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SCATTERING THEORY AND EFFECTIVE MEDIUM APPROXIMATIONS TO HETEROGENEOUS MATERIALS

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ABSTRACT

The formal analogy existing between problems studied in the microscopic theory of disordered alloys and problems concerned with the effective (macroscopic) behavior of heterogeneous materials is discussed. Attention is focused on 1) analogous approximations (effective medium approximations) developed for the microscopic problems by scattering theory concepts and techniques, but for the macroscopic problems principally by intuitive means, 2) the link, provided by scattering theory, of the intuitively developed approximations to a well-defined perturbative analysis, 3) the possible presence of conditionally convergent integrals in effective medium approximations.

INTRODUCTION

Many physical phenomena are associated with inhomogeneous medium. For example, a solid state physicist may study the electrical properties of disordered alloys; a geologist, the mechanical properties of polycrystalline rocks. Other scientists may ponder the twinkling of stars or water-seepage through concrete.

Various theoretical approaches to these diverse phenomena generally exhibit two common features. One feature is a statement of physics, usually in the context of a model. This statement may be the equation of motion for a solid continuum, the time independent Schrödinger equation, Helmholtz's equation, etc. These various equations regulate the dynamical variables and have as parameters stochastic variables associated with the inhomogeneous medium. The second common feature is an average of the dynamical variables or their products over the distribution of the stochastic parameters. Even when the statistical information is complete, only an approximation to the averaging, which for some problems is called an effective medium approximation, is generally possible. Most often effective medium approximations are developed by intuitive means.

In solid state physics in the study of disordered alloys, theorists stated the physics of their problem in terms of an integral equation and analyzed this equation by techniques developed in the quantum mechanical theory of scattering. This integral equation is equivalent to a perturbation series (an infinite series), and various effective medium approximations were developed usually by approximating the average of each term in the series and then summing an infinite series of terms. This approach, scattering theory, with infinite order perturbation summation, developed perturbatively several effective medium approximations. Some of

these approximations have direct analogs to approximations developed intuitively for other phenomena.

I will illustrate the application of the scattering theory approach to the computation of the effective dielectric constant of a polycrystal. I will state the problem in the form of an integral equation, recover several well-known intuitive approximations, and indicate, but not demonstrate, the connection of the approximations to perturbation theory. This example and its discussion hopefully clarify the meaning of several commonly used effective medium approximations.

For this same problem, I will indicate the existence of conditionally convergent terms that may appear in an improperly constituted perturbation series. These terms can cause the effective property or approximations to the effective property of the material to depend on the shape of the material. Batchelor¹⁻³ first noticed the possibility of such terms in an analogous problem and suggested a procedure for their removal. His procedure is discussed in light of standard practices in scattering theory.

STATEMENT OF THE PROBLEM

The example under consideration is a polycrystalline material that has a dielectric constant tensor $\underline{\epsilon}(\underline{r})$ which in general changes from grain to grain because of changes in material type, orientation of the grain, or grain size and shape. However, when measured, the material as a whole behaves effectively as a homogeneous medium with a dielectric constant $\underline{\epsilon}^*$. The problem is to calculate $\underline{\epsilon}^*$ from statistical information about $\underline{\epsilon}(\underline{r})$.

For a static problem the physics follows from

$$\nabla \cdot \underline{D} = 0 \quad (1)$$

where $\underline{D}$ is the electric displacement field. Modelling of the medium begins with the constitutive relation

$$\underline{D}(\underline{r}) = \underline{\epsilon}(\underline{r}) \underline{E}(\underline{r}) \quad (2)$$

where $\underline{E}$ is the electric field, and the effective dielectric constant is defined by

$$\langle \underline{D} \rangle = \underline{\epsilon}^* \langle \underline{E} \rangle \quad (3)$$

where the angular brackets denote ensemble averaging.

