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Long-wavelength electromagnetic propagation in heterogeneous media

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Existing effective-medium-type theories for the propagation of long-wavelength electromagnetic radiation in heterogeneous media are examined, and structural effects, neglected by such theories, are introduced by a multiple-scattering approach that yields an effective propagation wave vector. Results are presented for propagation through an infinite periodic array of small spheres immersed in a host of different permittivity (or permeability). The procedure is generalized to aperiodic systems to include the lowest-order corrections for small-sphere volume fill fraction η (for arbitrary scattering strength) and for weak scattering (for arbitrary η). In all cases significant effects due to structure-induced multipole fields are seen to occur. A simple parametrization of deviations from the lowest-order result, the Maxwell-Garnett expression, is proposed in order to extract information on structural multipoles or clustering effects from experimental data. We present the results of calculations for mixtures of real dielectrics and for small metal spheres embedded quasirandomly in a dielectric host, and describe generalizations to include the effects of particle coating and size distributions on optical properties.

I. INTRODUCTION

As Landauer has aptly noted[1] the electromagnetic properties of heterogeneous media have been of interest almost since the beginning of electrodynamics[2-5] as a field of study. Recently this problem has attracted more concentrated experimental attention because of the possible use of heterogeneous materials in the quest for efficient solar energy absorbers. On the theory side, efforts to understand electromagnetic propagation in such systems now go somewhat beyond the historically important quasistatic effective-medium approaches (recapitulated briefly below). In particular, Stroud and Pan[6] have given a finite-wavelength extension of the effective-medium theory, while McPhedran and McKenzie,[7,8] Doyle,[9] and Bergman[10,11] have all examined certain features of periodic systems, but in the infinite-wavelength limit.

An ideal selective surface for solar energy purposes might be fabricated from a material with the physical requirement that it absorbs nearly all of the incoming solar radiation (much of which falls in the visible and ultraviolet), but, in coming to a temperature determined largely by substrate design conditions, would not suffer serious infrared energy loss by reradiation. A promising class of materials for such applications is the cermets, heterogeneous systems typically composed of small (~100 Å) metallic particles embedded in an insulating host.[12,13] That they might well be expected to be good absorbers can be seen by considering an insulating host (frequency-dependent dielectric constant $\epsilon_1(\omega)$ containing just *one* metal sphere [dielectric constant $\epsilon_2(\omega)$]. Elementary analysis[14] of this classical problem in the quasistatic limit shows that large absorption occurs at the sphere dipole resonance ($2\epsilon_1 + \epsilon_2 \simeq 0$), which typically occurs in the visible, and by judicious choice of constituents even at the maximum insolation.

The purpose of this paper is to give a theoretical description of electromagnetic propagation in cermets, or in mixtures of dielectrics with an equivalent geometry. As we shall see, a complete treatment of the problem requires that we go beyond both the effective-medium approximations and the quasistatic restriction (defined below). To achieve this we develop for electromagnetic fields the Green's-function or Korringa, Kohn, and Rostoker (KKR) band-structure procedure,[15,16] particularly in the form given by Morse.[17] For simplicity we consider heterogeneous systems that can be described by the *macroscopic* Maxwell equations and whose components are characterized by dielectric constants ϵ_i and magnetic permitivities μ_i that are local, scalar, complex functions of frequency. (They need not, however, be necessarily the bulk values.) The requisite formalism is developed (mainly in Sec. III) for a two-component system conforming to the *cermet topology*. The importance of topology in a heterogeneous system is discussed in Sec. II, where a brief review of effective-medium theories is given. The Green's-function or multiple-scattering approach is first applied to periodic arrays of identical spherical inclusions in an otherwise uniform host (Sec. III). Aperiodic arrays are discussed in Sec. IV, and in Sec. V we generalize the theory to multicomponent systems and to systems in which the inclusions are dispersed in size.

Before proceeding it is helpful to state at the

outset what we mean by the condition of long wavelength. Let $k_i = (\epsilon_i \mu_i)^{1/2} 2\pi/\lambda$ be the wave vector in each constituent. Let k be the effective wave vector for the composite (defined precisely below). Finally, let a be the radius of the spherical inclusions in the composite, and should any clustering of the inclusions occur, let b be the largest length characterizing such clustering. Then in a two-component composite (1 denotes host, say) we shall encounter the five conditions: $|k_1|a \ll 1$, $|k_2|a \ll 1$, $|k|a \ll 1$, $|k_1|b \ll 1$, and $|k|b \ll 1$, each of them relevant. When the first is satisfied ($|k_1|a \ll 1$) we shall say that we are in the *long-wavelength limit*; if, on the other hand, the system is such that *all* five conditions are met, we shall refer to the situation as the *infinite-wavelength* or *quasistatic limit*. Our generalized KKR procedure will require the long-wavelength (rather than the quasistatic) limit for its validity. Notice that in the periodic case the quantity corresponding to b will be the largest primitive-lattice vector.

Except in the quasistatic limit the electromagnetic properties of a composite cannot be defined by either a single effective $\bar{\epsilon}$ or a single effective $\bar{\mu}$. We shall be concerned instead with the effective product $(\epsilon\mu)_{av} \equiv k^2c^2/\omega^2$, and we shall take the effective wave vector k to be that corresponding to a Bloch wave propagating through the composite. It will become evident that this means diffuse scattering and absorption within the composite will not be physically distinguished.

II. MEAN-FIELD THEORIES

There are at least two interesting topologies for composite materials: one is the "cermet topology" [Fig. 1(a)], in which each inclusion is *completely* surrounded by host material. The other is the aggregate topology [Fig. 1(b)], where in terms of connectedness all components occur on an equal footing. A common example of the aggregate topology is the spatial structure associated with an assembly of microcrystals: a polycrystal.

To understand the importance of the physical differences associated with these basic structures, we briefly recapitulate the arguments for the standard effective-medium approximations.[18] We work in the quasistatic limit, as defined above, and for simplicity we set $\mu_1 = \mu_2 = 1$; magnetic effects will be discussed later. We divide the composite into cells, defined more precisely below, each of which is considered to be embedded in an effective medium of dielectric constant $\bar{\epsilon}$. Since we consider composites to possess macroscopic uniformity and both translational and rotational isotropy, we replace our irregularly shaped cells by spherical *average* cells. The

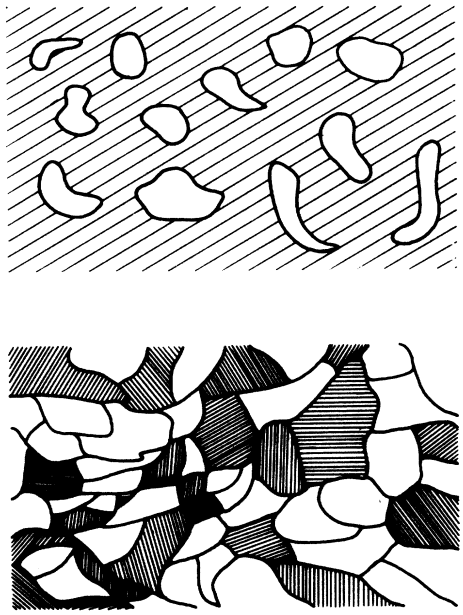

FIG. 1. Topology of two-component composite materials: (a) Cermet topology (isolated inclusions), (b) aggregate topology.

problem then reduces to one of treating, for a uniform field, the quasistatic electromagnetic properties of a spherical inclusion in the effective medium. It is to be solved subject to the requirement that when $\bar{\epsilon}$ is chosen *correctly* the scattering from an average cell shall vanish, i.e., the standard effective-medium ansatz. The procedure is the same for both topologies: The difference that occurs in the result simply reflects the underlying topology and its influence on the nature of the *average cell*.

In the cermet topology the cell is chosen as a spherical inclusion surrounded by a sufficient concentric layer of host so that each such average cell has the proper filling fraction η [η = (volume of inclusions)/(total volume of cermet)]. There *is* only one type of average cell; it can be described as a coated sphere (CS) which, though a composite body, can be approximately characterized (see Appendix A) by a single dielectric constant ϵ_{CS}. The no-scattering condition is then trivially satisfied if we take ($\epsilon_1 \equiv$ host, $\epsilon_2 \equiv$ inclusion, again),

$$\bar{\epsilon} = \epsilon_{CS} = \epsilon_1 \left(\frac{2\epsilon_1 + \epsilon_2 + 2\eta(\epsilon_2 - \epsilon_1)}{2\epsilon_1 + \epsilon_2 - \eta(\epsilon_2 - \epsilon_1)} \right). \tag{1}$$

This is the Maxwell-Garnett[19] result (MG).

For the aggregate topology each inclusion is taken as a cell and for a two-component composite there are two types of average cell now, viz., spheres of each constituent. The no-scattering condition then gives

$$\frac{3(1-\eta)}{2+\epsilon_1/\bar{\epsilon}}+\frac{3\eta}{2+\epsilon_2/\bar{\epsilon}}=1, \tag{2}$$

which is usually referred to as the effective-medium (EM) result.[20]

These two results are really quite different, as can be seen from typical cases. We note that (2), the EM result, is symmetric in the two components while (1), the MG result, is not. This difference is real and to be expected. In terms of the surface charges and field discontinuities established in a cermet, it *should* matter whether islands of medium 1 are completely surrounded by a sea of medium 2 or vice versa. In a polycrystal, in which a given microcrystal may never be completely surrounded by a different constituent, the appellations "host" or "inclusion" are hardly appropriate.

But the MG result has another meaning. For macroscopically uniform and isotropic systems with ϵ_1, ϵ_2 real, it can be shown by variational arguments that the MG result, and its complement resulting from interchange of ϵ_1 and ϵ_2, actually form a pair of bounds[21,22] for $\bar{\epsilon}$, irrespective of the topology of the system. These bounds are in principle achievable and so they serve to define a region of physically realizable $\bar{\epsilon}$, as a function of η, ϵ_1, and ϵ_2.

Although the effective-medium approach disregards information concerning the detailed structure of the cells and their arrangements, we expect qualitative accuracy in the predicted behavior of $\bar{\epsilon}$. This will be verified below for the cermet topology.

III. MULTIPLE-SCATTERING THEORY: PERIODIC SYSTEMS

As noted above, we shall restrict our attention in what follows to the cermet topology. We begin with a system of identical spheres of radius a, embedded as a periodic array in a host medium. For simplicity we shall consider systems with a single sphere in each primitive cell. The starting point for the generalization of the KKR band-structure procedure is the set of Maxwell equations written down *after* appropriate averaging for host and inclusions, which are regarded as macroscopic systems. We shall characterize the composite by specifying the constituent (scalar) dielectric functions ϵ_i and permeabilities μ_i. Thus

$$\epsilon(\omega,\vec{r})=\begin{cases}\epsilon_1(\omega) & (\vec{r}\text{ in the host}) \qquad (3a)\\ \epsilon_2(\omega,|\vec{r}-\vec{R}|) & (\vec{r}\text{ in the }\vec{R}\text{th sphere}),\end{cases} \tag{3b}$$

and similarly for μ. Here $\vec{R}$ locates the *center* of the $\vec{R}$th sphere. If $\epsilon(\vec{r})$ and $\mu(\vec{r})$ are known functions, then the magnetic field $\vec{H}(\vec{r})$ and electric field $\vec{E}(\vec{r})$ satisfy the wave equations

$$\vec{\nabla}\times[\vec{\nabla}\times\vec{H}(\vec{r})]-(\omega/c)^2\epsilon(\vec{r})\mu(\vec{r})\vec{H}(\vec{r}) - \epsilon^{-1}(\vec{r})[\vec{\nabla}\epsilon(\vec{r})]\times[\vec{\nabla}\times\vec{H}(\vec{r})]=0 \tag{4}$$

and

$$\vec{\nabla}\times[\vec{\nabla}\times\vec{E}(\vec{r})]-(\omega/c)^2\mu(\vec{r})\epsilon(\vec{r})\vec{E}(\vec{r}) - \mu^{-1}(\vec{r})[\vec{\nabla}\mu(\vec{r})]\times[\vec{\nabla}\times\vec{E}(\vec{r})]=0. \tag{5}$$

In much of the following development, equations occur in complementary pairs, (4) and (5) being an example. When it is unambiguous we shall present only one member of the complementary pair and shall comment further only if changes [other than reversing the role of $(\vec{H},\mu)$ and $(\vec{E},\epsilon)$] are needed.

