# Critical behavior of transport in percolation-controlled smart composites

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## ABSTRACT

The electrical transport properties of many smart composites and other technologically important materials are dominated by the connectedness, or percolation properties of a particular component. Predicting the critical behavior of such media near their percolation threshold, where one typically obtains the most interesting and useful material properties, is a formidable challenge, and not well understood from a modeling perspective. Here we report on recent mathematical results on lattice and continuum percolation models of these types of materials. In particular, we have found a direct, analytic correspondence between the critical behavior of transport in two component random media around a percolation threshold, and the critical behavior exhibited by phase transitions in statistical mechanics, such as by the magnetization of a ferromagnet around its Curie point. This correspondence has been used to establish that the critical exponents for DC conduction near a percolation threshold, for both lattice and continuum systems, satisfy the same scaling relations as their counterparts in statistical mechanics. Underlying our correspondence is an integral representation for the effective conductivity, which has exactly the same mathematical form as a corresponding representation for the magnetization of an Ising ferromagnet. The integral representation applies in general to many classical transport coefficients for two component media, and we have used it to obtain rigorous bounds on the complex permittivity of matrix-particle composites. A preliminary application of these bounds to insulator-conductor composites is investigated here, and even when the inclusions are near to touching (percolation), the new bounds give a dramatic improvement over the complex versions of the fixed volume fraction and Hashin-Shtrikman bounds found independently by Milton and Bergman in the late 1970's.

**Keywords:** percolation models, phase transitions, matrix-particle composites, complex permittivity

## 1. INTRODUCTION

A broad range of problems in the physics of materials involve highly disordered media whose effective behavior depends critically on the connectedness, or percolation properties of a particular component. Examples include smart materials such as piezoresistors and thermistors,[1] smart insulators, radar absorbing composites, cermets, porous media, doped semiconductors, thin metal films, and sea ice. In numerous smart materials, the microstructure can be characterized by conducting particles embedded in an insulating host, and one is interested in the effective DC conductivity (or complex permittivity for interactions with waves) near the critical volume fraction for percolation of the conducting phase. Such media frequently arise due to the desirability of light materials having the attractive mechanical properties of common polymers and the electrical conductivities of metals.[2] In modeling transport in such materials, one often considers a two component random medium with component conductivities $\sigma_1$ and $\sigma_2$, in the volume fractions $1-p$ and $p$. The medium may be discrete, like the random resistor network,[3–6] or continuous, like the random checkerboard[7–9] and Swiss cheese models.[10,6] In these systems, as $h = \frac{\sigma_1}{\sigma_2} \to 0$, the effective conductivity $\sigma^*(p,h)$ exhibits critical behavior near the percolation threshold $p_c$, $\sigma^*(p,0) \sim (p-p_c)^t$ as $p \to p_c^+$ (with $\sigma_1 = 0$ and $\sigma_2 = 1$), and at $p = p_c$, $\sigma^*(p_c,h) \sim h^{1/\delta}, h \to 0^+$.

In the lattice case of the random resistor network, it has been widely proposed[11–15,5,6] that the scaling behavior of $\sigma^*$ as a function of both $p$ and $h$ around $p = p_c$ and $h = 0$ (including crossover between the above laws), is similar to a phase transition in statistical mechanics, like that exhibited by the magnetization $M(T,H)$ of an Ising ferromagnet around its Curie point at temperature $T = T_c$ and applied field $H = 0$. However, this behavior of $\sigma^*(p,h)$ has been

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explicitly obtained only in mean-field theory around the critical dimension $d_c = 6$,[16] and in the effective medium approximation,[6,3] although renormalization arguments in two and three dimensions have supported its validity.[17,18] This situation should be contrasted with that for the underlying percolation model, where its Kasteleyn-Fortuin[19] representation as the $q \to 1$ limit of the $q$-state Potts model makes clear the connection to phase transitions. Indeed, the critical exponents of percolation have been shown to obey the standard scaling relations of statistical mechanics.[20,21] Similar efforts to use the connection between the random resistor network and the $q \to 0$ Potts model to analyze $\sigma^*$ when $h > 0$ have apparently been unsuccessful.[22,16] Nevertheless, for $h = 0$, a number of scaling laws relating $t$ to percolation exponents have been proposed, such as the Alexander-Orbach conjecture, although none of them seems to be exactly true.[4,5]

In the continuum, such as for the Swiss cheese model (a conducting host with random holes cut out), while the percolation exponents remain the same as for the lattice,[23] the transport exponents, such as $t$ in three dimensions, can be different from their lattice values.[10] For the random checkerboard in two dimensions, it has been argued[9] that the exponent $\delta$ is different from its lattice value, while the percolation exponents (and $t$) remain the same. These examples of non-universal behavior raise a fundamental question as to what features of the lattice problem remain true in the continuum.

