Exactly Solvable Microscopic Geometries and Rigorous Bounds for the Complex Dielectric Constant of a Two-Component Composite Material

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Exact bounds for the complex, bulk, effective dielectric constant ϵ_e of a two-component macroscopic composite that depend on the available information about the composite are presented and discussed. Some of these bounds are readily ascribable to special, exactly solvable, microscopic geometries. As a consequence, it is shown that there can exist composites where the real part of ϵ_e diverges as $\omega \to 0$ while the dc conductivity $\sigma_e \neq 0$.

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The problem of calculating the bulk, effective dielectric constant ϵ_e of a macroscopic composite material has been the subject of numerous investigations. An excellent review of the field, including an exhaustive list of references, has been written not long ago by Landauer.[1] Since it is often the case that the microscopic geometry of the composite is not known precisely, the derivation of rigorous upper and lower bounds for ϵ_e given partial information about this geometry has been a useful pursuit. The simplest examples of such sets of bounds for a real dielectric constant of a two-component composite are

$$\epsilon_1 \le \epsilon_e \le \epsilon_2, \quad \text{for} \quad \epsilon_1 < \epsilon_2, \tag{1}$$

$$\epsilon_e \le p_1\epsilon_1 + p_2\epsilon_2, \quad \frac{1}{\epsilon_e} \le \frac{p_1}{\epsilon_1} + \frac{p_2}{\epsilon_2}, \tag{2}$$

$$\epsilon_1 + \frac{p_2}{(\epsilon_2 - \epsilon_1)^{-1} + p_1/3\epsilon_1} \le \epsilon_e \le \epsilon_2 + \frac{p_1}{(\epsilon_1 - \epsilon_2)^{-1} + p_2/3\epsilon_2}, \quad \text{for } \epsilon_1 < \epsilon_2. \tag{3}$$

For Eq. (1) the only information are the values of ϵ_1, ϵ_2, for Eq. (2) the volume fractions of the two components $p_1, p_2 = 1 - p_1$ are also known, and for Eq. (3) the composite is also known to have isotropic or cubic point symmetry. The bounds of Eq. (3) are due to Hashin and Shtrikman.[2]

Interestingly enough, the extreme values in each case are attained in very simple geometries: Equality in Eq. (1) is attained when the entire composite is made of only one component. In Eq. (2), the extreme values are achieved when the composite is either in the form of parallel cylinders with the electric field $\vec{E}$ along the axes (the upper bound on ϵ_e), or in the form of parallel plates perpendicular to $\vec{E}$ (the lower bound). In Eq. (3), the extreme values occur when the entire composite is made of spheres of one component coated by a concentric spherical shell of the other component. The coated spheres can have any size (indeed, many different sizes must be present in order for the entire volume to be filled up), but they must all have the same volume fractions of the two components.

I have now succeeded in obtaining for the first time some rigorous bounds for the case of a complex dielectric constant in a two-component composite. These bounds are the analogs of Eqs. (1)–(3) for the real case. It is most convenient to state these bounds in terms of the function $F(s)$, where

$$s \equiv \epsilon_2/\epsilon_2 - \epsilon_1, \quad F(s) \equiv 1 - \epsilon_e/\epsilon_2.$$

Figure 1 shows these bounds in the form of regions of the complex F plane where the values of F must lie. While a detailed derivation of these bounds will be published elsewhere,[3] I note here that the bounds are obtained by treating as free parameters the poles s_n and residues B_n in the spectral representation of $F(s)$,

$$F(s) = \sum_n B_n/s - s_n,$$

and following the method of Bergman.[4] That is, if I assume that ImF is given and use it, as well as the other bits of available information, to impose constraints on the variation of these parameters, then the bounds are determined by maximixing or minimizing ReF.

All of the bounds obtained in this way are constructed from circles or straight lines that pass