The problem specified by (1)-(3) is analogous to many other problems. As $\underline{E}$ is a gradient of a potential, replacing $\underline{E}$ by the gradient of temperature and $\underline{D}$ by the heat current re-interprets $\underline{\epsilon}$ as a thermal conductivity. Through similar re-interpretations the problems of effective electrical conductivity, permeability, diffusivity, elastic stiffness, etc. are seen as directly analogous. The problem of effective elastic properties, of course, requires increases in tensorial rank.

It is useful to write $\underline{\epsilon}$ as the sum of two parts

$$\underline{\epsilon} = \underline{\epsilon}^{\circ} + \underline{\delta\epsilon} \quad (4)$$

where $\underline{\epsilon}^{\circ}$ is some arbitrarily, but in general conveniently, chosen spatially invariant (homogeneous) dielectric constant so that all stochastic variations are contained in the perturbation $\underline{\delta\epsilon}$. One can now show the equivalence of (1)-(4) to the integral equation

$$\underline{E} = \underline{E}^{\circ} + \int d\underline{r}' [\underline{\delta\epsilon}(\underline{r}') \underline{E}(\underline{r}') \cdot \underline{\nabla}'] g(\underline{r}, \underline{r}') \quad (5)$$

where g is the Green's function satisfying

$$\underline{\nabla} \cdot \underline{\epsilon}^{\circ} g = \delta(\underline{r} - \underline{r}')$$

and E° satisfies the homogeneous equation

$$\underline{\nabla} \cdot \underline{\epsilon}^{\circ} \underline{E}^{\circ} = 0$$

It is also useful to write the integral equation in several different forms. First, with a standard indicial notation

$$E_i = E_i^{\circ} + \int d\underline{r}' G_{ij} \delta\epsilon_{jk} E_k \quad (6a)$$

where

$$G_{ij} = G_{ji} = g_{i,1} = \phi_{,ij}$$

since g_i is expressible as the gradient of a potential ϕ . Next, in an operator notation

$$\underline{E} = \underline{E}^{\circ} + G \delta\epsilon \underline{E} \quad (6b)$$

where G is an integral operator

$$G_i \rightarrow \int d\underline{r}' G_{ij}(\underline{r}, \underline{r}') f_j(\underline{r}')$$

Equation (6) is a statement of the physics that is identical to (1)-(3).

The integral equation has a formal solution obtained by iteration and represented by the infinite series

$$\underline{E} = \underline{E}^{\circ} + G \delta\epsilon \underline{E}^{\circ} + G \delta\epsilon G \delta\epsilon \underline{E}^{\circ} + \dots$$

Different terms contain the perturbation $\delta\epsilon$ to different "powers". With the definition of T , the T-matrix,

$$T = \delta\epsilon + \delta\epsilon G \delta\epsilon + \delta\epsilon G \delta\epsilon G \delta\epsilon + \dots$$

the following equivalent to (6) is obtained

$$\underline{E} = \underline{E}^{\circ} + G T \underline{E}^{\circ} \quad (7)$$

Now T represents the perturbation series, and a formal summation of

T is obvious

$$T = \delta\epsilon (I - G\delta\epsilon)^{-1}$$

Since the explicit character of $\delta\epsilon$ is yet unspecified, (6) and (7) are general. The specification of $\delta\epsilon$ for a polycrystal assumes the following model:

$$\delta\epsilon(\underline{r}) = \sum_{\alpha} \delta\epsilon^{\alpha} \theta^{\alpha}(\underline{r}) \quad (8)$$

where $\theta^{\alpha}(\underline{r}) = 1$, $\underline{r}$ in grain α
0, otherwise.

The term "grain" is used in the broadest possible sense. For example, the region α could be a pore.

