Brief Reports

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Bounds on allowed values of the effective dielectric function of two-component composites at finite frequencies

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The exact solutions for electromagnetic wave propagation in laminar microstructures lead via a waveguide mechanism to values of the effective dielectric function that lie outside the absolute Wiener quasistatic bounds as well as the more restrictive Hashin-Shtrikman limits. The results explain recent refractive-index data of Egan and Hilgeman on pressed-powder composites.

Much work has been done on establishing various bounds to the allowed dielectric response, ϵ, of two-phase composite materials in the long-wavelength (quasistatic) limit.[1–5] It is now known that the original bounds of Wiener[1] can be made more restrictive if one takes advantage of measurable macroscopic attributes such as average composition[2] or the presence or absence of two- or three-dimensional isotropy.[3–5] However, the question naturally arises as to the validity of these bounds for more realistic finite-frequency conditions where the dimensions of the microstructure may be comparable to the wavelength of light. Previous efforts[6–11] to investigate finite-wavelength effects in composite materials have been concerned with the validity of the quasistatic approximation, and specifically, only with the accuracy by which Maxwell Garnett[12] or Bruggeman[13] effective-medium theories can reproduce beam attenuation for noninteracting spherical inclusions as calculated by Mie theory.[14] Whether values of ϵ that lie outside the quasistatic bounds can be obtained at finite wavelengths, and why, are problems that have not yet been considered.

Here, we take the simple and direct approach of investigating the behavior of the TE, TM, and TEM solutions[15,16] for wave propagation in the same laminar configuration that is used to obtain the least restrictive (Wiener) bounds to ϵ in the quasistatic limit. These solutions are exact for any wavelength. They show clearly that bounds derived in a quasistatic limit are relaxed at finite frequencies because a new mechanism, not contained in the quasistatic formulation, comes into play. In essence, the constituent with the larger value of $\mathrm{Re}(\epsilon)$ acts as a waveguide, concentrating the flux and thereby exerting an anomalously large influence on the value of ϵ. In striking contrast, it is the constituent with the smaller value of $|\epsilon|$ that always dominates in the quasistatic case simply because the more polarizable fraction develops more boundary charge and screens itself more effectively from the external field.

The model is as follows. Let constituents a and b having dielectric functions ϵ_a and ϵ_b form a composite of alternating layers of thicknesses d_a and d_b, with the y axis perpendicular to the layers. Within each layer,

$$c^2\vec{k}_a^2/\omega^2=\epsilon_a,\ \ c^2\vec{k}_b^2/\omega^2=\epsilon_b\ . \qquad (1)$$

We consider first the TE and TM modes which propagate in the $\hat{z}$ direction with electric and magnetic fields $\hat{x}E(\vec{r},t)$ and $\hat{x}H(\vec{r},t)$, respectively. If the continuity equations for tangential $\vec{E}$ and $\vec{H}$ and for normal $\vec{D}$ and $\vec{B}$ are to be realized, then the phase factor $\exp(ik_z z-i\omega t)$ must be the same at all boundaries. All the above conditions can be achieved simultaneously only if $\vec{k}_a$ and $\vec{k}_b$ also have components along $\hat{y}$. Thus the phase factors of the TE and TM waves will have the general form

$$\exp(ik_y y + ik_z z - i\omega t) .$$

If k_y is real, the solutions will combine to yield standing waves $\hat{x}E$, $\hat{x}H \sim \cos(k_y y)$ within the lamination. If k_y is imaginary, the wave will be evanescent in that layer.

The boundary conditions lead to the following equations[15,16]:

$$(k_y^a/\xi_a)\tan(k_y^a d_a/2) + (k_y^b/\xi_b)\tan(k_{y_b} d_b/2) = 0 , \tag{2a}$$

$$\epsilon = (ck_z/\omega)^2 , \tag{2b}$$

$$= \epsilon_a - (ck_y^a/\omega)^2 , \tag{2c}$$

$$= \epsilon_b - (ck_y^b/\omega)^2 , \tag{2d}$$

where $\xi_a = \xi_b = 1$ for the TE mode and $\xi_a = \epsilon_a$, $\xi_b = \epsilon_b$ for the TM mode. The solution is exact, valid for any values of the parameters. The propagation rate through the composite defines ϵ.