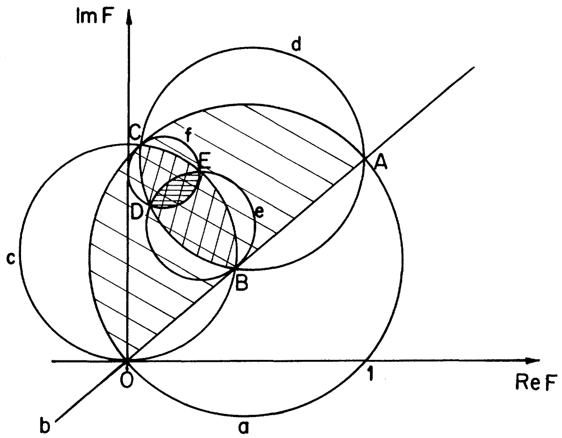

FIG. 1. Graphic description of the three sets of bounds in the complex F plane. The hatched region is where $F(s)$ must be if s (i.e., ϵ_1 and ϵ_2) is known. The cross-hatched region is where F must be if also the volume fractions p_1 and $p_2 = 1 - p_1$ are known. The triple-hatched region is where F must be if, in addition to that, the composite has either cubic or isotropic point symmetry. The lines a–f can all be constructed (with ruler and compass only, if desired) from a knowledge of the points A–E:

$$A = \frac{1}{s}, \quad B = \frac{p_1}{s}, \quad C = \frac{p_1}{s - p_2}, \quad D = \frac{p_1}{s - \frac{1}{3} p_2},$$

$$E = \frac{p_1}{3 - p_1}\left[\frac{2}{s} + \frac{p_2}{s - (1 - \frac{1}{3} p_1)}\right].$$

A parametric representation for the lines a–f, where s_0 or B_0 is the parameter, is

$$F_a(s) = \frac{B_0}{s - (1 - B_0)}, \quad F_b = \frac{B_0}{s},$$

$$F_c = \frac{p_1}{s - s_0}, \quad F_d = \frac{1}{s_0}\left[\frac{s_0 - p_2}{s} + \frac{p_2(1 - s_0)}{s - s_0}\right],$$

$$F_e = \frac{p_1}{s_0}\left(\frac{p_2}{3(s - s_0)} + \frac{s_0 - \frac{1}{3} p_2}{s}\right),$$

$$F_f = \frac{p_1(s - s_0 - \frac{2}{3} p_2)}{s^2 - s(p_2 + s_0) + p_2(s_0 - \frac{2}{3} p_1)}.$$

through some very simple points in the F plane. These points, which are specified in Fig. 1, determine the bounds completely, and allow them to be constructed by ruler and compass alone, if so desired, even without knowing their detailed equations (the detailed equations for the points and lines are given in the figure caption of Fig. 1).

As was found in the real case, here too the extreme values of $F(s)$ seem to be achieved for special microscopic geometries which happen to be exactly soluble: The circle a in Fig. 1 corresponds to a composite in the form of parallel plates perpendicular to $\vec{E}$. The straight line b corresponds to a composite in the form of cylinders parallel to $\vec{E}$.

The circle c corresponds to a composite made entirely of spheroids of ϵ_1 material, each of them coated by a shell of ϵ_2 material with an outer surface that is also a spheroid. The two spheroidal surfaces of a single-coated grain must be confocal, and the volume fractions, as well as the spheroidal axis, must be the same in all the coated grains, but the volume of a grain is arbitrary. (It can be shown that space can be packed completely in this fashion.) This is clearly a generalization of the Hashin-Shtrikman coated-sphere geometry. The reason why this geometry is exactly solvable is because when a coated spheroid of the right shape is placed in a homogeneous medium whose dielectric constant is ϵ_e, in which there exists a uniform field $\vec{E}$, there will be no distortion of the field outside the inclusion. This occurs when the polarization field created by the coating shell exactly cancels the polarization field created by the core. Such a cancellation is only possible with ellipsoidal-shaped inclusions, since only then is the induced field restricted to a single electrostatic multipole (dipole if the inclusion is a sphere). Clearly, the circle d corresponds to a similar microscopic geometry with the roles of ϵ_1 and ϵ_2 reversed.

In the case of the circles e and f, I have not yet been able to find a specific microgeometry where these extreme values of F are realized, though I believe that such a microgeometry does exist. Some clues as to its nature are already apparent from the equations for the two circles (see Fig. 1 and its caption): The function $F_e(s)$ corresponding to points on the boundary of the triple-hatched region satisfies $F_e(0) = \infty$ and $F_e(1) < 1$. This means that both components of the composite material must percolate. The function $F_f(s)$ for a similar range of points satisfies $F_f(0) < \infty$ and $F_f(1) = 1$. Therefore, in this case, neither component percolates. Clearly, it would be of great interest to identify the microgeometries for which $F_e(s)$ and $F_f(s)$ are exact.