To correspond to the piecewise behavior of $\delta\epsilon$, it is convenient to define a t-matrix associated with grain α

$$t^{\alpha} = \delta\epsilon^{\alpha} \theta^{\alpha} (I - G\delta\epsilon^{\alpha} \theta^{\alpha})^{-1} \quad (9)$$

With this definition T is expressible as

$$T = \sum_{\alpha} t^{\alpha} + \sum_{\alpha} \sum_{\beta \neq \alpha} t^{\alpha} G t^{\beta} + \sum_{\alpha} \sum_{\beta \neq \alpha} \sum_{\gamma \neq \beta} t^{\alpha} G t^{\beta} G t^{\gamma} + \dots \quad (10)$$

Although (10) is equivalent to (7), it shifts the focus of the perturbation series from $\delta\epsilon$ to t^{α} . The significance is that a truncation of (7) after the first term produces a perturbation series of first order in $\delta\epsilon^{\alpha}$, a truncation of (10) after the first term produces a perturbation of infinite order in $\delta\epsilon^{\alpha}$.

t^{α} has a physical meaning: If the deviation from homogeneity is confined solely to one region α , then

$$E = E^{\circ} + G\delta\epsilon^{\alpha} \theta^{\alpha} E$$

which when iterated and summed becomes

$$E = E^{\circ} + G t^{\alpha} E^{\circ}$$

Thus t^{α} is the T-matrix which solves the single inhomogeneity problem. Consequently, the first term in (10) represents contributions from regions α individually embedded in a homogeneous medium ϵ° . The remaining terms, all involving at least two regions, represent the interaction between regions.

THE AVERAGING

To compute ϵ^* , $\langle E \rangle$ and $\langle D \rangle$ are needed. $\langle E \rangle$ is determined directly from (7)

$$\langle E \rangle = E^{\circ} + \langle GT \rangle E^{\circ} \quad (11)$$

but the determination of $\langle D \rangle$ involves several steps. First, since $\epsilon = \epsilon^\circ + \delta\epsilon$,

$$D = \epsilon^\circ E + \delta\epsilon E$$

Next from a comparison of (6) and (7),

$$\delta\epsilon E = TE^\circ$$

Finally,

$$\langle D \rangle = \epsilon^\circ \langle E \rangle + \langle T \rangle E^\circ \quad (12)$$

Thus, (11) and (12) with (3) yield

$$\epsilon^* = \epsilon^\circ + \langle T \rangle (\epsilon^\circ + \langle T \rangle)^{-1} \quad (13)$$

This is an exact equation, independent of the assumed polycrystalline model.

As with most exact equations, exact evaluation is usually impossible. Approximations are needed. In the present case, one sees that approximations to T are especially important, and one possible approximation is to truncate (10) after the first term.

$$T \approx \sum_{\alpha} t^{\alpha} \quad (14)$$

For the standard problem of isotropic $\delta\epsilon^\alpha$ and spherical grains, the above, when used in (13), yields after several algebraic manipulations

$$\frac{\epsilon^* - \epsilon^\circ}{\epsilon^* + 2\epsilon^\circ} = \sum_j v_j \frac{\epsilon^j - \epsilon^\circ}{\epsilon^j + 2\epsilon^\circ} \quad (15)$$

where v_j is the volume fraction of material type j that has a dielectric constant ϵ^j . Often, a polarizability

$$\frac{4\pi\alpha^j}{3} = \frac{\epsilon^j - \epsilon^\circ}{\epsilon^j + 2\epsilon^\circ}$$

is associated with each grain, and (15) is written as

$$\frac{\epsilon^* - \epsilon^\circ}{\epsilon^* + 2\epsilon^\circ} = \frac{4\pi}{3} \sum_j v_j \alpha^j \quad (16)$$

This equation is now of the form of the famous Clausius-Mossotti equation.

