Bulk properties of two-phase disordered media. I. Cluster expansion for the effective dielectric constant of dispersions of penetrable spheres

S. Torquato
Department of Mechanical and Aerospace Engineering and Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7910

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We derive a cluster expansion for the effective dielectric constant ϵ^* of a dispersion of equal-sized spheres distributed with arbitrary degree of impenetrability. The degree of impenetrability is characterized by some parameter λ whose value varies between zero (in the case of randomly centered spheres, i.e., fully penetrable spheres) and unity (in the instance of totally impenetrable spheres). This generalizes the results of Felderhof, Ford, and Cohen who obtain a cluster expansion for ϵ^* for the specific case of a dispersion of totally impenetrable spheres, i.e., the instance $\lambda = 1$. We describe the physical significance of the contributions to the average polarization of the two-phase system which arise from inclusion-overlap effects. Using these results, we obtain a density expansion for ϵ^*, which is exact through second order in the number density ρ, and give the physical interpretations of all of the cluster integrals that arise here. The use of a certain family of equilibrium sphere distributions is suggested in order to systematically study the effects of details of the microstructure on ϵ^* through second order in ρ. We show, furthermore, that the second-order term can be written as a sum of the contribution from a *reference* system of totally impenetrable spheres and an excess contribution, which only involves effects due to overlap of pairs of inclusions. We also obtain an expansion for ϵ^* which is exact through second order in ϕ_2, where ϕ_2 is the sphere volume fraction. We evaluate, for concreteness, some of the integrals that arise in this study, for arbitrary λ, in the permeable-sphere model and in the penetrable concentric-shell model introduced in this study.

I. INTRODUCTION

The theoretical determination of effective properties of two-phase random materials is an outstanding problem in science. It was Maxwell[1] and Einstein[2] who obtained the effective electrical conductivity and viscosity of a dilute suspension of spheres, respectively, by making use of the solution of the appropriate boundary-value problem for a single inclusion in an infinite matrix. Brown[3] was the first to show the precise dependence of the bulk property on its microstructure by obtaining a perturbation expansion for the effective dielectric constant ϵ^* of any two-phase random composite in terms of absolutely convergent integrals that involve n-point correlation functions. (The n-point correlation functions give the probability of finding n points in one of the phases.[4–6]) Ramshaw[7] has recently obtained a wide variety of series representations for ϵ^* using general perturbation expansions of response kernels. For media composed of inclusions of dielectric constant ϵ_2 statistically distributed throughout a matrix of dielectric constant ϵ_1, Finkel'berg[8] obtained a cluster expansion for ϵ^* in terms of absolutely convergent integrals that involve n-particle probability density functions defined in the text. The work is formal in nature and very few details are provided. In another study he gives an explicit expression for the second-order term in ϵ^*.[9] Jeffrey[10] found and evaluated the same second-order term for dispersions of impenetrable spherical inclusions but used a method due to Batchelor[11] to make the integral involved here absolutely convergent. By extending Batchelor's technique to bypass conditionally convergent integrals to higher-order terms, Jeffrey[12] later obtained ϵ^* for suspensions of impenetrable spheres to all orders. Felderhof, Ford, and Cohen[13] have obtained a cluster expansion for ϵ^* of dispersions of nonoverlapping spherical inclusions using the procedure employed by Finkel'berg, but provide explicit expressions for the nth-order terms. They also elegantly prove that for such a dispersion the cluster integrals of any order are absolutely convergent, which implies that ϵ^* is well defined and independent of the shape of the sample in the limit of a large system.

The advantage of the technique first outlined by Brown,[3] for the perturbation expansion, and by Finkel'berg,[8] for the cluster expansion, is that it provides a systematic procedure to pass to the infinite-volume limit without shape-dependent integrals appearing in the expression for ϵ^*. The basic procedure for either expansion technique may be briefly summarized as follows. One first considers a large but finite sample of arbitrary shape in an arbitrary applied field $\mathbf{E}_0(\mathbf{r})$. The average polarization $\langle \mathbf{P} \rangle$ is then expressed as a formal operator acting on the applied field $\mathbf{E}_0(r)$. The formal operator, an ensemble averaged quantity, is then expanded either in a perturbation or cluster expansion. As is well known from macroscopic electrostatics, however, relations between average fields and $\mathbf{E}_0$ are dependent upon the shape of the sample and, hence, the integrals involved here must necessarily be conditionally convergent. Accordingly, one then seeks the appropriate series expression for $\mathbf{E}_0$ in terms of the average electric field $\langle \mathbf{E} \rangle$. Using this expression, the applied field $\mathbf{E}_0$ is eliminated in favor of $\langle \mathbf{E} \rangle$ in the expression for $\langle \mathbf{P} \rangle$ mentioned above. This resulting relation between $\langle \mathbf{P} \rangle$ and $\langle \mathbf{E} \rangle$ is localized, i.e., independent of the shape of the sample and, therefore, involves absolutely convergent integrals. One may now pass to the limit of an infinite volume without any ambiguity and obtain, from this localized relation, the particular expansion for ϵ^* of statistically homogeneous media.

This is the first in a series of papers on the bulk properties of two-phase disordered media. In this article we obtain a cluster expansion for ϵ^* of statistically homogeneous and isotropic two-phase medium composed of N identical mutually penetrable spheres of radius R and dielectric constant ϵ_2, statistically distributed throughout a matrix of dielectric constant ϵ_1. The degree of impenetrability of the spheres 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). Sphere distributions involving intermediate values of λ are easy to define. The permeable-sphere (PS) model proposed by Blum, Salacuse, and Stell[14] is an example of such a model. Here 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 that is $1-\lambda$, $0\leqslant\lambda\leqslant 1$, independent of r, whenever $r<2R$. Another example is a model we shall refer to as the penetrable concentric-shell (PCS) model in which spheres of radius R are statistically distributed in space subject only to the condition of a mutually impenetrable core region of radius λR, $0\leqslant\lambda\leqslant 1$. Each sphere of radius R may be thought of as being composed of an impenetrable core of radius λR, encompassed by a fully penetrable concentric shell of thickness $(1-\lambda)R$. Although the first example assumes a condition of thermal equilibrium, along with the aforementioned constraints, neither the second example nor the general results of this paper assume that the sphere distribution is constrained to be one of thermal equilibrium. The PCS model is a special case of the more general concentric-shell model described in the Appendix. In the latter model, λ is some finite real number which may be greater than unity. Chiew and Glandt[15] have used the PS model to study the percolation behavior of three-dimensional fluid systems. To our knowledge, the easily conceived concentric-shell model, however, has never been introduced in the study of random media.

Allowing the spheres to overlap introduces interesting microstructural features into the problem which would be absent if the spheres were totally impenetrable to one another (i.e., for $\lambda=1$). Chiew and Glandt,[16] e.g., have observed that in the case of fully penetrable spheres, $\lambda=0$, if the volume fraction of particle phase (phase 2) ϕ_2 is less than volume fraction at the percolation threshold of the region of space occupied by particles, ϕ_2^P, then the spheres are dispersed throughout a continuous matrix phase. When ϕ_2 is such that $\phi_2^P\leqslant\phi_2<\phi_2^M$, where ϕ_2^M is the ϕ_2 at the percolation threshold of the region of space which is the complement of the particle space (i.e., the matrix space), the "dispersion" is actually a bicontinuous medium. For still higher ϕ_2, i.e., $\phi_2^M<\phi_2\leqslant 1$, the matrix phase becomes the dispersed phase and the particle phase is the only continuous phase. A dispersion of fully penetrable spheres is a nontrivial model of a two-phase random medium and it has been employed with success, by Weissberg,[17] Weissberg and Prager,[18] DeVera and Strieder,[19] and Torquato and Stell[20] to rigorously bound various effective properties of two-phase disordered materials.

