2 + \frac{3}{2}a^2 x_{12} - \frac{1}{2}a^2 x_{12} \right], & x_{12} < 2a \\
\frac{2}{3} \pi a^3, & x_{12} > 2a
\end{cases}.
$$

(4.2)

Since the thermal distribution functions $g_n(1,\ldots,n)$ are identically equal to unity, in this case, each term in the inclusion–exclusion series (3.7) becomes a product of identical factors. The resulting series can be summed to yield

$$
F_{sw}(x_{12}) = \exp \left[ -\rho \int \mathcal{V}(x_{12},a)f(a) \, da \right].
$$

(4.3)

The argument of the exponential is explicitly

$$
\frac{2}{3} \rho \pi a^3 \right) \int_{x_{12}}^{a} f(a) \, da + \frac{1}{a^2} x_{12} \int_{x_{12}}^{a} f(a) \, da + \frac{1}{a^2} \int_{x_{12}}^{a} f(a) \, da + \frac{1}{a^2} \int_{x_{12}}^{a} f(a) \, da.
$$

(4.4)

The functions $F_{sw}(x_{12})$ and $F_{sp}(x_{12})$ are evaluated by similar means. The expression in curly brackets in Eqs. (3.14) and (3.15) can be factored out and the remaining series summed to give $F_{sw}(x_{12})$. The results can be written concisely as

$$
F_{sw}(x_{12}) = \frac{\mathcal{V}(x_{12},a_1,a_2) \cdot \mathcal{V}(x_{12},a_2)}{a_1(a_2)},
$$

(4.5)

$$
F_{sw}(x_{12}) = \frac{\mathcal{V}(x_{12},a_1,a_2) \cdot \mathcal{V}(x_{12},a_2)}{a_1(a_2)},
$$

(4.6)

with

$$
\hat{F}_{sw}(x_{12}) = \langle I_1(x_{12},a) \rangle, 
$$

(4.7)

$$
\hat{F}_{sw}(x_{12}) = \langle I_1(x_{12},a) \rangle^2 + \langle I_2(x_{12},a) \rangle. 
$$

(4.8)

Here $I_1(x_{12},a)$ is the probability density associated with finding the point $x_1$ on the surface of a trap of radius $a$, and the point $x_2$ outside that trap. It is given by

$$
I_1(x_{12},a) = \rho \int dx_3 \delta(x_{13} - a) \left[ 1 - m(x_{23},a) \right].
$$

(4.9a)

or

$$
I_1(x_{12},a) = \rho \int dx_3 \delta(x_{13} - a) \delta(x_{23} - a). 
$$

(4.9b)

The function $I_2(x_{12},a)$ is the probability density for finding the points $x_1$ and $x_2$ both on the surface of a single trap of radius $a$. It is

$$
I_2(x_{12},a) = \rho \int dx_3 \delta(x_{13} - a) \delta(x_{23} - a). 
$$

(4.10a)

or

$$
I_2(x_{12},a) = \left\{ \begin{array}{ll}
\rho \pi a^2 & x_{12} < 2a \\
0 & x_{12} > 2a
\end{array} \right.
$$

(4.10b)

Explicitly, in terms of the radius distribution function $f(a)$,
we have

\[ F_{\alpha}(x) = \left[ 2\pi \rho \int_0^x a^2 f(a) da + \pi \rho x \int_0^x a f(a) da \right. \\
\left. + 2\pi \rho \int_0^x a f(a) da \right] F_{\alpha}(x), \quad (4.11) \]

\[ F_{ss}(x) = \left[ \frac{2\pi}{x} \rho \langle a^3 \rangle + 4\pi^2 \rho \langle a^4 \rangle + 8\pi^2 \rho \langle a^5 \rangle \int_0^x a^2 f(a) da \right. \\
\left. + 4\pi^2 \rho^2 x \int_0^x a f(a) da \\
+ \pi \rho x^2 \int_0^x a^2 f(a) da \right] F_{\alpha}(x), \quad (4.12) \]

where \( F_{\alpha}(x) \) is given by Eq. (4.3). These expressions have been evaluated using both the gamma, or Schulz distribution

\[ f(a) = \frac{1}{a_0^{z+1}} \left( \frac{a}{a_0} \right)^{z+1} \exp \left[ - \left( \frac{a}{a_0} \right) \right] \]

and the lognormal distribution

\[ f(a) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma a_0} \exp \left[ - \frac{\left( \ln(a/a_0) \right)^2}{2\sigma^2} \right]. \quad (4.14) \]