It is important to note that (14) is used in (13), not in

$$\epsilon^* = \epsilon^\circ + \langle T \rangle \quad (17)$$

Since t^α solves the problem of a single grain α embedded in ϵ° , (17) is a simple sum of the average contribution of each grain. From elementary electrostatics, when an isotropic dielectric sphere is placed in a uniform electric field E° , the sphere is polarized; t^α is connected with this polarization. Equation (14) sums individual "dipoles" embedded in ϵ° and does not account for the fact that any given dipole sees a medium in which other "dipoles" are present. The factor $(1 + \langle GT \rangle)^{-1}$ in (13) is the Lorentz correction which accounts for the presence and the polarization of other grains by replacing these grains by a uniformly polarized medium. The important point is that in (16) the grain α is embedded not in ϵ° , as in (14), but in a uniformly "polarized" medium. However, interactions between grains are still neglected.

The approximation (14) has been used in many different contexts usually with $\epsilon^\circ = \langle \epsilon \rangle$, for example, in electrical conductivity problems by Maxwell⁴, (frequency dependent) dielectric problems by Maxwell-Garnett^{5,6}, thermal conductivity problem by deVries⁷, and in solid state physics by Elliott and Taylor⁸. For elastic problems, Kröner's⁹ result bears some relation to (17). In solid state physics, (14) is sometimes called the Average T-matrix Approximation (ATA).

A commonly used approximation is a self-consistent effective medium approximation. "Self-consistency" is a term used in different contexts, often incompatibly. In the present context, the self-consistency means the following: T in (13) depends on ϵ° through $\delta\epsilon$ and G . If ϵ° were chosen so that $\langle T \rangle = 0$, then $\epsilon^* = \epsilon^\circ$.

T , let alone $\langle T \rangle$, is not a quantity one expects to evaluate exactly. Self-consistent solutions, however, can be sought for approximations to T . If, for example, one takes

$$T \approx \sum_{\alpha} t^{\alpha} \quad (18a)$$

and requires

$$\langle T \rangle = 0 \quad (18b)$$

then for the standard problem of isotropic $\delta\epsilon^\alpha$ and spherical grains, he finds the following well-known self-consistent effective medium approximation

$$\sum_j v_j \frac{\epsilon^* - \epsilon^j}{\epsilon^* + 2\epsilon^j} = 0 \quad (19)$$

The self-consistency condition is significant. Both the ATA and self-consistent approximation are based on a perturbation series represented by

$$T \approx \sum_{\alpha} t^{\alpha}$$

i.e., the embedding of single grains in a homogeneous medium. Equation (16), however, does not equal (19). The difference is the ATA stops with the above and thereby ignores interactions between grains, while the self-consistent approximation through the additional condition (18b) incorporates interacting grains in an average manner.

The mathematical details of how (18b) incorporates some of the interactions is fully documented elsewhere.^{10,11} Physically, one considers a single grain α in a uniformly polarized medium that represents the presence of the other grains. This polarized medium polarizes α , but the polarization of α changes the polarization of the uniform medium, the change in this polarization changes the polarization of α , etc. until the polarization of α and the uniform medium representing the other grains are consistent on the average.

Self-consistent approximations, as defined in the present context, have been used by various investigators, for example, Bruggerman¹² and Landauer¹³ for electrical media, Hershey¹⁴, Hill¹⁵, and Budiansky¹⁶ for elastic media. In solid state physics this approximation was derived by Taylor¹⁷ and by Soven¹⁸ and is called the (single site) Coherent Potential Approximation (CPA).

REMARKS

From (10) corrections to ϵ^* beyond the ATA are easily seen to be second order in t . Corrections to ϵ^* beyond the CPA are not as obvious, but are known to be fourth order in t , which implies that the ATA is an approximation to the CPA. The important point is that analysis natural to the scattering theory with infinite order perturbation summation approach can connect condition (18) to a well-defined perturbation analysis and identify the next order corrections: The CPA is exact through the third order in t . Since the self-consistency condition is a formal expression of intuitive and physical conditions stated for a variety of related problems, the ad hoc flavor of many self-consistent effective medium approximations is placed on clearly defined theoretical grounds by their relation to an explicit perturbation series that has immediately identifiable corrections.

