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Dielectric Polarization in Random Media[1]

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The theory of dielectric polarization in random media is systematically formulated in terms of response kernels. The primary response kernel K(12) governs the mean dielectric response at the point $\mathbf{r}_1$ to the external electric field at the point $\mathbf{r}_2$ in an infinite system. The inverse of K(12) is denoted by L(12); it is simpler and more fundamental than K(12) itself. Rigorous expressions are obtained for the effective dielectric constant ϵ^* in terms of L(12) and K(12). The latter expression involves the Onsager–Kirkwood function $(\epsilon^* - \epsilon_0)(2\epsilon^* + \epsilon_0)/\epsilon_0\epsilon^*$ (where ϵ_0 is an arbitrary reference value), and appears to be new to the random medium context. A wide variety of series representations for ϵ^* are generated by means of general perturbation expansions for K(12) and L(12). A discussion is given of certain pitfalls in the theory, most of which are related to the fact that the response kernels are long ranged. It is shown how the dielectric behavior of nonpolar molecular fluids may be treated as a special case of the general theory. The present results for ϵ^* apply equally well to other effective phenomenological coefficients of the same generic type, such as thermal and electrical conductivity, magnetic susceptibility, and diffusion coefficients.

KEY WORDS: Dielectrics; random media; nonpolar fluids; diffusion; conduction; composites.

1. INTRODUCTION

The purpose of this paper is to provide a unified and systematic development of certain aspects of the theory of static dielectric polarization in

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random media. With appropriate reinterpretation of symbols, the development also applies to other phenomena governed by the same differential equations, such as thermal and electrical conduction, diffusion, and magnetization.

In contrast to the statistical-mechanical theory of molecular dielectrics, the statistical theory of dielectric behavior in random continuous media is of relatively recent inception. It appears to have originated with the elegant pioneering work of Brown[1,2] on random two-phase composites. This work was extended to more general random media by Finkel'berg.[3] There has subsequently been a steadily increasing interest in the dielectric (and analogous) properties of random media.[4–17] A substantial part of this work has been restricted to the important special case of two-phase composites or particulate suspensions. Within this restriction, considerable emphasis has been placed on expansions in the number density of particles or inclusions.[7,9–11,15,16] Much effort has also been devoted to establishing rigorous upper and lower bounds on the effective dielectric constant ϵ^* (and analogous parameters) for both composites and more general random media.[2,5,8,11,17] These aspects will not be considered in the present paper. Our attention is primarily focused on the relation of ϵ^* to the statistical correlations that exist in the random medium. The nature and constitution of the random medium are left arbitrary; we simply suppose that the medium exhibits a fluctuating dielectric constant $\epsilon(1)$ which is a random function of position with definite but unspecified statistical characteristics. The results obtained are thus possessed of considerable generality, and may be used as convenient starting points for the treatment of particular cases such as composites or suspensions.

For simplicity, and because it is the most common situation of interest, the random medium is taken to be statistically homogeneous and isotropic. However, the methods employed are not restricted to this case, and the development readily generalizes to anisotropic and/or inhomogeneous media at the cost of some additional complexity.

The theory leads to a variety of different series expansions for ϵ^*. The successive terms in these series contain successively higher-order spatial correlation functions involving $\epsilon(1)$. These series expressions for ϵ^* are considerably more general and flexible than those obtained in earlier work. They are formally rigorous, but their convergence properties are as yet unknown. It is conceivable that in some cases the series may be merely asymptotic.

Our development is based on the systematic use of response kernels, and in this respect it is rather closely analogous to our work on dielectric polarization in fluids composed of polar molecules.[18,19] Other aspects of the development, particularly those concerned with series expansions of the response kernels, have no analogs in the case of polar molecules but are related to the theory of *non*polar molecular dielectrics. Within the random medium context, the earlier work to which our approach is closest in spirit is that of Brown[1,2] and Finkel'berg.[3]

The basic response kernel of the theory is K(12), which determines the mean dielectric response at the point $\mathbf{r}_1$ (defined in terms of a natural generalization of the polarization) to the external electric field at the point $\mathbf{r}_2$ in an infinite system. The inverse of K(12), denoted by L(12), plays a central role in the theory, as it is a simpler and more fundamental quantity than K(12) itself.[18] Rigorous expressions are obtained for the effective dielectric constant ϵ^* in terms of K(12) and L(12). These expressions are formally identical to the corresponding expressions for the dielectric constant of molecular fluids,[18,20,21] except that they involve an arbitrary reference dielectric constant ϵ_0 which is ordinarily not introduced in the molecular case. The expression for ϵ^* in terms of L(12) is the general result corresponding to the series expansion of Brown.[1,2] The expression for ϵ^* in terms of K(12) involves the Onsager–Kirkwood function $(\epsilon^* - \epsilon_0)(2\epsilon^* + \epsilon_0)/\epsilon_0\epsilon^*$, and appears to be new to the random medium context.

The response kernels K(12) and L(12) are long ranged in character; they decay to zero like $|\mathbf{r}_1 - \mathbf{r}_2|^{-3}$ as $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$. This long-range behavior gives rise to certain subtleties and hazards in the theory, and it has not always been properly dealt with in earlier work. The dangers are particularly acute in contexts such as thermal conduction, where everything seems superficially local and one does not ordinarily think of the underlying physics in terms of long-range effects. We have therefore thought it worthwhile to devote a separate section to a discussion of some of the associated pitfalls.

In the literature on random media, it has become customary to refer collectively to the difficulties associated with these long-range effects as the "conditional convergence" problem.[10,15,22–24] This problem typically manifests itself as a dependence of certain integrals in a finite system on the shape of the sample volume. This shape dependence persists even in the infinite-volume limit, so that in such formulations the case of an infinite system becomes ambiguous. Various methods are now known for dealing with these complications,[10,15,22–24] but on the whole they seem needlessly cumbersome. In the present development, such difficulties are entirely circumvented by carefully accounting for all long-range effects from the outset. We are thereby able to formulate the infinite-system problem in a manifestly unambiguous way, so that conditionally convergent expressions never arise in the first place and hence need not be dealt with. The procedural details of our development may therefore be of some interest apart from the results to which they lead here, for they seem likely to be equally applicable and advantageous in other similiar problems, such as the determination of effective elastic constants and viscosities of solid and liquid suspensions.

The response kernels K(12) and L(12) are next expressed as infinite series by means of general perturbation expansions. The terms in these series involve spatial correlation functions of various rational functions of $\epsilon(1)$. A wide variety of different series representations may be generated as special cases of the general expansions. In this way each of the two rigorous expressions for ϵ^* leads to two different two-parameter families of series expansions for ϵ^*. One of the two parameters is the reference dielectric constant ϵ_0 mentioned above; the other parameter is related to the ambiguity in the dipole tensor.[25] These parameters lend a great deal of flexibility to the results, and it is hoped that it may prove possible to choose them in such a way as to accelerate convergence of the series.

The series expansions of the present work are weak-coupling expansions in the sense of Felderhof, Ford, and Cohen.[15] These authors considered the case of a random suspension, for which strong-coupling cluster and density expansions can also be developed. It is not immediately obvious how to formulate analogous strong-coupling expansions for more general random media, where there are no well-defined inclusions and hence no clusters or number density thereof. It should be noted, however, that even in situations where both types of expansions are available, either can converge faster than the other depending on the parameter regime of interest. (For example, in a nonpolar molecular fluid the weak-coupling expansion in powers of polarizability may be expected to converge rapidly even at high density,[26] where a density expansion would converge very slowly if at all.) Thus, although the terminology might suggest otherwise, the two types of expansion are actually complementary.

The question of whether an effective dielectric constant ϵ^* in fact *exists* is of interest, just as is the analogous question for molecular media.[18,26] This question will not be pursued here. Its investigation would require consideration of a finite sample of arbitrary shape, and would proceed along much the same outline as in the molecular problem. Here we forgo such an investigation in favor of the greater flexibility in the expressions for ϵ^* that an infinite sample affords. We merely remark that it is clear in a general way that the existence of ϵ^* will depend essentially on the spatial correlations in $\epsilon(1)$ being short ranged in character.[15,26]

Finally, we note that the dielectric constant of a nonpolar molecular fluid may be treated as a special case of the present development. This specialization is briefly outlined, both as an illustrative application of the general theory and because the nonpolar fluid is of interest in its own right. The flexibility in our expressions for ϵ^* fortunately survives the specialization, and one thereby obtains a somewhat more general class of expressions for the dielectric constant of a nonpolar fluid than have been presented previously. These expressions include as special cases the familiar Kirkwood–Yvon expansion in powers of the molecular polarizability, as well as expansions in density fluctuations of the type considered by Bedeaux and Mazur[(27)] and by Felderhof.[(28)]

2. DIPOLE TENSORS

The dipole tensor $\mathsf{T}(\mathbf{r}) = \boldsymbol{\nabla}\boldsymbol{\nabla}|\mathbf{r}|^{-1}$ (where $\mathbf{r}$ is the position vector) plays an important role in dielectric theory. As is well known, however, $\mathsf{T}(\mathbf{r})$ is not well defined as a factor in an integrand because of the type of singularity it exhibits at $\mathbf{r} = 0$.[(25,29)] This circumstance makes it possible to define a family of dipole tensors which differ only in their behavior at $\mathbf{r} = 0$. The basic member of this family is the dipole tensor with an infinitesimal spherical cutoff,

$$\mathsf{T}_0(\mathbf{r}) = H(|\mathbf{r}| - \sigma)\boldsymbol{\nabla}\boldsymbol{\nabla}|\mathbf{r}|^{-1} \tag{1}$$

where $H(x)$ is unity for $x \geqslant 0$ and zero otherwise, and it is understood that the limit $\sigma \to 0$ is ultimately to be taken. The use of $\mathsf{T}_0(\mathbf{r})$ for $\mathsf{T}(\mathbf{r})$ in an integrand is the three-dimensional analog of taking the Cauchy principal value of the integral. The remainder of the family is defined by

$$\mathsf{T}_\theta(\mathbf{r}) = \mathsf{T}_0(\mathbf{r}) - (4\pi\theta/3)\delta(\mathbf{r})\mathsf{U} \tag{2}$$

where $\delta(\mathbf{r})$ is the Dirac delta function and U is the unit dyadic.