The properties of these distributions are collected in Appendix A. We use them to assess the influence of polydispersity on the Doi bounds. To evaluate these bounds, we require expressions for the void fraction \( \phi_v \), and the specific surface \( s \), for this system. These expressions are provided by arguments of precisely the same form as those used in this section to derive the distribution functions. These have been previously derived by such a method, we simply give the results here. The porosity is given by

\[ \phi_v = \exp \left[ - \frac{1}{\pi \rho \langle a^3 \rangle} \right]. \quad (4.15) \]

The specific surface, or average trap–void interface area per unit volume, is given by

\[ s = 4\pi \langle a^2 \rangle \phi_v. \quad (4.16) \]

Even the simple two-phase geometry discussed in this paper shows complex, nonmonotone dependences of the system variables on trap density. We briefly describe two such dependences. The specific surface as a function of trap density is shown in Fig. 1. The different curves correspond to Schulz distributions with the same mean radius, but varying dispersivity. Under these conditions, at high dispersivity, the traps with large volume predominate. Increasing the density of such traps rapidly diminishes the reaction area; thus for larger dispersivity the specific surface has a maximum at lower trap density.

Similar reasoning gives the qualitative behavior of the material distribution function \( F_{\alpha}(x) \): at low trap densities, this is a monotone decreasing function of its argument. At higher trap densities, the function develops a minimum for small separation \( x \) and a nearby maximum for slightly larger \( x \). An increase in dispersivity broadens and separates these features. Further increase of the trap density has a very similar effect.

We have evaluated the Doi bound for a range of densities and for several different values of the index of polydispersity. A basic theme in this paper is the search for a proper

\[ \text{FIG. 1. Specific surface as a function of trap density. From bottom to top on right-hand side we show Schulz distribution data for randomly overlapping traps with } z = 0, 1, 6, 15. \text{ For larger dispersivity, the maximum occurs at higher densities of traps.} \]

\[ \text{FIG. 2. The distribution function } F_{\alpha}(x) \text{ for a system of random inclusions. Here, } \eta = 0.05, \text{ with the reduced density } \frac{x}{\eta \rho a_0^2}. \text{ From top to bottom, the curves correspond to a lognormal distribution with standard deviation } \sigma = 0.1, 0.6, 1.2, \text{ respectively.} \]

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lognormal distributions, respectively. One sees that this quantity is a useful scaling variable for the low and intermediate values of $\phi_e$. For very low values of $\phi_e = 1 - \phi_s$, one expects that the system will contain almost no pairs of overlapping traps. Thus the trapping rate should be given by the

radius averaged solution of Smoluchowski for a single trap. In Fig. 5, we replot the data of Fig. 3, for low inclusion densities, as a function of the scaling variable $\rho(a)$. Use of this variable is suggested by the Smoluchowski solution for the trapping rate due to a single trap, which is

$$k_s = 4\pi a.$$ (4.17)

Here the radius $a$ occurs on the right-hand side because the traps considered here are spherical; for an arbitrary shape of inclusion, this factor would be replaced by the capacity of the corresponding set.\textsuperscript{26} For low densities, one expects the trapping rate to be given approximately by

$$k = 4\pi \rho(a).$$ (4.18)

However, this approximation is only useful at extremely low densities, as shown by Fig. 5. One reason for this is the interference between traps, which becomes important at extremely low volume fractions (this effect becomes important at densities too low for there to be any substantial overlapping of traps.) Another reason is based in the limitations of the Doi bound and will be discussed in detail in Sec. VII.

**V. DOI BOUND FOR NONOVERLAPPING TRAPS**

In this section, we evaluate the Doi bound for trapping rate in a model two-phase medium. Here the absorbing phase is taken to consist of spherical traps of many sizes that do not overlap, imbedded in a matrix or void phase in which reactant particles diffuse. We determine the material distribution functions $F_{w_1}(x_{12})$, $F_{w_2}(x_{12})$, and $F_{v}(x_{12})$ for this case. As we show, they depend only on the two-point distribution function for the centers of the traps. The distribution functions of these centers are assumed to be those of a polydisperse system of hard spheres. We evaluate and discuss the
Percus–Yevick approximation for the latter quantity. The distribution functions are then evaluated numerically using the Schulz distribution for the inclusion radii. These solutions are then used to evaluate the Doi bound. The behavior of these bounds as a function of density and polydispersity is discussed.

