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

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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[1] and the activity of a catalyst[2] 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 λ 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 λ 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 λ have already been introduced into the study of composites by the authors. One of us (G.S.) has proposed the permeable-sphere model,[3] in which spherical inclusions of radius R are assumed to be noninteracting 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 $1 - \lambda$, $0 \leqslant \lambda \leqslant 1$, independent of r, when $r < 2R$. S. T. has recently introduced a somewhat different model, the penetrable-core model,[4] in which spheres of radius R have a mutually impenetrable core region of radius λR, $0 \leqslant \lambda \leqslant 1$. Although the first example assumes a condition of thermal equilibrium, along with the constraints explicitly stated above, neither the second example nor the general results of this note assume that the sphere distribution is constrained to be one of thermal equilibrium.[5] (For simplicity, however, we shall assume spatial homogeneity of the inclusions here.)

Debye, Anderson, and Brumberger[2] have already shown that the specific surface area s, for a system of arbitrarily shaped particles, is proportional to the slope of the two-point matrix probability function $S_2(r)$ at $r = 0$. [$S_2(r)$ is the probability of finding two points, separated by a distance r, in the matrix phase.[2]] Our expression for s is of a different type that becomes especially useful in the permeable-sphere model.

ANALYSIS AND RESULTS

The intersection or overlap volume of n mutually penetrable spheres of radius R centered at positions $\mathbf{r}_2$, $\mathbf{r}_3$, ..., $\mathbf{r}_{n+1}$, O_n is given by the volume integral

$$O_n(\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_{n+1};R) = \int d\mathbf{r}_1 \prod_{j=2}^{n+1} m(r_{1j};R), \tag{1}$$

where $m(r;R)$ is the step function such that

$$m(r;R) = \begin{cases} 1 & \text{if } r < R, \\ 0 & \text{if } r > R, \end{cases} \tag{2}$$

and $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$. The surface area of overlaps $A_n(\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_n;R)$ is given by

$$A_n = \frac{\partial O_n}{\partial R}. \tag{3}$$

Since the spheres are statistically distributed throughout the matrix we shall use ensemble averaging techniques to obtain the expected specific surface area of the two-phase system. The subsequent geometric argument used to obtain s is the same one employed by Torquato and Stell[7] to obtain S_1 (the probability of finding one point in the matrix phase). It is a paraphrase of the latter author's extension[8] of a method due to Boltzmann for finding such quantities, which are fundamental in considering the microstructure of a hard-sphere fluid.

Let $P_n(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_n)d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_n$ be the probability that particle 1 is in $d\mathbf{r}_1$, particle 2 is in $d\mathbf{r}_2$, ..., and particle n is in $d\mathbf{r}_n$. Then the expected or mean surface area of the particle-matrix interface, neglecting boundary effects, is at most the surface area of N spheres, which is

$$N \int A_1(\mathbf{r}_2;R)P_1(\mathbf{r}_2)d\mathbf{r}_2 = N 4\pi R^2. \tag{4}$$

However, there is expected overlapping of spheres that we must consider when the spheres are not totally impenetrable.

We must subtract the expected surface area of the overlap volume between all indistinguishable pairs of spheres:

$$\frac{N(N-1)}{2} \int\int A_2(\mathbf{r}_2,\mathbf{r}_3;R\,)P_2(\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_2 d\mathbf{r}_3 \ . \tag{5}$$

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:

$$s = s_1 - s_2 + s_3 - s_4 + \cdots , \tag{6}$$

where

$$s_n = \frac{\rho^n}{Vn!} \int\int \cdots \int A_n(\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_{n+1})$$
$$\times g_n(\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_{n+1})d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_{n+1} \ . \tag{7}$$

Here $\rho^n g^n = [N!/(N-n)!]P_n$, $\rho = N/V$. 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

$$s_n = \frac{\rho^n}{Vn!} \frac{\partial}{\partial R} \int\int \cdots \int O_n(\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_{n+1})$$
$$\times g_n(\mathbf{r}_2,\mathbf{r}_3,...,\mathbf{r}_{n+1})d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_{n+1} \tag{8a}$$

$$= \frac{\partial}{\partial R} \left\{ \frac{\rho^n}{n!} \int\int \cdots \int \left[\prod_{j=2}^{n+1} m(r_{1j};R\,) \right] \right.$$
$$\left. \times g_n(\mathbf{r}_2,\mathbf{r}_3,...\mathbf{r}_{n+1})d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_{n+1} \right\} \tag{8b}$$

$$= \frac{\partial}{\partial R} S_1^{(n)}(R\,) \ . \tag{8c}$$

The quantity $S_1^{(n)}$ is precisely the nth term of the series expression for $S_1(R\,)$, the volume fraction of matrix ϕ_1 [$S_1^{(0)} \equiv 1$].[7] Therefore, we have

$$s = -\frac{\partial S_1(R\,)}{\partial R} \tag{9a}$$

$$= \frac{\partial}{\partial R} \left[S_1^{(1)} - S_1^{(2)} + S_1^{(3)} - \cdots \right] \tag{9b}$$

$$= \frac{\partial}{\partial R} \phi_2(R\,) \tag{9c}$$

$$= -\frac{\partial}{\partial R} \phi_1(R) \ , \tag{9d}$$

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 ϕ_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.,

$$M(\mathbf{x};R\,) = \frac{\partial}{\partial R} J(\mathbf{x};R\,) \ , \tag{10}$$

where

$$J(\mathbf{x};R\,) = \begin{cases} 1 & \text{if } \mathbf{x}\epsilon D \\ 0 & \text{otherwise.} \end{cases} \tag{11}$$

