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Optical and dielectric properties of partially resonant composites

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We analyze the two-dimensional potential around a coated cylinder placed in a nonuniform field. In two special cases the system behaves as if the core of the cylinder were enlarged and the shell absent. These are when the shell dielectric constant is the negative of either the core dielectric constant or the matrix dielectric constant. When the shell dielectric constant has a small imaginary part, the field can exhibit large fluctuations which remain localized near the surface of the coated cylinder.

Under certain circumstances the dielectric response of a three-phase composite structured as a square array of coated cylinders embedded in a matrix of dielectric constant ε_m can be exactly the same as the response of a square array of solid cylinders embedded in the same matrix material.[1] This occurs when the core dielectric constant (ε_c) and the shell dielectric constant (ε_s) satisfy some special relations.

Two of these circumstances are genuinely surprising: $\varepsilon_s + \varepsilon_c = 0$, when the core properties are extended up to the outer boundary of the shell, and $\varepsilon_s + \varepsilon_m = 0$, the properties of the core being extended beyond the shell into the matrix. Both of these are what we call a *partially-resonant* system.

More generally, we take *partially-resonant* to mean a compound system, containing a component with a given volume fraction (f), whose properties are equivalent to those of a system with that component having a larger volume fraction.

In particular, it may be possible for a *partially-resonant* system with a vanishingly small concentration to exhibit properties like those of a concentrated system. In the cases studied here, the "magnified" component is the core, and this behavior is due to some new sort of resonance, what we might call *partial resonance* since the system has a finite, rather than an infinite, response to the applied field.

Here we will show that the notion of partial resonance extends to bodies containing any number of coated-cylinder inclusions, each aligned parallel to the z axis, and is not just particular to regular arrays. Also we will show the equivalence extends to coated inclusions with noncircular boundaries. Naturally, for either $\varepsilon_s + \varepsilon_c = 0$ or $\varepsilon_s + \varepsilon_m = 0$ to be satisfied, at least one dielectric constant must be the negative of another dielectric constant. Although seemingly unphysical, this condition comes close to being satisfied for various pairs of materials at frequencies in the visible and infrared. As an example, the pair SiC-voids has $\varepsilon_{\text{SiC}} = -1 + 0.1i$ and $\varepsilon_{\text{voids}} = 1$ at $\lambda = 10.550\ \mu$m.

For the equivalence to hold, the radii of the equivalent solid cylinders must be much smaller than λ. Otherwise, scattering becomes important and we need to use the full Maxwell equations, rather than just the quasistatic approximation used here.

From the viewpoint of electrical tomography (whereby the distribution of dielectric material within a body is to be determined by placing a set of test electrodes at the body surface and measuring the currents that result from various combinations of oscillating potentials applied to the electrodes)[2] the body containing the coated cylinders is indistinguishable from the body containing the equivalent solid cylinders, with respect to test fields that are independent of z.

There is another unusual effect associated with this equivalence. We will see that when the shell dielectric constant has a small imaginary part, with $\varepsilon_s = (-1 + i\delta)\varepsilon_m$ so that the relation $\varepsilon_s + \varepsilon_m = 0$ is only approximately satisfied, then the field in the vicinity of the coated cylinder can exhibit large fluctuations, with these fluctuations growing to infinity and becoming more rapid as $\delta \to 0$. The length scale of these oscillations is much shorter than the wavelength of the applied radiation (which is infinite in the quasistatic limit). By introducing molecules into the region of these high-field fluctuations, we would expect to see enhanced Raman scattering.[3] In contrast to the phenomena of resonance where there is global increase in the field magnitude as resonance is approached, these field fluctuations remain localized: at sufficiently large distances from the coated cylinder the field remains smooth and approximately equal to that found around the equivalent solid cylinder.