In Sec. II we describe the basic equations for the random medium problem. In Sec. III we describe, in some detail, the physical significance of the contributions to the average polarization of the system which arise from inclusion-overlap effects. Using the cluster expansion method first outlined by Finkel'berg,[8] we derive a cluster expansion for the effective dielectric constant of a statistically homogeneous and isotropic dispersion of N mutually penetrable spheres. In doing so, we adopt much of the notation used in the more comprehensive treatment of the problem by Felderhof, Ford, and Cohen.[13] In Sec. IV we obtain an expansion for ϵ^* which is exact though second order in ρ, where ρ is the number density, and give physical interpretations of all of the cluster integrals that arise there. Following Stell's general suggestions that the models of statistical mechanics be exploited in considering composite media,[21] we suggest, in Sec. V, the use of a certain family of equilibrium sphere distributions in order to systematically study the effects of details of the microstructure on ϵ^*, through second order in ρ. Here we also show that the second-order term can be written as a sum of the contribution from a *reference* system of totally impenetrable spheres and an excess contribution, which only involves effects due to overlap of pairs of inclusions. We evaluate, for concreteness, one of the cluster integrals involved here, for arbitrary λ, in the PS and PCS models. Lastly, in Sec. VI we give a general expression for ϵ^* through second-order in ϕ_2. Here we evaluate the sphere volume fraction ϕ_2 exactly, through the order ρ^2 and for arbitrary λ, in the PS and PCS mdoels.

II. BASIC EQUATIONS

The random medium is a domain of space D of volume V which is composed of two regions: a matrix phase D_1 with volume fraction ϕ_1 and dielectric constant ϵ_1, and a particle phase D_2 with volume fraction ϕ_2 and dielectric constant ϵ_2. It follows that the local dielectric constant at position $\mathbf{r}$ is given by

$$\begin{aligned}\epsilon(\mathbf{r}) &= \epsilon_1 I^{(1)}(\mathbf{r}) + \epsilon_2 I^{(2)}(\mathbf{r}) \\ &= \epsilon_1 + (\epsilon_2-\epsilon_1) I^{(2)}(\mathbf{r}),\end{aligned} \tag{2.1}$$

where

$$I^{(i)}(r) = \begin{cases} 1, & \text{if } \mathbf{r}D_i \\ 0, & \text{otherwise.}\end{cases} \tag{2.2}$$

For N overlapping spheres of radius R centered at $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N(=\mathbf{r}^N)$ it has been shown that[4]

$$I^{(2)}(\mathbf{r};\mathbf{r}^N) = 1-\prod_{i=1}^{N}[1-m(x_i)] \tag{2.3a}$$

$$= \sum_{i=1}^{N} m(x_i) - \sum_{i<j}^{N} m(x_i)m(x_j) + \sum_{i<j<k}^{N} m(x_i)m(x_j)m(x_k) - \cdots, \tag{2.3b}$$

where

$$m(r) = \begin{cases} 1, & \text{if } r<R \\ 0, & \text{if } r>R\end{cases} \tag{2.4}$$

and

$x_i = |\mathbf{r} - \mathbf{r}_i|$.

The nth sum in Eq. (2.3b) is over all distinguishable n-tuplets of particles and thus contains $N!/(N-n)!n!$ terms. It arises because n-tuplets of spheres may happen to simultaneously overlap. Clearly, the first sum is the contribution to $I^{(2)}$ neglecting overlap of the inclusions, whereas, the remaining sums account for the possibility of overlap of the spheres. The local governing field equations are given by Maxwell's electrostatic equations

$$\nabla \cdot \mathbf{D} = 4\pi\sigma, \tag{2.5a}$$

$$\nabla \times \mathbf{E} = 0, \tag{2.5b}$$

$$\mathbf{D} = \epsilon \mathbf{E}, \tag{2.5c}$$

where $\mathbf{D}$ is the dielectric displacement, $\mathbf{E}$ is the electric field, $\sigma \equiv (\nabla \cdot \epsilon_1 \mathbf{E}_0)/4\pi$ is the given charge density, and $\mathbf{E}_0$ is the applied electric field which is the solution of the Eqs. (2.5a)–(2.5e) with $\epsilon = \epsilon_1$. The electric field $\mathbf{E}(\mathbf{r};\mathbf{r}^N)$ is the solution of the same equations when N overlapping spheres are added to reference medium (or matrix) such that ϵ is given by Eq. (2.1).

The averaged field relations are given by

$$\nabla \cdot \langle \mathbf{D} \rangle = 4\pi\sigma, \tag{2.6a}$$

$$\nabla \times \langle \mathbf{E} \rangle = 0, \tag{2.6b}$$

$$\langle \mathbf{D} \rangle = \epsilon \langle \mathbf{E} \rangle, \tag{2.6c}$$

where angular brackets denote an ensemble average (defined below) and ϵ^* is the effective dielectric constant. By writing Eq. (2.6c) we have assumed the existence of ϵ^*, the quantity we desire to determine. If we define the induced polarization as

$$\mathbf{P} = (1/4\pi)(\epsilon - \epsilon_1)\mathbf{E}, \tag{2.7}$$

we have the alternative relation between the average polarization and the average electric field.

$$\langle \mathbf{P} \rangle = (1/4\pi)(\epsilon^* - \epsilon_1)\langle \mathbf{E} \rangle. \tag{2.8}$$

In arriving at Eq. (2.8) we have used Eqs. (2.1), (2.5c), (2.6c), and (2.7).

The solution of Eqs. (2.5a)–(2.5c) in the presence of inclusions may be formally expressed as

$$\mathbf{E}(\mathbf{r};\mathbf{r}^N) = \int d\mathbf{r}' \mathsf{K}(\mathbf{r},\mathbf{r}';\mathbf{r}^N) \cdot \mathbf{E}_0(\mathbf{r}') \tag{2.9}$$

or, in a more condensed notation,

$$\mathbf{E}(\mathbf{r}^N) = \mathsf{K}(\mathbf{r}^N) \cdot \mathbf{E}_0. \tag{2.10}$$

The polarization is then expressed as

$$\mathbf{P}(\mathbf{r}^N) = \chi(\mathbf{r}^N) \mathsf{K}(\mathbf{r}^N) \cdot \mathbf{E}_0, \tag{2.11}$$

where

$$\chi(\mathbf{r}^N) = (1/4\pi)[\epsilon(\mathbf{r}^N) - \epsilon_1] = (1/4\pi)[\epsilon_2 - \epsilon_1] I^{(2)}(\mathbf{r}^N) \tag{2.12}$$

is the relative dielectric susceptibility. It is clear that both χ and $\mathbf{P}$ vanish inside the matrix.

The particles are distributed throughout the matrix according to the probability density $P(\mathbf{r}^N)$, where $P(\mathbf{r}^N)d\mathbf{r}^N$ is the probability of simultaneously finding the center of particle 1 in the volume $d\mathbf{r}_1$ and $\mathbf{r}_1$, the center of particle 2 in the volume $d\mathbf{r}_2$ about $\mathbf{r}_2$,..., and the center of particle N in the volume $d\mathbf{r}_N$ about $\mathbf{r}_N$. Here $d\mathbf{r}^N \equiv d\mathbf{r}_1 \cdots d\mathbf{r}_2$. When convenient, we write the arguments of functions as 1,2,...and differentials as $d\,1, d\,2$,..., rather than $\mathbf{r}_1, \mathbf{r}_2$...and $d\mathbf{r}_1, d\mathbf{r}_2$,...,respectively. The degree of impenetrability of the particles is characterized by some parameter λ whose value varies between zero, in the case of fully penetrable spheres and unity, in the case of totally impenetrable spheres. The probability density $P(\mathbf{r}^N)$ implicitly depends upon λ. It is assumed that $P(\mathbf{r}^N)$ normalizes to unity and is invariant to interchange of the particles. The reduced n-particle probability density $P(\mathbf{r}^N)$ is given by

$$P(\mathbf{r}^n) = \int \cdots \int d(n+1) \cdots dN P(\mathbf{r}^N). \tag{2.13}$$

We let

$$\rho(\mathbf{r}^n) = [N!/(N-n)!] P(\mathbf{r}^n). \tag{2.14}$$

Therefore, $\rho(\mathbf{r}^n)d\mathbf{r}^n$ is the probability that the center of exactly one (unspecified) particle is in the volume $d\mathbf{r}_1$ about $\mathbf{r}_1$, the center of exactly one other (unspecified) particle is in $d\mathbf{r}_2$, etc. In the Appendix, we show there is a simple relationship between $\rho(\mathbf{r}^n;\lambda)$ and $\rho(\mathbf{r}^n;1)$ for isotropic distributions of spheres in the concentric-shell model.