D is the space occupied by particles. Torquato and Stell[6]

have shown that for a system of mutually penetrable spheres

$$J(\mathbf{x};R\,) = 1 - \prod_{i=1}^{N} [\,1 - m(|\mathbf{x} - \mathbf{r}_i|)] \tag{12a}$$

$$= \sum_{i=1}^{N} m(|\mathbf{x} - \mathbf{r}_i|) - \sum_{i<j}^{N} m(|\mathbf{x} - \mathbf{r}_i|)m(|\mathbf{x} - \mathbf{r}_j|)$$
$$+ \sum_{i<j<k}^{N} m(|\mathbf{x} - \mathbf{r}_i|)m(|\mathbf{x} - \mathbf{r}_j|)m(|\mathbf{x} - \mathbf{r}_k|)$$
$$- \cdots \ . \tag{12b}$$

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

$$M(\mathbf{x};R\,) = \sum_{i=1}^{N} \delta(R - |\mathbf{x} - \mathbf{r}_i|)$$
$$- \sum_{i<j}^{N} \delta(R - |\mathbf{x} - \mathbf{r}_i|)m(|\mathbf{x} - \mathbf{r}_j|)$$
$$- \sum_{i<j}^{N} \delta(R - |\mathbf{x} - \mathbf{r}_j|)m(|\mathbf{x} - r_i|) - \cdots \ . \tag{13}$$

Equation (13) demonstrates that the generalized function M may be looked upon as a characteristic function of the interface, i.e., the function $M(\mathbf{x};R\,)$ is nonzero when $\mathbf{x}$ 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 $M(\mathbf{x}_1)M(\mathbf{x}_2)\cdots M(\mathbf{x}_n)$. In particular, the expected specific surface area s is simply $\langle M(\mathbf{x})\rangle$. 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

$$s = \rho 4\pi R^2 \exp\left[-\rho\frac{4\pi}{3}R^3 \right]$$

$$= \rho 4\pi R^2 S_1(R\,) \ . \tag{14}$$

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.[8] Note that since $S_1 < 1$, $s(\lambda = 1) \geqslant s(\lambda = 0)$ which is expected. As aforementioned, Debye et al.[1] have obtained the result

$$s = -4\frac{dS_2(r)}{dr}\bigg|_{r=0} \ . \tag{15}$$

Using the results of Torquato and Stell[6] 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

$$\frac{dS_2}{dr}\bigg|_{r=0} = \frac{1}{4}\frac{\partial S_1(R)}{\partial R}. \tag{16}$$

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.[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[10]

$$g_n(\mathbf{r}_1,...,\mathbf{r}_n) = \prod_{1 \leq i < j \leq n} g_2(\mathbf{r}_i,\mathbf{r}_j). \tag{17}$$

For all values of the variables of integration in Eq. (8) for which no m is zero (i.e., every m is unity) we have $g_2 = 1 - \lambda$ in the permeable-sphere model. Thus, substituting Eq. (17) into Eq. (8) yields immediately

$$S_1(R) = 1 + \sum_{n=1}^{\infty} (-4\pi\rho R^3/3)^n (1 - \lambda)^{n(n-1)/2} \tag{18a}$$

$$s = 4\pi\rho R^2 \sum_{n=1}^{\infty} (-4\pi\rho R^3/3)^{n-1}(1 - \lambda)^{n(n-1)/2}. \tag{18b}$$

Equation (17) becomes exact for all n as either ρ or λ goes to

zero, and Eq. (18) is exact for all ρ when λ is 0 or 1. As long as λ is either small or close to 1, we would expect Eq. (18) to be quantitatively useful over a wide range of ρ. For $\lambda \approx 1/2$, Eq. (18) can only be used with confidence for ρR^3 small compared to 1 (say $\rho R^3 < 1/3$) until a more detailed assessment of its accuracy is made.

ACKNOWLEDGMENTS

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[2] P. Debye, H. R. Anderson, Jr., and H. Brumberger, J. Appl. Phys. **28**, 679 (1957).

[3] See, J. J. Salacuse and G. Stell, J. Chem. 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, Physica **29**, 517 (1963) and its footnote 23 for explicit expressions.

[4] S. Torquato (to be published).

[5] See 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).

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[10] See G. Stell in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964), pp. II-209, II-219, and II-220.