Equation (4) [or (5)] can be transformed into an integral for $\vec{H}(\vec{r})$ [or $\vec{E}(\vec{r})$] in a single primitive cell. The procedure is a straightforward generalization of the quantum-mechanical case[23] for the scalar field. If $\vec{r}'$ is restricted to the interstitial (i.e., host) region, then because of the periodicity we may write

$$\vec{H}(\vec{r}')=e^{i\vec{k}\cdot\vec{r}'}H_p(\vec{k},\vec{r}') \tag{6a}$$

$$=-\int_S ds\{[\hat{n}\cdot\vec{\nabla}G_{\vec{k},\kappa}(\vec{r}',\vec{r})]\vec{H}(\vec{r}) - G_{\vec{k},\kappa}(\vec{r}',\vec{r})\hat{n}\cdot\vec{\nabla}\vec{H}(\vec{r})\} \tag{6b}$$

with

$$\kappa=(\epsilon_1\mu_1)^{1/2}\omega/c, \tag{7}$$

and where the surface S consists of the cell boundary and a surface infinitesimally outside the spherical inclusion. We take $\hat{n}$ to be the outward (inward) normal on the cell (sphere) boundary. The Green's function appearing in (6) has the definition

$$G_{\vec{k},\kappa}(\vec{r}',\vec{r})=\frac{1}{4\pi}\sum_{\{\vec{R}\}}\frac{e^{i\kappa|\vec{r}'-\vec{r}-\vec{R}|}}{|\vec{r}'-\vec{r}-\vec{R}|}e^{i\vec{k}\cdot\vec{R}}. \tag{8}$$

The index $\vec{k}$ appearing in (6) and (8) is the Bloch wave vector, to be identified later with the effective propagation wave vector. The quantity $\vec{H}_p$ is periodic:

$$\vec{H}_p(\vec{k},\vec{r}+\vec{R})=\vec{H}_p(\vec{k},\vec{r}). \tag{9}$$

It is important to note that Bloch's theorem [Eq. (6a)] is valid even for dissipative systems. For these, $\vec{k}$ will be complex but the combination $G\vec{H}$ in (6) will be periodic and the integral over the *cell* boundary will vanish. We proceed from (6) by first performing an expansion of $\vec{H}$ in terms of electric and magnetic multipoles,[24]

$$\vec{H}(\vec{r})=\vec{H}_E(\vec{r})-\frac{ic}{\omega\mu}\vec{\nabla}\times\vec{E}_H(\vec{r}), \tag{10}$$

where

$$\vec{H}_E(\vec{r})=\sum_{lm} A^E_{lm} f^E_l(r)\vec{L}Y_{lm}(r) \tag{11}$$

and

$$\vec{L}=-i\vec{r}\times\vec{\nabla}. \tag{12}$$

The Y_{lm}'s are the usual spherical harmonics. (Note that in the equation complementary to (10) the minus is replaced with a plus.) The terms in (11) are referred to as electric multipoles (those of its complement are magnetic). It can be shown[25] that (10) and its complement automatically satisfy two of the Maxwell equations,

$$\vec{\nabla}\cdot\vec{B}=\vec{\nabla}\cdot\vec{D}=0. \tag{13}$$

We ensure that the other two are satisfied by requiring that the expansions satisfy the wave equations (4) and (5). Thus from the equation for $\vec{H}$, we obtain, after some manipulation, a radial equation for $f^E_l(r)$:

$$\left[\frac{\omega^2\epsilon\mu}{c^2}-\frac{l(l+1)}{r^2}-\frac{1}{\epsilon}\frac{d\epsilon}{dr}\left(\frac{d}{dr}+\frac{1}{r}\right)+\frac{1}{r}\frac{d^2}{dr^2}r\right]f^E_l(r)=0, \tag{14}$$

whose solutions for some particularly useful cases are given in Appendix A.

For $r'<r$ the Green's function may itself be expanded[26]:

$$G_{E,\kappa}(\vec{r}',\vec{r})=\sum_{lm;l'm';L} Y_{lm}(\hat{r}')Y^*_{l'm'}(\hat{r})\kappa j_l(\kappa r')$$
$$\times[ih^+_l(\kappa r)\delta_{ll'}\delta_{mm'}+4\pi i^{l-l'}j_{l'}(\kappa r)C(lm;l'm';L,m-m')M_{L,m-m'}(\vec{k},\kappa)], \tag{15}$$

where

$$C(lm;l'm';L,m-m')=\int d\hat{r}\,Y^*_{lm}(\hat{r})Y_{l'm'}(\hat{r})Y_{L,m-m'}(\hat{r}). \tag{16}$$

Structural information then resides in the structure constant M:

$$M_{L,m-m'}(\vec{k},\kappa)=i^{1-L}\sum_{\vec{R}\neq 0} e^{i\vec{k}\cdot\vec{R}}h^+_L(\kappa R)Y^*_{L,m-m'}(\hat{R})+\delta_{L0}\delta_{M0}\frac{i}{\sqrt{4\pi}}, \tag{17}$$

whose evaluation is treated in Appendix B.

Next, we take the expansion of $\vec{H}$ [Eqs. (10) and (11)], insert it into the integral equation (6), multiply the result by $[\vec{L}Y_{lm}(\hat{r}')]^*[l(l+1)]^{-1/2}$, and integrate over the surface of the spherical inclusion. This lengthy but straightforward procedure then generates a set of linear equations in the multipole coefficients A^α_{lm} (here $\alpha=E,H$). To fully describe these equations we need the definitions

(a) $$\Delta g^E_l(a^+)=-\frac{a}{f^E_l(r)}\frac{df^E_l(r)}{dr}\bigg|_{a^+}-g^0_l(a), \tag{18a}$$

where

$$g^0_l(a)=-a\frac{d}{da}j_l(\kappa a)/j_l(\kappa a) \tag{18b}$$

(these are the phase shifts[17]),

(b) $$B^E_{lm}=\left(\frac{l(l+1)}{\epsilon_1}\right)^{1/2}f^E_l(a^+)\Delta g^E_l(a^+)A^E_{lm} \tag{19}$$

(these are the normalized multipole strengths),

(c) $$J(lm;l'm';LM)=[l(l+1)l'(l'+1)]^{-1/2}\int d\hat{r}[\vec{L}Y_{lm}(\hat{r})]^*\cdot[\vec{L}Y_{l'm'}(\hat{r})]Y_{LM}(\hat{r}), \tag{20a}$$

$$T(lm;l'm';LM)=[l(l+1)l'(l'+1)]^{-1/2}\sum_{\tilde{m}\tilde{m}'}\int d\hat{r}[\vec{L}Y_{lm}(\hat{r})]Y^*_{l\tilde{m}}(\hat{r})$$
$$\cdot\int d\hat{r}'Y^*_{l\tilde{m}'}(\hat{r})\hat{r}Y_{l'-1,m'}(\hat{r})C(l\tilde{m};l'-1,\tilde{m}';LM), \tag{20b}$$

(d) $$\chi(l,l')=(l'+\tfrac{1}{2})(l'-l)+\tfrac{1}{2},$$

(e) $$\Theta(\kappa a,l)=\sum_{l'=l\pm1} j_{l'}(\kappa a)\{l(l+1)+\chi(l',l)[g^0_{l'}(a)-1]\},$$

and

$$\Gamma(\kappa a, l) = \sum_{l'=l\pm1} j_{l'}(\kappa a)(l(l+1)[1+g_l^0(a)-g_{l'}^0(a)] + \chi(l', l)\{[g_{l'}^0(a)-1][g_l^0(a)-1]-l(l+1)+(\kappa a)^2\}) .$$

We refer to J and T as selection constants, and their evaluation is given in Appendix C.

With these definitions the system of linear equations can be written

$$\sum_{l'm'\alpha'} \mathcal{K}_{lm;l'm'}^{\alpha\alpha'}(\vec{k}, \kappa) B_{l'm'}^{\alpha'} = 0 \quad (\alpha = E, H) \quad (\alpha' = E, H) \tag{21}$$

where

$$\mathcal{K}_{lm;l'm'}^{E,E}(\vec{k}, \kappa) = \left[\left(\frac{1}{\Delta g_l^E(a^+)} - i\kappa a j_l(\kappa a) h_l^+(\kappa a)\right)\delta_{ll'}\delta_{mm'} - 4\pi i^{l-l'}\kappa a j_l(\kappa a) j_{l'}(\kappa a)\sum_L J(lm; l'm'; L, m-m') M_{L,m-m'}(\vec{k}, \kappa)\right], \tag{22}$$

and

$$\mathcal{K}_{lm;l'm'}^{E,H}(\vec{k}, \kappa) = -4\pi i^l j_l(\kappa a)\sum_L T(lm; l'm'; L, m-m') \times M_{L,m-m'}(\vec{k}, \kappa)[\Theta(\kappa a, l') + \Gamma(\kappa a, l')/\Delta g_l^H(a^+)] . \tag{23}$$

Note that the equation for $\mathcal{K}^{H,E}$, complementary to (23), has the overall minus sign removed.

Equation (21) and the equations leading to it are formidably complex, but as we shall see the small-κa limit, in which we are principally interested, leads to considerable simplification. Observe that all the information on the physical properties of the inclusions is contained in the phase shifts Δg, while information on their location is condensed into the structure constants. Since (21) is a homogeneous equation it possesses solutions only when

$$\det \mathcal{K}(\vec{k}, \kappa) = 0 , \tag{24}$$

where $\kappa = (\epsilon_1\mu_1)^{1/2}\omega/c$ and $\vec{k}$ is the Bloch wave vector. For a prescribed ω the solutions to (21) determine the dispersion relation

$$\vec{k} = \vec{k}(\omega) .$$

Notice, however, that $\vec{k}$ is usually restricted to a single Brillouin zone, i.e., it can only be determined to within a reciprocal-lattice vector. In the band-structure case, a unique labeling of the electron levels is achieved by requiring that $\vec{k}$ be within the first Brillouin zone. In the electrodynamic case we shall also demand that if the wavelength greatly exceeds a lattice constant then $\vec{k}$ will likewise be taken to be in the first Brillouin zone. In general, however, we can assure uniqueness through the requirement

$$\lim_{\epsilon_2 \to \epsilon_1} k = \kappa .$$

With k obtained from the secular relation (and its uniqueness assured) we now define the *effective product* $(\epsilon\mu)_{av}$, a function of k and ω, by

$$(\epsilon\mu)_{av} = k^2(\omega)c^2/\omega^2 . \tag{25}$$

It is worth repeating that for $\omega \neq 0$ the electromagnetic properties of a composite cannot in general be specified by a single $\bar{\epsilon}$ and $\bar{\mu}$. Our choice of $(\epsilon\mu)_{av}$ is that which gives the correct change of phase and amplitude of a Bloch wave across a slab of composite. It is related to a transmission experiment in the forward direction. However, it does not *precisely* describe such an experiment, since we make no attempt to rigorously solve the boundary-value problem for a slab [matching the (composite) Bloch wave to (external) plane waves]. Thus our definition will ignore diffuse scattering at the composite *boundaries*, which appear as absorption in a transmission experiment; it does, however, treat diffuse scattering of the Bloch waves *within* the composite as absorption.

The practicality of the procedure for obtaining $(\epsilon\mu)_{av}$ just described depends on our ability to truncate the matrix $\mathcal{K}$ and yet still obtain reliable results. The question is therefore one of convergence and requires us to examine carefully the behavior of the off-diagonal elements of $\mathcal{K}$. Using the results of Appendices A–C, we find that in almost all cases of interest the single condition $|\kappa|a \lesssim 1$ is, in fact, sufficient to assure reasonable convergence. As might be expected, convergence, in the order of $\mathcal{K}$, is more rapid as both η and $\epsilon_2 - \epsilon_1$ become smaller.