For values of θ in the range $-2 \leqslant \theta \leqslant 1$, $\mathsf{T}_\theta(\mathbf{r})$ can be interpreted in terms of an excluded spheroidal cavity at $\mathbf{r} = 0$ whose ellipticity is determined by θ.[(30)] However, such an interpretation plays no role in our development, and it is preferable simply to define $\mathsf{T}_\theta(\mathbf{r})$ by Eq. (2). The value of θ is then unrestricted.

The following basic relation is frequently useful. If $\mathbf{G}(\mathbf{r})$ is an irrotational vector field (i.e., $\boldsymbol{\nabla}\times\mathbf{G} = 0$) which vanishes at infinity, then

$$\int d(2)\, \mathsf{T}_1(12)\cdot\mathbf{G}(2) = -4\pi\mathbf{G}(1) \tag{3}$$

where the integration extends over all space, and we have adopted the usual shorthand convention of representing $\mathbf{r}_k$ simply by (k). [It is further understood that in a function having only a single $\mathbf{r}$ argument, (jk) represents $(\mathbf{r}_j - \mathbf{r}_k)$.] Equation (3) is easily verified by using the relations[(25)] $\boldsymbol{\nabla}\cdot\mathsf{T}_1(\mathbf{r}) = -4\pi\boldsymbol{\nabla}\delta(\mathbf{r})$ and $\boldsymbol{\nabla}\times\mathsf{T}_1(\mathbf{r}) = 0$ to show that both sides have the same divergence and curl. Since $\mathsf{T}_1(\mathbf{r})$ is itself irrotational, the well-known relation

$$\int d(3)\, \mathsf{T}_1(13)\cdot\mathsf{T}_1(32) = -4\pi\mathsf{T}_1(12) \tag{4}$$

is seen to be a special case of Eq. (3).

The inverse of $\mathsf{T}_\theta(\mathbf{r})$ is denoted by $\mathsf{R}_\theta(\mathbf{r})$, and is defined by

$$\int d(3)\,\mathsf{T}_\theta(13)\cdot\mathsf{R}_\theta(32) = \delta(12)\mathsf{U} \tag{5}$$

Using Eq. (4), one readily verifies that

$$\mathsf{R}_\theta(\mathbf{r}) = -\left(\frac{3}{4\pi}\right)^2 \frac{1}{(\theta-1)(\theta+2)}\,\mathsf{T}_{-1-\theta}(\mathbf{r}) \tag{6}$$

Notice that the inverse does not exist for $\theta = -2$ or $\theta = 1$; $\mathsf{T}_1(\mathbf{r})$ and $\mathsf{T}_{-2}(\mathbf{r})$ are singular.

3. THE RESPONSE KERNELS

We consider an infinite medium whose dielectric constant is a random function of position $\epsilon(1)$. The function $\epsilon(1)$ is taken to be statistically homogeneous and isotropic. The medium is subjected to an external electric field $\mathbf{E}_0(1)$ which is assumed to vary slowly with position on the scale of the random inhomogeneities, and which vanishes at infinity. The latter condition eliminates certain ambiguities that would otherwise arise, as will be discussed in Section 5. This condition is most easily satisfied by requiring the sources of $\mathbf{E}_0(1)$ to be confined to a finite region inside the medium. To prevent this from violating the assumed statistical homogeneity and isotropy, it is necessary to imagine that the sources are ethereal; they coexist with the medium without displacing it. This is an admittedly artificial but perfectly well-defined situation, to which all the usual relations of electrostatics may be applied.

In a particular realization of the random medium, the total electric field $\mathbf{E}(1)$ is determined by

$$\nabla\cdot(\epsilon\mathbf{E}) = \nabla\cdot\mathbf{E}_0 \tag{7}$$

$$\nabla\times\mathbf{E} = 0 \tag{8}$$

Let ϵ_0 be an arbitrary reference value for the dielectric constant, which can be chosen at our convenience, and define $\epsilon'(1)$ by

$$\epsilon(1) = \epsilon_0 + \epsilon'(1) \tag{9}$$

Equation (7) can then be rewritten in the form

$$\nabla\cdot\left(\mathbf{E} - \frac{1}{\epsilon_0}\mathbf{E}_0\right) = -\frac{1}{\epsilon_0}\nabla\cdot(\epsilon'\mathbf{E}) \tag{10}$$

Furthermore, since $\nabla\times\mathbf{E}_0 = 0$ we have that

$$\nabla\times\left(\mathbf{E} - \frac{1}{\epsilon_0}\mathbf{E}_0\right) = 0 \tag{11}$$

We emphasize that ϵ_0 need not be a physically realizable dielectric constant. The value of ϵ_0 is unrestricted; it can even be negative.

Equations (10) and (11) are equivalent to the integral equation

$$\mathbf{E}(1) = \frac{1}{\epsilon_0}\mathbf{E}_0(1) + \frac{1}{4\pi\epsilon_0}\int d(2)\,\mathsf{T}_1(12)\cdot[\epsilon'(2)\mathbf{E}(2)] \tag{12}$$

It is convenient to define a quantity $\mathbf{F}(1)$ by

$$\mathbf{F}(1) = \frac{\epsilon'(1)}{4\pi\epsilon_0}\mathbf{E}(1) = \frac{\epsilon(1)-\epsilon_0}{4\pi\epsilon_0}\mathbf{E}(1) \tag{13}$$

When $\epsilon_0 = 1$, $\mathbf{F}(1)$ simply reduces to the polarization (dipole moment per unit volume) $\mathbf{P}(1)$. For arbitrary ϵ_0, $\mathbf{F}(1)$ still plays a role analogous to the polarization. In particular, Eqs. (12) and (13) combine to give the electric field produced by a given $\mathbf{F}(1)$,

$$\mathbf{E}(1) = \frac{1}{\epsilon_0}\mathbf{E}_0(1) + \int d(2)\,\mathsf{T}_1(12)\cdot\mathbf{F}(2) \tag{14}$$

The relation of $\mathbf{F}(1)$ to $\mathbf{E}_0(1)$ is obtained by eliminating the remaining $\mathbf{E}(1)$ in Eq. (14) by means of Eq. (13). This gives

$$\int d(2)\,\boldsymbol{\lambda}(12)\cdot\mathbf{F}(2) = \frac{1}{\epsilon_0}\mathbf{E}_0(1) \tag{15}$$

where

$$\boldsymbol{\lambda}(12) = \frac{4\pi\epsilon_0}{\epsilon'(1)}\delta(12)\mathsf{U} - \mathsf{T}_1(12) \tag{16}$$

The inverse of $\boldsymbol{\lambda}(12)$ is denoted by $\boldsymbol{\kappa}(12)$, so that Eq. (15) can be inverted to yield

$$\mathbf{F}(1) = \frac{1}{\epsilon_0}\int d(2)\,\boldsymbol{\kappa}(12)\cdot\mathbf{E}_0(2) \tag{17}$$

The above relations apply in any particular realization of the random medium. We now consider the average behavior. The appropriately weighted ensemble average over all possible realizations [i.e., all possible functions $\epsilon(1)$] will be denoted by angular brackets $\langle\cdots\rangle$. The average of Eq. (14) is then

$$\langle\mathbf{E}(1)\rangle = \frac{1}{\epsilon_0}\mathbf{E}_0(1) + \int d(2)\mathsf{T}_1(12)\cdot\langle\mathbf{F}(2)\rangle \tag{18}$$

and the average of Eq. (17) is

$$\langle\mathbf{F}(1)\rangle = \frac{1}{\epsilon_0}\int d(2)\,\mathsf{K}(12)\cdot\mathbf{E}_0(2) \tag{19}$$

where $\mathsf{K}(12) = \langle\boldsymbol{\kappa}(12)\rangle$. The inverse of $\mathsf{K}(12)$ is denoted by $\mathsf{L}(12)$, so that

Eq. (19) can be inverted to yield

$$\int d(2)\,\mathsf{L}(12)\cdot\langle\mathbf{F}(2)\rangle = \frac{1}{\epsilon_0}\,\mathbf{E}_0(1) \tag{20}$$

The relation of $\langle\mathbf{F}(1)\rangle$ to $\langle\mathbf{E}(1)\rangle$ is now obtained by combining Eqs. (18) and (20),

$$\langle\mathbf{E}(1)\rangle = \int d(2)\left[\mathsf{L}(12) + \mathsf{T}_1(12)\right]\cdot\langle\mathbf{F}(2)\rangle \tag{21}$$