One interesting application of the bounds described in this Letter is to the case where one component is a pure conductor with a dc conductivity σ_2, while the other is a pure insulator, with a real dielectric constant ϵ_1. In that case one can write

$$\epsilon_2 = 4\pi\sigma_2/i\omega,$$

$$s = \frac{\sigma_2}{\sigma_2 - i\omega\epsilon_1/4\pi} \cong 1 + i\,\frac{\omega\epsilon_1}{4\pi\sigma_2} \cong 1,$$

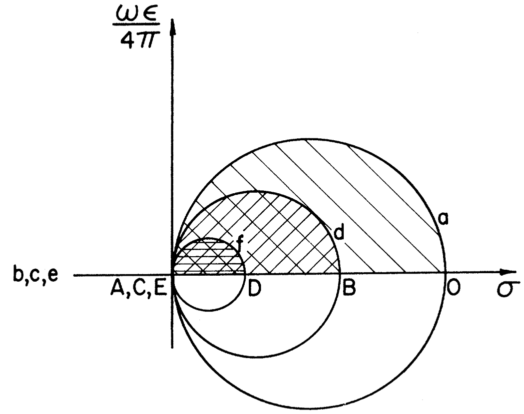

FIG. 2. Graphic description of the three sets of bounds in the σ, $\omega\epsilon/4\pi$ plane for the special case where ϵ_1 = real, $\epsilon_2 = 4\pi\sigma_2/i\omega$. The points, the lines, and the hatchings have the same meanings as in Fig. 1. In this case, the nonzero points are given by $O = \sigma_2$, $B = p_2\sigma_2$, $D = \frac{2}{3}p_2\sigma_2/1-\frac{1}{3}p_2$.

where $\omega\epsilon_1 \ll 4\pi\sigma_2$ is assumed in order to get the last result. In this case, the bounds of Fig. 1 degenerate to the bounds of Fig. 2. Some interesting consequences follow from this figure:

(a) If $\sigma_e = 0$ at $\omega \neq 0$, then one must also have $\epsilon_e = 0$. Note that this does not mean that at a dc conductivity threshold ϵ_e must vanish, since then $\omega = 0$.

(b) The bounds of Fig. 2 do not change with ω, therefore one can use them to analyze the behavior of a system at a dc conductivity threshold when $\omega \to 0$. If $\sigma_e \sim \omega^{\beta}$, then the divergence of ϵ_e is limited by the rigorous inequality

$$\epsilon_e \leq \text{const}\,\omega^{(\beta/2)-1}.$$

This is weaker than a result proven in the past by Bergman and Imry,[5] namely

$$\epsilon_e \sim \omega^{\beta-1},$$

but it is a rigorous result.

(c) Because all of the points within any of the allowed regions are probably attainable by an appropriate microgeometry, therefore, there exist systems for which $\sigma_e = 0$, and yet $\epsilon_e \to \infty$ as $\omega \to 0$.[6] This means that, in order for the real part of ϵ_e to diverge, it is sufficient but not necessary that the system be at a conductivity threshold. This divergence is limited by $\epsilon_e < \text{const}/\omega$. This result could help in understanding the anomalous behavior of the dielectric constant in some sedimentary rocks,[7] where ϵ_e has been observed to be as high as 10^6.

A similar approach to the calculation of bounds for complex ϵ_e has apparently been taken simutaneously by Milton,[8] although the methods he used have not been fully described. He quotes results for dimensionality $d = 2$, as well as $d = 3$. For $d = 3$, his results though less detailed, are the same as those reported here. For $d = 2$, he claims to have identified the microgeometry that yields the values of $F(s)$ on the boundary of the allowed region for the isotropic case (the analogs of the circles e and f). I think that this identification is erroneous, since the proposed microgeometry, namely, double coated circular cylinders (e.g., a circular cylinder ϵ_2 coated by a concentric cylindrical shell ϵ_1, coated by yet another concentric cylindrical shell ϵ_2), has exactly one component that percolates. By contrast, I have shown in the $d = 3$ case (but the same is true also in the $d = 2$ case), that on e and f either both or none of the components must percolate.

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[3] D. J. Bergman and P. Lacour-Gayet, to be published.

[4] D. J. Bergman, Phys. Rep. 43C, 377 (1978), also in *Solid State Devices—1977*, edited by C. W. Garland and D. Tanner AIP Conference Proceedings No. 40 (American Institute of Physics, New York, 1978), p. 46.

[5] D. J. Bergman and Y. Imry, Phys. Rev. Lett. 39, 1222 (1977).

[6] I am indebted to P. Sen for suggesting this possibility to me.

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[8] G. W. Milton, to be published.