III. GENERAL CLUSTER EXPANSION PROCEDURE

Let $F(\mathbf{r}^N)$ be any function of the coordinates of the N mutually penetrable spheres. Then it is rigorously true that

$$F(\mathbf{r}^N) = \overline{F}(\varnothing) + \sum_{i=1}^{N} \overline{F}(i) + \sum_{i<j}^{N} \overline{F}(i,j) + \sum_{i<j<k}^{N} \overline{F}(i,j,k) + \cdots + \overline{F}(1,...,N). \tag{3.1}$$

The physical meaning of the cluster functions $\overline{F}(\mathbf{r}^n)$ is as follows: $\overline{F}(\varnothing)$ is the contribution to F in the absence of inclusions, $\overline{F}(1)$ is the additional contribution to F when an inclusion with position 1 is added to the system, and, in general, $\overline{F}(\mathbf{r}^n)$ is the contribution to F, not included in the previous $n-1$ terms, when inclusions with positions 1,...,N are added to the system. Note that the nth sum in Eq. (3.1) is over all distinguishable s-tuplets of particles and thus contains $N!/(N-n)!n!$ terms. Equations (3.1) defines the cluster functions $\overline{F}$ associated with the many-body function F. In still shorter notation we have

$$F(\mathscr{L}) = \sum_{\mathscr{M} \subset \mathscr{L}} \overline{F}(\mathscr{M}), \tag{3.2}$$

where $\mathscr{M}$ is a set of inclusion labels and the sum is over all subsets of $\mathscr{M}$. It is clear that the inverse of this rule is

$$\overline{F}(\mathscr{L}) = \sum_{\mathscr{M} \subset \mathscr{L}} (-1)^{L-M} F(\mathscr{M}), \tag{3.3}$$

where L and M are the number of labels in $\mathscr{L}$ and $\mathscr{M}$, respectively.

The average electric field in the two-phase system is given by

$$\langle \mathbf{E} \rangle = \int \cdots \int d\mathbf{r}^N P(\mathbf{r}^N) \mathsf{K}(\mathbf{r}^N) \cdot \mathbf{E}_0. \tag{3.4}$$

Here we have used Eq. (2.10). Substitution of Eq.(3.1) into Eq. (3.4) with $F = \mathsf{K}$ and use of Eq. (2.14) gives

$$\langle \mathbf{E} \rangle = \sum_{n=0}^{N} (1/n!) \int \cdots \int d\mathbf{r}^n \rho(\mathbf{r}^n) \overline{\mathsf{K}}(\mathbf{r}^n) \cdot \mathbf{E}_0. \tag{3.5}$$

Clearly, $\overline{\mathsf{K}}$ is the cluster operator associated with the formal operator K. Note that when $n = 0$, $\rho(\varnothing) \equiv 1$ and $\overline{\mathsf{K}}(\varnothing) = \mathsf{U}$, where $\varnothing$ denotes the empty set and U is the unit dyadic, i.e., the first term in series (3.5) is precisely $\mathbf{E}_0$.

The average polarization in the presence of the inclusions is given by

$$\langle \mathbf{P} \rangle = \int \cdots \int d\mathbf{r}^n P(\mathbf{r}^N) \chi(\mathbf{r}^N) \mathsf{K}(\mathbf{r}^N) \cdot \mathbf{E}_0. \tag{3.6}$$

Here we have used Eq. (2.11). Before obtaining the cluster expansion of $\langle \mathbf{P} \rangle$ it is useful to first reexpress Eq. (3.6) by expanding the relative dielectric susceptibility, appearing in Eq. (3.6), in terms of the characteristic function $I^{(2)}$ [Eq. (2.3b)]. We have, for the first few terms, that

$$\begin{aligned} \langle \mathbf{P} \rangle = {} & N \int \cdots \int d\mathbf{r}^N P(\mathbf{r}^N) \chi_1(1) \mathsf{K}(\mathbf{r}^N) \cdot \mathbf{E}_0 \\ & - \frac{N(N-1)}{2!} \int \cdots \int d\mathbf{r}^N P(\mathbf{r}^N) \chi_2(1,2) \mathsf{K}(\mathbf{r}^N) \cdot \mathbf{E}_0 \\ & + \frac{N(N-1)(N-2)}{3!} \int \cdots \int d\mathbf{r}^N P(\mathbf{r}^N) \chi_3(1,2,3) \\ & \times \mathsf{K}(\mathbf{r}^N) \cdot \mathbf{E}_0 - \cdots, \end{aligned} \tag{3.7}$$

where

$$\chi_n(\mathbf{r}^n) = \frac{(\epsilon_2 - \epsilon_1)}{4\pi} \prod_{i=1}^{n} m(x_i). \tag{3.8}$$

In general, we have

$$\langle \mathbf{P} \rangle = \sum_{n=1}^{N} \frac{(-1)^{n+1} N!}{n!(N-n)!} \int \cdots \int d\mathbf{r}^N P(\mathbf{r}^N) \mathsf{M}_n(\mathbf{r}^N) \cdot \mathbf{E}_0, \tag{3.9}$$

where

$$\mathsf{M}_n(\mathbf{r}^N) = \chi_n(\mathbf{r}^n) \mathsf{K}(\mathbf{Y}^N) \tag{3.10}$$

Note that in the nth term of (3.9), the labels $1,...,n$ are singled out. The factor $\chi_1(1)\mathsf{K}(\mathbf{r}^N)\cdot\mathbf{E}_0$, appearing inside the first integral of Eq. (3.7) or Eq. (3.9) is the polarization induced in an inclusion centered at $\mathbf{r}_1$, in a field $\mathbf{E}_0$, for a particular configuration of the remaining $N-1$ penetrable spheres. Excluding the factor N, the first integral is the average polarization induced in a single inclusion of the system neglecting any overlap with this reference sphere. The first term of Eq. (3.10), therefore, is the contribution to $\langle \mathbf{P} \rangle$ neglecting inclusion-overlap effects.

Clearly, this term is the only contribution to $\langle \mathbf{P} \rangle$ if the spheres are totally impenetrable to one another (i.e., $\lambda = 1$), since the quantity $\chi_n(\mathbf{r}^n)P(\mathbf{r}^n)$ is identically zero for all $n \geqslant 2$, for such a distribution. The first term of Eq. (3.7) is the only contribution to $\langle \mathbf{P} \rangle$ that Felderhof, Ford, and Cohen[13] needed to consider. The remaining terms in Eq. (3.7) provide the corrections to $\langle \mathbf{P} \rangle$ when average effects due to overlap of the spheres must be considered. The factor $\chi_2(1,2)\mathsf{K}(\mathbf{r}^N)\cdot\mathbf{E}_0$, appearing inside the second integral of Eq. (3.7), is the polarization induced in the volume of overlap between an inclusion centered at $\mathbf{r}_1$ and another inclusion centered at $\mathbf{r}_2$, in a field $\mathbf{E}_0$, for a particular configuration of the remaining $N-2$ penetrable spheres. Since the spheres may overlap, in general, we must subtract from the first term of Eq. (3.7) the contribution of $\langle \mathbf{P} \rangle$ due to the overlap volume between all distinguishable pairs of spheres. Apart from the minus sign, this contribution is precisely the second term of Eq. (3.7). We must now add the contribution to the average polarization coming from the overlap volume between all distinguishable triplets of spheres, i.e., we must add the third term of Eq. (3.7). This line of reasoning may be extended to give the physical significance of the general nth term of Eq. (3.9).

