Microstructure of two-phase random media. IV. Expected surface area of a dispersion of penetrable spheres and its characteristic function

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(Received 7 September 1983; accepted 29 September 1983)

A new expression is derived for the expected surface area of a dispersion of spheres distributed with arbitrary degree of penetrability. A convenient representation of the characteristic function of the interfacial surface is also introduced.

INTRODUCTION

In a wide variety of applications it is important to determine the expected specific surface area $s$ of a two-phase random material. For example, the fluid conductivity or permeability of a porous medium and the activity of a catalyst are known to be dependent upon $s$.

Here we consider a two-phase random medium composed of a dispersion of $N$ mutually penetrable spheres embedded in a matrix. The degree of impenetrability is characterized by some parameter $\lambda$ whose value varies between zero (in the case where the sphere centers are randomly centered and thus completely uncorrelated, i.e., fully penetrable spheres) and unity (in the instance of totally impenetrable spheres). One of our main results is an expression for the expected specific surface area $s$ (the surface area of the interface between particle and matrix phase per unit volume) in terms of probability density functions associated with the configuration of $n$ spheres in three-dimensional space. For the special cases of $\lambda = 0$ and $\lambda = 1$, we recover simple closed-form expressions for $s$ that are already known. For intermediate $\lambda$ we find an expression for $s$ in terms of a set of $n$-particle distribution functions that characterize the microstructure of the dispersion. Sphere distributions involving such intermediate $\lambda$ have already been introduced into the study of composites by the authors. One of us (G.S.) has proposed the permeable-sphere model, in which spherical inclusions of radius $R$ are assumed to be nonintersecting when nonintersecting (i.e., when $r > 2R$, where $r$ is the distance between sphere centers), with the probability of intersecting given by a radial distribution function $g(r)$ that is $1 - \lambda$, $0 < \lambda < 1$, independent of $r$, when $r < 2R$. S. T. has recently introduced a somewhat different model, the penetrable-core model, in which spherical inclusions of radius $R$ are assumed to be mutually impenetrable when nonintersecting (i.e., when $r > 2R$, where $r$ is the distance between sphere centers), with the probability of intersecting given by a radial distribution function $g(r)$ that is $1 - \lambda$, $0 < \lambda < 1$, independent of $r$, when $r < 2R$. S. T. has recently introduced a somewhat different model, the penetrable-core model, in which spherical inclusions of radius $R$ are assumed to be mutually impenetrable when nonintersecting (i.e., when $r > 2R$, where $r$ is the distance between sphere centers), with the probability of intersecting given by a radial distribution function $g(r)$ that is $1 - \lambda$, $0 < \lambda < 1$, independent of $r$, when $r < 2R$.
We must subtract the expected surface area of the overlap volume between all indistinguishable pairs of spheres:

\[
\frac{N(N-1)}{2} \int A_2(r_2, r_3; R) P_2(r_2, r_3) dr_2 dr_3.
\]

We have now overestimated this surface area because we have overcounted the overlap whenever three or more spheres happen to simultaneously overlap. This line of reasoning may be continued until we obtain an expression for \(s\):

\[
s = s_1 - s_2 + s_3 - s_4 + \ldots,
\]

where

\[
s_n = \frac{\rho^2}{V n!} \int \ldots \int A_n(r_2, r_3, \ldots, r_{n+1})
\]

\[
\times g_n(r_2, r_3, \ldots, r_{n+1}) dr_2 dr_3 \ldots dr_{n+1}.
\]

Here \(\rho g^n = [N^{n}(N-n)/n!]P_n, \rho = N/V\). Equation (6) is our general expression for \(s\). For the permeable-sphere model, as well as for fully penetrable and hard spheres, \(\partial g_n/\partial R = 0\) for all \(r_i\) in Eq. (7) such that \(A_n \neq 0\). For such a model

\[
s_n = \frac{\rho^2}{V n!} \int \ldots \int O_n(r_2, r_3, \ldots, r_{n+1})
\]

\[
\times g_n(r_2, r_3, \ldots, r_{n+1}) dr_2 dr_3 \ldots dr_{n+1},
\]

\[
= \frac{\partial}{\partial R} \left[ \frac{1}{n!} \int \ldots \int \prod_{i=2}^{n+1} m(r_i; R) \right]
\]

\[
\times g_n(r_2, r_3, \ldots, r_{n+1}) dr_2 dr_3 \ldots dr_{n+1},
\]

\[
= \frac{\partial}{\partial R} S^{(n)}(R).
\]