The kernels $\boldsymbol{\kappa}(12)$ and $\boldsymbol{\lambda}(12)$ are the random counterparts of the kernels $\mathsf{K}(12)$ and $\mathsf{L}(12)$ that characterize the average response behavior. The average and random response kernels are connected by the relation $\mathsf{K}(12) = \langle\boldsymbol{\kappa}(12)\rangle$. We note that $\mathsf{L}(12) \neq \langle\boldsymbol{\lambda}(12)\rangle$, because $\langle\boldsymbol{\kappa}(13)\cdot\boldsymbol{\lambda}(32)\rangle \neq \langle\boldsymbol{\kappa}(13)\rangle\cdot\langle\boldsymbol{\lambda}(32)\rangle$. We also note that an explicit expression for $\boldsymbol{\lambda}(12)$ in terms of $\epsilon(1)$ is provided by Eq. (16). In contrast, an explicit expression for $\boldsymbol{\kappa}(12)$ is not available; if it were, the theory would be largely trivial. The main complication in the theory is that the random kernel whose average is required is not the simple known kernel $\boldsymbol{\lambda}(12)$, but rather the more complicated kernel $\boldsymbol{\kappa}(12)$ which cannot be expressed in closed form. This is why perturbation expansions are necessary; they enable one to express $\boldsymbol{\kappa}(12)$ in terms of $\epsilon(1)$ as an infinite series so that $\langle\boldsymbol{\kappa}(12)\rangle$ can then be evaluated.

Just as $\boldsymbol{\lambda}(12)$ is simpler in structure than $\boldsymbol{\kappa}(12)$, so $\mathsf{L}(12)$ is a simpler and more fundamental quantity than $\mathsf{K}(12)$. In particular, $\mathsf{L}(12)$ has a universal asymptotic form: it becomes asymptotic to $-\mathsf{T}_1(12)$ [or, if one prefers, the negative of any other $\mathsf{T}_\theta(12)$] at long range (see Appendix). This simple asymptotic behavior is analogous to that of the direct correlation function in a molecular fluid, which also may be interpreted in terms of an inverse response kernel.[31] (The universal asymptotic form of the direct correlation function is simply the negative of the intermolecular pair potential divided by kT.) We remark in passing that the simplicity of $\mathsf{L}(12)$ relative to $\mathsf{K}(12)$ is even more pronounced in a finite system, in which $\mathsf{L}(12)$ remains asymptotic to $-\mathsf{T}_1(12)$ at long range (except in a thin surface layer), whereas $\mathsf{K}(12)$ acquires a complicated shape-dependent behavior. However, we shall not consider finite-system effects here.

We now proceed to relate the effective dielectric constant of the random medium to the response kernels $\mathsf{K}(12)$ and $\mathsf{L}(12)$.

4. THE EFFECTIVE DIELECTRIC CONSTANT

Since $\mathsf{L}(12)$ is asymptotic to $-\mathsf{T}_1(12)$ at long range, we can write

$$\mathsf{L}(12) = \mathsf{L}_0(12) - \mathsf{T}_1(12) \tag{22}$$

where $\mathsf{L}_0(12)$ is a short-ranged kernel. The range of $\mathsf{L}_0(12)$ may be expected to be of the same order of magnitude as the correlation lengths associated with the fluctuations in the random medium. Equation (21) can hence be written as

$$\langle \mathbf{E}(1) \rangle = \int d(2)\, \mathsf{L}_0(12) \cdot \langle \mathbf{F}(2) \rangle \tag{23}$$

We now restrict attention to external fields that vary slowly with position in comparison to the characteristic correlation lengths of the medium. Then it is clear that $\langle \mathbf{E}(1) \rangle$ and $\langle \mathbf{F}(1) \rangle$ will also be slowly varying, so that $\langle \mathbf{F}(2) \rangle$ in Eq. (23) can be evaluated at the point $\mathbf{r}_2 = \mathbf{r}_1$ and taken outside the integral. This yields

$$\langle \mathbf{E}(1) \rangle = \left[\int d(2)\, \mathsf{L}_0(12) \right] \cdot \langle \mathbf{F}(1) \rangle \tag{24}$$

By virtue of the assumed statistical homogeneity and isotropy, $\int d(2)\, \mathsf{L}_0(12)$ must be independent of $\mathbf{r}_1$ and proportional to U. Equation (24) therefore reduces to

$$\langle \mathbf{E}(1) \rangle = \Phi \langle \mathbf{F}(1) \rangle \tag{25}$$

where

$$\Phi = \frac{1}{3} \int d(2)\, \mathsf{U} : \mathsf{L}_0(12) \tag{26}$$

The effective dielectric constant ϵ^* of the random medium may be introduced by the relation $\langle \epsilon(1)\mathbf{E}(1) \rangle = \epsilon^* \langle \mathbf{E}(1) \rangle$, which is equivalent to

$$\langle \mathbf{F}(1) \rangle = \frac{\epsilon^* - \epsilon_0}{4\pi\epsilon_0} \langle \mathbf{E}(1) \rangle \tag{27}$$

Comparing Eqs. (25) and (27), we see that $\Phi = 4\pi\epsilon_0/(\epsilon^* - \epsilon_0)$, which combines with Eq. (26) to yield ϵ^* in terms of $\mathsf{L}_0(12)$. It is desirable, however, to express ϵ^* directly in terms of $\mathsf{L}(12)$. This is easily done using Eq. (22) and the fact[25] that $\mathsf{U} : \mathsf{T}_1(12) = -4\pi\delta(12)$. We thereby obtain

$$\frac{3}{4\pi} \left(\frac{\epsilon^* - \epsilon_0}{\epsilon^* + 2\epsilon_0} \right) = \left[\frac{1}{3} \int d(2)\, \mathsf{U} : \mathsf{L}(12) \right]^{-1} \tag{28}$$

which is our final expression for ϵ^* in terms of the inverse kernel $\mathsf{L}(12)$. When $\epsilon_0 = 1$, Eq. (28) becomes identical in form to an expression previously derived for the dielectric constant of a molecular fluid.[18]

Our next task is to express ϵ^* in terms of $\mathsf{K}(12)$. This may be done by the following procedure.[20] We first combine Eqs. (18) and (27) to obtain

$$\int d(2) \left[\frac{4\pi\epsilon_0}{\epsilon^* - \epsilon_0} \delta(12)\mathsf{U} - \mathsf{T}_1(12) \right] \cdot \langle \mathbf{F}(2) \rangle = \frac{1}{\epsilon_0} \mathbf{E}_0(1) \tag{29}$$

Comparison with Eq. (20) now shows that $\mathsf{L}(12)$ is *macroscopically equiva-*

lent (i.e., equivalent for slowly varying test functions) to the kernel

$$\mathsf{L}_m(12) = \frac{4\pi\epsilon_0}{\epsilon^* - \epsilon_0}\,\delta(12)\mathsf{U} - \mathsf{T}_1(12) \tag{30}$$

Therefore $\mathsf{K}(12)$ will be macroscopically equivalent to the inverse of $\mathsf{L}_m(12)$, call it $\mathsf{K}_m(12)$. Using the results of Section 2, one readily finds that

$$\mathsf{K}_m(12) = \frac{(\epsilon^* - \epsilon_0)(2\epsilon^* + \epsilon_0)}{12\pi\epsilon_0\epsilon^*}\,\delta(12)\mathsf{U} + \frac{\epsilon_0}{\epsilon^*}\left(\frac{\epsilon^* - \epsilon_0}{4\pi\epsilon_0}\right)^2 \mathsf{T}_0(12) \tag{31}$$

It then follows that

$$\int d(2)\,\mathsf{U} : \mathsf{K}_m(12) = \frac{(\epsilon^* - \epsilon_0)(2\epsilon^* + \epsilon_0)}{4\pi\epsilon_0\epsilon^*} \tag{32}$$

where we have made use of the fact[25] that $\mathsf{U} : \mathsf{T}_0(12) = 0$. But since $\mathsf{K}(12)$ is macroscopically equivalent to $\mathsf{K}_m(12)$, we may rewrite Eq. (32) as

$$\frac{(\epsilon^* - \epsilon_0)(2\epsilon^* + \epsilon_0)}{4\pi\epsilon_0\epsilon^*} = \int d(2)\,\mathsf{U} : \mathsf{K}(12) \tag{33}$$

which is our final formula for ϵ^* in terms of $\mathsf{K}(12)$. When $\epsilon_0 = 1$, Eq. (33) becomes identical in form to the well-known Onsager–Kirkwood expression for the dielectric constant of a molecular fluid.[21] In contrast to Eq. (28), which is implicit in the earlier work of Brown,[1,2] Eq. (33) appears to be new to the random medium context.

Equations (28) and (33) are rigorous, but to be useful they require expressions for $\mathsf{K}(12)$ and $\mathsf{L}(12)$ in terms of the correlations that exist in the random medium. We shall pursue the development of series representations for $\mathsf{K}(12)$ and $\mathsf{L}(12)$ below. First, however, we pause in the next section to consider some pitfalls related to the preceding development. Readers not interested in how the development might have gone astray may proceed directly to Section 6 without loss of continuity.