We first evaluate the expansions Eqs. (3.14) and (3.15) for the distribution functions. At first glance, these appear quite formidable. However, the only nonzero terms are those containing the one- and two-point correlation functions. To see this, note that the kth term in the inclusion–exclusion series takes account of the possibility of k different inclusions each overlapping one of the two points x1 and x2. Since the inclusions in this model cannot overlap each other, a maximum of two can satisfy this condition. The resulting material distribution functions are

\[
F_m(x_{12}) = 1 - \rho \int da_1 f(a_1) V(x_{12}, a_1) + \frac{1}{2!} \int da_1 \, da_2 \, f(a_3) f(a_4) \rho(x_3, a_3, x_4, a_4) \\
\otimes \int dx_3 \, dx_4 \rho(x_{13}, a_3) \rho(x_{24}, a_4) \rho(x_3, a_3, x_4, a_4)
\]

(5.1)

\[
F_m(x_{12}) = \rho \int da_1 f(a_1) \delta(x_{13} - a_1) - \int da_1 \, da_2 f(a_1) f(a_2) \rho(x_{13}, a_1, x_4, a_4) \\
\otimes \int dx_3 \, dx_4 \delta(x_{13} - a_1) \rho(x_{24}, a_4) \rho(x_3, a_3, x_4, a_4)
\]

(5.2)

\[
F_m(x_{12}) = \rho \int da_1 f(a_1) \int dx_3 \delta(x_{13} - a_1) \delta(x_{23} - a_1) + \int da_1 \, da_2 f(a_1) f(a_2) \rho(x_{13}, a_1, x_4, a_4) \\
\otimes \int dx_3 \, dx_4 \delta(x_{13} - a_1) \delta(x_{24} - a_4)
\]

\[\otimes \rho(x_3, a_3, x_4, a_4).
\]

(5.3)

The analytic solution for the Percus–Yevick equation has been extended to a polydisperse mixture of hard spheres. In previous work, however, the solution has been used indirectly, either to obtain the direct correlation function in density-functional theory, or to obtain the structure factor for scattering experiments. The spatial dependence of the solution has only been briefly noted in the literature. In Fig. 6 we plot this function for reduced density \(\rho a_0^2 = 0.05\) and four different values of the polydispersity. As the distribution of hard-sphere particles becomes more disperse, i.e., as \(\rho(a^2)\) increases, the central maximum becomes broader and moves to larger separations.

We employ this function to evaluate the distribution functions as follows: the expressions involving the two-point distribution function all have the structure of multiple convolutions. Thus, their Fourier transforms are easily written as products of the transforms of the individual factors in the convolution. These products, which are known analytically, can then be averaged over the radius distribution function.
The inverse Fourier transform of the result then gives the material distribution functions.

Calculating the Doi bounds for this system requires also an expression for the void fraction and specific surface. These are quite simple, because the inclusions are nonoverlapping. One has

\[ \phi_v = 1 - \phi_n \]
\[ = 1 - \frac{1}{4\pi}(a^2) \]
\[ = 4\pi \rho \langle a^2 \rangle. \quad (5.4) \]

In Fig. 7, we show the Doi bounds for this system, for a range of densities, and for several values of the polydispersity parameter. The scaling variables \( \rho(a) \) is used in this figure. This variable, for the Schulz distribution employed here, corresponds to the mean number density of inclusions. One sees that, both for low and intermediate inclusion densities, the number of inclusions is a better scaling variable than one might expect. Of course, for low inclusion density, the Smoluchowski solution (4.18) is valid, and thus the Doi bound should depend only on \( \rho(a) \). But this quantity is a good approximate scaling variable well beyond this regime. We discuss the theoretical basis for this result in Sec. VI.