Felderhof *et al.* have elegantly proven the absolute convergence of the integrals involved in the expression relating $\langle \mathbf{P} \rangle$ to $\langle \mathbf{E} \rangle$, for totally impenetrable spheres. Such an expression is obtained by obtaining a cluster expansion for the first term of Eq. (3.9), i.e., a cluster expansion of the many-body operator that we denote by $\mathsf{M}_1(\mathbf{r}^N) = \chi_1(1)\mathsf{K}(\mathbf{r}^N)$, and eliminating $\mathbf{E}_0$ in favor of $\langle \mathbf{E} \rangle$ through use of Eq. (3.5). By utilizing information concerning the asymptotic behavior of the cluster operators $\overline{\mathsf{M}}_1$ (the cluster operator associated with M_1) and $\overline{\mathsf{K}}$, and the n-particle probability densities $\rho(\mathbf{r}^n)$, for large separation of the inclusions, they show that the general integrand, which arises in the relation between $\langle \mathbf{P} \rangle$ and $\langle \mathbf{E} \rangle$, vanishes sufficiently rapidly for widely separated configurations of the inclusions, and thus prove the absolute convergence of the general integral involved. Allowing the spheres to overlap does not spoil the absolute convergence of the integrals involved in the expression relating $\langle \mathbf{P} \rangle$ to $\langle \mathbf{E} \rangle$ for arbitrary λ; an expression that we are about to derive. To be sure, note that for $n \geqslant 2$, the asymptotic behavior of the operator $\mathsf{M}_n(\mathbf{r}^N)$ of Eq. (3.10) (when the condition $|\mathbf{r} - \mathbf{r}^i| < R$ is satisfied for all i such that $1 \leqslant i \leqslant n$) for widely separated configurations of the inclusions $n+1,...,N$ is the same as the corresponding asymptotic behavior of the operator considered by Felderhof *et al.*, i.e., $\mathsf{M}_1(\mathbf{r}^N)$. For $n \geqslant 2$, moreover, $\mathsf{M}_n(\mathbf{r}^N) = 0$ if $|\mathbf{r} - \mathbf{r}_i| \geqslant R$, for any i such that $1 \leqslant i \leqslant n$. Using such information concerning M_n and given the fact that the integrals involved in a cluster expansion of $\langle \mathbf{P} \rangle$ in terms of $\langle \mathbf{E} \rangle$ for the specific case $\lambda = 1$ are absolutely convergent, one may demonstrate the absolute convergence of the integrals involved in the corresponding expression for the arbitrary λ [i.e., Eq. (3.15) give below]. We, however, shall not explicitly prove this here.

Instead of obtaining cluster expansions of the individual terms in Eq. (3.9) in order to obtain the desired relation between $\langle \mathbf{P} \rangle$ and $\langle \mathbf{E} \rangle$ for arbitrary λ, we employ an equivalent expression for the average polarization, Eq. (3.6), and Eqs. (2.14) and (3.1), to find that

$$\langle \mathbf{P} \rangle = \sum_{n=1}^{N} \frac{1}{n!} \int \cdots \int d\mathbf{r}^n \rho(\mathbf{r}^n) \overline{\mathsf{M}}(\mathbf{r}^n) \cdot \mathbf{E}_0. \tag{3.11}$$

Here $\overline{\mathsf{M}}$ is the cluster operator associated with the formal operator $\chi(\mathbf{r}^N)\mathsf{K}(\mathbf{r}^N)$ which appears in Eq. (3.6).

It is useful to write out the cluster operators $\overline{\mathsf{K}}(\mathbf{r}^n)$ and $\overline{\mathsf{M}}(\mathbf{r}^n)$ in terms of the operators K and $\chi\mathsf{K}$, respectively, for $n = 0,1$, and 2 using Eq. (3.3):

$$\overline{\mathsf{K}}(\varnothing) = \mathsf{K}(\varnothing) = \mathsf{U}, \tag{3.12a}$$

$$\overline{\mathsf{K}}(1) = \mathsf{K}(1) - \mathsf{K}(\varnothing), \tag{3.12b}$$

$$\overline{\mathsf{K}}(1,2) = \mathsf{K}(1,2) - \mathsf{K}(1) - \mathsf{K}(2) + \mathsf{K}(\varnothing), \tag{3.12c}$$

and

$$\overline{\mathsf{M}}(\varnothing) = 0, \tag{3.13a}$$

$$\overline{\mathsf{M}}(1) = \chi(1)\mathsf{K}(1) = [(\epsilon_2 - \epsilon_1)/4\pi]m(1)\mathsf{K}(1), \tag{3.13b}$$

$$\overline{\mathsf{M}}(1,2) = \chi(1,2)\mathsf{K}(1,2) - \chi(1)\mathsf{K}(1) - \chi(2)\mathsf{K}(2) = [(\epsilon_2 - \epsilon_1)/4\pi]\{[m(1) + m(2) - m(1)m(2)] \times \mathsf{K}(1,2) - m(1)\mathsf{K}(1) - m(2)\mathsf{K}(2)\}. \tag{3.13c}$$

Note that $\overline{\mathsf{M}}(\varnothing) = 0$, since the induced polarization must be zero in the absence of inclusions. In Eqs. (3.13b) and (3.13c), we have expressed the relative dielectric susceptibility [Eq. (2.12)] using the expanded form of the characteristic function of the particle phase [Eq. (2.3b)].

The object now is to eliminate $\mathbf{E}_0$ between the series (3.5) and (3.11) in order to obtain the desired relation between $\langle \mathbf{P} \rangle$ and $\langle \mathbf{E} \rangle$. This is done by solving Eq. (3.5) for $\mathbf{E}_0$ in terms of $\langle \mathbf{E} \rangle$ by successive substitutions and rearranging terms according to the number of inclusions involved. This new series representation of $\mathbf{E}_0$ is then substituted into the right-hand side of Eq. (3.11) to yield the desired cluster expansion. The first few terms of this expansion are

$$\langle \mathbf{P} \rangle = \int d\,1 \rho(1)\overline{\mathsf{M}}(1)\cdot\langle \mathbf{E} \rangle + \frac{1}{2!}\int\int d1\, d2[\rho(1,2)\overline{\mathsf{M}}(1,2) - 2\rho(1)\overline{\mathsf{M}}(1)\cdot\rho(2)\overline{\mathsf{K}}(2)]\cdot\langle \mathbf{E} \rangle + \frac{1}{3!}\int\int\int d\,1\, d\,2\, d\,3[\rho(1,2,3)\overline{\mathsf{M}}(1,2,3) - 3\rho(1,2)\overline{\mathsf{M}}(1,2)\cdot\rho(3)\overline{\mathsf{K}}(3) - 3\rho(1)\overline{\mathsf{M}}(1)\cdot\rho(2,3)\overline{\mathsf{K}}(2,3) + 6\rho(1)\rho(2)\rho(3)\overline{\mathsf{M}}(1)\cdot\overline{\mathsf{K}}(2)\cdot\overline{\mathsf{K}}(3)]\cdot\langle \mathbf{E} \rangle + \cdots. \tag{3.14}$$

In general, we have the following expression relating $\langle P \rangle$ to $\langle E \rangle$ for a dispersion of penetrable spheres:

$$\langle P \rangle = \sum_{n=1}^{N} \frac{1}{n!}\int\cdots\int d\mathbf{r}^n \sum_{(B)} (-1)^{k-1}\rho(B_1)\overline{\mathsf{M}}(B_1)\rho(B_2)\overline{\mathsf{K}}(B_2)\cdots\rho(B_k)\overline{\mathsf{K}}(B_k)\cdot\langle \mathbf{E} \rangle, \tag{3.15}$$

where in the nth term the sum $\Sigma_{(B)}$ in the integrand is over all ordered partitions of the labels $1,\ldots,n$ into disjoint subsets. Here, $k = k(B)$ is the number of subsets in the partition $(B) = (B_1|B_2|\cdots|B_k)$ with slashes indicating the partitioning into disjoint subsets, where B_1 is the first subset, B_2 is the second subset,..., and B_k is the kth subset. Within the integral involving three inclusions of Eq. (3.14), e.g., the third term corresponds to the three partitions $(1|2,3)$, $(2|1,3)$, and $(3|1,2)$. The labels within a subset are not ordered, however.

Relation (3.15) generalizes the corresponding expression obtained by Felderhof *et al.* which is valid for the specific case $\lambda = 1$, i.e., totally impenetrable spheres. Formally, the general functional structure of relation (3.15) is very similar to the analogous expression [Ref. 13, Eq. (3.17)] they obtained. The former relationship, however, involves contributions to $\langle \mathbf{P} \rangle$ due to overlap effects (embodied in the cluster operator $\overline{\mathsf{M}}$), which obviously do not arise in the latter expression. The genesis of these additional terms has been explicitly described above.