5. PITFALLS

In this section we discuss some of the subtleties and pitfalls with which it is advisable to be familiar before attempting a serious study of the effective parameters of random media. Most of these pitfalls are related, in one way or another, to the long-range nature of the response kernels. They are therefore particularly hazardous in contexts (e.g., heat conduction) where the governing equations are traditionally thought of in purely local terms and the underlying long-range effects receive little or no emphasis. Workers in such areas are often lulled into a false sense of local behavior which can be very dangerous. The danger is aggravated by the fact that in many treatments the response kernels appear only implicitly, in the form of infinite series such as those considered in Section 6 below. One is then liable to be misled by the fact that the first few terms in the most common series for K(12) [see Eq. (56) and the subsequent discussion] are short ranged. This unfortunate circumstance has been a major impediment to the crucial realization that long-range effects are present.

5.1. Ambiguity of the Dipole Tensor

Perhaps the simplest pitfall is the ambiguity in the tensor $\nabla\nabla|\mathbf{r}|^{-1}$, which was discussed in Section 2. Although this issue and its proper treatment are well understood, one still occasionally encounters a development in which $\nabla\nabla|\mathbf{r}|^{-1}$ is treated as well defined with no special comment. In such cases care is needed to determine whether $\nabla\nabla|\mathbf{r}|^{-1}$ is being consistently identified with a single $\mathsf{T}_\theta(\mathbf{r})$, and if so what the value of θ is. The two most common values are $\theta = 1$ and $\theta = 0$. The choice $\theta = 1$ is often implicitly adopted in the course of formally differentiating under the integral sign or integrating by parts, for as a rule it is found that the resulting equations become correct if all factors of $\nabla\nabla|\mathbf{r}|^{-1}$ that thereby arise are interpreted as $\mathsf{T}_1(\mathbf{r})$. On the other hand, authors who are attuned to improper integrals frequently think of such integrals as Cauchy principal values, and they therefore tend to interpret $\nabla\nabla|\mathbf{r}|^{-1}$ as $\mathsf{T}_0(\mathbf{r})$.

5.2. Inversion of Singular Kernels

As was noted in Section 2, the kernels $\mathsf{T}_1(\mathbf{r})$ and $\mathsf{T}_{-2}(\mathbf{r})$ are singular and cannot be inverted. Notice that $\mathsf{T}_{-2}(\mathbf{r}) = \mathsf{T}_1(\mathbf{r}) + 4\pi\delta(\mathbf{r})\mathsf{U}$, so that $\mathsf{T}_{-2}(\mathbf{r})$ can effectively appear even in treatments based upon the use of $\mathsf{T}_1(\mathbf{r})$. And of course any kernel that can be expressed as the convolution of another kernel with $\mathsf{T}_1(\mathbf{r})$ or $\mathsf{T}_{-2}(\mathbf{r})$ will also be singular. The fact that such kernels cannot be inverted is sometimes lost sight of, and the use of the resulting nonexistent inverses can then lead to incorrect or meaningless expressions.(32,33)

5.3. Shape Dependence and Infinite-System Ambiguities

The present development is based upon consideration of an infinite sample. Alternatively, one can formulate the theory for a sample contained in a finite volume V, of some definite convenient shape, subjected to an external field $\mathbf{E}_0(\mathbf{r})$ whose sources lie outside of V. In this way one can derive expressions for ϵ^* in terms of integrals of the finite-system response kernel $\mathsf{K}_V(12)$ over the volume V. For example, consideration of an ellipsoidal sample suspended in vacuum ($\epsilon_0 = 1$) leads to the formula

$$\sum_{k=1}^{3} \frac{\epsilon^* - 1}{1 + (\epsilon^* - 1)D_k} = \frac{4\pi}{V} \int_V d(1)\, d(2)\, \mathsf{U} : \mathsf{K}_V(12) \tag{34}$$

where the D_k are the depolarizing factors for the ellipsoid,[34] which are known functions of the ratios of the principal axes. Such expressions are perfectly valid, provided that a definite sample shape is selected and consistently adhered to throughout the development, but they are of limited utility. The reason is that the integrals therein depend on the shape of V, so that the form of the expression for ϵ^* is different for different sample shapes. These features are clearly evident in Eq. (34), the left member of which depends on the shape of the ellipsoid through the D_k. The integral in the right member must therefore exhibit the same shape dependence to maintain the equality. This situation is entirely analogous to that encountered in the older theories of molecular dielectrics. One might naively hope to eliminate the shape dependence by taking the limit $V \to \infty$, but the shape dependence unfortunately persists in this limit. This means that, in some respects at least, the case of an infinite system is ambiguous. That is, it is not enough to specify that the system is infinite; one must also say what shape the infinite system is. The need to evaluate such shape-dependent expressions in formulations of the type mentioned is a severe obstacle in any attempt to actually compute numerical results from the theory. Just as in the molecular theory,[18] shape-dependent expressions can be avoided by appropriate introduction of the inverse response kernel $\mathsf{L}(12)$. A satisfactory formulation for finite systems then results, and the limit $V \to \infty$ can be uneventfully taken if desired. The resulting expression for ϵ^* is just Eq. (28).

The preceding discussion points up two related pitfalls: (a) A naive formulation for finite systems leads to expressions such as Eq. (34) which depend on the shape of the sample volume V, even in the limit $V \to \infty$; and (b) The case of an infinite system is in some respects ambiguous. Nothing further need be said about (a), but (b) raises the question of how properly to deal with an infinite system in such a way that ambiguous expressions do not arise in the theory. The key to resolving this question is the realization that ambiguous expressions arise only when long-range quantities such as $\mathsf{K}(12)$ are integrated over all space *with no tempering at infinity*. But in the present context, $\mathsf{K}(12)$ is inherently tempered by $\mathbf{E}_0(2)$ [see Eq. (19)], so that ambiguity arises only when $\mathbf{E}_0(\mathbf{r})$ does not vanish as $|\mathbf{r}| \to \infty$, i.e., when $\mathbf{E}_0(\mathbf{r})$ has sources at infinity. Such a situation occurs, in particular, when $\mathbf{E}_0(\mathbf{r})$ is considered to be uniform. Formally, Eq. (19) then becomes

$$\langle \mathbf{F} \rangle = \frac{1}{\epsilon_0} \left[\int d(2)\, \mathsf{K}(12) \right] \cdot \mathbf{E}_0 \tag{35}$$

But this equation is meaningless because the integral in square brackets does not have a unique value. This integral should, of course, be defined as the limit of $\int_V d(2)\,\mathsf{K}(12)$ as $V \to \infty$, but the limit depends on the shape of V and is therefore ambiguous. The shape dependence is a consequence of the fact that $\mathsf{K}(12)$ is long ranged. The integral in square brackets in Eq. (35) is a typical example of the "conditionally convergent" integrals that often arise when sufficient caution is not exercised in the formulation of the theory.

We therefore see that *the situation of an infinite system in a uniform field is inherently ambiguous* and should not be used as a basis for theoretical developments (cf. Felderhof[24]). Thus, contrary to what one might naively have expected, the assumption of a uniform field is not an advantageous simplification but rather a severe and even fatal complication. The ambiguity can also be appreciated from a slightly different point of view. Consider again a dielectric ellipsoid of volume V suspended in a uniform external field $\mathbf{E}_0$. The mean Maxwell field $\langle \mathbf{E} \rangle$ inside the ellipsoid is then also uniform with a value that depends on the shape of the ellipsoid through the depolarizing factors D_k.[34] In the limit $V \to \infty$ one obtains an infinite sample in a uniform field, but if only $\mathbf{E}_0$ is given one does not know $\langle \mathbf{E} \rangle$ (and vice versa). One might hope that $\langle \mathbf{E} \rangle$ could be unambiguously inferred from $\mathbf{E}_0$ via the well-known relation[34]

$$\epsilon^* \langle \mathbf{E}(1) \rangle = \mathbf{E}_0(1) \tag{36}$$

for slowly varying fields in an infinite system. However, this relation is derived under the assumption that the fields vanish at infinity, and it therefore does not apply when they are uniform.

Once the nature of the ambiguity is understood, it becomes clear that all such difficulties are avoided simply by restricting attention to situations in which there are no sources at infinity, so that $\mathbf{E}_0(\mathbf{r}) \to 0$ as $|\mathbf{r}| \to \infty$. (A similar approach has been used for molecular dielectrics by Høye and Stell[35] in their Appendix D.) With this restriction, the case of an infinite system becomes perfectly well defined and one can exploit the convenience it affords. This is the approach taken in the present work. It has the advantage that ambiguous or "conditionally convergent" integrals never arise, so they need not be interpreted or dealt with. It also avoids any considerations of the transition from finite to infinite volume.

Of course, a nonuniform $\mathbf{E}_0(1)$ entails a nonuniform $\langle \mathbf{E}(1) \rangle$, but this presents no problems. It does not violate the assumed statistical homogeneity because this assumption applies only to the material properties of the medium, in particular $\epsilon(1)$, and not to the fields.