To analyze the equivalence let us consider a coated cylinder embedded in a body, possibly containing other coated cylinders. The coated cylinder, centered on the origin of coordinates, is characterized by the core radius (r_c), the shell radius (r_s), and the corresponding dielectric constants ($\varepsilon_c, \varepsilon_s$). We suppose the external medium has dielectric constant ε_m, at least within a radius r_m

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around the cylinder center. Assuming the quasistatic approximation is valid, the two-dimensional electrical potential can be expressed in the form $\mathcal{V}(x,y) = \mathrm{Re}[V(z)]$, in which $z = x + iy = r\exp(i\theta)$ and $V(z)$ is a complex potential satisfying $\nabla\cdot(\varepsilon\nabla V) = 0$. Since $V(z)$ is an analytic function of z in each of the three regions it has the expansions (see Fig. 1)

$$V_e(z) = A_0 + \sum_{\ell=1}^{\infty}(A_\ell z^\ell + B_\ell z^{-\ell}) \quad \text{for } r_s \le r \le r_m, \tag{1}$$

$$V_s(z) = C_0 + \sum_{\ell=1}^{\infty}(C_\ell z^\ell + D_\ell z^{-\ell}) \quad \text{for } r_c \le r \le r_s, \tag{2}$$

$$V_c(z) = E_0 + \sum_{\ell=1}^{\infty} E_\ell z^\ell \quad \text{for } r \le r_c. \tag{3}$$

Let us introduce the dimensionless parameters

$$\eta_{ms} = \frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + \varepsilon_s}, \quad \eta_{sc} = \frac{\varepsilon_s - \varepsilon_c}{\varepsilon_s + \varepsilon_c}, \tag{4}$$

which characterize the jumps in dielectric constant across the boundary separating the external medium from the shell (η_{ms}) and across the boundary separating the shell from the core (η_{sc}). With these notations, by means of the boundary conditions of continuity of the potential and the normal component of the electric displacement at the core and shell surfaces, we may express the coefficients $B_\ell, C_\ell, D_\ell, E_\ell$ in terms of the A_ℓ:

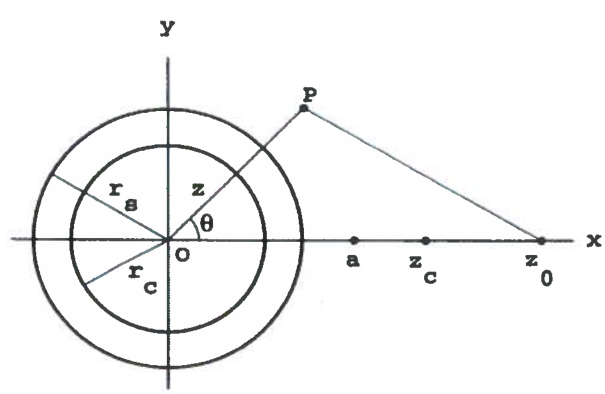


FIG. 1. A coated cylinder in the field of a dipole at the finite distance z_0. There are marked also the points at distances $a = r_s^2/r_c$ and $z_c = a^2/r_s$ along the x axis.

$$B_\ell = [\eta_{ms} + \eta_{sc}(r_c/r_s)^{2\ell}]r_s^{2\ell}A_\ell/\Delta, \tag{5}$$

$$C_\ell = (1+\eta_{ms})A_\ell/\Delta, \tag{6}$$

$$D_\ell = \eta_{sc}(1+\eta_{ms})r_c^{2\ell}A_\ell/\Delta, \tag{7}$$

$$E_\ell = (1+\eta_{ms})(1+\eta_{sc})A_\ell/\Delta, \tag{8}$$

where $\Delta = 1 + \eta_{ms}\eta_{sc}(r_c/r_s)^{2\ell}$.

Analyzing the relationship between the coefficients A_ℓ and B_ℓ which defines the response of a coated cylinder to an external field, we may distinguish six special cases when the coated cylinder is equivalent to a solid cylinder, i.e., when the relation between A_ℓ and B_ℓ is exactly the same as that for a solid cylinder. First, we find the two banal equivalences corresponding to $\varepsilon_s = \varepsilon_m$ (solid cylinder of radius r_c and dielectric constant ε_c) and $\varepsilon_s = \varepsilon_c$ (solid cylinder of radius r_s and dielectric constant ε_c). Second, for $\varepsilon_s = 0$ or $\varepsilon_s \to \pm\infty$ the shell shields the core and the coated cylinder resembles a solid cylinder of radius r_s and dielectric constant $\varepsilon_s = 0$ or $\varepsilon_s \to \pm\infty$, respectively.