In order to indicate the structure of (22) we specifically truncate at $l=1$. For the sake of simplicity we take $\kappa a \ll 1$, $\vec{k}$ in the z direction, and restrict attention to a cubic system. We then have

$$\mathcal{K}^{E,E}_{1m,1m'} = \delta_{mm'}\left[D_1^E - \delta_{m,\pm1}\left(\tfrac{1}{6}\eta\,\frac{k^2+2\kappa^2}{k^2-\kappa^2} - \frac{1-\eta}{2}\,\delta P^{(1)}\right) + \delta_{m,0}\left(\tfrac{1}{3}\eta - (1-\eta)\delta P^{(1)}\right)\right], \tag{26}$$

where

$$D_l^E = \frac{1}{\Delta g_l^E(a^*)} - \frac{1}{2l+1} \tag{27}$$

and

$$\delta P^{(1)} = \frac{i}{1-\eta}\left(\frac{4\pi}{5}\right)^{1/2} \kappa a\, j_1^2(\kappa a) \times\left(\sum_{\vec{R}\neq 0} - \rho\int d\vec{R}\right)\left[e^{i\vec{k}\cdot\vec{R}} h_2^*(\kappa R) Y_{20}(\hat{R})\right]. \tag{28}$$

Here ρ is the number density of inclusions, and the sum is taken over lattice vectors. In addition

$$\mathcal{K}^{E,H}_{1m,1m'} = -\mathcal{K}^{H,E}_{1m,1m'} = \delta_{mm'}\frac{i\eta m}{2}\,\frac{k\kappa}{k^2-\kappa^2}\,. \tag{29}$$

It follows that the 6×6 block of equations for $l=1$ decouples (in m) to give 3 blocks of 2×2. The $m=0$ (longitudinal) block is diagonal and gives ($\alpha = E, H$),

$$D_1^\alpha - (1-\eta)\delta P^{(1)} + \tfrac{1}{3}\eta = 0, \tag{30}$$

which has solutions only for certain small ranges of ω since for small kb and κb (b is the lattice constant) the k dependence of $\delta P^{(1)}$ is weak [in fact $\delta P^{(1)} \sim (kb)^2$]. This solution corresponds physically to a shifted surface-plasmon type of excitation. The transverse blocks ($m=\pm1$) give us

$$\begin{pmatrix} \bar{D}_1^E - \frac{1}{6}\eta\,\frac{\xi+2}{\xi-1} & -\frac{i\eta m}{2}\,\frac{\sqrt{\xi}}{\xi-1} \\ \frac{i\eta m}{2}\,\frac{\sqrt{\xi}}{\xi-1} & \bar{D}_1^H - \frac{1}{6}\eta\,\frac{\xi+2}{\xi-1} \end{pmatrix}\begin{pmatrix} B^E_{1,m} \\ B^H_{1,m} \end{pmatrix} = 0\,. \tag{31}$$

Here,

$$\xi = (k/\kappa)^2 = (\epsilon\mu)_{av}/\epsilon_1\mu_1\,,$$

and

$$\bar{D}_1^\alpha = D_1^\alpha + \tfrac{1}{2}(1-\eta)\delta P^{(1)}\,. \tag{32}$$

This equation has two solutions, one of which ($\xi = 1$) is unphysical. The physical solution is

$$(\epsilon\mu)_{av} = \epsilon_1\left(\frac{\bar{D}_1^E + \frac{1}{3}\eta}{\bar{D}_1^E - \frac{1}{6}\eta}\right)\mu_1\left(\frac{\bar{D}_1^H + \frac{1}{3}\eta}{\bar{D}_1^H - \frac{1}{6}\eta}\right), \tag{33}$$

and we see from this that we arrive at a product of an effective $\bar{\epsilon}$ and an effective $\bar{\mu}$. In the small-k_2a limit we have

$$\bar{\epsilon} = \epsilon_1\,\frac{\epsilon_1 + [P^E(1-\eta)+\eta](\epsilon_2-\epsilon_1)}{\epsilon_1 + P^E(1-\eta)(\epsilon_2-\epsilon_1)}\,, \tag{34}$$

where

$$P^E = \tfrac{1}{3} + \delta P^{(1)}\,.$$

This form of $\bar{\epsilon}$ is exactly that arising from the mean-field arguments of Sec. I as applied to oriented *ellipsoids* with depolarizing factor P^E. Notice also that in the quasistatic limit $\delta P^{(1)}$ vanishes, so that (31) becomes

$$(\epsilon\mu)_{av} = \epsilon_{MG}\mu_{MG}\,, \tag{35}$$

i.e., the product of the Maxwell-Garnett results.[27]

It is important to note that for small η the small ka and small κa limits differ greatly from the small kb and small κb conditions. In dilute systems this means that the effects of $\delta P^{(1)}$ can remain relatively important even when ka and κa are assumed to be small.

Several features of the solutions obtained above are more general than the derivation given would indicate. The unphysical root $\xi = 1$ will occur, as we shall see, for all structures, both periodic and aperiodic. The uncoupling in m is, however, not a general feature and certainly does not occur in structures of lower symmetry. Otherwise, we shall frequently encounter situations in which the solutions will be very much the *form* of (33) and (34). We can see this first for the case of higher l values.

To include higher l we can use (21) directly or reduce the $l>1$ problem to an effective $l=1$ problem by the device of matrix folding. To do this, note that the equations

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix}\begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0\,, \tag{36}$$

where M_{ij} are matrices, can be replaced by

$$(M_{11} - M_{12}M_{22}^{-1}M_{21})v_1 = 0\,. \tag{37}$$

In a cubic system with k in the z direction we find that for small κa the folding correction is diagonal in all indices and furthermore the $m=\pm1$ terms are equal. It follows that the solutions for ξ must continue to have the *form* of (31) but with

$$\bar{D}_l^\alpha = D_l^\alpha + \tfrac{1}{2}(1-\eta)(\delta P^{(1)} + \delta P_\alpha^{(2)})\,, \tag{38}$$

where

$$\delta P_\alpha^{(2)} = \frac{-2}{1-\eta}\sum_{\substack{m,m'\\ \alpha',\alpha''}}\sum_{l,l'>1}\mathcal{K}^{\alpha;\alpha'}_{11;lm}(\mathcal{K}'-1)^{\alpha',\alpha''}_{lm;l'm'}\mathcal{K}^{\alpha''\alpha}_{l'm';11}\,. \tag{39}$$

Here $\mathcal{K}'$ is $\mathcal{K}$ with rows and columns with $l=1$ deleted. In the quasistatic limit $\delta P^{(2)}$ remains finite even though $\delta P^{(1)}$ vanishes. Thus in this limit the result for $\bar{\epsilon}$ (or $\bar{\mu}$) is of the form (32) but with

$$P^{\alpha}=\tfrac{1}{3}+\delta P_{\alpha}^{(2)}. \tag{40}$$

That $\delta P_{\alpha}^{(2)}$ is finite emerges as a consequence of the physical fact that a given inclusion can induce various multipoles ($l>1$) in its neighbors in a manner specifically dependent on their mutual arrangement. Such effects may be termed "structural multipoles" and are not included in the simple mean-field approach of Sec. II. They are nevertheless important in the condensed systems we are treating, even in the quasistatic limit. From their appearance, formulas of the type (33) and (34) bear a certain similarity to the Maxwell-Garnett result except for the alterations in the effective depolarizing factor stemming from the induced multipoles. Henceforth we shall refer to formulas of the type (33) and (34) as multipole-modified Maxwell-Garnett results (MMMG). In periodic systems with lower than cubic symmetry a few differences should be noted. First, $\delta P^{(1)}$ can be finite in the quasistatic limit. Second, for a given propagation direction there can be different values of $(\epsilon\mu)_{\rm av}$ corresponding to different polarizations. Finally, there are at least three directions (along the principal axes) for which

$$(\epsilon\mu)_{\rm av}=\bar{\epsilon}_{\rm MMMG}\bar{\mu}_{\rm MMMG}. \tag{41}$$

It may be helpful at this point to give an example. We consider a simple cubic lattice in a system for which $\kappa b\ll 1$ and $kb\ll 1$. From Appendix B we find, in this limit

$$\mathcal{K}^{E,E}_{lm;l'm'}=(-1)4\pi J(lm;l'm';l+l',m-m')a^{l+l'-1}\frac{[2(l+l')-1]!!}{(2l+1)!!\,(2l'+1)!!}$$

$$\times\sum_{R\neq 0}Y^{*}_{l+l',m-m'}(\hat{R})/R^{l+l'+1}+\delta_{ll'}\delta_{mm'}D_l, \quad (l \text{ or } l'>1). \tag{42}$$

As a consequence of the cubic symmetry the sum is nonzero only for $l+l'$ even and for m an integral multiple of 4. (In contrast to the procedure used by McPhedran and McKenzie[8] *no* sums involving shifted origins are involved here.) Using these properties we arrive at a much simplified form of (39), namely

$$\delta P_{\alpha}^{(2)}=\frac{2}{1-\eta}\sum_{\substack{l,l' \text{ odd};\\ m,m'=1+4\,(\text{integer})}}\mathcal{K}^{\alpha\alpha}_{11;lm}(\mathcal{K}''-1)^{\alpha\alpha}_{lm;l'm'}\mathcal{K}^{\alpha\alpha}_{l'm';11}, \tag{43}$$

where $\mathcal{K}''$ means that only elements with l, l' odd and $m, m'=1+4$ (integer) are to be included. For our example we retain only the lowest order nonvanishing corrections, i.e., $l=3$. After some manipulation we have

$$\delta P_{\alpha}^{(2)}=\frac{32(3\eta/4\pi)^{10/3}U_4^2}{(1-\eta)[(3/28)(D_3^{\alpha})^{-1}-20(3\eta/4\pi)^{7/3}U_6^2]}, \tag{44}$$

where

$$U_l=\sum_{R\neq 0}P_l(z/R)(b/R)^{l+1}. \tag{45}$$

For a simple cubic lattice (using the numerical values of the sums U_l given by McPhedran and McKenzie[8]) this becomes

$$\delta P_{\alpha}^{(2)}=\frac{24.351\eta^{10/3}}{(1-\eta)[(D_3^{\alpha})^{-1}-0.1364\eta^{7/3}]}. \tag{46}$$

This is precisely the result of McPhedran and McKenzie in the limit $k_2a\ll 1$ when b_1 and all c's are taken to be zero.

Figure 2 now shows results for the quasistatic case and the choices $\epsilon_1=1$, $\epsilon_2=8$ (and vice versa), and $\mu_1=\mu_2=1$. Plotted there as a function of filling fractions are effective dielectric constants for (a) Maxwell-Garnett (MG), (b) the formula of McPhedran and McKenzie[8] (SC) for the simple-cubic case, and (c) the aperiodic MMMG (weak scattering) case discussed below. Note that the simple cubic result stays within the Maxwell-Garnett results as required by the Hashin-Shtrikman bounds. Note also that the simple cubic results terminate at a maximum filling fraction of $\pi/6$, the simple cubic close-packing limit. In Fig. 3 we show MG, sc, and aperiodic MMMG (small η) results for the absorption coefficient. These are plotted for a model representation of (20%) fine gold particles in KBr ($\epsilon_1=2.34$). The gold itself is represented by a Drude model. The significant aspects of the results are the sharp dips in the sc curve which occur whenever $D_l^E\sim 0$ or, quasistatically,

$$\frac{\epsilon_2(\omega)-\epsilon_1}{(l+1)\epsilon_1+l\epsilon_2(\omega)}\sim 0 \quad (l>1). \tag{47}$$