In recent work[24] which we report on in section 2 below, we have shown that although the critical exponents of transport in the continuum may be different from their lattice values, they still satisfy the standard scaling relations of statistical mechanics, as do their lattice counterparts. This is accomplished through an analytic correspondence between transport in two component random media and the magnetization $M$ of an Ising ferromagnet,[25] which has been developed further and applied to critical behavior.[24] In particular, we obtain a new Stieltjes integral representation for $\sigma^*$ which is the direct analogue of Baker's formula for $M$,[26] making the connection to statistical mechanics almost transparent. Then, methods which have been used to analyze the critical behavior of the Ising model[26–28] can be appropriately modified for transport in lattice and continuum percolation models. Our scaling laws are obtained under the standard assumption of existence of the critical exponents for transport, and a technical assumption concerning the asymptotic behavior of the Stieltjes representation, which was also used for the Ising model.[28] We have also investigated the zeros of the conductivity partition function in the complex $p-$ and $h-$planes introduced earlier,[25] and found further numerical evidence in the case of the two dimensional random resistor network that the percolation threshold $p = p_c = \frac{1}{2}$ is an accumulation point of these zeros. We also discuss the existence of gaps in the distributions of the zeros (or spectral gaps) around $h = 0$ (for $p > p_c$) and around $p = p_c$ (for $h > 0$) in both lattice and continuum settings. It should be remarked that our results can be viewed as a culmination of the suggestion[14] that the analytic properties of $\sigma^*(p, h)$ are related to the scaling hypothesis of statistical mechanics.

The Stieltjes integral representation above has been used previously in a different form to obtain rigorous, general bounds on the effective complex permittivity of two component random media in the continuum.[29–31] These bounds are obtained under statistical constraints on the microstructure, such as known volume fractions and statistical isotropy, and are valid in the quasistatic regime where the wavelength is much larger than the microstructural scale. For real component parameters these bounds are known as the arithmetic and harmonic mean bounds (fixed volume fraction), or elementary bounds, and the Hashin-Shtrikman (isotropic) bounds.[32] Unfortunately, for high contrast materials, such as insulator-conductor composites, the bounds are very broad, and give little practical information about the effective behavior. However, in a seminal work, Bruno[33] found that if one assumes further that the geometry of the composite is characterized by the condition that one phase is contained in separated inclusions embedded in a matrix of the other material (matrix-particle assumption), then there is a gap in the support of the measure in the integral representation (a spectral gap around the endpoints). He used this finding to derive tighter versions of the Hashin-Shtrikman bounds in the case of real parameters. Subsequently, we[34,35] have found complex versions of the elementary and Hashin-Shtrikman bounds for matrix-particle composites. Even when the inclusions are fairly close to touching, the new bounds give a dramatic improvement over the original complex bounds.[29–31] Our work on these matrix-particle bounds was motivated by trying to capture more tightly effective permittivity data at around 5 GHz for sea ice, which we originally compared[36] with the older complex bounds. Interestingly, the microstructure of sea ice, which consists of a pure ice (insulating) host with random brine (conducting) and air inclusions, is strikingly similar to the microstructure of many insulator-conductor composites of interest in smart materials technology. Furthermore, the sea ice exhibits a percolation threshold around a critical temperature of $T_c \approx -5°C$ where the brine phase becomes connected and the ice becomes porous, significantly affecting its electromagnetic, fluid and thermal transport properties. In section 3 we describe the new bounds and give a preliminary application of them to insulator-conductor composites. This approach gives an alternative to widely used effective medium theories.[2,1]