5.4. Nonuniqueness of the Response Kernels

A potential source of confusion and error is the fact that the response kernels $\lambda(12)$, $\kappa(12)$, $\mathsf{K}(12)$, and $\mathsf{L}(12)$ are not uniquely determined by the response equations (15), (17), (19), and (20) in which they appear. The origin of this nonuniqueness is Eq. (3), which shows that the long-ranged kernel $\mathsf{T}_l(12)$ has the same effect on an irrotational function as the short-ranged kernel $-4\pi\delta(12)\mathsf{U}$. Since $\mathbf{E}_0(1)$ and $\mathbf{E}(1)$ are irrotational, Eq. (3) can be used to rewrite the response equations in various alternative forms which lead to different identifications of the response kernels. For this purpose it is convenient to use an equivalent form of Eq. (3); namely, if $\mathbf{G}(1)$ is irrotational then

$$\int d(2)\,\mathsf{T}_{-2}(12)\cdot\mathbf{G}(2)=0 \tag{37}$$

Equation (17), for example, can therefore be rewritten as

$$\mathbf{F}(1)=\frac{1}{\epsilon_0}\int d(2)\left[\boldsymbol{\kappa}(12)+\xi\mathsf{T}_{-2}(12)\right]\cdot\mathbf{E}_0(2) \tag{38}$$

where ξ is an arbitrary constant. Thus the validity of Eq. (17) is invariant to the replacement of $\boldsymbol{\kappa}(12)$ by $\boldsymbol{\kappa}(12)+\xi\mathsf{T}_{-2}(12)$. Similarly, the validity of Eq. (15) is invariant to the replacement of $\boldsymbol{\lambda}(12)$ by $\boldsymbol{\lambda}(12)+\xi\mathsf{T}_{-2}(12)/\epsilon'(2)$. One therefore has choices for the response kernels other than those resulting from Eq. (16); i.e., the response kernels are nonunique. However, the response kernels cannot be chosen independently of one another, for $\boldsymbol{\kappa}(12)$ is required to be the unique inverse of $\boldsymbol{\lambda}(12)$, and $\mathsf{L}(12)$ is defined as the unique inverse of $\mathsf{K}(12)=\langle\boldsymbol{\kappa}(12)\rangle$. A definite choice of either $\boldsymbol{\kappa}(12)$ or $\boldsymbol{\lambda}(12)$ therefore uniquely determines the other three kernels as well. It is convenient to regard $\boldsymbol{\lambda}(12)$ as the fundamental response kernel from which the others follow. The nonuniqueness can then be associated with $\boldsymbol{\lambda}(12)$, or more precisely with the fact that there exist different possible identifications of $\boldsymbol{\lambda}(12)$ that preserve the validity of Eq. (15).

It is essential to realize that the different possible choices for $\boldsymbol{\lambda}(12)$ have different asymptotic forms at long range (i.e., different coefficients of T_1). Corresponding differences in the asymptotic behavior of $\boldsymbol{\kappa}(12)$, $\mathsf{K}(12)$, and $\mathsf{L}(12)$ then result. In particular, $\boldsymbol{\lambda}(12)$ and $\mathsf{L}(12)$ are simply asymptotic to $-\mathsf{T}_1(12)$ only for the choice of Eq. (16), upon which the present development is based. It is this simple asymptotic form that favorably distinguishes this particular choice, for the asymptotic forms of $\boldsymbol{\lambda}(12)$ and $\mathsf{L}(12)$ are then independent of the random medium and its statistical properties. Other choices would introduce a dependence on $\epsilon(2)$ into the asymptotic form of $\boldsymbol{\lambda}(12)$, and a corresponding dependence on ϵ^* into the asymptotic form of $\mathsf{L}(12)$.

Because of these differences in asymptotic behavior, the expressions for ϵ^* in terms of $\mathsf{L}(12)$ and $\mathsf{K}(12)$ will also be different in form for different choices of $\boldsymbol{\lambda}(12)$, and only when Eq. (16) is adopted will Eqs. (28) and (33) obtain. That is, *the validity of Eqs.* (28) *and* (33) *for* ϵ^* *depends specifically on* *the particular choice of Eq.* (16) *for the random inverse response kernel* $\lambda(12)$. In the present development, of course, this choice has been clearly made and consistently adhered to, but it is important to realize that other possibilities exist and to be aware of their consequences.

5.5. Incorrect Representations of the External Field

In the present development, the external electric field $\mathbf{E}_0(1)$ serves as the source of the total electric field $\mathbf{E}(1)$. This is reflected, in particular, in the presence of the $\mathbf{E}_0$ term in the fundamental Eq. (12). In contrast, in contexts other than dielectric polarization (such as heat conduction) it has not been customary to explicitly introduce an external source term analogous to $\mathbf{E}_0$. Instead, most workers have in effect regarded the mean field $\langle\mathbf{E}\rangle$ as the source, under the supposition that $\langle\mathbf{E}\rangle$ can be specified at will by proper choice of the boundary conditions. This can indeed be done in a finite sample of volume V, but difficulties arise in the limit $V\to\infty$. One source of trouble is that $\langle\mathbf{E}\rangle$ is commonly taken to be uniform, which gives rise to the problems already discussed in Section 5.3 above. But even if $\langle\mathbf{E}\rangle$ is nonuniform and vanishes at infinity, the problem remains of how to properly introduce it as a source term into the relevant integral equations such as Eq. (12). This is easily done if one starts with a formulation in terms of $\mathbf{E}_0$, for if the fields vary slowly and vanish at infinity (and if ϵ^* in fact exists) then the simple relation (36) obtains. Thus the correct introduction of $\langle\mathbf{E}\rangle$ as a source term consists in the replacement of $\mathbf{E}_0/\epsilon_0$ by $(\epsilon^*/\epsilon_0)\langle\mathbf{E}\rangle$ in any of the equations of the present development. However, in the absence of $\mathbf{E}_0$ it is unclear how to proceed, and as a result many authors have incorrectly introduced $\langle\mathbf{E}\rangle$ into the integral equations of the theory.[4,6,12,13] In particular, it is not uncommon to encounter Eq. (12) with $\mathbf{E}_0/\epsilon_0$ simply replaced by $\langle\mathbf{E}\rangle$, the factor of (ϵ^*/ϵ_0) being erroneously omitted.[6,12,13]

The explicit presence of the external field $\mathbf{E}_0$ is seen to be distinctly advantageous, as it eliminates any uncertainty about the proper form of the source terms in the various integral equations. [Of course, it is eventually necessary to eliminate $\mathbf{E}_0$ in favor of $\langle\mathbf{E}\rangle$, but this is easily done at an appropriate stage in the development, either by the procedure of Section 3 or by use of Eq. (36) as discussed above.] From this point of view, a dielectric formulation of the random medium problem is rather easier to treat correctly than an equivalent formulation in terms of, say, heat conduction, because the external field $\mathbf{E}_0$ is naturally present in the description from the beginning. (A corollary is that in contexts where an external field does not naturally appear, it may be useful to introduce one and then eliminate it later.) Moreover, a dielectric formulation has the further advantage that long-range effects, and the shape dependence to which they give rise in a finite sample, are more familiar and hence less likely to be dealt with incorrectly.

5.6. Improper Manipulations Involving Long-Ranged Kernels

As discussed above, when $\mathbf{E}_0(1)$ varies slowly with position it can be eliminated in favor of $\langle \mathbf{E}(1) \rangle$ by use of Eq. (36). If this is done in Eq. (19), one obtains

$$\langle \mathbf{F}(1) \rangle = \frac{\epsilon^*}{\epsilon_0} \int d(2)\, \mathsf{K}(12) \cdot \langle \mathbf{E}(2) \rangle \tag{39}$$

which is a relation between $\langle \mathbf{F} \rangle$ and $\langle \mathbf{E} \rangle$. One might be tempted to think of it as the statistically derived constitutive relation, from which ϵ^* could be inferred simply by comparison with Eq. (27). Unfortunately, the long-range nature of $\mathsf{K}(12)$ invalidates the simple manipulations upon which this plan depends. It is instructive to consider these manipulations in some detail. We first combine Eqs. (27) and (39) to obtain

$$\frac{\epsilon^* - \epsilon_0}{4\pi\epsilon^*} \langle \mathbf{E}(1) \rangle = \int d(2)\, \mathsf{K}(12) \cdot \langle \mathbf{E}(2) \rangle \tag{40}$$

Therefore $\mathsf{K}(12)$ has a local effect on $\langle \mathbf{E}(2) \rangle$, in spite of the fact that it is long ranged. The reason is that $\mathsf{K}(12)$ is asymptotically proportional to $\mathsf{T}_1(12)$ at long range, and the local behavior then results from Eq. (3). However, an insufficient awareness of the underlying long-range effects might lead one to erroneously conclude from Eq. (40) that $\mathsf{K}(12)$ is a local kernel, and that $\langle \mathbf{E}(2) \rangle$ could therefore be evaluated at the point $\mathbf{r}_2 = \mathbf{r}_1$ and taken outside the integral. One would thereby obtain

$$\frac{\epsilon^* - \epsilon_0}{4\pi\epsilon^*} \langle \mathbf{E}(1) \rangle = \left[\int d(2)\, \mathsf{K}(12) \right] \cdot \langle \mathbf{E}(1) \rangle \tag{41}$$

which of course is meaningless since it contains the same ambiguous integral encountered in Section 5.3. However, if one were unaware of this difficulty he would go on to infer from Eq. (41) that $\int d(2)\, \mathsf{K}(12)$ is proportional to U and hence is equal to $(1/3)[\int d(2)\, \mathsf{U} : \mathsf{K}(12)]\mathsf{U}$. Equation (41) would then reduce to the *incorrect expression*

$$\frac{\epsilon^* - \epsilon_0}{4\pi\epsilon^*} = \frac{1}{3} \int d(2)\, \mathsf{U} : \mathsf{K}(12) \tag{42}$$

which is particularly dangerous because the integral therein is no longer ambiguous. The *correct* expression for ϵ^* in terms of $\mathsf{U} : \mathsf{K}(12)$ is of course Eq. (33). The error arises because the simple manipulations leading to Eq. (42), which would have been perfectly legitimate if $\mathsf{K}(12)$ had been short ranged, are invalid for long-ranged kernels.