We consider statistically homogeneous and isotropic two-phase media and thus take the thermodynamic limit ($N\to\infty\to$, $V\to\infty$, and $\rho = N/V$ fixed). In order for relation (2.8) to hold, Eq. (3.15) must reduce to a local relationship between $\langle \mathbf{P} \rangle$ and $\langle \mathbf{E} \rangle$, i.e., the dielectric constant is given by

$$\epsilon^* = \epsilon_1 + \frac{4\pi}{3}\sum_{n=1}^{\infty}\frac{1}{n!}\int\cdots\int d\,2\cdots dN(0|\mathsf{Q}(\mathbf{r}^n)|0):\mathsf{U}, \tag{3.16}$$

where

$$\mathsf{Q}(\mathbf{r}^n) = \sum_{(B)}(-1)^{k-1}\rho(B_1)\rho(B_2)\cdots\rho(B_k)\overline{\mathsf{M}}(B_1) \times\overline{\mathsf{K}}(B_2)\cdots\overline{\mathsf{K}}(B_k) \tag{3.17}$$

and

$$(0|\mathsf{Q}(\mathbf{r}^n)|0) = \int\int d\mathbf{r}\, d\mathbf{r}'\, \mathsf{Q}(\mathbf{r},\mathbf{r}';\mathbf{r}^n). \tag{3.18}$$

The sum in Eq. (3.17) is again over all ordered partitions of the labels $1,\ldots,n$ into disjoint subsets. Because of the assumption of statistical homogeneity, the quantity $(0|\mathsf{Q}(\mathbf{r}^n)|0)$ appearing in Eq. (3.16) depends only upon the relative positions $\mathbf{r}_{1j} = \mathbf{r}_j - \mathbf{r}_1$ where $j = 2,3,\ldots,n$. The shape independence of the effective dielectric constant is reflected in the absolute convergence of the integrals in Eq. (3.16). Note that Eq. (3.16) is not an expansion in powers of density since the $\rho(\mathbf{r}^n)$ contained therein are dependent upon density.

IV. EFFECTIVE DIELECTRIC CONSTANT THROUGH ORDER ρ^2

In order to study the effects of overlap of pairs of spheres on ϵ^*, we obtain a density expansion of the effective dielectric constant ϵ^* of a statistically homogeneous dispersion of mutually penetrable spheres which is exact through order ρ^2 or η^2, where $\eta = \rho V_1$ and V_1 is the volume of a spherical inclusion. If we assume that such a dispersion possesses no long-range order, then in the limit $|r_i - r_j|\to\infty$ for all $1\leqslant i<j\leqslant n$, i.e., as the mutual distances between n inclusions increases without bound, the n-body probability density $\rho(r^n)$ factorizes into ρ^n. We shall assume that the $\rho(\mathbf{r}^n)$ may be expanded in powers of density and that the leading term of the density expansion is of order ρ^n. Consequently, in order to obtain ϵ^* through order ρ^2, we need only consider the first two terms of the sum of Eq. (3.16) and the leading-order term of the density expansion of $\rho(\mathbf{r}_1,\mathbf{r}_2)$, which must be of the general form $\rho^2 g_0(x)$ for isotropic media, where $x = |\mathbf{r}_2 - \mathbf{r}_1|$. The quantity $g_0(x)$ is the zero-density limit of the pair distribution or radial distribution function. Clearly, $g_0(x)$ is a density-independent function of the relative distance x whose precise functional form depends upon the model of the distribution of spheres and, assuming no long-range order, must tend to unity as $x\to\infty$. Therefore, for a statistically homogeneous and isotropic dispersion of mutually penetrable spheres, Eq. (3.16) gives ϵ^*/ϵ_1, through order η^2, to be exactly

$$\epsilon^*/\epsilon_1 = 1 + k_1\eta + k_2\eta^2, \tag{4.1}$$

where

$$k_1 = (4\pi/3\epsilon_1 V_1)(0|\overline{\mathsf{M}}(1)|0):\mathsf{U} \tag{4.2}$$

and

$$k_2 = \frac{4\pi}{6\epsilon_1 V_1^2}\int d\mathbf{x}(0|g_0(x)\overline{\mathsf{M}}(1,2) - 2\overline{\mathsf{M}}(1)\cdot\overline{\mathsf{K}}(2)|0):\mathsf{U}. \tag{4.3}$$

Note that evaluation of k_1 requires the solution of the electrostatic equations (2.5a)–(2.5c) for an isolated sphere (given below) since Eq. (4.2) involves the one-body operator $\overline{\mathsf{M}}(1)$. Clearly, k_1 is independent of the degree of penetrability of the particles and hence implies, for the models considered here, that k_1 is independent of λ. The contribution to k_2 which involves $\overline{\mathsf{M}}(1)\cdot\overline{\mathsf{K}}(2)$ requires only the solution of the one-sphere boundary-value problem. The remaining contribution to k_2 requires specification of the zero-density limit of the radial distribution function $g(x)$ of the model for the distribution of the penetrable spheres and, due to the presence of $\overline{\mathsf{M}}(1,2)$, the solutions of the boundary-value problems for an isolated sphere and two penetrable spheres for all relative separations of the spheres, i.e., $0 \leqslant x \leqslant \infty$. Satisfaction of the boundary conditions for the two-sphere electrostatic problem makes the task of determining the electric field a formidable one. The solution for two nonoverlapping spheres, however, was obtained long ago.[22] By contrast, the solution for two overlapping spheres ($0 \leqslant x \leqslant 2R$), to our knowledge, does not exist in the literature.

Using the arguments given in Sec. III to physically interpret the polarization and the average polarization for the general case of overlapping spheres in an applied field $\mathbf{E}_0$, it is easy to relate the quantities in Eq. (4.1) to induced dipole moments in the inclusions. For example, for a uniform applied field $\mathbf{E}_0$, the electric field $\mathbf{E}$ at the field point $\mathbf{r}$ in the presence of a single inclusion at $\mathbf{r}_1$, in the expanded notation of Eq. (2.9), is

$$\mathbf{E}(\mathbf{r};1) = \int d\mathbf{r}'\mathsf{K}(r,r';1)\mathbf{E}_0 = \begin{cases}\mathbf{E}_0 + (\beta R^3/y^3)[3(\hat{\mathbf{y}}\cdot\mathbf{E}_0)\hat{\mathbf{y}} - \mathbf{E}_0], & y > R\\ (1-\beta)\mathbf{E}_0 & y < R,\end{cases} \tag{4.4}$$

where

$$y = |\mathbf{r} - \mathbf{r}_1|,\ \hat{\mathbf{y}} = (\mathbf{r} - \mathbf{r}_1)/|\mathbf{r} - \mathbf{r}_1|$$

and

$$\beta = (\epsilon_2 - \epsilon_1)/(\epsilon_2 + 2\epsilon_1).$$

In Sec. III, we interpreted the quantity $\chi_1(1)\mathsf{K}(\mathbf{r}^N)\cdot\mathbf{E}_0$, which is equal to $\chi_1(1)\mathbf{E}(\mathbf{r};\mathbf{r}^N)$ using the expanded notation (2.9), as the polarization induced in an inclusion centered at $\mathbf{r}_1$, in a field $\mathbf{E}_0$, for a particular configuration of the remaining N-1 spheres. Therefore, $\overline{\mathsf{M}}(1)\cdot\mathbf{E}_0$, which according to Eq. (3.13b) is equal to $\chi_1(1)\mathbf{E}(\mathbf{r};1)$, is the polarization (the electric dipole moment per unit volume) induced in an isolated inclusion at $\mathbf{r}_1$ in an applied field $\mathbf{E}_0$. The dipole moment induced in the isolated inclusion, $\mu(1)$, therefore is obtained by integrating the polarization induced within the inclusion, $\chi_1(1)\mathbf{E}(r;1)$, over the volume of the inclusion, i.e., $\mu(1)$ is given by $(0|\overline{M}(1)|0)\cdot\mathbf{E}_0$. Since the polarizability tensor of a single inclusion $\boldsymbol{\alpha}(1)$ is defined through the relation $\mu(1) = \boldsymbol{\alpha}(1)\cdot\mathbf{E}_0$, we have, upon use of Eq. (4.4), that

$$\boldsymbol{\alpha}(1) = (0|\overline{\mathsf{M}}(1)|0) = \alpha\mathsf{U}, \tag{4.5}$$

where $\alpha = \beta\epsilon_1 R$ is the scalar polarizability of a sphere. Substitution of Eq. (4.5) into Eq. (4.2) gives the first-order term to be

$$k_1 = (4\pi/\epsilon_1 V_1)\alpha = 3\beta; \tag{4.6}$$

a result first obtained by Maxwell.[1] Using the arguments of Sec. III and the reasoning used above for an isolated inclusion, the interpretation of the terms in the second-order term k_2 follows in a very straightforward manner, i.e., we have, for a uniform applied field $\mathbf{E}_0$:

$$(0|\overline{\mathsf{M}}(1,2)|0)\cdot\mathbf{E}_0 = \boldsymbol{\alpha}(1;2)\mathbf{E}_0 + \boldsymbol{\alpha}(2;1)\mathbf{E}_0 - \boldsymbol{\alpha}_0(1,2)\mathbf{E}_0 - \boldsymbol{\alpha}(1)\mathbf{E}_0 - \boldsymbol{\alpha}(2)\mathbf{E}_0, \tag{4.7}$$

and

$$(0|\overline{\mathsf{M}}(1)\cdot\overline{\mathsf{K}}(2)|0)\cdot\mathbf{E}_0 = \boldsymbol{\alpha}(1|2)\mathbf{E}_0 - \boldsymbol{\alpha}(1)\mathbf{E}_0. \tag{4.8}$$