VI. DISCUSSION OF THE SCALING PROPERTIES OF TRAPPING BOUNDS AND A NEW POLYDISPERSE DOI BOUND

Here we discuss our findings on the influence of polydispersity on the bulk properties of materials, in light of both previous studies of bounds, and of the relevant mathematical literature on diffusion processes. We emphasize the importance of choosing the proper scaling variables in order to minimize the importance of polydispersity. We show, in particular, that the commonly used bounds for reaction rate in polydisperse two-phase materials do not have the proper low-density behavior. We show how to generalize the Doi bound to give a bound without this defect.

Perhaps the simplest class of calculations of effective bulk properties are those termed effective medium theories. In these theories, one considers a single discrete element (e.g., one inclusion) from a random material, surrounded by a homogeneous continuum with constant material properties. The response of the inclusion in the effective medium to an external force (e.g., a pressure gradient or imposed electric field) is calculated and employed to choose the effective medium bulk property self-consistently.

Early attempts to describe disordered media in this fashion involved lattices whose bonds have randomly chosen properties, e.g., random resistances to model conductivity, or random tube diameters to model flow in porous media. A study by Koplik showed that effective medium theories were reliable as a description of these models except when the distribution from which bond variables were chosen was extremely broad. Because effective medium theories are similar to mean field theories, and since the latter break down near critical points (where fluctuations have a very broad distribution), one expects effective medium theories to be invalid for systems in which the various moments of the random distribution functions employed become large, or cease to exist. One goal of the research reported here is to understand how to modify effective medium formulas to account for polydispersity.

Richards has developed an effective medium theory for the area accessible to a random walker in time \( t \), and a corresponding approximation for the trapping rate. This predicts that \( k/k_i \) is a function only of the variable

\[ y^2 = \rho \frac{\langle a \rangle^2}{\langle a^2 \rangle}. \quad (6.1) \]

Here \( k_i \) is the Smoluchowski solution of Eq. (4.18). The quantity \( k/k_i \), as given by our rescaled Doi bounds for a system of random traps is graphed as a function of \( y^2 \) in Fig. 8. As the figure shows, data that is plotted in this manner collapses very well, at least for intermediate densities. Thus, the variable \( y^2 \) must be taken seriously as a candidate for a scaling variable to describe polydisperse, random systems. Of course, deciding which variable is best for plotting the actual transport coefficients of polydisperse systems will require numerical simulations of such systems. These are very demanding computationally, and have not yet been carried out.

Previous experience with evaluating the standard bounds for a number of bulk properties, for systems of random inclusions, also indicates that these bounds, when plotted as functions of \( \phi_n \), the void fraction, and \( z \), the index of polydispersity, are relatively insensitive to the latter. Milton has computed bounds on the thermal conductivity to fourth order in the conductivities of the pure states. These numerical calculations for two-dimensional systems are vir-

![Graph](image.png)

**FIG. 8.** This shows a different way to plot the data in Fig. 5. Here we normalize the data by the low-density Stokes value \( k_{\text{St}} = 4\pi \rho \langle a \rangle^2 \) and use for abscissa the scaling variable \( \phi_n = \rho \langle a^2 \rangle / \langle a \rangle \) suggested by the analysis of Richards. The bounds were derived with our improved trial functions, and thus they behave correctly at low densities. This method of collapsing the Doi bounds for different distributions onto a single graph works quite well at low and intermediate densities for both the Schulz and lognormal distributions.
truly insensitive to polydispersity. Similar results are found for the bounds developed by Milton for shear and bulk modulus. This work has been extended to three dimensions, and the same conclusion was reached. These series, like many perturbation series for bulk materials properties, have the property that their Padé approximants furnish upper and lower bounds. Equivalently, for these problems, low-order bounds give extremely good approximations, at least for low and moderate densities. This shows that the insensitivity to particle size distribution is a fact about the bulk properties themselves (at least for some classes of problems) and not merely an artifact due to approximation.