The last two special cases, namely $\varepsilon_c + \varepsilon_s = 0$ and $\varepsilon_s + \varepsilon_m = 0$, are completely different. The first leads us to the relations

$$B_\ell = \frac{\varepsilon_m - \varepsilon_c}{\varepsilon_m + \varepsilon_c} r_s^{2\ell} A_\ell,$$

i.e., without changing the external potential V_e we can replace the coated cylinder by a solid cylinder having the radius r_s and dielectric constant ε_c (the core properties being extended up to the outer boundary of the shell). It follows that the dielectric properties of a solid cylinder of dielectric constant ε_s and radius r_s change dramatically if we insert a core of radius r_c and dielectric constant $-\varepsilon_s$. Even when r_c is infinitesimal the dielectric properties transform to those of a solid cylinder of dielectric constant $-\varepsilon_s$ and radius r_s. In the second case the coefficients of the external potential satisfy the relations

$$B_\ell = \frac{\varepsilon_m - \varepsilon_c}{\varepsilon_m + \varepsilon_c} a^{2\ell} A_\ell, \quad a = r_s^2/r_c, \tag{9}$$

which indicate an extension of the core properties beyond the limits of the shell, into the matrix, the equivalent solid cylinder having radius $a > r_s$ and dielectric constant ε_c. In other words we can replace the coated cylinder by a solid cylinder of dielectric constant ε_c and radius a without altering the potential outside the radius a provided $a < r_m$. In the special case when both $\varepsilon_c + \varepsilon_s = 0$ and $\varepsilon_s + \varepsilon_m = 0$, the coated cylinder can be replaced by matrix material without disturbing the external field. A related equivalency occurs in two-dimensional elasticity. Mansfield[4] found that certain reinforced holes can be introduced in a plane sheet without altering the stress distribution in the main body of the sheet, assuming the loading acts within the plane of the sheet. In contrast to the coated cylinder, where the electrical equivalence holds for all imposed fields, the elastic equivalence of Mansfield is limited to a particular (but arbitrary) loading: the shape of the reinforced holes needs to be adjusted according to the loading.

In order to clarify this remarkable behavior, let us now specialize to the case of a coated cylinder embedded in an infinite medium, subject to a nonuniform external field created by a line dipole of prescribed magnitude parallel to the coated-cylinder axis and located at z_0 (see Fig. 1). This specialization can be made without loss of generality since an arbitrary external field can be generated by a superposition of such dipole source terms, with possibly complex coefficients. Also let us choose our axes so that z_0 is located on the positive x axis, i.e., so that z_0 is real and positive. The magnitude of the dipole is chosen such that its potential is $1/(z-z_0)$, and may be expanded in z, with coefficients $A_\ell = -(1/z_0)^{\ell+1}$.

Since the analysis for the case $\varepsilon_s+\varepsilon_c=0$ is similar to that for case $\varepsilon_s+\varepsilon_m=0$, let us focus on the latter. From (5)–(8) and (1)–(3) we see that when $z_0 > z_c = a^2/r_s$ the potential is

$$\tilde{V}_e(z) = \frac{1}{z-z_0} - \frac{\varepsilon_m-\varepsilon_c}{\varepsilon_m+\varepsilon_c}\frac{a^2/z_0^2}{z-a^2/z_0} \quad \text{for } |z|\geq r_s, \quad (10)$$

$$\tilde{V}_s(z) = -\frac{2\varepsilon_c}{\varepsilon_m+\varepsilon_c}\frac{1}{z_0} + \frac{\varepsilon_m-\varepsilon_c}{\varepsilon_m+\varepsilon_c}\frac{r_s^2/a^2}{z-z_0r_s^2/a^2} - \frac{r_s^2/z_0^2}{z-r_s^2/z_0} \quad \text{for } r_c\leq|z|\leq r_s, \quad (11)$$

$$\tilde{V}_c(z) = \frac{\varepsilon_m-\varepsilon_c}{\varepsilon_m+\varepsilon_c}\frac{1}{z_0} + \frac{2\varepsilon_m}{\varepsilon_m+\varepsilon_c}\frac{r_s^2/a^2}{z-z_0r_s^2/a^2} \quad \text{for } 0\leq|z|\leq r_c. \quad (12)$$

We will call this the *partially-resonant* potential. Naturally the expression for $\tilde{V}_e(z)$ coincides for $r > a$ with that for the solid cylinder of radius a and can be regarded as resulting from a dipole at z_0 and an image dipole at a^2/z_0. This image dipole, which has no physical significance for the solid-cylinder problem, begins to take on a physical meaning for the coated-cylinder problem as z_0 approaches z_c. When this happens the image dipole approaches the surface of the coated cylinder, and accordingly the potential and fields start to diverge to infinity there.