These are referred to as the multipole resonances,

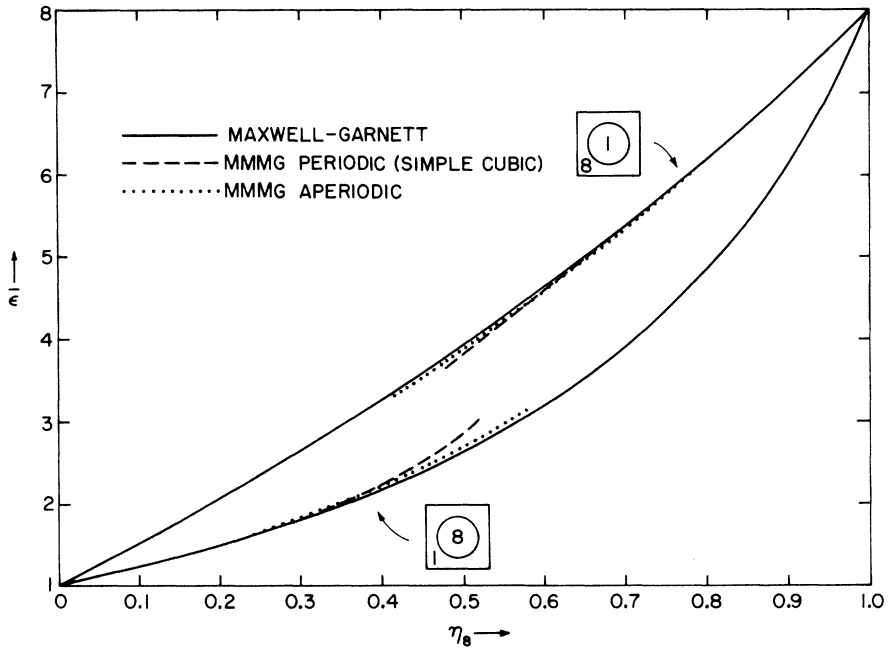

FIG. 2. Hashin-Shtrikman bounds (Maxwell-Garnett result) and multipole-modified Maxwell-Garnett (MMMG) curves for the effective dielectric constant in periodic (simple cubic) and aperiodic arrangements of small dielectric spheres ($\epsilon_2 = 8$ or 1) in a dielectric host ($\epsilon_1 = 1$ or 8). Here η_8 is the volume fraction of the $\epsilon = 8$ component.

and can be considered as the higher "excited states" of the free spherical inclusion. From the structure of (44) it is apparent that $\delta P_\alpha^{(2)}$ is the ratio of two polynomials each of degree l in D_l (for even l) and this guarantees such resonant behavior. (Actually there can be some cancellation of common factors in the polynomials, but the resonances persist.) For periodic systems that

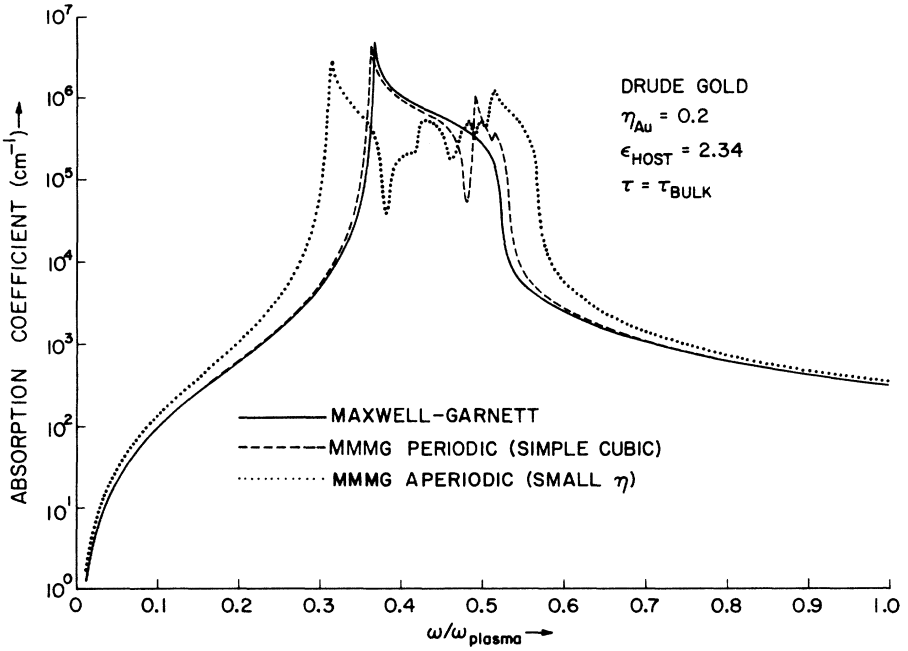

FIG. 3. Maxwell-Garnett, MMMG (periodic) and MMMG (aperiodic) results for absorption coefficient of a dispersion of small Drude Au spheres in KBr ($\epsilon_1 \cong 2.34$) with a metal volume filling fraction of 20%; the Drude relaxation time equals the bulk Au value.

lack inversion symmetry (for which a basis is necessary) even-l resonances will occur. This gives a clear indication of the necessity to go beyond the MG result for cermets. Finally, it should be noted that the results derived for periodic systems by quasistatic methods can easily be generalized to lift the restriction $k_2 a \ll 1$ (which in fact is readily violated for metallic inclusions). It is only necessary to replace

$$\frac{(l+1)\epsilon_1 + l\epsilon_2}{(l+1)(2l+1)(\epsilon_2 - \epsilon_1)}$$

by D_l^E (and similarly for D_l^H) and to use the product rule (35). In this way the quasistatic results can be generalized to include magnetic multipoles (eddy currents), which can certainly be important.[6]

IV. APERIODIC SYSTEMS

In this section we return to the system of identical spherical inclusions but relax the restriction that they be arranged periodically. To the extent that the fine metallic particles in a cermet can be considered as monodispersed in size, this situation begins to approach physical reality. For a bulk system (N' inclusions, where N' is very large) we may take a macroscopic cubic fragment of the material and extend it periodically with no significant changes expected in its electromagnetic properties. The aperiodic system may therefore be replaced by a periodic system with a large basis. Correspondingly, there is a quasicontinuous distribution of reciprocal-lattice vectors.

For a lattice with a basis, we may proceed as in Sec. III until we reach equation (6), the basic integral equation, whose *form* is unchanged except that the Green's function is modified to read

$$G_{\vec{k},\kappa}(\vec{r}', \vec{r}) = \frac{1}{4\pi} \sum_{ij\rho} \frac{e^{i\kappa|(\vec{r}'-\vec{R}_i)-(\vec{r}-\vec{R}_j)-\vec{R}_\rho|}}{|(\vec{r}'-\vec{R}_i)-(\vec{r}-\vec{R}_j)-\vec{R}_\rho|} e^{i\vec{k}\cdot\vec{R}_\rho}, \tag{48}$$

where $\vec{R}_\rho$ are lattice vectors and $\vec{R}_i$, basis vectors. Proceeding, we divide each unit cell into regions V_i surrounding a spherical inclusion located at $\vec{R}_i$ and bounded by the corresponding Voronoy polyhedron. We then perform a multipole expansion as before, but we now find that within V_i, (11) is replaced by

$$\vec{H}_E(\vec{r}_i) = \sum_{lm} A_{lm}^{E,i} f_l^E(r_i) \vec{L}^{(i)} Y_{lm}(\hat{r}_i) e^{i\vec{k}\cdot\vec{R}_i} \quad (r \in V_i), \tag{49}$$

where

$$\vec{r}_i = \vec{r} - \vec{R}_i$$

and

$$\vec{L}^{(i)} = -i\vec{r}_i \times \vec{\nabla}_i .$$

The radial equation (14) also remains the same except for a change in origin. Since the inclusions are all identical (for the moment) the phase shifts will be independent of site index.

Next, we define

$$\vec{r}_{i\rho} = \vec{r} - \vec{R}_i - \vec{R}_\rho ,$$

and we note that for $r_{i\rho} > r_{i'\rho'}$ (when $\vec{r} \in V_i$ in the ρth cell and $\vec{r}' \in V_i$ in the ρ'th cell) we can expand the Green's function

$$G_{\vec{k},\kappa}(\vec{r}', \vec{r}) = \sum_{lmi'l'm'} Y_{lm}(\hat{r}_{i\rho}) Y_{l'm'}^*(\hat{r}_{i'\rho'}) \kappa j_{l'}(\kappa r_{i'\rho'})$$
$$\times \Big(\delta_{ll'}\delta_{mm'}\delta_{ij}\delta_{\rho\rho'} i h_l^+(\kappa r_{i\rho}) - (1 - \delta_{ij}\delta_{\rho\rho'}) 4\pi i^{l-l'} j_l(\kappa r_{i\rho})$$
$$\times \sum_{L,\rho,-\rho'} C(lm; l'm'; L, m-m') i^{1-L} Y_{L,m-m'}^*(\hat{R}_{\mu'\mu}) h_L^+(\kappa R_{\mu'\mu}) e^{i\vec{k}\cdot(\vec{R}_\rho - \vec{R}_{\rho'})} \Big), \tag{50}$$

where

$$\vec{R}_{\mu'\mu} = \vec{R}_{\mu'} - \vec{R}_\mu$$

with

$$\vec{R}_{\mu'} = \vec{R}_{i'} - \vec{R}_{\rho'}$$

and

$$\vec{R}_\mu = \vec{R}_i - \vec{R}_\rho .$$

We use this expansion, and Eq. (49) above in the integral equation. We then multiply the result by

$$e^{i\vec{k}\cdot\vec{R}_i} [\vec{L}^{(i)} Y_{lm}(\hat{R}_i)]^* [l(l+1)]^{-1/2},$$

and for each i integrate over the surface of the ith sphere. What emerges is a matrix equation whose elements are now decorated by the *basis* index i as well as the indices of (21). Thus

$$\sum_{l'm'i\alpha'i'} \mathcal{K}_{lm,l'm'}^{\alpha i,\alpha' i'}(\vec{k}, \kappa) B_{l'm'}^{\alpha' i'} = 0, \tag{51}$$

where again the B's are the normalized multipole strengths [see (19)] and

$$\mathcal{K}^{Ei,Ei'}_{lm,l'm'} = \delta_{ll'}\delta_{mm'}\delta_{ii'}\left(\frac{1}{\Delta g_l^E(a^+)} - i\kappa a j_l(\kappa a)h_l^*(\kappa a)\right) - 4\pi i^{l-l'}\kappa a j_l(\kappa a)j_{l'}(\kappa a)\sum_{L,pp'} J(lm;l'm';L,m-m')$$

$$\times e^{i\vec{k}\cdot(\vec{R}_p-\vec{R}_{p'})}i^{1-L}Y^*_{L,m-m'}(\hat{R}_{\mu\mu'})h^*_L(\kappa R_{\mu\mu'})(1-\delta_{\mu\mu'}), \tag{52}$$

and

$$\mathcal{K}^{Ei,Hi'}_{lm,l'm'} = -4\pi i^l j_l(\kappa a)\Bigg[\sum_L T(lm;l'm';L,m-m')$$

$$\times\Bigg(\sum_{pp'} e^{i\vec{k}\cdot(\vec{R}_p-\vec{R}_{p'})}i^{1-L}Y^*_{L,M-M'}(\hat{R}_{\mu'\mu})h^*_L(\kappa R_{\mu'\mu})(1-\delta_{\mu\mu'})\Bigg)$$

$$\times[\Theta(\kappa a,l') + \Gamma(\kappa a,l')/\Delta g^H_{l'}(a^+)]\Bigg]. \tag{53}$$

Since the reciprocal-lattice vectors for this system are quasicontinuous it follows that for an arbitrary choice of κ we may encounter propagation in a gap. As a consequence we may then expect k to be complex even in the absence of intrinsically dissipative elements in the system. Bragg reflections in the extended periodic system correspond to diffuse scattering in the original system. It is important to note once again that our choice of k and hence of $(\epsilon\mu)_{av}$ is that in which absorption and diffuse scattering (within the composite) are *not* physically distinguished.

As far as computation is concerned Eq. (51) is certainly not practical primarily because of the explicit appearance of the (unrestricted) basis position indices. We shall proceed to eliminate these position indices by applying a matrix folding technique to (51). This folding will involve the inversion of a matrix that is also in practice too large to handle directly. However, as we shall see, it is possible to develop a reasonable and systematic approximation to this inversion procedure.

We begin by eliminating the (spurious) periodicity of our extended system (which was introduced chiefly to ensure that k was well defined) by considering each inclusion of the system to be specified by a position vector instead of a lattice-plus-basis vector. The resulting equations continue to have the same form as above except for the absence of lattice summations in (48)–(53). The basis indices now become position indices. This, of course, increases the number of such indices from N' (large) to N ($\to\infty$), but as we shall soon see this creates no additional difficulty.