## 2. STATISTICAL MECHANICS OF TRANSPORT NEAR A PERCOLATION THRESHOLD

To present our results, we briefly review the relevant theory for the nearest neighbor Ising model of a ferromagnet in a field $H$ and at temperature $T$. When $H = 0$, as $T \to T_c^-$ the magnetization $M(T) = -\frac{\partial f}{\partial H} \sim (T_c - T)^\beta$, where $f$ is the free energy per site, and the magnetic susceptibility $\chi = \frac{\partial M}{\partial H} = -\frac{\partial^2 f}{\partial H^2} \sim (T - T_c)^{-\gamma}$. Along the critical isotherm $T = T_c$, $M(H) \sim H^{1/\delta}$ as $H \to 0^+$ (where $\delta$ and the other exponents have different numerical values from their analogues in transport). Now, in 1952 Lee and Yang[37] found that the zeros of the partition function of the Ising ferromagnet (or lattice gas) lie on the unit circle in the $z$-plane, where $z = exp(-2\beta H)$ is the "activity," $\beta = 1/kT$, and $k$ is Boltzmann's constant. Equivalently they lie on the imaginary axis in the $H$-plane. For $T > T_c$, there is a gap $\theta_H$ in these zeros around $H = 0$, which collapses as $T \to T_c^+$, with $\theta_H \sim (T - T_c)^\Delta$. In the $T$-plane the situation is more complicated, although in $d = 2$ for $H = 0$, "Fisher's zeros" lie on two circles in the complex $v = \tanh(2\beta J)$ plane,[38] where $J$ is the interaction strength. In 1968, Baker[26] used the Lee -Yang property to show that the magnetization has the following special analytic structure in the variable $\tau = \tanh(\beta H)$,

$$M(\tau) = \tau + \tau(1 - \tau^2)G(\tau^2), \qquad G(\tau^2) = \int_0^\infty \frac{d\psi(t)}{1 + \tau^2 t}, \tag{1}$$

where $G$ is a Stieltjes (or Herglotz) function of $\tau^2$, and $\psi$ is a positive measure which for $T > T_c$ is supported only in $[0, S(T)]$, where $S(T) \sim (T - T_c)^{-2\Delta}, T \to T_c^+$. Note that $M$ is analytic throughout the $\tau^2$-plane except $(-\infty, 0]$. This analytic representation was used to obtain the scaling relations $\beta = \Delta - \gamma$ and $\delta = \Delta/(\Delta - \gamma)$,[27,28] (which are satisfied by the mean field exponents $\beta = 1/2, \gamma = 1, \delta = 3, \Delta = 3/2$, and the exact exponents for $d = 2, \beta = 1/8, \gamma = 7/4, \delta = 15$), as well as *Baker's inequalities* $\gamma_{n+1} - 2\gamma_n + \gamma_{n-1} \geq 0$ for the critical exponents $\gamma_n$ of the higher field derivatives of the free energy $f$, with $\gamma_0 = \gamma$.[26]

We have observed that the Lee-Yang-Baker critical theory outlined above applies to transport problems, and in particular, we rigorously establish direct analogues of (1) and the associated scaling relations and inequalities for lattice and continuum percolation models of conduction in two component random media. Our results apply as well to electrical permittivity, magnetic permeability, thermal diffusivity, fluid permeability for Darcy flow in a porous medium, and effective diffusivity for turbulent transport,[39] which all share the Lee -Yang property.

We now formulate the effective conductivity problem in general for two component random media in the continuum $\mathbf{R}^d$, which includes the lattice $\mathbf{Z}^d$ as a special case.[40,25] Let the local conductivity $\sigma(x,\omega) = \sigma_1\chi_1(x,\omega) + \sigma_2\chi_2(x,\omega)$ be a two-valued stationary random field in $x \in \mathbf{R}^d$ and $\omega \in \Omega$, where $\Omega$ is the set of realizations of the random medium, $\chi_1(x,\omega) = 1$ if $x$ is in medium 1, and 0 otherwise, and $\chi_2 = 1 - \chi_1$. For the random resistor network and checkerboard, $\Omega$ is identified with a product of Bernoulli trials, and for the Swiss cheese model with random distributions of points (centers of possibly overlapping spheres or discs) in $\mathbf{R}^d$. Let $E(x,\omega)$ and $J(x,\omega)$ be stationary random electric and current fields which are related by $J = \sigma E$ and satisfy $\nabla \cdot J = 0$ and $\nabla \times E = 0$, with $< E(x,\omega) >= e_k$, where $e_k$ is a unit vector, and $< \cdot >$ denotes ensemble average over $\Omega$, or an appropriate infinite volume limit. For the random resistor network the differential equations become difference equations (Kirchoff's laws). For isotropic media, the effective conductivity $\sigma^*$ is defined by $< J >= \sigma^* < E >$, or $\sigma^* =< (\sigma_1\chi_1 + \sigma_2\chi_2)E_k >$. Since $\sigma^*$ is homogeneous $\sigma^*(\lambda\sigma_1, \lambda\sigma_2) = \lambda\sigma^*(\sigma_1, \sigma_2)$, we consider $m(h) = \frac{\sigma^*}{\sigma_2}, h = \frac{\sigma_1}{\sigma_2}$.