If $z_0 < z_c$, the ratio test shows the series (1) for $V_e(z)$ fails to converge for $r_s < r < a^2/z_0$ and shows the series (2) for $V_s(z)$ fails to converge for $z_0r_s^2/a^2 < r < r_s$. Also the solution (10) is no longer appropriate since the image dipole at a^2/z_0 is located in the matrix, creating an unphysical singularity, at which the expansion of V_e diverges; there appears also an image dipole at $z_0r_s^2/a^2$ in the shell, producing an unphysical singularity of V_s. Consequently, there is no physical solution of the problem if $\varepsilon_s=-\varepsilon_m$ and $z_0 < z_c$.

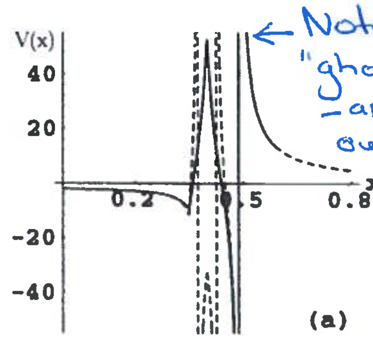
To guarantee the existence of a physical solution we need to add a small imaginary part to the dielectric constant of the shell so that it becomes lossy. If we take the dielectric constant of the shell to be $\varepsilon_s = (-1+i\delta)\varepsilon_m$, where $|\delta|\ll 1$, then the potential remains close to the value given by (10)–(12) except in the annulus $z_0r_s^2/a^2 \leq r \leq a^2/z_0$ (when $z_0 < z_c$). Inside this annulus the potential has a completely different behavior.

Starting from (5) with $A_\ell = -(1/z_0)^{\ell+1}$, we find, in the first-order approximation:

$$B_\ell \approx \frac{1}{z_0}\left(1+\frac{2i}{\delta}\right)\left(\frac{r_s^2}{z_0}\right)^\ell \quad \text{for } \ell > \left|\frac{\ln\delta}{\ln(r_c/r_s)}\right|.$$

This asymptotic behavior guarantees the convergence of the series expansions (1)–(3) provided only that $z_0 > r_s$. Consequently, the problem has a physical solution for a source dipole placed at any position $z_0 > r_s$ and the potential is finite over the entire x-y plane excepting at the point $z = z_0$. Since the potential is harmonic in the core, shell, and matrix it follows by the maximum principle that any local maxima or minima of the potential must be located at the interface between phases or at z_0.

As an example, Fig. 2(a) shows that the nonanalytic potential $\tilde{V}(x)$ exhibits singularities in the shell and in the matrix. By contrast, the actual potential remains finite, but exhibits local extrema on the core and shell boundaries (so long as $\varepsilon_c > 0$). As $\delta \to 0$, these extrema tend to $-\infty$ and ∞, respectively. At the same time, the potential around the outer shell boundary $r = r_s$ exhibits large fluctuations which are particularly intense in the vicinity of $\theta = 0$ [see Fig. 2(b)]. These fluctuations become less pronounced at larger and smaller r, dying out in the limit $\delta \to 0$ for all $r > a^2/z_0$ and for all $r < z_0r_s^2/a^2$, with the potential $V(z)$ converging to $\tilde{V}(z)$ in these regions.



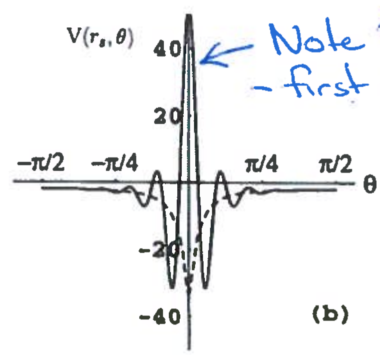


FIG. 2. The case $a < z_0 < z_c$, displaying the potentials (a) $V(x)$ and (b) $V(r_s,\theta)$ given by (10)–(12) (dashed curve) and for $\varepsilon_s = -1+i\delta$ (solid curve), with $\delta = 0.01$, $\varepsilon_c = 5$, and $\varepsilon_m = 1$. The geometry of the system is characterized by $r_c = 0.35$, $r_s = 0.40$, $a = 0.46$, $z_c = 0.52$, $z_0 = 0.49$.