On physical grounds the approximation,

$$T \approx \sum_{\alpha} t^{\alpha}$$

because it neglects interactions between grains and clustering effects is expected to work for well-separated grains of different species embedded in ϵ^0 . For two-phase systems, this means small concentrations of one species hosted in the other. Because the CPA is also based on this same approximation to T , it too is often regarded as a small concentration approximation. This is not completely correct since comparisons with experiment suggest otherwise. Apparently, for many problems the interactions between grains and such clustering effects as "touching" grains are on the average not as important as one would a priori suppose.

For a two-phase medium the CPA is exact for the low concentration limit for either species. One interpretation of the CPA is that of an interpolation formula between these limits, an interpolation performed according to a specific approximation. The interpretation, of course, is not always useful for problems involving porous materials.

Another important point about the CPA is that it is the best possible approximation using statistical information about single grains, e.g. volume fraction, texture, etc. It is the best possible in the sense that it evaluates every perturbation term that can be evaluated with only single grain distribution functions. Corrections to the CPA require knowledge of two-grain distribution functions. To be precise, the CPA is the best single site approximation in the sense that all single-site diagrams are taken into account.

An interesting, new effective medium approximation, called the self-consistent cumulant approximation (SCA), was recently proposed by Hori and Yonezawa.¹⁹⁻²⁵ When they compared the SCA to the results of a computer experiment on a network of resistors randomly placed on Bravais lattice, they found that near the percolation limit the SCA matched the computed results better than the CPA given in (19). Since clustering phenomena becomes important near the percolation threshold and since the CPA ignores clustering, it would appear that the SCA includes some clustering effects. Indeed, Hori and Yonezawa²² identify these contributions.

The SCA, however, is based on a special model of a heterogeneous material, called the perfectly disordered material. In this model the value of the dielectric constant at $\underline{r}$ is statistically independent of the value at $\underline{r}'$. (In a polycrystal, the values of ϵ at different points within each grain are strongly correlated; hence, a polycrystal does not fit the above definition of a perfectly disordered material.) Additionally, the SCA also based on a infinite summation of a perturbation series that includes various terms in the series more than once. In the jargon of scattering theory, the propagator is not renormalized in a self-consistent fashion so different diagrams are multiply counted. The physical and mathematical basis of the SCA needs further study.

There is more than one way to relate effective medium approximations to perturbation theory. Elliott et al.¹⁰ and Yonezawa and Morigaki¹¹ review these ways for solid state physics problems. In a series of papers¹⁹⁻²⁵ and with a specific approach, Hori and Yonezawa do an extensive analysis of electrical, thermal, and magnetic problems. Gubernatis and Krumhansl^{26,27} discuss the analysis as applied to elastic problems. Other references²⁸⁻⁴⁰ treat a variety of problems both from the intuitive and more formal viewpoints. In some cases comparisons with experiment are given. This list is not close to being definitive.

CONDITIONALLY CONVERGENT INTEGRALS

Several years ago, Batchelor¹⁻³ noted that if one attempts to calculate the effective properties of a heterogeneous material by looking for a solution in terms of an expansion of the volume

fraction v of particles in a "dilute suspension", integrals that are only conditionally convergent can arise. If such integrals are evaluated for a finite volume which is allowed to go to infinity without change of shape, then the limit depends on the shape of the volume chosen.^{41,42} Thus, the appearance of such integrals seemingly makes the effective property dependent on the shape of the sample. In the effective dielectric problem discussed above, conditionally convergent integrals with integrands $O(r^{-3})$ arise from the dipole character of the G_{ij} in (6a),

$$G_{ij} = \frac{1}{4\pi\epsilon^0} \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} \frac{1}{|\underline{r} - \underline{r}'|} \quad (20)$$

(the i^{th} component of an electric field at $\underline{r}$ because of the j^{th} component of dipole placed at $\underline{r}'$ in a medium with dielectric constant ϵ^0). To be properly convergent, the integrand at large r must vary as $r^{-(3+\eta)}$ where $\eta > 0$.