If d_a, $d_b \rightarrow 0$, then Eqs. (2) reduce to

$$\epsilon = f_a\epsilon_a + f_b\epsilon_b, \quad \text{TE} \tag{3a}$$

$$\epsilon^{-1} = f_a\epsilon_a^{-1} + f_b\epsilon_b^{-1}, \quad \text{TM} \tag{3b}$$

where $f_{a,b} = d_{a,b}/(d_a + d_b)$ is the volume fraction of the phase a, b. For $0 \le f_a = 1 - f_b = \le 1$, Eqs. (3) trace out the absolute Wiener bounds.[1] The bounds are absolute because the region of the complex ϵ plane enclosed by them must contain all physically realizable quasistatic values of ϵ for two-phase composites regardless of composition or microstructure. This follows because there can never be less screening than no screening [all boundaries parallel to the electrostatic field, Eq. (3a)] nor more screening than maximum screening [all boundaries perpendicular to the electrostatic field, Eq. (3b)]. If the macroscopic compositions $f_a = 1 - f_b$ are known, then all physically realizable values of ϵ, regardless of microstructure, must lie within a smaller enclosed region bounded by the Hashin-Shtrikman limits.[2] For real ϵ_a and ϵ_b, the Hashin-Shtrikman limits reduce to the two points given by Eqs. (3).

It is already clear that quasistatic bounds may no longer be rigorously valid when the wavelength becomes comparable to the microstructural dimensions simply because the electric field can now have components both parallel and perpendicular to the internal boundaries. We show next that a waveguide mechanism favors the component with the larger Re(ϵ) and is responsible for relaxing these bounds. Suppose for simplicity that ϵ_a and ϵ_b are both real, with $\epsilon_a < \epsilon_b$. Since no absorption mechanism is present, ϵ must also be real and must satisfy the general inequality $\epsilon_a \le \epsilon \le \epsilon_b$. Then Eqs. (2c) and (2d) show that k_y^a must be purely imaginary and k_y^b purely real. Therefore, the wave is evanescent in a and concentrated in b. Using the inequalities $\tanh(x) \le x \le \tan(x)$, we find that for real ϵ_a, ϵ_b:

$$f_a\epsilon_a + f_b\epsilon_b \le \epsilon \le \epsilon_b, \quad \text{TE} \tag{4a}$$

$$\epsilon_b^{-1} \le \epsilon^{-1} \le f_a\epsilon_a^{-1} + f_b\epsilon_b^{-1}, \quad \text{TM} . \tag{4b}$$

Thus for finite frequencies ϵ lies between the appropriate Hashin-Shtrikman limit and ϵ_b.

In more quantitative terms, we show in Fig. 1 calculated values of ϵ for layers (a) of SiO_2 separating layers (b) of amorphous Si as a function of D/λ, where $D = d_a + d_b$ is the period of structure. In this example, we chose $d_a = d_b$ and $E = 1.75$ eV ($\lambda = 7084$Å), so $\epsilon_a = 2.12$ and $\epsilon_b = 19.05 + i0.13 \cong 19.0$. The Hashin-Shtrikman limits calculated from Eqs. (3) are shown as the straight lines. For $D/\lambda << 0.1$ the quasistatic limits are reasonably accurate; the lowest-order correction, $\sim(\omega D/c)^2 (\epsilon_b - \epsilon_a)^2$ is, as usual,[8,16] quadratic in D/λ. However, the results for the TE and TM modes deviate markedly from the quasistatic values near $D/\lambda = 0.1$ and 0.15, respectively. For $D/\lambda > 1$, the waveguide effect completely dominates and $\epsilon \cong \epsilon_b$. We note that the Hashin-Shtrikman limits are exceeded for *all* D/λ for the TE mode and for all $D/\lambda > 0.32$ for the TM mode.