Here

$$\boldsymbol{\alpha}(i;j) = (0|\chi_1(i)\mathsf{K}(i,j)|0);\quad i \neq j, \tag{4.9}$$

$$\boldsymbol{\alpha}_0(1,2) = (0|\chi_2(1,2)\mathsf{K}(1,2)|0), \tag{4.10}$$

and

$$\boldsymbol{\alpha}(1|2) = (0|\chi_1(1)\mathsf{K}(1)\cdot\mathsf{K}(2)|0). \tag{4.11}$$

In arriving at Eqs. (4.7)–(4.11), we have used the relations (3.8), (3.12b), (3.13b), and (3.13c). Clearly, for a uniform $\mathbf{E}_0$, $\boldsymbol{\alpha}(i;j)\mathbf{E}_0$ is the dipole moment induced in a sphere centered at $\mathbf{r}_i$ in the presence of another sphere centered at $\mathbf{r}_j$ and $\boldsymbol{\alpha}_0(1,2)\mathbf{E}_0$ is the dipole moment induced in the overlap volume of two spheres, one centered at $\mathbf{r}_1$ and the other centered at $\mathbf{r}_2$. This latter contribution must be subtracted from the first two terms in Eq. (4.7) since the sum $\boldsymbol{\alpha}(1;2)\mathbf{E}_0 + \boldsymbol{\alpha}(2;1)\mathbf{E}_0$, overestimates the total dipole moment induced in two spheres in the uniform field $\mathbf{E}$, which we denote by $\boldsymbol{\alpha}(1,2)\mathbf{E}_0$, by an amount exactly equal to $\boldsymbol{\alpha}_0(1,2)\mathbf{E}_0$ whenever the spheres happen to overlap. The quantity $\boldsymbol{\alpha}(1|2)\mathbf{E}_0$ is the dipole moment induced in a sphere centered at $\mathbf{r}_1$ for a nonuniform field $\mathbf{E}(2) = \mathsf{K}(2)\cdot\mathbf{E}_0$ which results from a sphere centered at $\mathbf{r}_2$ in a uniform field $\mathbf{E}_0$.

Clearly, the quantities $\boldsymbol{\alpha}(1,2)$ and $\boldsymbol{\alpha}(1|2)$ are polarizability tensors which take into account the effects of pairs of spheres in a uniform field $\mathbf{E}_0$ and, in general, depend upon the relative position $\mathbf{x}$ and the scalar parameter α. Felderhof, Ford, and Cohen[23] have expressed k_2 [Eq. (4.3)] for totally impenetrable spheres, in terms of the induced dipole moments of the inclusions. Hence, the only term of Eqs. (4.7) and (4.8) they did not have to consider is the one involving $\boldsymbol{\alpha}_0$, since $\boldsymbol{\alpha}_0 g_0$ is identically zero for totally impenetrable spheres.

Employing Eqs. (4.3) and (4.7)–(4.11), we have

$$k_2 = \frac{2\pi}{\epsilon_1 V_1^2}\int d\mathbf{x}\{g_0(x)[\boldsymbol{\alpha}(1,2) - \boldsymbol{\alpha}(1) - \boldsymbol{\alpha}(2)]:\mathsf{U} - 2[\boldsymbol{\alpha}(1|2) - \boldsymbol{\alpha}(1)]:\mathsf{U}\}, \tag{4.12}$$

where

$$\boldsymbol{\alpha}(1,2) = \boldsymbol{\alpha}(1;2) + \boldsymbol{\alpha}(2;1) - \boldsymbol{\alpha}_0(1,2) \tag{4.13}$$

and where $\boldsymbol{\alpha}(i;j)$ and $\boldsymbol{\alpha}_0(1,2)$ are given by Eqs. (4.9) and (4.10), respectively. The evaluation of $\boldsymbol{\alpha}(1,2)$, for overlapping particles, requires the solution to the boundary-value problem for two interpenetrating spheres. This boundary-value problem, as aforementioned, does not appear to have been solved.

V. SECOND-ORDER TERM k_2

A. Sensitivity of k_2 to the details of the microstructure

The determination of the sensitivity of the effective property of a composite material to the details of the microstructure is an important fundamental question and one for which there are relatively few quantitative results. For example, the second-order term k_2 has been evaluated for a very limited number of models of spheres of dielectric constant ϵ_2 statistically distributed throughout a matrix of dielectric constant ϵ_1. Firstly, no such results exist for dispersions of penetrable spheres. Jeffrey[10] and, later, Felderhof, Ford, and Cohen[23] evaluated k_2 for totally impenetrable spheres by obtaining the solution of boundary-value problem for two totally nonoverlapping spheres and by assuming that

$$g_0(x) = H(x - 2R), \tag{5.1}$$

where $H(r)$ is the Heaviside step function. (Actually the integrand in Jeffrey's expression for the second-order term is different than one obtained by Felderhof, Ford, and Cohen,[23] but the former authors prove the value of the integral is the same.) A dispersion consisting of totally impenetrable spheres and possessing a radial distribution function specified by Eq. (5.1) has been referred to as a "well-stirred" dispersion.[10] A $g_0(x)$ given by Eq. (5.1) is equal to the leading-order term of the density expansion of the radial distribution function of equilibrium distribution of spheres[24] and certain nonequilibrium distributions, such as random sequential addition of hard spheres.[25] Chiew and Glandt[16] have noted that Eq. (5.1) is not general for totally impenetrable spheres and, as an example, they point out that the zero-density limit of the radial distribution function is given by

$$g_0(x) = H(x - 2R) + \tfrac{2}{3} R\delta(x - 2R)$$

for a dispersion prepared by uniform growth of random seeds. McCoy and Beran[26] have been the only ones to evaluate k_2 for a dispersion of totally impenetrable spheres using probability densities other than the one given by Eq. (5.1). They follow the approach used by Jeffrey, but, instead of using the Batchelor procedure to make the second-order conditionally convergent integral an absolutely convergent one, McCoy and Beran employ nearest-neighbor distributions rather than the distribution of all the neighbors $g_0(x)$, in order to avoid convergence problems. Jeffrey[27] has noted, however, that the use of nearest-neighbor functions in lieu of $g_0(x)$ lead to incorrect results for problems which involve longer range interactions than are present in the dielectric case (e.g., the sedimentation problem).