From (5) and (4) it can be seen that the multipole coefficients B_ℓ, for any finite order ℓ, tend to the corresponding multipole coefficients in (9). In other words, the multipole coefficients always exhibit the nonanalytic property, even at radii where the potential series diverges as $\delta \to 0$.

From these results we can analyze the dielectric properties of composites containing random distributions of coated cylinders. For example, suppose we start with a regular square lattice of coated cylinders each with core radius r_c, shell radius r_s, and with spacing d between cylinder centers such that d is only slightly larger than $2r_s^2/r_c$. The core, shell, and surrounding matrix material have dielectric constants ε_c, ε_s, and ε_m. Now suppose we randomly select lattice sites and remove the coated cylinder situated there (replacing it by matrix material) until a proportion p of the original coated cylinders remain. When $\varepsilon_s = (-1+i\delta)\varepsilon_m$ and δ is sufficiently small, the effective dielectric constant of this random array will be close to that of the equivalent, nonanalytic, array of nearly touching solid cylinders, each of radius $a = r_s^2/r_c \approx d/2$. In particular, when $\varepsilon_c \gg \varepsilon_m$ and p is above the percolation threshold, the field will be concentrated across the gaps between these nearly touching cylinder pairs, and the effective dielectric constant of this random array will be close to that of an associated random capacitor network, where each capacitor represents the capacitance across the small gap between neighboring solid-cylinder pairs. Critical exponents which describe the behavior of the effective dielectric constant of the network when p is close to the site percolation threshold[5] will also be appropriate to describing the behavior of the effective dielectric constant of both the random array of solid cylinders and the equivalent array of coated cylinders. In other words, the description involving critical exponents is appropriate even though there is no obvious geometrical percolation in the random array of coated cylinders: unlike the equivalent two-phase composite, the connectedness of this three-phase composite is insensitive to perturbations in p, r_c, or r_s. In the vicinity of the coated cylinders the field will oscillate wildly (due to the presence of image charges which lie outside the radius r_s in the equivalent solid-cylinder problem), but at $r = d/2$ the field will be smooth and concentrated at the midpoints between the coated-cylinder pairs.

This equivalence also extends to coated cylinders with noncircular boundaries. Indeed, suppose $\varphi(z)$ represents a conformal mapping from the disk of radius r_m to some region $\Omega(r_m)$. Let $\Omega(r)$ denote the image under this conformal mapping of a disk of radius r. Then a coated inclusion with the core and shell occupying the regions $\Omega(r_c)$ and $\Omega(r_s)$ excluding $\Omega(r_c)$ and surrounded by matrix material at least within the region $\Omega(r_m)$ is equivalent to a solid inclusion occupying the region $\Omega(r_s)$ when $\varepsilon_s + \varepsilon_c = 0$ and $r_m > r_s$, and is equivalent to a solid cylinder occupying the region $\Omega(r_s^2/r_c)$ when $\varepsilon_s + \varepsilon_m = 0$ and $r_m > r_s^2/r_c$. This is because the equations of two-dimensional electrostatics are preserved under conformal transformations, the dielectric constant and the potential at any point $z' = \varphi(z)$ being taken equal to their former values at the point z. To prove this equivalence, one maps the potential around the coated noncircular cylinder to the corresponding potential around the coated circular inclusion, replaces it by the equivalent solid cylinder, and then maps the potential back to the solid noncircular cylinder. The field in the exterior region, outside the equivalent solid inclusion, is left undisturbed by this procedure. By the Riemann mapping theorem[6] we can find a mapping $\varphi(z)$ which takes the disk $r < r_m$ to an arbitrarily shaped simply connected region $\Omega(r_m)$. Since $\Omega(r)$ is almost circular when r is sufficiently small, it follows that an infinitesimal coated cylinder with almost circular boundaries can be equivalent to an arbitrarily shaped solid cylinder when $\varepsilon_s + \varepsilon_m = 0$. In other words the shape of the equivalent solid cylinder is extremely sensitive to the shape of the coated cylinder when $r_c \ll r_s$.

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