Next we execute a change in basis of real-space position vectors from $|i\rangle$ for $i=1,\ldots,N$, to

$$|\tilde{o}\rangle = \frac{1}{\sqrt{N}}\sum_{i=1}^{N}|i\rangle \tag{54}$$

and

$$|\tilde{i}\rangle \quad \text{for } \tilde{i}=1,\ldots,N-1.$$

The $|\tilde{i}\rangle$ need not be further specified except to demand that

$$\langle\tilde{i}\,|\tilde{j}\rangle = \delta_{\tilde{i}\tilde{j}} \qquad 0\le\tilde{i},\tilde{j}\le N-1. \tag{55}$$

(For notational simplicity we will now temporarily abandon the indices l, m, α.) We now proceed to separate $\mathcal{K}$ as follows:

$$\mathcal{K}_{ij} = D\delta_{ij} + (1-\delta_{ij})\hat{\mathcal{K}}_{ij}. \tag{56}$$

Then the result of (a) matrix folding, and (b) the usual expansion of an inverse matrix, allows us to write (51) as

$$(\mathcal{K}_{\tilde{o}\tilde{o}} - \Delta_{\tilde{o}\tilde{o}})B_{\tilde{o}} = 0, \tag{57}$$

where

$$\Delta_{\tilde{o}\tilde{o}} = \sum_{\tilde{i}\tilde{j}=1}^{N-1}\mathcal{K}_{\tilde{o}\tilde{i}}(D^{-1}\delta_{\tilde{i}\tilde{j}} - D^{-1}\mathcal{K}_{\tilde{i}\tilde{j}}D^{-1} + \cdots)\mathcal{K}_{\tilde{j}\tilde{o}}.$$

We can simplify this further by defining a projection operator

$$P = |\tilde{o}\rangle\langle\tilde{o}|,$$

and a new matrix

$$\bar{\mathcal{K}} = (1-P)\hat{\mathcal{K}}(1-P).$$

Then

$$\Delta_{\tilde{o}\tilde{o}} = \frac{1}{N}\sum_{ij,kl}^{N}\hat{\mathcal{K}}_{ij}(D^{-1}\delta_{jk} - D^{-1}\bar{\mathcal{K}}_{jk}D^{-1} + \cdots)\hat{\mathcal{K}}_{kl}, \tag{58}$$

(after changing back to the original basis). Finally we make the separation

$$\Delta_{\tilde{o}\tilde{o}} = \sum_{n=2}^{\infty}\Delta^{(n)}, \tag{59}$$

where $\Delta^{(n)}$ contains only those terms containing n distinct indices. Let

$$g^{(n)}(\vec{R}^{(1)}, \vec{R}^{(2)}, \ldots, \vec{R}^{(n-1)})$$

$$= \frac{1}{N}\sum_{ij_k}^{N} \delta(\vec{R}^{(1)} - \vec{R}_{j_1} + \vec{R}_i)\delta(\vec{R}^{(2)} - \vec{R}_{j_2} + \vec{R}_i)$$

$$\times \cdots \times \delta(\vec{R}^{(n-1)} - \vec{R}_{j_{n-2}} + \vec{R}_i) \tag{60}$$

be an n-particle distribution operator (site coincidences removed). Evidently the $\Delta^{(n)}$ will involve $n-1$ volume integrals over an integrand containing $g^{(n)}$ and must therefore be proportional to ρ^{n-1}, where ρ is the number density. It follows that $\Delta^{(n)} \sim \eta^{n-1}$. Also, each $\Delta^{(n)}$ contains an overall factor of D^{2-n}, except $\Delta^{(2)}$ which contains D^{-1}.

Before turning to an explicit evaluation of the $\Delta^{(n)}$, we examine the problem corresponding to the complete neglect of Δ. We are then led to consider the solution of

$$\sum_{l'm'\alpha'} \mathcal{K}^{\alpha\tilde{o},\alpha'\tilde{o}}_{lm,l'm'}(\vec{k}, \kappa) B^{\alpha'\tilde{o}}_{l'm'} = 0\,, \tag{61}$$

which happens to be exact for periodic systems. Now if $\kappa a \ll 1$, then (Appendix D)

$$\mathcal{K}^{\alpha\tilde{o},\alpha'\tilde{o}}_{lm,l'm'} = \delta_{ll'}\delta_{mm'}\delta_{\alpha\alpha'}D^{\alpha}_{l}\,, \tag{62}$$

and if the system consists of an isotropic distribution of inclusions then for $\vec{k}$ in the z direction, $\mathcal{K}^{\tilde{\alpha}o,\tilde{\alpha}'o}_{1m,1m}$ is the same as is given in (26)–(29) except that

$$\delta P^{(1)} = \frac{8\pi}{1-\eta}(\kappa a) j_1^2(\kappa a)\rho \int_0^\infty R^2 dR\, h(R)[j_2(kR)h_2^*(\kappa R) + j_0(kR)h_0^*(\kappa R)] \tag{63}$$

and

$$\mathcal{K}^{E\tilde{o},H\tilde{o}}_{1m,1m'} = -\mathcal{K}^{H\tilde{o},E\tilde{o}}_{1m,1m'} = \delta_{mm'}\,\frac{i\eta m}{2}\,\frac{k\kappa}{k^2-\kappa^2}\,, \tag{64}$$

where

$$h(R) = g(R) - 1 = g^{(2)}(R) - 1\,.$$

From Appendix D we now see that as in the cubic (crystalline) case, we again arrive at leading-order corrections $O((kb)^2)$ and $O((\kappa b)^2)$, where b is now some characteristic length which determines the scale of variation of the inclusion pair correlation function $h(R)$. If we had a "frozen liquid" type of distribution, for example, then a Percus-Yevick[28,29] hard-sphere solution to the distribution problem[29] will give $b \sim a$. But if there is *clustering* on some larger scale, then physically we expect b to be the clustering length. Evidently $\delta P^{(1)}$ can then still be important even for very small ka and κa. It is worth recalling that in this regime diffuse scattering becomes important when $\lambda \sim b$. We suggest that this is the mechanism which produces the anomalously high far-infrared "absorption" observed in transmission experiments.[30-31] This can be tested by looking off axis in the experiment.

This completes the analysis in which Δ is neglected. We now consider the case in which Δ is retained. After some manipulation we again find results of the form (33), with

$$\bar{D}^{\alpha}_{l} = D^{\alpha}_{l} + \tfrac{1}{2}(1-\eta)(\delta P^{(1)} + \delta P^{(2)}_{\alpha}) \tag{65}$$

and

$$\delta P^{(2)}_{\alpha} = \left(\frac{2}{1-\eta}\right) \times \left(\Delta_{11,11} - \sum_{\substack{l>1,m \\ l>1,m'}} \Delta_{11,lm}(D+\Delta)^{-1}_{lm,l'm'}\Delta_{l'm',11}\right), \tag{66}$$

where we have omitted the position indices $\tilde{o}, \tilde{o}$ on Δ but have made explicit the multipole indices. It can easily be shown that in the weak-scattering (D_l large) or small-η limits (except perhaps very near to multipole resonances), the second term of (66), which results from multipole folding, is small. This seems likely to always be the case (at any rate we shall ignore it henceforth).

For our first attempt at determining $\delta P^{(2)}_{\alpha}$ we consider the weak-scattering case. Then we need retain only the leading corrections in D_l^{-1}. These in turn involve only the contributions to $\Delta^{(2)}$ and $\Delta^{(3)}$. Using the results of Appendix C, and some considerable algebra, we obtain for $\kappa a \ll 1$,

$$\delta P^{(2)}_{\alpha} = \frac{-\eta}{3(1-\eta)}\sum_{l=1} \frac{l}{D^{\alpha}_{l}}\,\frac{(2a)^{2l+1}}{2^{l}}(\Lambda^{(2)}_{l} + \rho\Lambda^{(3)}_{l})\,, \tag{67}$$

where

$$\Lambda^{(2)}_{l} = \int_0^\infty dR\, g^{(2)}(R) R^{-(2l+2)} \tag{68a}$$

and

$$\Lambda^{(3)}_{l} = \int d\vec{R} \int d\vec{R}' g^{(3)}(R, R'; |\vec{R} - \vec{R}'|) \times \frac{Y_{l+1,0}(\hat{R})}{R^{l+2}}\,\frac{Y_{l+1,0}(\hat{R}')}{R'^{l+2}}\, e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\,. \tag{68b}$$

An exact evaluation of (63) and (67) requires a complete knowledge of $g^{(2)}$ and $g^{(3)}$ for the system. Unfortunately, these are seldom available, particularly $g^{(3)}$. We know, however, that the inclusions do not interpenetrate. The excluded volume (EV) distributions defined by

$$g^{(2)}(R) = \begin{cases} 1, & R > 2a \\ 0, & R < 2a \end{cases} \tag{69a}$$

and

$$g^{(3)}(R,R';|\vec{R}-\vec{R}'|)=\begin{cases}1, & R>2a,\ R'>2a,\\ & |\vec{R}-\vec{R}'|>2a\\ 0, & \text{otherwise}\end{cases} \tag{69b}$$

partially take this requirement into account. This distribution is exact (in the absence of clustering) only in the small-η limit. But even for larger packing fractions, as we shall see, excluded volume effects, as represented by (69) turn out to be major contributors to $\delta P_\alpha^{(2)}$! Taking the limit $kb \ll 1$ we now have

$$\delta P_\alpha^{(2)}=\frac{-\eta}{6(1-\eta)}\sum_{l=1}^{\infty}\frac{l}{D_l^{\alpha}2^l(2l+1)}(1-\eta\gamma_l), \tag{70}$$

where

$$\gamma_l=3a^3\Lambda_l^{(3)}/4\pi\Lambda_l^{(2)},$$

with $\Lambda_l^{(3)}$ evaluated at $k=0$. If, in addition $k_2a\ll 1$, then

$$\delta P_E^{(2)}=\frac{-\eta}{6(1-\eta)}\sum_{l=1}^{\infty}\frac{l(l+1)}{2^l}\frac{\epsilon_2-\epsilon_1}{(l+1)\epsilon_1+l\epsilon_2}(1+\eta\gamma_l). \tag{71}$$

The quantities γ_l are a measure of the relative importance of the pair and triplet contributions. For the excluded volume distribution (69), we have

$$\begin{aligned}\gamma_1^{EV}&=-\tfrac{15}{4},\\ \gamma_2^{EV}&=-\tfrac{53}{32},\\ \gamma_3^{EV}&=-\tfrac{25}{64},\end{aligned} \tag{72}$$

and we may extrapolate for large l by

$$\gamma_l^{EV}=A_2l^{-2}+A_4l^{-4}+A_6l^{-6}, \tag{73}$$

where

$$A_2=+0.2087,\quad A_4=+33.04,\quad \text{and}\quad A_6=-29.50.$$

For the true distribution (and $k=0$), we use (60) and (68) to obtain

$$\Lambda_l^{(2)}+\rho\Lambda_l^{(3)}=\frac{1}{N\rho}\sum_{i=1}^{N}\left(\sum_{j=1}^{N}\frac{Y_{l+1,0}(\hat{u}_{\vec{R}_i-\vec{R}_j})}{|\vec{R}_j-\vec{R}_i|^{l+2}}\right)^2. \tag{74}$$

We note that this quantity is positive definite, or equivalently $\eta\gamma_l>-1$. However, γ_1^{EV} does not satisfy this condition for $\eta>\frac{4}{15}$.

Now, in monodispersed cermets, the physical range of η is $0\le\eta\le 0.582$, the upper limit having been determined by Vissher[32] from computer experiments involving the random dropping of identical spheres. However, experimentally $\eta\sim 0.4$ is more typical of an upper limit that remains compatible with the cermet topology. Nevertheless, we shall see the range $\sim 0.2<\eta<\sim 0.4$ still presents a difficulty in the $l=1$ term. Although the use of the exact $g^{(2)}$ will typically increase the importance of the pair term relative to the triplet term, it appears that even for relatively small filling fractions ($\eta\sim 0.25$) corrections must be sought for the excluded volume $g^{(3)}$.