A very general theorem about diffusion-dominated processes also sheds light on the proper choice of a scaling variable, at least for a system of impenetrable inclusions. Consider an open domain \( V \) containing equal-sized spherical inclusions of radius \( a \). If a field \( \Phi(x) \) satisfies the diffusion equation with Neumann boundary conditions in \( V \), and vanishes on the surface of the inclusions, then \( \Phi \) may be expanded in eigenfunctions \( \phi_n \) of the Laplacian, each with its corresponding eigenvalue. If \( \lambda_1 \) is the largest eigenvalue, one has

\[
- \lambda_1 \leq \frac{2\Phi(a)}{|V|} |1 + O(pa)|,
\]

where \( |V| \) is the volume of \( V \) and \( \phi_n \) is the volume fraction of the inclusions. If the inclusions are evenly spaced, such that the volume they cover is proportional to their number, then there exist positive constants \( c_1, c_2 \), such that

\[
- \lambda_1 > c_1 pa - c_2.
\]

This theorem has direct application, both to cooling problems and to creeping flow problems (which are closely related to the trapping problems studied here). Its validity can be ultimately traced to the fact that the hitting probability (the probability that a Brownian path intersects a region) is proportional, for a spherical region, to the radius of that region. This theorem generalizes immediately to polydisperse systems and shows that one should expect the exact trapping rate, and not merely its bounds, at least for systems of nonoverlapping traps, to depend only on the scaling variable \( \rho(a) \).

For systems of impenetrable traps, we saw in Sec. IV that \( \rho(a) \) is a good scaling variable for low and intermediate values of density. Since the derivation of the bounds discussed in this paper ignores many-body effects, these bounds are not expected to give a good estimate at high densities. We are presently evaluating the Doi and Weissberg/Prager bounds with a realistic assessment of three-body effects to extend the limits of the scaling hypotheses explored here.

For random, freely penetrable inclusions, one expects that the data for low inclusion density should still collapse when plotted against \( \rho(a) \), up to a density such that, on the average, overlaps begin to appear. However, Fig. 5 does not show an appreciable scaling range of this kind. One reason for this is a basic inadequacy of the Doi bound: it fails, in the polydisperse case, to reproduce the correct low-density limit. In this limit, one wants a bound to equal the average over inclusion radii of the Smoluchowski solution for trapping by a single spherical inclusion. This is

\[
k = 4\pi \rho(a).
\]

At first glance, it is reasonable to expect such agreement from the Doi bound, since our trial function \( \xi(x) \) of Sec. II was chosen to be a one-particle trial function. One expects the correct low-density form to have this structure. However, we can see that the low density limit is incorrect by inserting Eqs. (4.3)–(4.12) into Eqs. (2.16)–(2.20) and expanding in powers of density. The dominant term gives

\[
k \geq 4\pi \rho \left< \frac{a^2}{2a^2} \right>.
\]

The same result is obtained for a system of impenetrable traps. Using the results of Appendix A for the moments of \( a \) shows that when the Schulz distribution is used, this term is indistinguishable from that given by the Stokes solution, except for very large polydispersity, i.e., for \( z \) very small. On the other hand, this equality is badly violated for the lognormal distribution. These considerations explain why the standard Doi bound on trapping rate has been considered quite adequate for moderately disperse distributions of traps. Indeed, Chiew found that simulation data from a binary distribution of trap sizes were well approximated by the form (6.5).

However, for extremely disperse trap distributions, the standard Doi bound is unsatisfactory. Indeed, in the extreme polydisperse limit, the bound given by Eq. (6.5) may trivialize; i.e., the quantity on the right-hand side of this equation will be zero for some distributions of trap radii. This shortcoming seems not to have been noticed before. Here, we generalize the Doi bound to apply to this case by repeating the calculation of Sec. II, but allowing the single-particle trial function \( \xi_1(x) \) to depend on particle radius. The algebra can be carried out just as in Sec. II; again, we simply provide the result and discuss its probabilistic interpretation. For this purpose, we need to generalize the material distribution functions. Define \( \bar{F}_{a} (x_1, a_1, x_2, a_2) \) to be the reduced distribution function associated with the expectation density that the point \( x_1 \) is on the surface of an inclusion of radius \( a_1 \), and the point \( x_2 \) is on the surface of an inclusion of radius \( a_2 \). This quantity can be divided into \( \bar{F}_{a_1} \) and \( \bar{F}_{a_2} \), associated, respectively, with the expectation densities for finding \( x_1 \) and \( x_2 \) on two different inclusions and that for finding \( x_1 \) and \( x_2 \) on the same inclusion. For example, for randomly overlapping traps, these two terms are given by the first and second terms in Eq. (4.8), respectively. For a polydisperse medium, one has