If ϵ_a or ϵ_b is complex, then ϵ is not constrained to lie along the real axis and the bounds become

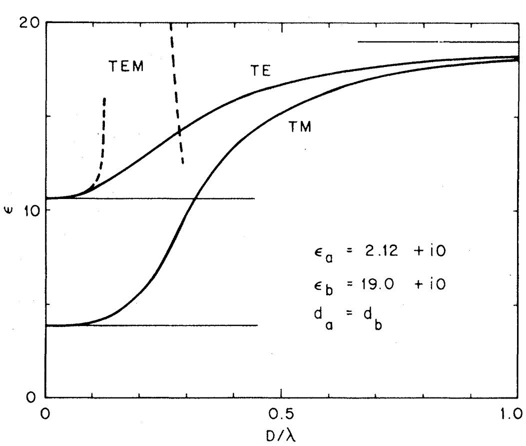

FIG. 1. Variation of ϵ with D/λ for a hypothetical laminar composite of amorphous Si and SiO_2. The Hashin-Shtrikman limits are shown as the two horizontal lines on the left. The horizontal line on the right indicates the limit $\epsilon = \epsilon_b$.

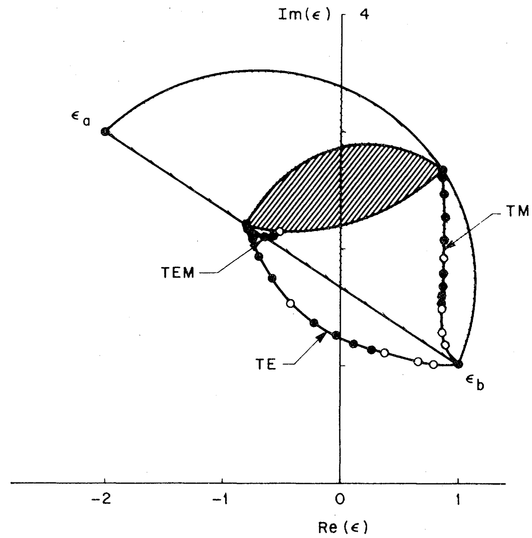

FIG. 2. Two-dimensional quasistatic limits and the variation of ϵ with D/λ for the complex values of ϵ_a and ϵ_b used by Milton (Ref. 4). Increments of 0.1 and 0.5 in D/λ are indicated by closed and open circles, respectively.

two-dimensional in the complex ϵ plane. We consider the example given by Milton[3]: $\epsilon_a = -2+i\,3$, $\epsilon_b = 1+i\,1$, and $f_a = 0.60$. The absolute Wiener bounds,[1] given by Eqs. (3), define the large semicircular region in Fig. 2. But because the composition $f_a = 0.60$ is fixed, ϵ is now restricted to the crosshatched region determined by the Hashin-Shtrikman limits.[2] Superimposed on the figure are traces that show the evolution of ϵ with increasing D/λ for the laminar configuration for both TE and TM modes. The dots signify increments of 0.1 in D/λ. The results show that the calculated values of ϵ lie outside the Hashin-Shtrikman limits for all finite λ. Moreover, with a second dimension available, the Wiener bounds for the TE mode are also exceeded for all finite λ. For small wavelengths, the waveguide mechanism again causes ϵ to converge to the dielectric function with the largest value of Re(ϵ).

TEM propagation perpendicular to the laminations is qualitatively different because multiple reflections cause waves to propagate in both directions. If ϵ is to have meaning, then the coefficients of both waves must differ by the same factor $\eta = \exp(ik_zD)$ upon a displacement by one full period D. This restriction leads to an eigenvalue equation for k_z which reduces to Eq. (3a) when $D \to 0$. The TEM branches of ϵ are also plotted in Figs. 1 and 2. They tend initially to follow the TE branch, but in general there exist ranges of D/λ for which propagation is not possible.