To our knowledge, no one has ever examined the question of the sensitivity of k_2 and thus of ϵ^*, through $O(\eta^2)$, to the details of the microstructure by employing various equilibrium sphere distributions. The obvious advantage in studying equilibrium configurations is that the well-established techniques and results of equilibrium statistical mechanics may be employed, as Stell has observed.[21] It is known that the zero-density limit of the radial distribution function for an equilibrium distribution of spheres is given by[24]

$$g_0(x) = \exp[-\Phi(x)/kT], \tag{5.2}$$

where $\Phi(x)$ is the interaction potential for pairs of particles, k is Boltzmann's constant, and T is absolute temperature. Specifically, we suggest that k_2 be evaluated for equilibrium sphere distributions using the $g_0(x)$ that results by using the following class of pair potentials:

$$\Phi(x;\lambda) = \begin{cases} \infty, & x < 2R\lambda \\ \lambda\Phi_0(x), & x > 2R\lambda, \end{cases} \tag{5.3}$$

where λ is some real number such that $0 \leqslant \lambda \leqslant k$ and k is some bounded integer such that $k \geqslant 1$. Here Φ_0 is any pair potential which may be either due to attractive or repulsive interparticle forces. The parameter λ multiplies Φ_0 in Eq. (5.3) to ensure that $\Phi(x) \to 0$ for all x. When $\lambda < 1$ and Φ_0 is nonzero in Eq. (5.3), the particles may be regarded as possessing an "outer" penetrable core of outer radius R and an "inner" impenetrable core of radius λR. There are a variety of Φ_0 that have been employed in the study of the liquid state that we may choose from as reasonable model potentials for random two-phase materials. For example, in order to study the effects of agglomeration of particles on k_2 one could take Φ_0 to be the attractive part of the potential of the adhesive-sphere model proposed by Baxter.[28] This model introduces attractive interaction which is infinitely short-ranged and has been considered by Chiew and Glandt in the study of percolation behavior of three-dimensional fluid systems.[15] The effects of repulsive interactions (in addition to the infinite repulsive forces which exist when $x < 2R\lambda$), on the other hand, could be examined by considering Φ_0 to be a Yukawa-like potential when $x > 2R\lambda$. Such potentials have been used extensively in statistical-mechanical investigations of Coulombic systems.[29] Note that if $T \to \infty$ or if $\Phi_0 = 0$ in Eq.(5.3), we recover the equilibrium version of the concentric-shell model described in the Appendix. The absolute temperature, which appears in Eq. (5.2), does not have the same physical significance in the random-medium problem as it does in liquid state theory. In the context of disordered media, it may be looked upon as a parameter which allows us to systematically control the effect of either attractive or repulsive forces, on the microstructure, which act when the distance between sphere centers is greater than $2R\lambda$. Note that for the models considered here, ϵ^* will depend not only upon ϕ_2 and ϵ_2/ϵ_1 but upon λ, T, and the parameters that are embodied in Φ_0. In these series of papers, however, we shall not study the effects of k_2 of interparticle forces that act when the spheres do not intersect one another, but instead, shall focus our attention on the sensitivity of k_2 to inclusion-overlap effects for sphere models in which the range of the impenetrability parameter λ is restricted to be $0 \leqslant \lambda \leqslant 1$, (e.g., aforementioned permeable-sphere and penetrable concentric-shell models).

B. Rearrangement of the terms involved in k_2

It is convenient to divide up the integration region of the integral k_2, given by Eq.(4.3), into two parts, $x < 2R$ and $x \geqslant 2R$, in order to recast it in the following way:

$$k_2 = \hat{k}_2 + \Delta k_2 \quad (5.4)$$

where

$$\hat{k}_2 = A + B, \quad (5.5)$$

$$\Delta k_2 = C + D, \quad (5.6)$$

$$A = \frac{2\pi}{\epsilon_1 V_1^2} \int_{x>2R} dx \{ g_0(x) [\boldsymbol{\alpha}(1,2) - 2\boldsymbol{\alpha}(1)] : \mathsf{U} - 2[\boldsymbol{\alpha}(1|2) - \boldsymbol{\alpha}(1)] : \mathsf{U} \}, \quad (5.7)$$

$$B = \frac{-4\pi}{\epsilon_1 V_1^2} \int_{x<2R} dx [\boldsymbol{\alpha}(1|2) - \boldsymbol{\alpha}(1)] : \mathsf{U}, \quad (5.8)$$

$$C = \frac{2\pi}{\epsilon_1 V_1^2} \int_{x<2R} dx\, g_0(x) \boldsymbol{\alpha}(1,2) : \mathsf{U}, \quad (5.9)$$

and

$$D = \frac{-4\pi}{\epsilon_1 V_1^2} \int_{x<2R} dx\, g_0(x) \boldsymbol{\alpha}(1) : \mathsf{U}. \quad (5.10)$$

Here $\boldsymbol{\alpha}(1)$, $\boldsymbol{\alpha}(1|2)$, and $\boldsymbol{\alpha}(1,2)$ are given by relations (4.5), (4.11), and (4.13), respectively.

The quantities on the right-hand side of Eq. (5.4) have an especially simple physical significance. The term $\hat{k}_2$ is the contribution to k_2 for a *reference* system of a dispersion of totally impenetrable spheres. Note that although the region of integration of the integral B is specified to be $x < 2R$, it contributes to k_2 even when the spheres are totally impenetrable to one another. [This last point is made clear by noting that B originates from the term involving $\overline{\mathsf{M}}(1)\cdot\overline{\mathsf{K}}(2)$ in Eq. (4.3) and can be seen there to make a contribution to k_2 whether or not the spheres intersect.] If we consider models in which $g_0(x) = 1$ whenever $x \geqslant 2R$, then k_2 is precisely equal to the second-order term evaluated by Jeffrey[10] and Felderhof, Ford, and Cohen,[23] for a dispersion of totally impenetrable spheres. From Jeffrey, we find that

$$A = 3\beta^2 \sum_{n=6}^{\infty} \frac{C_n}{(n-3)2^{(n-3)}}, \quad (5.11)$$

$$B = 3\beta^2, \quad (5.12)$$

where the coefficients C_n are functions of β (and are equivalent to $B_n - 3A_n$ in Jeffrey's notation). Therefore, for dispersions of penetrable spheres characterized by a $g_0(x)$ equal to unity for all $x \geqslant 2R$, the *reference* system is a dispersion of totally impenetrable spheres which possesses a $g_0(x)$ given by Eq. (5.1) and a value of k_2 given by the sum of Eqs. (5.11) and (5.12).

The quantity Δk_2 is, therefore, the contribution to k_2 in excess of the contribution from the reference system $\hat{k}_2$ and, hence, accounts for effects due to penetrability of the spheres. Note that the excess quantity Δk_2 must tend to zero as $\lambda \to 1$, since $g_0(x)$, which appears in the cluster integrals C [Eq. (5.9)] and D [Eq. (5.10)] must tend to zero as $\lambda \to 1$ for all x such that $x < 2R$.

The evaluation of the integral D for arbitrary λ is straightforward in the permeable-sphere and penetrable concentric-shell models. In the PS model the zero-density limit of the radial distribution function is given by[14]

$$g_0(x;\lambda) = \begin{cases} 1-\lambda, & x < 2R \\ 1, & x > 2R \end{cases}. \quad (5.13)$$

In the PCS model, the $g_0(x;\lambda)$ is not uniquely given. We choose, however, to consider the following expression for such a model:

$$g_0(x;\lambda) = \begin{cases} 0, & x < 2R\lambda \\ 1, & x > 2R\lambda \end{cases}. \quad (5.14)$$

From the discussion in Sec. IV, it is clear that Eq. (5.14) applies not only to equilibrium configurations of spheres, but also to certain nonequilibrium distributions, such as random sequential addition.[25] Note that both Eqs. (5.13) and (5.14) tend to unity for all x as $\lambda \to 0$ (i.e., we recover the fully penetrable-sphere case in this limit) and are equal to the zero-density limit of the radial distribution function for totally impenetrable spheres as given by Eq. (5.1). In the PS model and in a PCS model characterized by a $g_0(x)$ given by Eq. (5.14), the reference system is the so-called "well-stirred" dispersion and, therefore, k_2 is the sum of Eqs. (5.11) and (5.12). Substituting Eqs. (5.13) and (5.14) into Eq. (5.10) gives

$$D_{\rm PS}(\lambda) = -24\beta(1-\lambda) \quad (5.15)$$

and

$$D_{\rm PC}(\lambda) = -24\beta(1-\lambda^3), \quad (5.16)$$

where Eqs. (5.13) and (5.14) give the integral D in the PS and PCS models, respectively, as specified above.

The evaluation of the two-body cluster integral C requires knowledge of the polarizability tensor $\boldsymbol{\alpha}(1,2)$ for $x < 2R$ and, thus, the solution of the boundary-value problem for two interpenetrating spheres. Clearly, whenever $x < 2R$, $\boldsymbol{\alpha}(1,2)$ may be interpreted to be the polarizability tensor of a single "irregularly shaped" inclusion which is composed of two interpenetrating spheres, one being centered at $\mathbf{r}_1$ and the other being centered at $\mathbf{r}_2$. In the next article in this series, we shall obtain an expression for the integral C, for arbitrary λ in the permeable-sphere model, which is exact through order $\kappa^3 (\kappa \equiv \epsilon_2/\epsilon_1 - 1)$ without making direct use of the electrostatic solution for two interpenetrating spheres. There we also obtain rigorous upper and lower bounds on C and thus on k_2, through all orders in κ and for arbitrary λ, in the PS model.