\[
\bar{F}_{a_1} (x_1, a_1, x_2, a_2) = \int \int \bar{F}_{a_1} (x_1, a_1, x_2, a_2) f(a_1) f(a_2) da_1 da_2
\]

\[
+ \int \bar{F}_{a_2} (x_1, x_2, a_1) f(a_1) da_1,
\]

where \( f(a) \) is the radius distribution function. The first term in the bracket in the Doi bound (2.20) is \( 2 F_{a_1} (x_1, x_2) \). Allowing the trial function \( \xi \) to depend on the trap radius has the effect of replacing this with

\[
\left< \bar{F}_{a_1} (x_1, a_1, x_2, a_2) \xi(a_1) \xi(a_2) \right>.
\]

where we here use the angle bracket to indicate an average.
over the trap radii $a_1$ and $a_2$. Explicitly, this is
\begin{equation}
F_{w_1}(x_1,x_2) = \int \int \tilde{F}_{w_1}(x_1,a_1,x_2,a_2) f(a_1) \rho(a_2) \xi_1(a_1) \xi_2(a_2) da_1 da_2
+ \int \tilde{F}_{w_2}(x_1,x_2,a_1) f(a_1) \xi_1(a_1) \xi_2(a_1)^2 da_1.
\end{equation}

(6.8)

Similarly, the second term becomes
\begin{equation}
-2(\tilde{F}_{w_1}(x_1,x_2,a_1) \xi(a_1)).
\end{equation}

(6.9)

The third term is unchanged. The form of the one-particle function $\xi(x,a)$ can be determined by requiring that:
(1) The averaged Smoluchowski solution (6.4) is regained in the low-density limit.
(2) The integrand in the Doi bound provided by Eq. (2.20) should vanish for widely separated arguments.
This is necessary for the Doi bound to be nontrivial.
These conditions fix the choice of one-particle function both for a medium composed of randomly overlapping traps
\begin{equation}
\xi(x,a) = \frac{1}{4\pi \rho(a) a_i}
\end{equation}
and for a medium containing nonoverlapping traps
\begin{equation}
\xi(x,a) = \frac{1}{4\pi \rho(a) a_i} - \frac{a_i}{3}.
\end{equation}

(6.10)

(6.11)

In the latter case, a detailed analogy to electrostatic problems is available. This has been used to show that the Doi bound with the choice (6.11) is an optimal bound, as discussed at the end of Sec. II.

The polydisperse Doi bounds given by the procedure described above seem to be new. They give numerical values substantially different from the naive bounds developed in Sec. II only for low trap density. However, this is the regime in which bounds on transport quantities are the most valuable; thus the improvement is important in practical terms.

In Fig. 9, we graph the polydisperse Doi bounds, as a function of the quantity $\rho(a)$ for a system of randomly overlapping traps with the Schulz radius distribution. This graph should be compared with the one given by the naive Doi bounds, as shown in Fig. 5. The data now show a substantial low-density scaling regime, as discussed at the end of Sec. IV. Our improvement to the Doi bound causes very little difference in the case of traps with a less polydisperse distribution of radii. This is discussed in detail in Appendix A. Here we note that this difference in behavior merely reflects the fact that no single parameter can fully describe the statistics, e.g., the dispersity, of a distribution.

VII. THE POLYDISPERSE WEISSBERG-PRAKER BOUNDS FOR TRAPPING RATE

In this section, we show that the Weissberg–Prager-type bounds for trapping rate, in a system of randomly placed polydisperse traps, give the wrong low-density limit. We then show that the method of generalizing the Doi bounds developed in Sec. VI to deal with this problem also corrects the Weissberg–Prager bounds.

The Weissberg–Prager bounds for freely overlapping traps can be evaluated immediately. The second term in Eq. (2.23) does not contribute in this case. The result is simply
\begin{equation}
k \geq 4\pi \rho \left\{ \int_0^\infty \frac{1}{z^2} \int_0^z f(a) da dz \right\}^{-1}.
\end{equation}

(7.1)

Integration by parts then shows that this bound is trivial if $f(0) \neq 0$, in the sense that its right-hand side will be zero. If $f(0) = 0$, the bound (7.1) becomes
\begin{equation}
k \geq 4\pi \rho \left( \frac{1}{a} \right)^{-1}.
\end{equation}

(7.2)