The tendency of wave energy to concentrate in the more dense constituent, as seen in the simple laminar case treated here, will clearly also occur for more complex microstructures. The calculations could easily be extended to cylindrical microstructures appropriate to columnar materials such as glow-discharge-deposited a-Si(H).[17] The quasistatic limit should remain a good approximation for $d/\lambda \lesssim 0.1$, but for larger ratios the more dense columnar material should dominate. The present development also indicates why effective-medium models describe[18] microscopically rough surfaces: the impinging wave front is refracted into the more dense medium as the TE amd TM components realize local boundary conditions and preserve a common phase factor. But the distortion will be small, and the quasistatic limit a good approximation if the microstructural dimensions are small compared to λ. This appears to be the case for microscopically rough amorphous Si films.[19]

Finally, we consider the recent remarkable results of Egan and Hilgeman,[20] who measured refractive indices for selected transparent materials in pressed-powder form with independently determined packing fractions. For $MgCO_3$ and $BaSO_4$ with average bulk dielectric functions of 2.692 at 5890 Å for each material,[21] the void fractions were 0.50 and 0.48, respectively. Because the packing fractions are known, the relevant quasistatic limits for any microstructure are given by Eqs. (3a) and (3b).[2] For samples that are macroscopically isotropic in three dimensions, the more restrictive Bergman-Milton limits will apply.[3–5] Evaluating both sets of limits explicitly, we calculate

$$1.46 < 1.66 < \epsilon(MgCO_3) < 1.75 < 1.85$$

and

$$1.49 < 1.69 < \epsilon(BaSO_4) < 1.78 < 1.85 \; .$$

The measured values of 2.161 ($MgCO_3$) and 2.076 ($BaSO_4$) lie well outside both sets of allowed ranges. Consequently, these data cannot be explained by microstructural effects alone.

It is significant that these materials were the two for which the constituent particle dimensions ($0.1 \times 1.0\ \mu m^2$ platelets for $MgCO_3$, $0.1-1.0\ \mu m$ spheroids for $BaSO_4$) were of the order of λ. A waveguide effect should therefore be expected. The calculated values of ϵ for all modes as a function of D/λ are shown in Fig. 3. The TEM mode can be neglected because the conditions for the development of a forbidden band obviously cannot be realized in these samples. The actual depen-

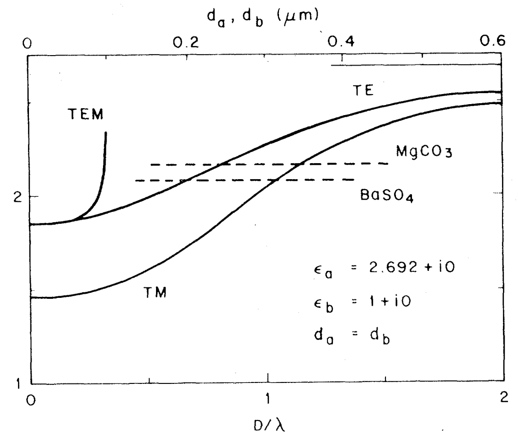

FIG. 3. As Fig. 1, but for the parameters of the samples used in Ref. 20. Measured values are indicated by the dashed lines.

dence of ϵ on D/λ will undoubtedly differ from the predictions of the simple laminar model, but a mean value should be representative. The experimental values intersect the TE and TM branches near d_a, $d_b \sim 0.3$ μm, of the order of the mean particle dimensions determined by electron microscopy. Thus the anomalously large values of ϵ are explained with microstructural parameters in agreement with experiment.

In conclusion, we have shown by means of a model calculation that values of ϵ can be obtained at finite wavelengths that not only lie outside the quasistatic Hashin-Shtrikman limits, but also lie outside the more general absolute Wiener bounds. These results can explained the recent data of Egan and Hilgeman, who observed the refractive index values that were impossibly large according to quasistatic theory. It would now be of interest to determine whether absolute bounds, analogous to those derived in the quasistatic limit, can also be obtained for finite wavelengths. This work is in progress and will be reported elsewhere.

I wish to thank W. G. Egan for verifying the macroscopic uniformity of $MgCO_3$ and $BaSO_4$ samples.

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