The pitfalls discussed above, either singly or more often in various combinations, have given rise to many errors in the literature on random media. It is therefore prudent to approach this literature with a great deal of caution. The presence of error is frequently indicated by the appearance of meaningless expressions, such as $\int d(2)\mathsf{K}(12)$ or the inverse of $\mathsf{T}_1(12)$. Such expressions may appear in a variety of different forms and are not always obvious on casual inspection. Their recognition is complicated by the fact that in many treatments the result for ϵ^* is generated directly in series form. In such cases it may be helpful to compare with the series expansions for $\mathsf{K}(12)$ and $\mathsf{L}(12)$ developed in the next section, of which many of the series in the literature are special cases. Another complication is that the long-range quantity $\mathsf{T}_\theta(12)$, from which most of the difficulties arise, frequently does not appear explicitly in the formulas. However, its presence can often be revealed by use of the identity

$$\int d(2)\,\nabla_1|\mathbf{r}_1-\mathbf{r}_2|^{-1}\nabla_2\cdot\mathbf{f}(2)=\int d(2)\,\mathsf{T}_1(12)\cdot\mathbf{f}(2) \tag{43}$$

where $\nabla_i = \partial/\partial\mathbf{r}_i$. It should also be emphasized that the absence of meaningless expressions in the final results is not necessarily a good omen, as the incorrect Eq. (42) illustrates.

Finally, we note that there has been a growing interest in applying formal operator techniques, of the type used in scattering theory and elsewhere, to the theory of random media.[3,22,36–38] These techniques afford a great deal of convenience, compactness, and elegance, and we shall utilize them to some degree in developing series expansions for $\mathsf{K}(12)$ and $\mathsf{L}(12)$ in the next section. However, a note of caution is in order. By their very compactness, these operator techniques may increase the danger of some of the pitfalls discussed above. In performing the operator algebra manipulations, there is a natural tendency to lose sight of the mathematical character of the kernels which the operators represent. Attention is distracted, in particular, from the fact that some of these operators may be nonunique, singular, or long ranged. [For example, Eq. (40) can be written in an obvious operator notation as $[(\epsilon^*-\epsilon_0)/4\pi\epsilon^*]\langle E\rangle = K\langle E\rangle$, which might lead one to thoughtlessly identify $(\epsilon^*-\epsilon_0)/4\pi\epsilon^*$ with K. This identification is of course impermissible, for it equates an isotropic short-ranged operator to an anisotropic long-ranged one.] A keen awareness of the various pitfalls is therefore especially important in developments based on formal operator techniques.

6. SERIES EXPANSIONS

We now proceed to develop series representations for the kernels $\mathsf{K}(12)$ and $\mathsf{L}(12)$ in terms of spatial correlations in the random field $\epsilon(1)$. The resulting series then immediately provide series expansions for ϵ^* via Eqs.

(28) and (33). The development is facilitated by the introduction of a compact operator notation, so that function arguments, dot products, convolutions, etc. need not be written out explicitly. The operator corresponding to a kernel $\mathsf{A}(12)$ will simply be denoted by A. Operator multiplication corresponds to a combined dot product and convolution. That is, the product AB of two operators A and B is the operator corresponding to $\int d(3)\,\mathsf{A}(13)\cdot\mathsf{B}(32)$. The unit operator corresponds to the kernel $\delta(12)\mathsf{U}$ and is denoted by I. In operator notation, the relation between $\mathsf{K}(12)$ and $\mathsf{L}(12)$ becomes simply $KL = I$, or $L = K^{-1}$. Similarly, the relation between the random kernels $\boldsymbol{\kappa}(12)$ and $\boldsymbol{\lambda}(12)$ is expressed by the operator equation $\kappa\lambda = I$, or $\kappa = \lambda^{-1}$.

The series expansions to be considered here are based on the separations

$$\kappa = \kappa_0 + \kappa' \tag{44}$$

$$\lambda = \lambda_0 + \lambda' \tag{45}$$

where $\kappa_0\lambda_0 = I$, and λ_0 is to be chosen in such a way that $\lambda_0^{-1} = \kappa_0$ can be obtained explicitly in closed form. A major point of interest is that this constraint is remarkably unrestrictive. A wide variety of choices for λ_0 is possible, and this lends a great deal of flexibility to the series expansions for K and L and to the expressions for ϵ^* that result from their use.

The basic series expansion for K is obtained simply by ensemble averaging the series for κ in powers of λ'. The latter is easily generated by expanding the inverse operator in the relation $\kappa = (I + \kappa_0\lambda')^{-1}\kappa_0$. The result is

$$\kappa = \sum_{k=0}^{\infty} (-1)^k (\kappa_0\lambda')^k \kappa_0 \tag{46}$$

from which it follows that

$$K = \sum_{k=0}^{\infty} (-1)^k \langle(\kappa_0\lambda')^k \kappa_0\rangle \tag{47}$$

The series expansions of K to be considered here are all special cases of Eq. (47).

Generation of the corresponding series expansion for L in powers of λ' is less straightforward, because $L \neq \langle\lambda\rangle$. Of course, this expansion can always be obtained by manual term-by-term inversion of Eq. (47), but this is inconvenient and cumbersome. Fortunately a more elegant approach is available, in which the series for L in powers of λ' may be directly generated by the introduction of an appropriate projection operator.[22,37] When λ_0 is nonrandom, this expansion takes the form

$$L = \lambda_0 + \langle(I + \lambda'\kappa_0 P)^{-1}\lambda'\rangle = \langle\lambda\rangle + \sum_{k=1}^{\infty} (-1)^k \langle(\lambda'\kappa_0 P)^k \lambda'\rangle \tag{48}$$

where the projection operator P is defined by

$$Pf = f - \langle f \rangle \tag{49}$$

for an arbitrary random function f. In contrast to a common careless statement, we note that the operator PA is *not* simply equal to $A - \langle A \rangle$, for $PAf = Af - \langle Af \rangle$, and this does not reduce to $(A - \langle A \rangle)f$ for random f. However, it is clear that PA may be *replaced* by $A - \langle A \rangle$ when there is no further randomness to the right of the operator A, and this fact may be used to expand the terms in Eq. (48) by repeated elimination of the rightmost factor of P.

The corresponding expansion when λ_0 is random is unfortunately a bit more cluttered, but it may be derived by a straightforward generalization of the procedure[37] used to obtain Eq. (48). The result is

$$\begin{aligned} L &= L_0 + L_0 \langle \kappa_0 (I + \lambda' Q \kappa_0)^{-1} \lambda' \kappa_0 \rangle L_0 \\ &= L_0 + \sum_{k=0}^{\infty} (-1)^k L_0 \langle \kappa_0 (\lambda' Q \kappa_0)^k \lambda' \kappa_0 \rangle L_0 \end{aligned} \tag{50}$$

where $L_0 = \langle \kappa_0 \rangle^{-1}$, and the projection operator Q is defined by

$$Qf = f - \kappa_0 L_0 \langle f \rangle \tag{51}$$

Again, of course, the operator QA differs from $A - \kappa_0 L_0 \langle A \rangle$, but the former may be *replaced* by the latter when there is no further randomness to the right of the operator A. One readily verifies that Eq. (50) properly reduces to Eq. (48) when λ_0 is nonrandom, for L_0 then reduces to λ_0, adjacent factors of L_0 and κ_0 annihilate each other, Q reduces to P, and P commutes with κ_0.

Equipped with the above general series expansions for K and L, we now proceed to consider different possible choices for λ_0. Additional flexibility is obtained by rewriting Eq. (16) in the equivalent form

$$\lambda(12) = \frac{1}{\chi_\theta(1)} \delta(12)\mathsf{U} - \mathsf{T}_\theta(12) \tag{52}$$

where

$$\chi_\theta(1) = \frac{3}{4\pi} \left(\frac{\epsilon(1) - \epsilon_0}{(1-\theta)\epsilon(1) + (2+\theta)\epsilon_0} \right) \tag{53}$$

and θ is an arbitrary parameter at our disposal.[3] In operator notation, Eq. (46) becomes simply

$$\lambda = \chi_\theta^{-1} - T_\theta \tag{54}$$

[3] The parameter θ was introduced into dielectric theory by Høye and Stell,[35] although they did not explicitly incorporate it into the dipole tensor as we do here.

where χ_θ is the operator corresponding to the kernel $\chi_\theta(1)\delta(12)\mathsf{U}$. We now observe that both terms in Eq. (52) or (54) can separately be inverted explicitly, so that either term can be identified with λ_0. We therefore have a choice of two types of expansions. Each choice actually represents a two-parameter family, since the free parameters ϵ_0 and θ may be selected at our convenience.