This bound has exactly the same type of defect as the naive form of the Doi bound; for very polydisperse systems, it may become trivial. We generalize this bound in exactly the manner described in Sec. VI. If we choose the single particle function $\xi_1(x,a)$ in the trial function (2.21) to depend on particle radius:
\begin{equation}
\xi(x,a) = \frac{1}{\rho(a) a_i}
\end{equation}
the resulting bound is
\begin{equation}
k \geq 4\pi \rho(a).
\end{equation}

(7.3)

(7.4)

The same one-particle function (7.3) will also correct the Weissberg–Prager bound (2.23) in the case of nonoverlapping traps. The two-point and three-point bounds are corrected by the same choice of $\xi(x,a_i)$.

VIII. CONCLUSIONS

A basic conclusion of the work reported here is that the influence of polydispersity upon bounds for trapping rate...
can be largely ignored, providing 

(1) One uses the generalized bounds developed in this paper, which have the correct low-density limit for arbitrary polydispersity. 

(2) One uses the proper scaling variable to plot data. 

Each of these developments has practical utility. But each also provokes further questions of a theoretical nature. We address these in turn.

The trapping rate is not as "universal" (i.e., independent of inclusion size distribution) as other previously studied quantities no matter which scaling variable is chosen. Apart from its practical importance, an understanding of this matter seems basic to our knowledge of transport processes in random media. In studies of two-phase systems composed of randomly overlapping inclusions, the irrelevance of polydispersity to the calculation of transport quantities such as conductivity has been noted before. The explanation for this phenomenon that suggests itself is that each inclusion does not feel the presence of the others, as a result of their complete lack of spatial correlation. Thus, averages over the size of each inclusion can be carried out separately. This type of argument, applies in general both to low-order bounds of the type discussed here, and to effective-medium theories. For bounds on trapping, however, this argument is clearly inadequate.

The use of one-particle functions tailored to specific inclusion geometry is evidently a very general technique. We have applied it to obtain, for a number of problems, new classes of optimal bounds. These developments will be treated separately.29

The modification made here to the Doi and Weissberg-Prager bounds seems to be new. For certain distributions of inclusion sizes, it can cause substantial change in the low density behavior of the bounds. This is quite important because the bounds are most useful at low densities. The change in the bounds at higher densities is rather small. The $F$ functions entering the Doi bounds are each a sum of a linear, or one-body, and a nonlinear, or two-body term, as shown, e.g., in Eq. (3.13). The former is more important at low densities and also seems to be more sensitive to polydispersity. It would be useful to have a general explanation for this observation. Also, it is interesting to note that, when both original and rescaled bounds are plotted against the proper scaling variable, the two curves are almost indistinguishable; the rather small change in each data point moves it along this universal curve, rather than changing the curve.

The proper scaling variable, at least for the classes of bounds studied here, is $\rho(a)$ for impenetrable traps, and $\rho(a^+)$ for freely overlapping traps. What is a general scaling variable that applies to traps with an arbitrary degree of penetrability? No direct analytical approach to the system of partly penetrable traps is known.33 It would be very interesting to have the results of computer simulation in this case as a guide to a complete scaling theory.

We attempt to place the work reported here in perspective by mentioning the formidable difficulties that still await future research. The available, low-order bounds on trapping rate do not either tightly bracket or closely approximate this quantity even for monodisperse materials. Despite extensive work, during the past thirty years, on the classes of models for random materials studied here, we still have few simulation results for the behavior of transport processes on them. New classes of lattice gas simulations now being conducted may, for the first time, make it possible to handle the complex boundary conditions involved. However, the irregularity of statistics involved in modeling polydisperse materials will necessitate very large sample sizes. These problems require both careful thought and new approaches.

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**APPENDIX: PROPERTIES OF TWO DISTRIBUTION FUNCTIONS**

In this appendix, we gather for ready reference the basic information about the two probability distributions, the gamma and Schulz distribution and the lognormal distribution, that we use in this study. These are commonly used distributions for the radii of particles in many polydisperse systems of practical interest. We use them to sample the radii of inclusions.