One approach is to take $g^{(2)}$ to be the hard-sphere fluid result and to approximate $g^{(3)}$ by the Kirkwood superposition approximation:

$$g^{(3)}(R,R';|\vec{R}-\vec{R}'|)=g^{(2)}(R)g^{(2)}(R')g^{(2)}(|\vec{R}-\vec{R}'|).$$

This will likely prove adequate, although calculations to confirm this are not yet available. Another (rather simple) approach to this problem that has the correct *qualitative* features without requiring the (currently unavailable) distribution $g^{(3)}$ is the following: In the close-packing (CP) limit ($\eta=\eta_c\sim 0.74$) each particle has 12 nearest neighbors in a local fcc arrangement, regardless of whether the overall packing is fcc, hcp, or random. Since the nearest neighbors ordinarily provide the bulk of the contributions to the sum in (74), we approximate the sum at $\eta=\eta_c$ by the corresponding sum over an fcc lattice. We can express our results using Eq. (70), where

$$\begin{aligned}\gamma_1^{CP}&=\gamma_{2l}^{CP}=-1/\eta_c,\\ \gamma_3^{CP}&=-7.251137,\\ \gamma_5^{CP}&=-58.8766,\end{aligned} \tag{75}$$

and

$$\gamma_{2l-1}^{CP}=-1/\eta_c+\frac{(4l-1)(4l+1)}{6\eta_c^2}\times[P_{2l}(0)+2P_{2l}(1/\sqrt{2})]\quad(\text{large } l).$$

Since we lack the specific information about the true distribution that would select one of the physically possible values of $\delta P^{(2)}$ as a function of η, in the interests of simplicity we will interpolate between small η and close packing by

$$1/\gamma_l=(1/\gamma_l^{EV})(1-\eta/\eta_c)+(1/\gamma_l^{CP})(\eta/\eta_c). \tag{76}$$

If exact information becomes available we can always use (67) and (68).

Another regime where we can calculate $\delta P_\alpha^{(2)}$ is that of small η (low filling fraction). Here we need consider only $\Delta^{(2)}$, but we are still required to consider all powers of D. Again the manipulations are lengthy but straightforward. We find for $\Delta^{(2)}$:

$$\Delta^{(2)}=\rho\int_0^{\infty}dR\,R^2g^{(2)}(R)\{\hat{\mathcal{K}}(\vec{R})[D^{-1}+D^{-1}\hat{\mathcal{K}}(-\vec{R})D^{-1}\hat{\mathcal{K}}(\vec{R})D^{-1}+\cdots]\hat{\mathcal{K}}(-\vec{R})$$
$$-\hat{\mathcal{K}}(\vec{R})[D^{-1}\hat{\mathcal{K}}(-\vec{R})D^{-1}+\cdots]\hat{\mathcal{K}}(\vec{R})e^{i\vec{k}\cdot\vec{R}}+O(1/N)\}. \tag{77}$$

In the small κa, ka limits, we can carry out the angular averages provided we assume that we are near at most *one* of the multipole resonances. This assumption is justifiable except for large l resonances which, in any case, are of diminishing physical importance. Then

$$\delta P_\alpha^{(2)} = \frac{-\eta}{3(1-\eta)} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \frac{l}{C_{lm}(2l+1)} \int_0^\infty dR \, \frac{g(R)}{R^{2l+2}} \left[D_l^\alpha + (-1)^{l+1} C_{lm} \left(\frac{a}{R}\right)^{2l+1} \right]^{-1}, \tag{78a}$$

where

$$C_{lm} = (-1)^m \frac{l}{(2l+1)(l+1)} \frac{(2l)!}{(l+,m)!\,(l-m)!}. \tag{78b}$$

We note that for any reasonable $g^{(2)}$ the principal effect of correlation for small η, as usual, is a consequence of excluded volume. Using such an excluded volume distribution we then have

$$\delta P_\alpha^{(2)} = \frac{-\eta}{3(1-\eta)} \sum_{l=1}^{\infty} \frac{l(-1)^{l+1}}{(2l+1)^2} \sum_{m=-l}^{l} \frac{1}{C_{lm}} \ln \left| 1 + (-1)^{l+1} C_{lm} \times 2^{-(2l+1)} (D_l^\alpha)^{-1} \right|, \tag{79}$$

which in the small-$k_2 a$ limit gives

$$\delta P_E^{(2)} = \frac{-\eta}{3(1-\eta)} \sum_{l=1}^{\infty} \frac{l(-1)^{l+1}}{(2l+1)^2} \sum_{m=-l}^{l} \ln \left| 1 + (-1)^{l+1} C_{lm} \times 2^{-(2l+1)} \frac{(l+1)(2l+1)(\epsilon_2 - \epsilon_1)}{(l+1)\epsilon_1 + l\epsilon_2} \right|. \tag{80}$$

Clearly, further corrections to these expressions can be obtained but we will not pursue them here.

We are now ready to compare the effects of structural multipoles in periodic *and* aperiodic systems. In periodic systems, particle equivalence ($B_{lm}^{\alpha i}$ independent of i) means that multipole effects emerge after the folding procedure in multipole space. In aperiodic systems a particle equivalence *approximation* would result in the absence of structural multipole effects. However, these effects, which *are* important, emerge from corrections to the particle equivalence approximation. Because of the lack of symmetry in aperiodic systems, multipole resonances can occur for all l, although typically they are less pronounced than in periodic systems.

In periodic systems higher multipoles are associated with terms carrying corresponding powers of η. Contrast this with aperiodic systems, where all multipole corrections are initially linear in η.

The reason that structural multipole effects are more important in aperiodic systems with small η is that close approaches between inclusions are permitted. However, the relative importance of these effects is reversed near the periodic close-packing η, since here there are more close approaches in the periodic system.

To recapitulate the major results of this section, we can state that providing $\kappa a \ll 1$, we have a product rule

$$(\epsilon\mu)_{av} = \bar{\epsilon}_{\mathrm{MMMG}} \bar{\mu}_{\mathrm{MMMG}}, \tag{81}$$

where

$$\bar{\epsilon}_{\mathrm{MMMG}} = \epsilon_1 \frac{D_1^E + (1-\eta)\delta P/2 + \eta/6}{D_1^E + (1-\eta)\delta P/2 - \eta/3} \tag{82}$$

and similarly for $\bar{\mu}_{\mathrm{MMMG}}$. If, in addition $k_2 a \ll 1$, then (82) becomes

$$\bar{\epsilon}_{\mathrm{MMMG}} = \epsilon_1 \frac{\epsilon_1 + [(1-\eta)P + \eta](\epsilon_2 - \epsilon_1)}{\epsilon_1 + (1-\eta)P(\epsilon_2 - \epsilon_1)}, \tag{83}$$

where

$$P^\alpha = \tfrac{1}{3} + \delta P^{(1)} + \delta P_\alpha^{(2)}.$$

In the limit $kb \ll 1$, $\kappa b \ll 1$, $\delta P^{(1)}$ vanishes. In the weak-scattering case ($\epsilon_2 \sim \epsilon_1$), $\delta P_\alpha^{(2)}$ is given by (67) or (71) while for small η it is given by (76), (78), or (79). In general δP is a function of k and κ and hence of $\bar{\epsilon}$. The dependence of δP on $\bar{\epsilon}$ is weak when $\kappa a \ll 1$ and in that case (82) or (83) can be solved by iteration. If $kb \ll 1$ and $\kappa b \ll 1$, δP will become independent of k and κ. We note that the product rule has been presented elsewhere[33] and that the results of several experiments have been accounted for using depolarizing factors interpreted as shape effects or effective multipole interactions.[34] However, these were *real* (rather than the frequency-dependent complex quantities above). In both cases their use was introduced in an intuitive and less general context. Our results indicate that at least part of the observed δP might be traced instead to structural multipoles.

As already mentioned, in Fig. 2, we compare MG, sc, and the *aperiodic* MMMG (weak scattering) for a two-dielectric composite. As argued above the effects of multipoles are far more pronounced in aperiodic systems. Figure 3 compares the same three cases for the model of (Drude) gold particles dispersed in a dielectric. Note that the sharp structure of the simple-cubic case does not appear in the aperiodic MMMG (small η) case although considerable analytic structure in the latter still persists.

V. SIZE DISTRIBUTIONS AND MULTICOMPONENT SYSTEMS

In this section we consider aperiodic systems in which the condition that the inclusions be identical is finally relaxed. In fact we shall allow them to vary both in size *and* in composition. At the outset it is important to note that when a $\lesssim 100$ Å, ϵ_2 and μ_2 can both depend on a, and in fact, depart appreciably from their bulk values.[35] In this regime, therefore, even a system which has two components when the spherical inclusions are of identical size, becomes a putative multicomponent system when the sizes are dispersed, i.e., the size of the inclusion at $\vec{R}_j$ is a_j.

As before, we can set up a multipole scattering formalism and obtain

$$0=\sum_{l'm'j}\Bigg\{\Bigg[\delta_{ll'}\delta_{mm'}\delta_{ij}\left(\frac{1}{\Delta g_l^E(a_i^+)}\,\frac{1}{\kappa a_i j_l^2(\kappa a_i)}-\frac{ih_l^+(\kappa a_i)}{j_l(\kappa a_i)}\right)$$
$$-4\pi i^{l-l'}\sum_{L,pp'}J(lm;l'm';L,m-m')e^{i\vec{k}\cdot(\vec{R}_p-\vec{R}_{p'})}Y^*_{L,m-m'}(\hat{R}_{\mu'\mu})h_L^+(\kappa R_{\mu'\mu})i^{1-L}\Bigg]B^{Ej}_{lm}$$
$$-4\pi i^{l}\Bigg[\sum_{L,pp'}T(lm;l'm';L,m-m')e^{i\vec{k}\cdot(\vec{R}_p-\vec{R}_{p'})}Y^*_{L,m-m'}(\hat{R}_{\mu'\mu})h_L^+(\kappa R_{\mu'\mu})$$
$$\times\left(\frac{\Theta(\kappa a_j,l')}{(\kappa a_j)j_{l'}(\kappa a_j)}+\frac{\Gamma(\kappa a_j,l')}{\kappa a_j j_{l'}(\kappa a_j)\Delta g_l^H(a_j^+)}\right)\Bigg]\tilde{B}^{Hj}_{l'm'}\Bigg\} \tag{84}$$

instead of (51). Here

$$\tilde{B}^{Ej}_{l'm'}=(\kappa a_j)j_{l'}(\kappa a_j)B^{Ej}_{l'm'}\,. \tag{85}$$

Again, for $\kappa a\ll 1$ we have a matrix equation of the type

$$\sum_{l'm\alpha'j}(\tilde{D}_i^\alpha\delta_{ll'}\delta_{mm'}\delta_{\alpha\alpha'}\delta_{ij}+\tilde{\mathcal{K}}^{\alpha i\alpha' j}_{lm\,l'm'})\tilde{B}^{\alpha' j}_{l'm'}=0\,, \tag{86}$$

where all size *and* composition dependence is in the $\tilde{D}_i^\alpha$ (note that the phase-shift problem is different for each inclusion). We proceed as in Sec. III, except that the diagonal term now depends on position. However, we make the reasonable assumption that size and composition are *not* correlated with position. Further, we assume that physical conditions can be chosen such that κa_i, ka_i, κb, and kb are all small, for all i. After quite considerable manipulation we again arrive at a product rule similar to (81) with

$$\bar{\epsilon}_{\mathrm{MMG}}=\epsilon_1\left(\frac{\bar{D}_1^E+(1-\eta)\delta P_E+\eta/6}{\bar{D}_1^E+(1-\eta)\delta P_E-\eta/3}\right), \tag{87}$$

where

$$\bar{D}_1^E=\langle\tilde{D}_1^E\rangle[2-\langle\tilde{D}_1^E\rangle\langle(\tilde{D}_1^E)^{-1}\rangle]\,, \tag{88}$$

and

$$\tilde{D}^E_{l,i}=D^E_{l,i}\langle aj_l^2(\kappa a)\rangle/a_i j_l^2(\kappa a)\,, \tag{89}$$

and $\langle\ \rangle$ stands for an average over size and composition distribution.