The series expansions that result from the choice $\lambda_0 = \chi_\theta^{-1}$ will be referred to as *expansions of the first kind.* With this choice we have $\kappa_0 = \chi_\theta$ and $\lambda' = -T_\theta$, so that Eq. (47) for K becomes

$$K = \sum_{k=0}^{\infty} \langle (\chi_\theta T_\theta)^k \chi_\theta \rangle \tag{55}$$

Conversion of Eq. (55) back into kernel form yields

$$\mathsf{K}(12) = \langle \chi_\theta(1) \rangle \delta(12)\mathsf{U} + \langle \chi_\theta(1)\chi_\theta(2) \rangle \mathsf{T}_\theta(12) + \int d(3) \langle \chi_\theta(1)\chi_\theta(2)\chi_\theta(3) \rangle \mathsf{T}_\theta(13) \cdot \mathsf{T}_\theta(32) + \cdots \tag{56}$$

We remark parenthetically that Eq. (56), with $\theta = 1$, is the expansion for $\mathsf{K}(12)$ that results from the common pedestrian procedure of combining Eqs. (13) and (14), solving the resulting integral equation for $\mathbf{F}(1)$ by iteration, and averaging the result. Substitution of Eq. (56) into Eq. (33) yields an expression for ϵ^* in terms of spatial correlations in the random function $\chi_\theta(1)$. In general $\langle \chi_\theta(1) \rangle \neq 0$, so Eq. (56) is not a true expansion in fluctuations. However, one can choose ϵ_0 and θ so that $\langle \chi_\theta(1) \rangle = 0$ [although this will in general require knowledge of the single-point probability distribution of $\epsilon(1)$], and then one has a true fluctuation expansion. In particular, the choice $\theta = 1$ makes $\chi_\theta(1)$ proportional to $\epsilon(1) - \epsilon_0$, and setting $\epsilon_0 = \langle \epsilon(1) \rangle$ then yields an expansion in correlations of the dielectric constant fluctuations $\epsilon(1) - \langle \epsilon(1) \rangle$. These choices for ϵ_0 and θ have frequently been adopted at the outset in previous work.

Notice that when $\langle \chi_\theta(1) \rangle = 0$, the first three terms in Eq. (56) are short ranged! In the absence of other information, one might erroneously conclude on this basis that $\mathsf{K}(12)$ itself is short ranged, whereupon several of the pitfalls discussed in Section 5 would rapidly befall him. Upon examination, however, the next term in Eq. (56) (which involves four-point correlations) is found to be long ranged even when $\langle \chi_\theta(1) \rangle = 0$.

Although duly noted on numerous other occasions in the literature, it is worthwhile to observe that the two-point correlation function $\langle \chi_\theta(1)\chi_\theta(2) \rangle$ contributes to ϵ^* in only a trivial way that does not involve its full dependence on $|\mathbf{r}_2 - \mathbf{r}_1|$. This follows from the fact that the contribution of the second term in Eq. (56) to the right member of Eq. (33) is simply $-4\pi\theta\langle [\chi(1)]^2 \rangle$, which involves only single-point statistical information. This contribution can even be made to vanish entirely by taking $\theta = 0$.

Setting $\lambda_0 = \chi_\theta^{-1}$ makes λ_0 random, so the expansions of the first kind for L are special cases of Eq. (50). Since $\kappa_0 = \chi_\theta$, $L_0 = \langle \chi_\theta \rangle^{-1} = (1/\beta)I$, where $\beta \equiv \langle \chi_\theta(1) \rangle$ is simply a constant. Equation (50) therefore becomes

$$L = \frac{1}{\beta} I - \frac{1}{\beta^2} \sum_{k=0}^{\infty} \langle \chi_\theta (T_\theta Q \chi_\theta)^k T_\theta \chi_\theta \rangle \tag{57}$$

or, in kernel form,

$$\begin{aligned} \mathsf{L}(12) = {} & \frac{1}{\beta} \delta(12) \mathsf{U} - \frac{1}{\beta^2} \langle \chi_\theta(1) \chi_\theta(2) \rangle \mathsf{T}_\theta(12) \\ & - \frac{1}{\beta^2} \int d(3) \left[\langle \chi_\theta(1) \chi_\theta(2) \chi_\theta(3) \rangle - \frac{1}{\beta} \langle \chi_\theta(1) \chi_\theta(3) \rangle \langle \chi_\theta(3) \chi_\theta(2) \rangle \right] \\ & \times \mathsf{T}_\theta(13) \cdot \mathsf{T}_\theta(32) + \cdots \end{aligned} \tag{58}$$

Substitution of Eq. (58) into Eq. (28) yields a second expression for ϵ^* in terms of spatial correlations of $\chi_\theta(1)$. The quantity β is somewhat analogous to the polarizability in the dielectric theory of nonpolar molecular fluids. Successive terms in Eq. (58) are seen to be of successively higher orders in β, the nth term being of order β^{n-2}. The expression for ϵ^* obtained by combining Eqs. (28) and (58) therefore has somewhat the character of a polarizability expansion. In this connection, it is noteworthy that if $\theta = 0$, the second term in Eq. (58) makes no contribution to Eq. (28). This choice consequently eliminates the term of order β^2 in the expansion of the generalized Clausius–Mossotti function $(3/4\pi)[(\epsilon^* - \epsilon_0)/(\epsilon^* + 2\epsilon_0)]$. The first correction to the term of order β is then the term of order β^3, just as in the corresponding expansion for nonpolar molecules.[26]

Series expansions resulting from the choice $\lambda_0 = -T_\theta$ will be called *expansions of the second kind*. With this choice we have $\lambda' = \chi_\theta^{-1}$ and $\kappa_0 = (3/4\pi)^2[(\theta - 1)(\theta + 2)]^{-1} T_{-1-\theta}$. The choices $\theta = 1$ and $\theta = -2$ are of course not available now. The present λ_0 is nonrandom, so the appropriate expansion for L is Eq. (48). From the above treatment of expansions of the first kind, it should now be clear how to specialize Eqs. (47) and (48) for K and L to the present situation. The details will therefore be omitted. The resulting series for $\mathsf{K}(12)$ and $\mathsf{L}(12)$ involve correlations of the random function $\psi_\theta(1) \equiv 1/\chi_\theta(1)$. Substitution of the series for $\mathsf{K}(12)$ into Eq. (33) yields a series expansion for ϵ^* in terms of these same correlations, and a second such series for ϵ^* is obtained by substituting the series for $\mathsf{L}(12)$ into Eq. (28). If desired, attention may be restricted to fluctuation expansions for ϵ^* by choosing the free parameters ϵ_0 and θ so that $\langle \psi_\theta(1) \rangle = 0$. For a given value of ϵ_0, this requires that

$$\theta = \left\langle \frac{\epsilon(1) + 2\epsilon_0}{\epsilon(1) - \epsilon_0} \right\rangle \tag{59}$$

This condition has the further consequence that $\lambda_0 = \langle\lambda\rangle$, which intuitively seems desirable.

We remark parenthetically that the terms in the series for L possess a cluster property that is lacking in the series for K. Early manifestations of this property are already evident in the contrast between Eqs. (56) and (58). This cluster property is a consequence of the projection operators in the series for L, and it plays a crucial role in determining that L is simply asymptotic to $-T_1$ at long range. These matters will not be discussed here, as they are rather intricate and bear only a peripheral relation to the present development.

In summary, we have constructed two different types of series expansions for the response kernels $\mathsf{K}(12)$ and $\mathsf{L}(12)$, the expansions of the first and second kinds. Each of them can be used in conjunction with the exact Eqs. (28) and (33) for ϵ^*. We thereby obtain four distinct series expansions for ϵ^* in terms of the spatial correlations that characterize the random medium. Each of these four series in fact represents a two-parameter family of similar series, in which the free parameters ϵ_0 and θ may be chosen in any desired manner. These parameters determine the form of the quantities $\chi_\theta(1)$ and $\psi_\theta(1)$ whose spatial correlations appear, and the parameter θ also determines which dipole tensor appears. The formulation as a whole is therefore possessed of considerable generality and flexibility, and encompasses a wide variety of series representations for ϵ^*.

7. NONPOLAR MOLECULES

The preceding development derives considerable generality from the fact that the nature of the random medium has been left arbitrary. In this section we shall briefly illustrate the specialization to a particular random medium of interest, namely, a simple fluid composed of nonpolar molecules. The dielectric behavior of such fluids is of considerable interest in its own right, and it has received much study from the point of view of conventional statistical mechanics.[26–28]

Since the present theory is a continuum theory, it is necessary to represent the molecules as small particles of continuous material surrounded by vacuum. This is perfectly permissible provided that the structure and material properties of the particles are chosen so that they exhibit the same external electrostatic behavior as the molecules. In the simplest model of a nonpolar fluid, the electrostatic behavior of the molecules is completely characterized by an isotropic molecular polarizability α, and this is the molecular model we shall consider. We therefore need only ensure that our particles of continuous material have this same polarizability. This is easily accomplished by letting the particles be uniform spheres of radius R and dielectric constant ϵ_α, where[34]

$$\frac{\epsilon_\alpha - 1}{\epsilon_\alpha + 2} R^3 = \alpha \tag{60}$$

For concreteness, R may be thought of as some suitable measure of the molecular radius, and the value of ϵ_α is then determined as well. However, the formulation will not involve R and ϵ_α separately; only the value of α matters.