The gamma, or Schulz, distribution is defined by

$$f(a) = \frac{1}{a!} \left[ \frac{z + 1}{a_0} \right]^{z+1} a^z \exp \left[ - \left( \frac{z + 1}{a_0} \right) a \right]. \quad (A1)$$

Here $f(a)$ is the probability density for inclusions of radius $a$; that is $f(a) da$ is the probability that an inclusion chosen at random have radius between $a$ and $(a + da)$. The moments of this distribution are given by

$$\langle a^n \rangle = \frac{(z + n)!}{z!} \left( \frac{1}{a_0} \right)^z \int_0^\infty \frac{1}{(z + 1)^n} a^n e^{-a/a_0} da. \quad (A2)$$

We note that the first moment of this distribution is identically equal to $a_0$; it is independent of the polydispersity. In calculating the surface-surface and surface-void distribution functions, we require the integrals

$$\int_0^\infty a^z f(a) da = \frac{1}{z!} \left( \frac{1}{z + 1} \right)^z a_0^n \int_0^\infty x^{z+n} e^{-x/a_0} dx, \quad (A3)$$

where $y = (z + 1) (a/a_0)$ and the integral on the right-hand side is the incomplete gamma function.

The parameter $a_0$ is the average inclusion radius; we choose units so that this is equal to unity. The parameter $z$ measures the polydispersity. The case $z = \infty$ gives a statistically sharp distribution in which all inclusions have radius $a_0$. The case $z = 0$ gives an exponential distribution in which many particles have extremely small radii.

The lognormal distribution is defined by the probability density

$$f(a) = \frac{1}{\sqrt{2\pi}} \frac{1}{a_0} \exp \left[ - \left( \frac{\ln(a/a_0)}{\sigma_0^2} \right)^2 \right]. \quad (A4)$$

The moments of this distribution are given by

$$\langle a^n \rangle = a_0^n Q_n, \quad (A5)$$
with
\[ Q_n = \exp \left[ \frac{3n^2}{4} \right]. \tag{A6} \]

In calculating the surface–surface and surface–void distribution functions, we require the integrals
\[ \int_0^{a_n} a^nf(a) \, da = \frac{1}{a_0^3} Q_n \left[ 1 - \text{erf}(A_n) \right], \tag{A7} \]
\[ \int_0^{a_n} a^nf(a) \, da = \frac{1}{a_0^3} Q_n \left[ 1 + \text{erf}(A_n) \right]. \tag{A8a} \]

Here we define
\[ A_n = \frac{\ln(a_n/a_0)}{\sigma \sqrt{2}} - \frac{n\sigma}{\sqrt{2}}. \tag{A8b} \]

Also, \( Q_n \) is defined by Eq. (A6), and \( \text{erf}(x) \) is the incomplete error function.

One would like to have a single measure for polydispersity so that we could readily compare distributions with different functional form, such as the two above. However, it is easily seen that there is no such unique measure. One that is widely used (see, e.g., Ref. 8) is the parameter \( A_3 \):
\[ A_3 = \frac{\langle a^3 \rangle}{\langle a^2 \rangle} - 1. \tag{A9} \]

For the Schulz distribution, this is given by
\[ A_3 = \frac{(z+6)(z+5)(z+4)}{(z+3)(z+2)(z+1)} - 1. \tag{A10} \]

This diverges as \( z \) approaches \( -1 \); it tends to zero as \( z \) approaches infinity. For the lognormal distribution, Eq. (A9) is
\[ A_3 = \exp \left[ 9\sigma^2 \right] - 1. \tag{A11} \]

This diverges as \( \sigma \) approaches infinity; it tends to zero as \( \sigma \) approaches zero.

The measure of dispersity relevant to determining the behavior of the naive Doi bounds is
\[ \frac{\langle a^3 \rangle}{\langle a^2 \rangle} \frac{\langle a \rangle}{\langle a^2 \rangle}. \tag{A12} \]

For the Schulz distribution, this quantity is bounded; it varies from 0.5 to 1. For the lognormal distribution, it becomes unbounded as the index \( \Lambda_3 \) does, but at a much slower rate. This explains why the modifications to the Doi bound made in Sec. III cause no major change in the low-density behavior of that bound if the Schulz distribution is used. The effect can be quite substantial for the lognormal distribution, but only at very large values of \( \Lambda_3 \).

33. A very general Ornstein–Zernike method for describing this class of models has recently been developed. See J. A. Given and G. Stell, J. Chem. Phys. (to be published).