Batchelor suggested a procedure^{1-3,41-3} to circumvent the apparent difficulties to $O(v^2)$. (If v is small, terms $O(v^2)$ exhibit the first order effects of interaction between two particles.) Qualitatively, his procedure is as follows: Subtract from the given conditionally convergent integral another conditionally convergent integral whose integrand has the same asymptotic behavior as the integrand of the integral in question and whose ensemble average is zero. Then the ensemble average of the given integral is unchanged, but the troublesome asymptotic behavior of the integrand is removed. The result is now shape independent.

The source of difficulty is the long-ranged nature of the dipole field. Traditionally, in scattering theory (and many-body theory), long-ranged interactions are replaced by shorter-ranged screened interactions obtained by a partial, but infinite, summation of perturbation series. Possibly, such a renormalization is related to Batchelor's intuitive approach and would be a systematic way to generalize and extend his procedure.

A question of more immediate interest is whether the effective constant defined by (13) is well-defined, i.e. shape independent. I believe it is.

Briefly, relying heavily on results of Yonezawa and coworkers^{11,22}, I reason in the following manner: First, write* $\langle GT \rangle = G\langle T \rangle$, then from (13) define $\epsilon^* \equiv \epsilon^0 + \Sigma$ where

$$\Sigma = \langle T \rangle (I + G\langle T \rangle)^{-1} \quad (21)$$

is analogous to the self-energy that appears in the solid state physics of disordered alloys. One has that

*Although T contains all the statistical information, I prefer, because of G being an integral operator, to write the average of GT as $\langle GT \rangle$ to indicate that the integration GT is averaged and not that the averaged T is integrated. Convention, along with Yonezawa and coworkers, uses $G\langle T \rangle$.

$$\Sigma = \Sigma^{(1)} + \Sigma^{(2)} + \Sigma^{(3)} + \dots \quad (22)$$

where

$$\Sigma^{(1)} = \langle \delta \epsilon \rangle \quad (23a)$$

$$\Sigma^{(2)} = \langle \delta \epsilon G \delta \epsilon \rangle - \langle \delta \epsilon \rangle G \langle \delta \epsilon \rangle \quad (23b)$$

$$\begin{aligned} \Sigma^{(3)} &= \langle \delta \epsilon G \delta \epsilon G \delta \epsilon \rangle - \langle \delta \epsilon G \delta \epsilon \rangle G \langle \delta \epsilon \rangle \\ &\quad - \langle \delta \epsilon \rangle G \langle \delta \epsilon G \delta \epsilon \rangle + \langle \delta \epsilon \rangle G \langle \delta \epsilon \rangle G \langle \delta \epsilon \rangle \end{aligned} \quad (23c)$$

or in terms of cumulants

$$\Sigma^{(1)} = \langle \delta \epsilon \rangle_c \quad (24a)$$

$$\Sigma^{(2)} = \langle \delta \epsilon G \delta \epsilon \rangle_c \quad (24b)$$

$$\begin{aligned} \Sigma^{(3)} &= \langle \delta \epsilon G \delta \epsilon G \delta \epsilon \rangle_c - \langle \delta \epsilon G \delta \epsilon \rangle_c G \langle \delta \epsilon \rangle_c \\ &\quad \vdots \end{aligned} \quad (24c)$$

where $\langle \dots \rangle_c$ denotes the cumulant. Equation (23) is composed of both reducible and irreducible terms where the "irreducible" has the usual meaning: A diagram that cannot be divided into two separate parts just by cutting the propagator (the Green's function) once. (Yonezawa called these proper diagrams.) On the other hand, (24) is composed of only irreducible terms.