For weak-scattering systems, and $\kappa b\ll 1$ and $kb\ll 1$, δP_α is as in (71) or (72) except that D^{-1} is replaced by $\langle\tilde{D}^{-1}\rangle$. For small η (and $\kappa b\ll$ and $kb\ll 1$) we have for the excluded volume distribution

$$\delta P_\alpha=\frac{-\eta}{6(1-\eta)}\sum_{l=1}^{\infty}\frac{l}{2l+1}\sum_{m=-l}^{l}\frac{1}{C_{lm}}\frac{1}{N^2}\sum_{i,j=1}^{N}\Bigg[\frac{\langle\tilde{D}_l\rangle^2}{(\tilde{D}_{l,i})^2}(-1)^{l+1}\left(\frac{\tilde{D}_{li}}{\tilde{D}_{lj}}\right)^{1/2}\ln\left|\frac{1+C_{lm}\times 2^{-(2l+1)}(\tilde{D}_{li}^{-1}\tilde{D}_{ij}^{-1})^{1/2}}{1-C_{lm}\times 2^{-(2l+1)}(\tilde{D}_{li}^{-1}\tilde{D}_{ij}^{-1})^{1/2}}\right|$$
$$-\frac{\langle\tilde{D}_l^2\rangle}{\tilde{D}_{l,i}\tilde{D}_{l,j}}\ln|1-\tilde{D}_{li}^{-1}\tilde{D}_{ij}^{-1}C_{lm}^2\times 2^{-(4l+2)}|\Bigg]. \tag{90}$$

To get triplet corrections *three* averages over size or composition distributions are required, and so on, for higher than triplet distributions. Since even the double average is quite cumbersome for continuous distribution of sizes we observe that for many multicomponent systems a more reasonable starting point may be the effective medium theory (in the spirit of Sec. II) at least for those systems possessing the cermet topology. An expression for $\bar{\epsilon}$ for this case has already been given.[20] It appears that if there is a distribution of sizes only (the $\epsilon_i\mu_i$ being unaltered by site) then there should be some broadening of resonances, but generally little change from a monodispersed system with the same filling fraction.

As noted above, there is implicit composition dependence which emerges from a distribution of *sizes*. Such effects can be crudely taken into account in cermets by replacing $1/\tau$ in the Drude

model by $1/\tau + v_F/2a$, where v_F is the Fermi velocity. In principle this should be taken care of by applying (88). If instead we consider only the average size, we obtain Fig. 4. It shows the absorption coefficient for (Drude) gold in KBr for (i) MMMG Bulk, (ii) MMMG (average size), and (iii) MG (average size). The introduction of a size-dependent ϵ_2 (via $1/\tau \to 1/\tau + v_F/2a$) greatly smoothes the structure of the bulk result. Since we expect only some small further smoothing due to size averaging, the full multicomponent formalism is probably not required in order to take such size averaging into account.

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APPENDIX A

The purpose of this Appendix is to give the solutions of the radial equation (14) and to compute the phase shifts Δg_l^E [defined by Eq. (18)] for the case of a layered sphere. The layered sphere is formed by taking a homogeneous inner sphere of radius r_n (described by ϵ_n and μ_n) surrounded by a series of concentric spherical shells whose outer radii are r_i $(2 \leq i < n,\ r_2 > r_i > r_n)$ composed of homogeneous material described by ϵ_i and μ_i. As usual the host is described by ϵ_1 and μ_1.

Of particular interest are the cases $n=2$, the uniform sphere, and $n=3$, a singly coated sphere. Though we shall consider Δg_l^E, the complementary results are obtained from the standard changes $(\epsilon, E) \leftrightarrow (\mu, H)$.

Since the ϵ_i and μ_i are constants the radial equation in each layer is

$$\left(\frac{1}{r}\frac{d^2}{dr^2}r - \frac{l(l+1)}{r^2} + k_i^2\right) f_l^E(r) = 0, \tag{A1}$$

where $k_i^2 = (\omega/c)^2 \epsilon_i \mu_i$. The solutions to (A1) are well known[36] and can be written as

$$f_l^E(r) = c_i^E j_l(k_i r) + d_i^E n_l(k_i r) \quad (r_{i-1} > r > r_i), \tag{A2}$$

where c_i^E and d_i^E are arbitrary constants. Now $f_l^E(r)$ must be finite everywhere, so it follows that in the innermost sphere (where r may vanish) the constant d_n^E must vanish. In addition, Eq. (A1) is linear, and since we therefore have an arbitrary overall constant, we may set $c_n^E = 1$.

To complete the solution we need the remaining

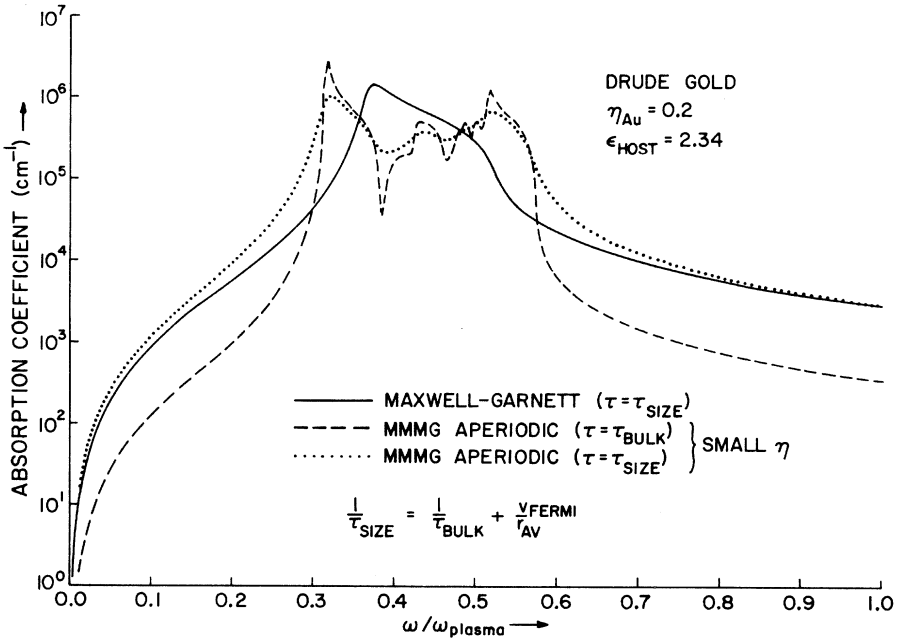

FIG. 4. MG and MMMG (aperiodic) curves for the system of Fig. 3; comparing results for bulk and size-modified Drude relaxation times for Au; $r_{av} = 50$ Å.

c_i and d_i. These we determine from the boundary conditions. First, the solutions of (14) must be continuous and hence

$$c^E_{i-1} j_l(k_{i-1}r_{i-1}) + d^E_{i-1} n_l(k_{i-1}r_{i-1}) = c^E_i j_l(k_i r_{i-1}) + d^E_i n_l(k_i r_{i-1}) . \quad \text{(A3)}$$

Next, we integrate the radial equation (14) over an infinitesimal range including the point r_{i-1}; this gives

$$c^E_{i-1} J_l(k_{i-1}r_{i-1}) + d^E_{i-1} N_l(k_{i-1}r_{i-1}) = c^E_i J_l(k_i r_{i-1}) + d^E_i N_l(k_i r_{i-1}) , \quad \text{(A4)}$$

where

$$J_l(k, r) = \left(j_l(kr) + r \frac{d}{dr} j_l(kr)\right) \Big/ \epsilon(r) \quad \text{(A5)}$$

and

$$N_l(k, r) = \left(n_l(kr) + r \frac{d}{dr} n_l(kr)\right) \Big/ \epsilon(r) . \quad \text{(A6)}$$

Note that (A3) and (A4) can also be derived from the continuity of, respectively, the tangential components of $\vec{H}$ and $\vec{E}$.

After a little manipulation we find for the phase shift

$$\Delta g^E_l = -\epsilon_1 \frac{J_l(k_2 a) + (d_2/c_2) N_l(k_2 a)}{j_l(k_2 a) + (d_2/c_2) n_l(k_2 a)} - g^0_l ,$$

where

$$g^0_l = -ka \left(\frac{d}{d(ka)} j_l(ka)\right) \Big/ j_l(ka) .$$

It remains, therefore, to determine the quantity $s_2 = d_2/c_2$, which in fact requires us to determine the $s_i = d_i/c_i$, where the d's and c's are related by (A3) and (A4).

After much manipulation we find

$$s_{i-1} = \frac{J_l(k_i r_{i-1}) j_l(k_{i-1} r_{i-1}) - J_l(k_{i-1} r_{i-1}) j_l(k_i r_{i-1}) + s_i [J_l(k_{i-1} r_{i-1}) n_l(k_i r_{i-1}) - N_l(k_i r_{i-1}) j_l(k_{i-1} r_{i-1})]}{N_l(k_{i-1} r_{i-1}) j_l(k_i r_{i-1}) - J_l(k_{i-1} r_{i-1}) n_l(k_i r_{i-1}) + s_i [N_l(k_i r_{i-1}) n_l(k_i r_{i-1}) - N_l(k_{i-1} r_{i-1}) n_l(k_{i-1} r_{i-1})]} ,$$

but since $s_n = 0$ we immediately have an iteration scheme enabling us to generate s_2. For the uniform sphere case ($n = 2$) this procedure gives

$$\Delta g^E_l = -\frac{\epsilon_1}{\epsilon_2} \frac{k_2 a}{j_l(k_2 a)} \frac{d}{d(k_2 a)} j_l(k_2 a) - \frac{k_1 a}{j_l(k_1 a)} \frac{d}{d(k_1 a)} j_l(k_1 a)$$

which reduces, in the limits $k_1 a \ll 1$, $k_2 a \ll 1$ to

$$\Delta g^E_l \simeq \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2}\right)(l+1) + \frac{(k_1 a)^2}{2l+3} \left(\frac{\mu_2 - \mu_1}{\mu_2}\right) .$$

Unlike the quantum-mechanical case,

$$\lim_{l \to \infty} \Delta g^E_l \neq 0 .$$

The reason for this is that (A4) requires $f^E_l(r)$ to possess a *discontinuous* derivative, in contrast to the quantum-mechanical requirement of *continuity* of the derivative of the wave function.

For the other case of interest, the coated sphere ($n = 3$), we find in the quasistatic limit

$$\Delta g^E_l = (l+1) \times \left(1 - \frac{\epsilon_1}{\epsilon_2} \frac{[(l+1)\epsilon_2 + l\epsilon_3] + l(\epsilon_2 - \epsilon_3)\xi^{2l+1}}{[(l+1)\epsilon_2 + l\epsilon_3] - (l+1)(\epsilon_2 - \epsilon_3)\xi^{2l+1}}\right) ,$$

where

$$\xi = r_3/r_2 .$$

It should be noted, in particular, that *only for* $l = 1$ can Δg^E_l for a coated sphere be obtained from Δg^E_l for an equivalent uniform sphere whose equivalent ϵ_2 is given by ϵ_{CS} as prescribed by (1). Thus, even in the quasistatic limit a coated sphere cannot be *completely* characterized by a *single* effective dielectric constant.

APPENDIX B: EVALUATION OF THE STRUCTURE CONSTANTS

We consider here the structure constants $M_{LM}(\vec{k}, \kappa)$ for a periodic lattice, first in the quasistatic limit, and then more generally. For the quasistatic case we divide M as follows:

$$M_{LM}(\vec{k}, \kappa) = \left(\sum_{\vec{R} \neq 0} - \rho \int d\vec{R}\right) m_{LM}(\vec{R}, \vec{k}, \kappa) + \rho \int d\vec{R}\, m_{LM}(\vec{R}, \vec{k}, \kappa) + \delta_{L0}\delta_{M0} \frac{i}{\sqrt{4\pi}} , \quad \text{(B1)}$$

where

$$m_{LM}(\vec{R}, \vec{k}, \kappa) = i^{1-L} e^{i\vec{k}\cdot\vec{R}} h^+_L(\kappa R) Y^*_{LM}(\hat{R}) . \quad \text{(B2)}$$

Next we note that for $R > R_0$ (where R_0 is a few times the largest primitive-lattice vector) the sum and integral are equal. On the other hand, if $R < R_0$ it is a consequence of the quasistatic condition that for $L > 0$ the angular integral will vanish. Accordingly,

$$M_{LM}(\vec{k}, \kappa) = \sum_{\substack{\vec{R} \neq 0 \\ R < R_0}} m_{LM}(\vec{R}, \vec{k}, \kappa) - \rho \int d\vec{R}\, m_{LM}(\vec{R}, \vec{k}, \kappa) \quad (L > 0) , \quad \text{(B3)}$$

and if we now expand m in powers of κ, retain only the leading terms, and evaluate the integrals we get

$$M_{LM}(\vec{k},\kappa)=i^{-L}(2L-1)!!\sum_{\vec{R}\neq 0}\frac{Y^*_{LM}(\hat{R})}{(\kappa R)^{L+1}} - (-1)^L\frac{4\pi\rho k^L Y^*_{LM}(\hat{k})}{\kappa^{2(L+1)}(k^2-\kappa^2)}\quad (L>0). \tag{B4}$$

Note that the upper cutoff on the sum can now be omitted (it is superfluous). We observe that for $L=1$ the second term dominates the first. For $L\geq 3$ the first dominates; and for $L=2$, both contribute. The case $L=0$ gives

$$M_{00}(\vec{k},\kappa)=\frac{1}{\sqrt{4\pi}\kappa}\left(\sum_{\substack{\vec{R}\neq 0\\ R<R_0}}-\rho\int d\vec{R}\right)\frac{1}{R} -\rho\sqrt{4\pi}\,\frac{1}{\kappa(k^2-\kappa^2)}+\frac{i}{\sqrt{4\pi}} \tag{B5}$$

and here the second term clearly dominates.