The quantity \(S^{(n)}\) is precisely the \(n\)th term of the series expression for \(S(R)\), the volume fraction of matrix \(\phi_1\) \([S^{(0)} = 1]\). Therefore, we have

\[
s = -\frac{\partial S(R)}{\partial R} \quad (9a)
\]

\[
= \frac{\partial}{\partial R} \left[ S^{(1)}_1 - S^{(1)}_2 + S^{(1)}_3 - \ldots \right] \quad (9b)
\]

\[
= \frac{\partial}{\partial R} \phi_3(R) \quad (9c)
\]

\[
= -\frac{\partial}{\partial R} \phi_1(R), \quad (9d)
\]

where \(\phi_2 = 1 - \phi_1\) is the volume fraction of particles. Equation (9) states that the expected specific surface area is equal to the derivative of \(\phi_2\) (or \(-\phi_1\)) with respect to the radius of the spheres. As explained below Eq. (7), Eq. (9) is a less general result than Eq. (6).

It is of interest to consider the derivative of the characteristic function of the particle phase \(J\) with respect to the radius of the spheres, i.e.,

\[
M(x; R) = \frac{\partial}{\partial R} J(x; R),
\]

where

\[
J(x; R) = \begin{cases} 1 & \text{if } x \in D \\ 0 & \text{otherwise.} \end{cases}
\]

\(D\) is the space occupied by particles. Torquato and Stell\(^6\) have shown that for a system of mutually penetrable spheres

\[
J(x; R) = 1 - \prod_{i=1}^{N} \left[ 1 - m(|x - r_i|) \right] \quad (12a)
\]

\[
= \sum_{i=1}^{N} m(|x - r_i|) - \sum_{i<j}^{N} m(|x - r_i|) m(|x - r_j|)
\]

\[
+ \sum_{i<j<k}^{N} m(|x - r_i|) m(|x - r_j|) m(|x - r_k|) - \ldots.
\]

Substituting Eq. (12b) into Eq. (10) gives

\[
M(x; R) = \sum_{i=1}^{N} \delta(R - |x - r_i|)
\]

\[
- \sum_{i<j}^{N} \delta(R - |x - r_i|) m(|x - r_j|)
\]

\[
+ \sum_{i<j<k}^{N} \delta(R - |x - r_i|) m(|x - r_j|) m(|x - r_k|) - \ldots. \quad (13)
\]

Equation (13) demonstrates that the generalized function \(M\) may be looked upon as a characteristic function of the interface, i.e., the function \(M(x; R)\) is nonzero when \(x\) describes a position on the interfacial surface. Such a function, to our knowledge, has never been used before (or even defined) in the study of two-phase media.

Equation (13) gives the explicit dependence of \(M\) on the positions of the \(N\) spheres. The usefulness of Eq. (13) lies in the way it permits one to explicitly evaluate ensemble averages of \(M\) and any other many-body random function in terms of \(n\)-body distribution functions \(g_n\). There are two important instances of such averages that readily come to mind, the first of which is the ensemble average of \(M(x_1)M(x_2)\cdots M(x_n)\). In particular, the expected specific surface area \(s\) is simply \(\langle M(x) \rangle\). It is of interest to calculate \(s\) for both the impenetrable-sphere case \((\lambda = 1)\) and the fully penetrable-sphere case \((\lambda = 0)\). For \(\lambda = 1\),

\[
S_1(R) = 1 - \rho \frac{4\pi}{3} R^3
\]

and thus from Eq. (9d) we obtain the obvious result that the specific surface areas \(s\) equals \(\rho 4\pi R^2\). For \(\lambda = 0\),

\[
S_1(R) = \exp \left[ -\rho \frac{4\pi}{3} R^3 \right],
\]

and hence

\[
s = \rho 4\pi R^2 \exp \left[ -\rho \frac{4\pi}{3} R^3 \right] = \rho 4\pi R^2 S_1(R). \quad (14)
\]