The next step is to determine the function $\epsilon(1)$. Clearly $\epsilon(1) = 1 + S(1)(\epsilon_\alpha - 1)$, where $S(1)$ is unity if $\mathbf{r}_1$ lies inside any of the particles and zero otherwise. It follows that

$$\frac{\epsilon(1) - 1}{\epsilon(1) + 2} = \frac{\alpha}{R^3} S(1) \tag{61}$$

We now observe that the integral of $(3/4\pi R^3)S(1)$ over an arbitrary region of space is simply the number of particles in that region. Thus $(3/4\pi R^3)$ $S(1)$ can be identified with the particle number density $\rho(1)$, so that Eq. (61) becomes

$$\frac{3}{4\pi}\left(\frac{\epsilon(1) - 1}{\epsilon(1) + 2}\right) = \alpha\rho(1) \tag{62}$$

This expresses the random function $\epsilon(1)$ in terms of the random function $\rho(1)$, so that correlations involving $\epsilon(1)$ can be expressed in terms of correlations involving the more basic variable $\rho(1)$. The latter are of course simply related to the familiar generic distribution functions.[26,31,34] Equation (62) shows that for spherical particles, the Clausius–Mossotti equation is exact in the random variables. Deviations from this equation are therefore entirely due to the statistical averaging, which may be thought of as effecting a renormalization of the dielectric constant as a function of number density.

Solving Eq. (62) for $\epsilon(1)$, we find

$$\epsilon(1) = \frac{3 + 8\pi\alpha\rho(1)}{3 - 4\pi\alpha\rho(1)} \tag{63}$$

which combines with Eq. (53) to yield

$$\chi_\theta(1) = \frac{3}{4\pi}\left\{\frac{3(1 - \epsilon_0) + 4\pi(2 + \epsilon_0)\alpha\rho(1)}{3\left[(1 - \theta) + (2 + \theta)\epsilon_0\right] + 4\pi\left[2(1 - \theta) - (2 + \theta)\epsilon_0\right]\alpha\rho(1)}\right\} \tag{64}$$

With the use of this expression for $\chi_\theta(1)$, the various series of Section 6 become series expansions for the dielectric constant of a nonpolar fluid in terms of various density correlation functions. An extensive discussion of special cases would be inappropriate here, but it is worthwhile to briefly consider some simple examples of the expansions of the first kind.

We first consider the case $\epsilon_0 = 1$ and $\theta = 0$, in which $\chi_\theta(1)$ reduces simply to $\alpha\rho(1)$. The expansion for ϵ^* obtained by combining Eqs. (28) and (58) then reduces to the well-known Kirkwood–Yvon expansion in powers of α.[26,34] This expansion involves simple density correlations of the form $\langle\rho(1)\rho(2)\ldots\rho(k)\rangle$. An alternative expansion for ϵ^* in terms of the same correlations, but involving the Onsager–Kirkwood function of ϵ^* instead of the Clausius–Mossotti function, is provided by Eqs. (33) and (56). These expansions are not fluctuation expansions because $\langle\rho(1)\rangle \neq 0$.

Expansions in density fluctuations, of the type considered by Bedeaux and Mazur[27] and by Felderhof,[28] may be obtained by requiring ϵ_0 to satisfy the Clausius–Mossotti equation,

$$\frac{3}{4\pi}\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\right) = \alpha\langle\rho(1)\rangle \tag{65}$$

and setting

$$\theta = -2\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\right) = -\frac{8\pi}{3}\alpha\langle\rho(1)\rangle \tag{66}$$

Equation (64) then reduces to

$$\chi_\theta(1) = \frac{9\alpha\left[\rho(1) - \langle\rho(1)\rangle\right]}{(3 + 8\pi\alpha\langle\rho(1)\rangle)(3 - 4\pi\alpha\langle\rho(1)\rangle)} \tag{67}$$

and the expansions of the first kind now become expansions in correlations of the density fluctuations $\rho(1) - \langle\rho(1)\rangle$. The presence of α in the denominator of Eq. (67) means that these expansions are no longer power series in α. The choice of Eqs. (65) and (66) for ϵ_0 and θ has had the effect of *resumming* the polarizability expansions that were obtained by setting $\epsilon_0 = 1$ and $\theta = 0$. The resummation has effectively collected terms in such a way as to bring in the density fluctuations instead of the density itself. The power and convenience of the formulation is illustrated by the fact that this resummation has been very simply accomplished in a purely analytic manner, with no need to consider the detailed structure of the terms in the series.

8. CONCLUDING REMARKS

Let us briefly summarize what has been accomplished. Rigorous general expressions have been established for ϵ^* in terms of the response kernels $\mathsf{K}(12)$ and $\mathsf{L}(12)$ for an infinite system. These expressions have been used in conjunction with perturbation expansions to construct very general and flexible families of series expansions for ϵ^* in terms of statistical correlations in the random medium. Throughout the development, particular attention has been paid to the careful treatment of long-range effects, so that shape-dependent or conditionally convergent expressions do not arise and therefore need not be interpreted or dealt with.

We have not considered the problem of establishing rigorous upper and lower bounds for ϵ^* in terms of the statistical correlations that characterize the medium. It is hoped, however, that the series for ϵ^* developed here may prove useful in future work as a basis for the construction of such bounds.

As already mentioned, the present results also apply to other effective parameters of the same type, such as conductivities and diffusion constants. The procedures by which these results have been obtained, however, are of potentially wider interest, for it seems likely that other classes of effective parameters will be susceptible to entirely similar treatments. Indeed, the conceptual and procedural aspects of our development should carry over, in essentially their present form, to virtually any linear constitutive relation between forcelike and fluxlike vector or tensor fields. (Of course, the actual equations may be somewhat more complicated owing to the presence of additional tensor indices, etc., but this is a mere technical detail.) In this way, the distinctive advantages of the present development, in particular its flexibility and freedom from difficulties with long-range effects, may be realized in many other contexts as well. Two obvious examples, of some current interest, are the effective elastic constants and viscosities of random solid and liquid suspensions.

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APPENDIX. ASYMPTOTIC FORM OF $\mathsf{L}(12)$

The constitutive relation between $\langle \mathbf{F}(1) \rangle$ and $\langle \mathbf{E}(1) \rangle$ must be local in nature for an effective dielectric constant ϵ^* to exist.[18] It might then appear from Eq. (21) that if ϵ^* exists, $\mathsf{L}(12)$ must be asymptotic to $-\mathsf{T}_1(12)$ at long range. Unfortunately, this reasoning is invalidated by Eq. (3), which shows that the long-ranged kernel $\mathsf{T}_1(12)$ has a *local effect* on irrotational functions such as $\langle \mathbf{E}(1) \rangle$. Thus the mere fact that an integral relation involving $\langle \mathbf{E}(1) \rangle$ must *reduce* to a local relation does not imply that the kernel therein is short ranged. Failure to appreciate this point can lead to serious error, as discussed in Section 5.

The fact that $\mathsf{L}(12)$ is asymptotic to $-\mathsf{T}_1(12)$ therefore cannot be inferred from Eq. (21) and the existence of ϵ^* without further justification. The asymptotic behavior of $\mathsf{L}(12)$ could be directly investigated by examining the terms in a series expansion of $\mathsf{L}(12)$ (see Section 6), taking into account the assumed short-ranged nature of the correlations in $\epsilon(1)$. However, such an analysis would be lengthy and intricate, and it is preferable for present purposes simply to adopt a slightly stronger assumption about the constitutive relation between $\langle \mathbf{F}(1) \rangle$ and $\langle \mathbf{E}(1) \rangle$. We shall assume that this relation remains local for transverse as well as longitudinal electric fields, i.e., even when $\mathbf{E}_0$ and $\mathbf{E}$ are no longer required to be irrotational. The development of Section 3 can readily be extended to this more general situation. Since $\mathbf{E}_0$ is an arbitrary external field, its curl can also be arbitrary. However, the curl of $\mathbf{E}$ must be specified to determine a unique solution. This is conveniently done by requiring Eq. (11) to remain valid; the curl of $\mathbf{E}$ is then simply proportional to that of $\mathbf{E}_0$. The retention of Eq. (11) means that Eqs. (12)–(21) continue to apply as before. Now, however, neither $\langle \mathbf{E}(1) \rangle$ nor $\langle \mathbf{F}(1) \rangle$ is irrotational, so Eq. (3) becomes irrelevant to the relation between them. Thus one *can* now infer from Eq. (21) that $\mathsf{L}(12)$ must be asymptotic to $-\mathsf{T}_1(12)$ at long range, for otherwise $\langle \mathbf{E}(1) \rangle$ would bear a nonlocal relation to $\langle \mathbf{F}(1) \rangle$ contrary to assumption.

Physically, the continued existence of a local relation between $\langle \mathbf{F}(1) \rangle$ and $\langle \mathbf{E}(1) \rangle$ for transverse as well as longitudinal electric fields is intuitively very plausible, if not obvious. In effect, it simply means that a local macroscopic constitutive law should hold in the presence of an arbitrary *vector* source function, not merely a scalar one. When $\mathbf{E}_0$ and $\mathbf{E}$ are irrotational, it is really only the scalar function $\nabla \cdot \mathbf{E}_0$ that serves as the source of the vector fields $\mathbf{E}$ and $\mathbf{F}$. One is then in the rather incongruous position of calculating a vector response to what is in effect a scalar stimulus. This incongruity is removed by allowing $\mathbf{E}_0$ and $\mathbf{E}$ to be rotational. However, the usual restriction to irrotational (longitudinal) electric fields has been retained everywhere except in this appendix, as it presents no serious difficulties in the main development. (It does, however, give rise to a potentially confusing nonuniqueness in the response kernels, as discussed in Section 5.4.)

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