In the general case, we note that the direct sum in $\vec{R}$ space converges exponentially fast if κ has a positive imaginary part but otherwise the convergence is slow. This problem is treated by dividing the sum into two quickly convergent sums (one on the lattice and one on its reciprocal) in the spirit of the Ewald method.[37] We can obtain the result in closed form, in contrast to the asymptotic expansion given by Morse.[38] Specifically, we separate

$$M_{LM}(\vec{k},\kappa)=M^R_{LM}(\vec{k},\kappa)+M^K_{LM}(\vec{k},\kappa), \tag{B6}$$

where

$$M^R_{LM}(\vec{k},\kappa)=\sum_{\vec{R}\neq 0} m_{LM}(\vec{R},\vec{k},\kappa)A_L(\gamma,R) +\delta_{L0}\delta_{M0}i/\sqrt{4\pi}, \tag{B7}$$

with A_L defined below. Transforming the complementary sum to the reciprocal lattice we obtain

$$M^K_{LM}(k,\kappa)=\frac{i}{2\pi^2}\left(\rho\sum_{\vec{K}}-\int d\vec{K}\right)Y^*_{LM}(\hat{u}_{\vec{k}+\vec{K}}) \times\int_0^\infty dR\,R^2 j_L(|\vec{k}+\vec{K}|R)h^+_L(\kappa R) [1-A_L(\gamma,R)]. \tag{B8}$$

Here $\{\vec{K}\}$ is the set of reciprocal-lattice vectors.

The function A_L and the parameter γ of the argument are chosen for convenience: we may take, for example,

$$A_L(\gamma,R)=1-\frac{2^{L+1}R^{2L+1}}{\sqrt{\pi}(2L-1)!!}\int_0^\gamma dt\,t^{2L}e^{-t^2R^2} \tag{B9a}$$

or, equivalently,

$$A_L(\gamma,R)=1-\operatorname{erf}(\gamma R)+\frac{2\gamma R}{\sqrt{\pi}}\sum_{l=0}^{L-1}\frac{2^l(\gamma R)^l}{(2l+1)!!}e^{-(\gamma R)^2}. \tag{B9b}$$

We find, after considerable manipulation that

$$M^K_{LM}(\vec{k},\kappa)=\frac{-2^{L-2}k^L\kappa^L}{(2L-1)!!}\left(\frac{1}{k}\frac{\partial}{\partial k}\right)^L\left(\frac{1}{\kappa}\frac{\partial}{\partial\kappa}\right)^L\frac{1}{K}\frac{1}{\kappa} \left((k+\kappa)^{2L-1}\int_{(k+\kappa)/\gamma}^\infty dz\,z^{1-2L}e^{-z^2/4}+(\kappa\to-\kappa)\right) \tag{B10}$$

$$=\frac{-i}{2k\kappa}\left(\frac{e^{-(k+\kappa)^2/4\gamma}}{k+\kappa}P_L(k,\kappa)+(\kappa\to-\kappa)\right).$$

For relatively modest values of L, the functions P_L are easily determined. Let $\alpha=(k+\kappa)^2/k\kappa$ and $\beta=(k+\kappa)^2/2\gamma^2$. Then

$$\begin{aligned}
P_0&=1,\\
P_1&=\alpha-1+\beta,\\
P_2&=\alpha^2-3\alpha+1+\beta(\alpha-2)+\tfrac{1}{3}\beta^2,\\
P_3&=\alpha^3-5\alpha^2+6\alpha-1+\beta(\alpha^2-4\alpha+3)\\
&\quad+\beta^2(2\alpha-5)/5+\beta^3/15,\\
P_4&=\alpha^4-7\alpha^3+15\alpha^2-10\alpha+1+\beta(\alpha^3-6\alpha^2+10\alpha-4)\\
&\quad+\beta^2(3\alpha^2-14\alpha+14)/7+\beta^3(10\alpha-28)/105\\
&\quad+\beta^4/105,
\end{aligned} \tag{B11}$$

and

$$\begin{aligned}
P_5&=\alpha^5-9\alpha^4+28\alpha^3-35\alpha^2+15\alpha-1\\
&\quad+\beta(\alpha^4-8\alpha^3+21\alpha^2-20\alpha+5)\\
&\quad+\beta^2(4\beta^3-27\alpha^2+54\alpha-30)/9\\
&\quad+\beta^3(7\alpha^2-30\alpha+42)/63+\beta^4(\alpha-3)/63+\beta^5/945.
\end{aligned}$$

Notice that the integral contribution to M^K, which is simply the $R=0$ term in M^R, clearly vanishes.

The choice of A used here provides excellent Gaussian convergence. If we take $\gamma\sim 1$, both sums converge quite rapidly. Finally, it should be noted that if both $\vec{k}$ and κ are real it is necessary to add to κ a small positive imaginary part in order to recover the δ functions that must arise when $|\vec{k}+\vec{K}|-\kappa=0$.

APPENDIX C

Here we present formulas for the selection constants for some of the more useful cases. In addition we give some identities necessary for deriving (22). The manipulations, many of which we omit, are straightforward but quite lengthy. We have

(i) $J(lm;l'm';00)=\delta_{ll'}\delta_{mm'}/\sqrt{4\pi}$, (C1)

$$\text{(ii)}\quad J(lm;l'm';l+l',M)=(-)\delta_{M,m-m'}\left(\frac{(2l+1)(2l'+1)(2l+2l'+1)}{4\pi l(l+1)l'(l'+1)}\right)^{1/2}$$
$$\times\frac{(2l)!(2l')!(l+l')!}{(l-1)!(l'-1)!(2l+2l'+1)!}\times(-1)^{m'}$$
$$\times\left(\frac{(l+l'-m+m')!(l+l'+m-m')!}{(l+m)!(l-m)!(l'+m')!(l'-m')!}\right)^{1/2}, \tag{C2}$$

$$\text{(iii)}\quad J(lm;l'm';LM)=0 \quad \text{unless } L=|l-l'-1|,\ |l-l'-1|+2,\ \ldots,\ |l+l'| \tag{C3}$$

$$\text{(iv)}\quad T(1m;1m';1,0)=-\delta_{mm'}\frac{m}{2\sqrt{3\sqrt{4\pi}}}, \tag{C4}$$

and

$$\text{(v)}\quad T(lm';l'm;LM)=0$$
unless
$$M=m-m',\ \text{ and }\ L=|l-l'-1|,\ |l-l'-1|+2,\ \ldots,\ |l+l'-1|. \tag{C5}$$

Next, we define

$$Q^{(i)}(lm;l'm';l';LM)=[l(l+1)l'(l'+1)]^{1/2}\sum_{\tilde m,\tilde m'}\int d\hat r\,\vec L Y_{l\tilde m}(\hat r)[Y_{l\tilde m}(\hat r)]^*\int d\hat r' Y^*_{l'\tilde m'}(\hat r')\vec Q^{i}(\hat r')Y_{l'm'}(\hat r')$$
$$\times C(l\tilde m;\tilde l'\tilde m';LM), \tag{C6}$$

where

$$\vec Q^{(1)}=\hat r',\quad \vec Q^{(2)}=\hat r'\times\vec L.$$

Note first that the Q^i are nonzero only if $l'=l\pm1$. The following identities are useful:

$$\begin{aligned}T(lm;l'm',L,m-m')&\equiv Q^{(1)}(lm,l'm';l'-1;L,m-m')\\&=-Q^{(1)}(lm,l'm';l'+1;L,m-m')\\&=\tfrac12 Q^{(2)}(lm,l'm';l'-1;L,m-m')\\&=Q^{(2)}(lm;l'm';l'+1;L,m-m').\end{aligned} \tag{C7}$$

APPENDIX D

In this Appendix we consider the calculation of the (average) matrix elements for an aperiodic system. We have

$$\mathcal{K}_{\delta\delta',lm,l'm'}(\vec k,\kappa)=D\delta_{ll'}\delta_{mm'}-4\pi i^{l-l'}\kappa a\, j_l(\kappa a)j_{l'}(\kappa a)$$
$$\times\sum_{LM}J(l,m;l',m';L,M)\langle M_{LM}(\vec k,\kappa)\rangle, \tag{D1}$$

where

$$\langle M_{LM}(\vec k,\kappa)\rangle=i^{1-L}\rho\int_0^\infty d\vec R\,g(R)e^{i\vec k\cdot\vec R}h_L^+(\kappa R)Y^*_{LM}(\hat R)$$
$$+\delta_{L0}\delta_{M0}i/\sqrt{4\pi}. \tag{D2}$$

Since $g(R)=0$ for $R<\sigma\equiv2a$ and using the expansion of $e^{i\vec k\cdot\vec R}$ in spherical Bessel functions, and defining $h(R)=g(R)-1$, we have

$$\langle M_{LM}(k,\kappa)\rangle=i^{1-2L}\rho\int_0^\infty dR\,R^2j_L(kR)h_L^+(\kappa R)$$
$$+i^{1-2L}\rho\int_0^\infty dR\,R^2h(R)j_L(kR)h_L^+(\kappa R)$$
$$+\delta_{L0}\delta_{M0}i/\sqrt{4\pi}. \tag{D3}$$

Using standard results,[38] we have

$$\int_0^\infty dR\,R^2j_L(\kappa R)h_L^+(\kappa R)$$
$$=\frac{kaj_{L-1}(ka)h_L^+(\kappa a)-\kappa aj_L(ka)h_{L-1}^+(\kappa a)}{k^2-\kappa^2}. \tag{D4}$$

For $ka\ll1$ and $\kappa a\ll1$, using the usual expansions, we find

$$i^{1-2L}\rho\int_0^\infty dR\,R^2j_L(kR)h_L^+(\kappa R)=(-)^L4\pi\rho\frac{k^LY^*_{LM}(\hat k)}{\kappa^{L+1}(k^2-\kappa^2)}$$
$$+O((ka)^2,(\kappa a)^2). \tag{D5}$$

Suppose now that $h(R)$ has a natural scale length, say b, due to clustering. Then we have, changing variables,

$$\int_0^\infty dR\, R^2 j_L(kR) h_L^*(\kappa R) h(R) = b^3 \int_{a/b}^\infty dx\, x^2 j_L(kbx) h_L^*(\kappa b x) h(bx) . \quad \text{(D6)}$$

If $kb \ll 1$ and $\kappa b \ll 1$ we can use the expansions of the spherical Bessel functions, and we find

$$\int_0^\infty dR\, R^2 j_L(kR) h_L^*(\kappa R) h(R) \sim \frac{b^2 k^L}{\kappa^{L+1}} \frac{1}{2L+1} \int_{a/b}^\infty dx\, x^2 h(bx) , \quad \text{(D7)}$$

where the final integral is of order one. Thus the leading correction to the quasistatic result is of order $(kb)^2$ relative to the other contributions to $\langle M \rangle$. This implies that even if $ka \ll 1$ and $\kappa a \ll 1$ there can be significant corrections if there is clustering. If there is no clustering, however, $b \sim a$ and these corrections are small in this limit.

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