Only the reducible diagrams, however, can be conditionally convergent. The integrands of reducible terms are the product of G times a function which may tend to a constant as $r \rightarrow \infty$ leaving an integrand $O(r^{-3})$ and the integral conditionally convergent. This remark is exemplified by (23b): If the $\delta \epsilon$ refer to different grains, $\langle \delta \epsilon G \delta \epsilon \rangle$ is reducible, and the principal contribution to the term is the integration

$$\iint d\underline{r} d\underline{r}' G(\underline{r}, \underline{r}') P_2(\underline{r}, \underline{r}')$$

where $P_2(\underline{r}, \underline{r}')$ is the probability of finding a grain centered at $\underline{r}$ if one is centered at $\underline{r}'$. As $|\underline{r} - \underline{r}'| \rightarrow \infty$, $P_2 \rightarrow \text{constant}$, i.e. the grains become statistically independent, and the integrand is $O(r^{-3})$. If the $\delta \epsilon$ refer to the same grain, $\langle \delta \epsilon G \delta \epsilon \rangle$ is irreducible, and the finite size of the grain eliminates any question of conditional convergence. The second part of (23b), $\langle \delta \epsilon \rangle G \langle \delta \epsilon \rangle$, is also conditionally convergent; the $\delta \epsilon$'s are averaged independently and the integration involves simply the bare G with $\delta \epsilon$.

The two terms in (23b) combine to give (24b) which is irreducible and absolutely convergent. Equation (24b) is proportional to

$$\iint d\underline{r} d\underline{r}' G(\underline{r}, \underline{r}') [P_2(\underline{r}, \underline{r}') - P_1(\underline{r}) P_1(\underline{r}')]]$$

where $P_1(\underline{r}) = v$ is the one-point correlation function. As $|\underline{r} - \underline{r}'| \rightarrow \infty$

$$P_2(\underline{r}, \underline{r}') - P_1(\underline{r})P_1(\underline{r}') \rightarrow 0$$

and the integral is well-behaved since for any physically reasonable specification of P_2 , it now goes to zero at least as fast as $r^{-(3+\eta)}$ where $\eta > 0$. A simple and, in the present context, an important property of cumulants is illustrated: Contributions from statistically independent stochastic variables are not present.

Irreducibility with the non-local character of the Green's function imply another mechanism to produce properly convergent integrals. A general character of irreducibility is convoluted multiple integrals. In individual terms or portions of such terms involving multiple integrations, a given integrand because of the non-locality of G depends on at least one other integration also involving a G . As a result, the entire integration falls off faster than r^{-3} . This is illustrated in the second term in (24c) which is proportional to

$$\iint d\underline{r} d\underline{r}' [P_2(\underline{r}, \underline{r}') - P_1(\underline{r})P_1(\underline{r}')] \int d\underline{r}'' G(\underline{r}, \underline{r}'') G(\underline{r}'', \underline{r}')$$

In light of the above remarks, I believe an examination of the $\Sigma(1)$ to all orders indicates that ϵ^* is well-defined, i.e. shape independent. The key is the ability of $\sum (I + G(T))^{-1}$ to subtract out the conditionally convergent terms in $\langle T \rangle$ on a one-to-one basis. The expansion of Σ in cumulants is a convenient, but not necessary, vehicle to discuss this. If (17) was the basis for defining ϵ^* , which essentially is Batchelor's basis, ϵ^* would be inherently shape dependent and hence ill-defined.

One should note that implicit in the above discussion is the need for caution in approximating (13). The CPA, (18), is directly expressible as a sum of corrected cumulants and thus is expected to be a shape independent approximation.

Admittedly, I have not presented a proof; a proof has been developed by Baker.⁴³ My intention was to be heuristic. The question of improperly convergent terms in the perturbation series has gone unnoticed for nearly eighty years and the existence of these difficulties is still unknown to many interested in the effective behavior of heterogeneous materials. I myself just heard of the difficulties several weeks ago. Hopefully, the problems now have the attention and interest of a wider community.

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referred to papers by D. J. Jeffery and J. R. Willis in the proceedings of that meeting.) In this paper the section on conditionally convergent integrals benefited from a helpful discussion with George A. Baker, Jr.

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