Equation (14) has a simple interpretation. It states that \(s\) is equal to the specific surface area of fully penetrable spheres multiplied by the probability of finding one point in the matrix (the volume fraction of matrix). This specific result for fully penetrable spheres has already been expressed by Weissberg and Prager.\(^*\) Note that since \(S_1 < 1, \lim_{\lambda \to 0} S_1(\lambda = 0) = 0\) which is expected. As aforementioned, Debye et al.\(^1\) have obtained the result

\[
s = -\frac{4}{3} \frac{dS_1(r)}{dr} \bigg|_{r=0}. \quad (15)
\]
Using the results of Torquato and Stell\textsuperscript{4} for $S_2$, one can show that Eq. (15) yields the expression for $s$ in the cases $\lambda = 0$ and $\lambda = 1$ that we have obtained above. We can also combine Eqs. (9) and (15) to obtain for permeable spheres the result
\begin{equation}
\frac{dS_2}{dr} \bigg|_{r=0} = \frac{1}{4} \frac{dS_1(R)}{dR}.
\end{equation}
(16)
The significance of higher-order correlations involving $M$ remains to be investigated.

A second important example that can be systematically treated once Eq. (13) is introduced is the ensemble average that arises when one is interested in obtaining the integral of some local physical quantity (which is a random function of position) over the surface area of the interface. This is seen in the study of flow through porous media where one is confronted with the task of integrating the local stress in the fluid over the interfacial surface.\textsuperscript{9}

The functions $S_1(R)$ and $s$ cannot be exactly evaluated in our permeable-sphere or penetrable-core models mentioned in the Introduction. For the permeable-sphere model, however, both functions can be easily expressed in the context of a generalized superposition approximation\textsuperscript{10}
\begin{equation}
s_1(r_1,...,r_n) = \prod_{1<i<j<n} g_2(r_i,r_j).
\end{equation}
(17)
For all values of the variables of integration in Eq. (8) for which no function of position is unity we have $g_2 = 1 - \lambda$ in the permeable-sphere model. Thus, substituting Eq. (17) into Eq. (8) yields immediately
\begin{equation}
S_1(R) = 1 + \sum_{n=1}^{\infty} (-4\pi R^3/3)^n (1 - \lambda)^{n-1}.
\end{equation}
(18a)
\begin{equation}
s = 4\pi R^2 \sum_{n=1}^{\infty} (-4\pi R^3/3)^n - 1(1 - \lambda)^{n-1/2}.
\end{equation}
(18b)
Equation (17) becomes exact for all $n$ as either $\rho$ or $\lambda$ goes to zero, and Eq. (18) is exact for all $\rho$ when $\lambda$ is 0 or 1. As long as $\lambda$ is either small or close to 1, we would expect Eq. (18) to be quantitatively useful over a wide range of $\rho$. For $\lambda \approx 1/2$, Eq. (18) can only be used with confidence for $\rho R^3$ small compared to 1 (say $\rho R^3 < 1/3$) until a more detailed assessment of its accuracy is made.

ACKNOWLEDGMENTS

S. Torquato gratefully acknowledges support of the National Science Foundation through Grant No. CPE-82-11966. G. Stell wishes to acknowledge support of the Office of Basic Energy Sciences, U. S. Department of Energy. We are indebted to Per Rikvold for crucial criticism of an earlier draft of this article.

3See, J. J. Salacuse and G. Stell, \textit{J. Chern. Phys.} 77, 2071 (1982) and references therein to the "permeable sphere" model. In this model the $n$-particle distributions $g_n$ for $n > 2$ are all uniquely defined functionals of $g(r)$ and the sphere volume fraction. See the Appendix of G. Stell, \textit{Physica} 29, 517 (1963) and its footnote 23 for explicit expressions.
4S. Torquato (to be published).
5See the remarks in this connection concerning our basic formulation by G. Stell in his Lecture Notes, Proceedings for the Workshop on the Mathematics and Physics of Disordered Media: Percolation, Random Walk, Modeling, and Simulation (Feb. 14–19, 1983); Institute for Mathematics and its Applications, University of Minnesota (Springer Lecture Notes in Mathematics Series).