VI. ϵ^* FOR A DISPERSION OF PENETRABLE SPHERES THROUGH ORDER ϕ_2^2

The volume fraction ϕ_2 is a more general parameter of dispersions than the number density since the former quantity remains well-defined for systems in which there are no well-defined inclusions. It is useful, therefore, to obtain an expansion for ϵ^* of statistically homogeneous dispersion of N mutually penetrable spheres, in powers of ϕ_2. This is accomplished by using the expansion of ϵ^* through order η^2, given by Eq. (4.1), and by eliminating η in favor of ϕ_2 in Eq. (4.1) using the expression (derived below) which gives η exactly through order ϕ_2^2 for dispersions of penetrable spheres.

Using the results of Torquato and Stell,[4] it is easy to show that ϕ_2, for statistically homogeneous and isotropic suspensions of penetrable spheres is, through order η^2, given exactly by

$$\phi_2 = \eta - I\eta^2, \quad (6.1)$$

where

$$I=\frac{1}{2V_1^2}\int\int d\mathbf{r}_2\,d\mathbf{r}_3\,g_0(r_{23})m(r_{12})m(r_{13}), \tag{6.2}$$

and where $r_{23}=|r_3-r_2|$. Here each volume integral is over the volume of the sample V. Note that I is equivalent to following integral:

$$I=\frac{1}{2V_1^2}\int d\mathbf{r}_{23}\,g_0(r_{23})\int d\mathbf{r}_1\,m(r_{12})m(r_{13}). \tag{6.3}$$

The volume integral over $\mathbf{r}_1$ is recognized to be a three-dimensional convolution integral of the step function m with itself and, hence, is equal to the volume common to two spheres of radius R whose centers are separated by a distance r_{23}, $V_2^{\rm int}(r_{23})$.

We have, therefore, that

$$I=\frac{1}{2V_1^2}\int d\mathbf{r}\,g_0(r)V_2^{\rm int}(r), \tag{6.4}$$

where

$$V_2^{\rm int}(r)=\begin{cases}\frac{4\pi}{3}R^3\left[1-\frac{3}{4}\frac{r}{R}+\frac{1}{16}\frac{r^3}{R^3}\right], & r<2R\\ 0, & r>2R.\end{cases} \tag{6.5}$$

Finally, by inverting Eq. (6.1) we have

$$\eta=\phi_2+I\phi_2^2, \tag{6.6}$$

which is exact through order ϕ_2^2. Note that for the general case of dispersions of penetrable spheres we have that $\phi_2\leqslant\eta$, since $I\geqslant0$; the equality sign applying to totally impenetrable-sphere systems.

Before proceeding to obtain ϵ^* through order ϕ_2^2, we evaluate the integral I, in the permeable-sphere and penetrable concentric-shell models, in order to shed some light on its geometrical significance. Substituting Eqs. (5.13) and (5.14) into Eq. (6.4) we have

$$I_{\rm PS}(\lambda)=[(1-\lambda)/2] \tag{6.7}$$

and

$$I_{\rm PCS}(\lambda)=4(1-\lambda^3)-\tfrac{9}{2}(1-\lambda^4)+(1-\lambda^6), \tag{6.8}$$

where Eqs. (6.7) and (6.8) give the integral I in the PS and PCS, respectively, as specified in Sec. V. In Table I we compare $I_{\rm PS}$ and $I_{\rm PCS}$ for various values of λ. Equations (6.7) and (6.8) are both montonically decreasing functions of λ and yield the same value at $\lambda=\lambda_0$, where $\lambda_0\simeq0.535$. From Table I we see that whenever $\lambda>\lambda_0$, $I_{\rm PS}(\lambda)>I_{\rm PCS}(\lambda)$ and that whenever $\lambda<\lambda_0$, $I_{\rm PS}(\lambda)<I_{\rm PCS}(\lambda)$. Referring to Eq. (6.1), this implies that $I\eta^2$, the expected overlap volume between all distinguishable pairs of spheres,[5] is greater in the permeable-sphere model whenever $\lambda>\lambda_0$, with the converse applying whenever $\lambda<\lambda_0$. Clearly, for fixed η and through order η^2, this implies that $\phi_2^{\rm PS}<\phi_2^{\rm PCS}$ whenever $\lambda<\lambda_0$ and that $\phi_2^{\rm PS}>\phi_2^{\rm PCS}$ whenever $\lambda>\lambda_0$, where $\phi_2^{\rm PS}$ and $\phi_2^{\rm PCS}$ are the ϕ_2 associated with the PS and PCS models, respectively.

Through use of relations (4.1), (4.2), (5.4), and (6.1), we find that for a statistically homogeneous and isotropic dispersion of penetrable spheres, ϵ^*/ϵ_1 through order ϕ_2^2 is given exactly by

$$\frac{\epsilon^*}{\epsilon_1}=1+k_1\phi_2+[\hat{k}_2+\Delta k_2']\phi_2^2, \tag{6.9}$$

$$\Delta k_2'=C+D+k_1I. \tag{6.10}$$

Here k_1, k_2, C, D, and I are given by Eqs. (4.6), (5.5), (5.9), (5.10), and (6.4), respectively. The quantity $\Delta k_2'$ is the second-order excess coefficient associated with the expansion of ϵ^*/ϵ_1 in powers of ϕ_2. The first-order coefficients of Eqs. (4.1) and (6.9) are identical. Whereas, the contributions to the second-order coefficients in these expansions from the reference system are identical, the excess coefficients of Eqs. (4.1) and (6.9) differ by an amount k_1I.

APPENDIX: CONCENTRIC-SHELL MODEL

In the concentric-shell model, N identical spheres (in three dimensions) or disks (in two dimensions) of radius R are statistically distributed in space subject only to the constraint that each particle possesses an impenetrable core region of radius λR, where λ is any real number such that $0\leqslant\lambda<k$ and k is some bounded integer greater than or equal to one. Using the notation of Sec. II, this means the N-body probability density P must obey the condition

$$P(r^N;\lambda)=0,\quad \text{if } |r_i-r_j|<2R\lambda \tag{A1}$$

for any i and j such that $i\neq j$. For $\lambda<1$, we may think of each sphere (disk) of radius R as being composed of an impenetrable core of radius λR surrounded by a fully penetrable concentric shell of thickness $(1-\lambda)R$. In cases when $\lambda>1$, an impenetrable concentric shell of thickness $(1-\lambda)R$ encompasses the sphere (disk) of radius R. Note that the concentric-shell model is not restricted to conditions of thermal equilibrium. The only constraints imposed on the sphere distribution are those stated explicitly above.

For the concentric-shell model, assuming statistical homogeneity and isotropy, the n-particle probability density for arbitrary λ and reduced η, $\rho(\mathbf{r}^n;\eta,\lambda)$, can be related to the n-particle probability density for totally impenetrable spheres ($\lambda=1$), in the following manner:

$$\rho(\mathbf{r}_{12}/R,...,\mathbf{r}_{1n}/R;\eta,\lambda)=\rho(\mathbf{r}_{12}/\lambda R,...,\mathbf{r}_{1n}/\lambda R;\eta\lambda^3,1). \tag{A2}$$

For $n=2$ and $\lambda<1$, e.g., Eq. (A2) states that the two-particle probability density at the reduced distance r_{12}/R and reduced density η is equal to the two-particle probability density, for a system of totally impenetrable spheres, at the larger reduced distance $r_{12}/\lambda R$ and smaller reduced density

TABLE I. Evaluation of the integral I in the permeable-sphere model [Eq. (6.7)] and the penetrable-concentric-shell model [Eq. (6.8)].

λ	$I_{\rm ps}$	$I_{\rm pcs}$
0.0	0.50	0.50
0.1	0.45	0.496
0.2	0.40	0.475
0.3	0.35	0.428
0.4	0.30	0.355
0.5	0.25	0.266
0.6	0.20	0.173
0.7	0.15	0.091
0.8	0.10	0.033
0.9	0.05	0.005
1.0	0.00	0.000

$\eta\lambda^3$. Clearly, as $\lambda \to 0$, we find that the pair of particles become spatially uncorrelated $[\rho(r_{12}) \to \rho^2]$,i.e., we recover the ρ_2 for the fully-penetrable-sphere model.

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