The following analytic properties of $m(h)$ have been established[41,30,31]: (i) $m(h)$ is analytic everywhere in the $h$-plane except $(-\infty, 0]$, and (ii) $Im(m) > 0$ when $Im(h) > 0$. These properties of $m$ were used to prove[31] the following representation formula for $F(s) = 1 - m(h), s = 1/(1 - h)$ (based on earlier conjectures[41,30]),

$$F(s) = \int_0^1 \frac{d\mu(u)}{s - u}, \tag{2}$$

where $\mu$ is a positive measure on [0,1] depending only on the geometry of the medium. Representation (2) was also proven by applying the spectral theorem to the resolvent representation $F(s) =< \chi_1[(s + \Gamma\chi_1)^{-1}e_k] \cdot e_k >$, where $\Gamma = \nabla(-\Delta)^{-1}\nabla\cdot$, and $\mu$ is the spectral measure of $\Gamma\chi_1$. As we have mentioned, this formula has been used quite successfully to obtain bounds on effective transport coefficients under microstructural constraints.[41,30,31] It was shown[25] how (2) could be derived from a free energy $\Phi(s) = \int_0^1 \log(s-u)d\mu(u)$, with $F = \frac{\partial\Phi}{\partial s}$. For the Ising model $f(T,H)$ has a similar representation.[37] For a finite resistor network with N resonances $s_n \in [0,1]$, $\Phi(s)$ is the infinite volume limit of finite volume free energies $\Phi_N(s) = \frac{1}{N}\log Z_N(s)$, where $Z_N(s) = \prod_{n=1}^{N}(s-s_n)$ is the partition function, (whose zeros become distributed according to $\mu$), serving as the analogue of $Z_N(z) = a_N \prod_{n=1}^{N}(z-z_n), |z_n| = 1$, for an Ising model with $N$ sites. We remark that (2) leads to $\frac{\partial^2 m}{\partial h^2} \leq 0$, the analog of the G.H.S inequality $\frac{\partial^2 M}{\partial H^2} \leq 0$.

We now focus on applying (2) to conductivity functions $\sigma(x,\omega)$ describing lattice and continuum percolation models. We assume the existence of the critical exponents $t$ and $\delta$, defined above, as well as $\gamma$, defined via a conductive susceptibility $\chi(p) = \frac{\partial m}{\partial h} \sim (p-p_c)^{-\gamma}, p \to p_c{}^+, h = 0$ (which is different from[42] and numerous subsequent works). Furthermore, for $p > p_c$, we assume that there is a gap $\theta_h \sim (p-p_c)^{\Delta}$ in the support of $\mu$ around $h = 0$ or $s = 1$, which is discussed further below. Now, one of the key features of (1) is that the coefficients in the Taylor expansion of $G$ around $\tau^2 = 0$ are the moments of $\psi$, which is not the case for (2), when expanded around $h = 0$ or $s = 1$. However, a simple change of variables $u = \frac{t}{t+1}$ (here $t$ is a variable, and not the critical exponent) in (2) yields the direct analogue of (1) for conductivity

$$m(h) = 1 + (h-1)g(h), \qquad g(h) = \int_0^\infty \frac{d\phi(t)}{1+ht}, \tag{3}$$

which is a general formula holding for two component stationary random media in lattice and continuum settings. In (3), $g$ is a Stieltjes function of $h$, and $\phi$ is a positive measure which for our percolation models with $p > p_c$ is supported only in $[0, S(p)]$, where $S(p) \sim (p-p_c)^{-\Delta}, p \to p_c{}^+$. The moments $\phi_n = \int_0^\infty t^n d\phi(t)$ satisfy the inequalities $\phi_n\phi_m \leq \phi_0\phi_{n+m}$, and form the coefficients of the expansion of $g$ around $h = 0$, $g(h) = \phi_0 - \phi_1 h + \phi_2 h^2 - \ldots$, where $(-1)^n n!\phi_n = \frac{\partial^n g}{\partial h^n}(0) (\sim -\frac{\partial^n m}{\partial h^n}(0)$ as $p \to p_c{}^+)$. We assume that $\phi_n(p) \sim (p-p_c)^{-\gamma_n}$, so that $\gamma_0 = 0$ and $\gamma_1 = \gamma$,which differs from the Ising model. The moment inequalities yield *Baker's inequalities* for transport

$$\gamma_{n+1} - 2\gamma_n + \gamma_{n-1} \geq 0, \tag{4}$$

which imply that the gap exponents $\Delta_n = \gamma_n - \gamma_{n-1}$ form an increasing sequence $\Delta_{n+1} \geq \Delta_n$.

Now, we have used (3) to show[24] that the critical exponents of transport above satisfy the same scaling relations as their counterparts in statistical mechanics, obtaining

$$\delta = \frac{\Delta}{\Delta - \gamma}, \qquad t = \Delta - \gamma. \tag{5}$$

These two relations for the exponents $t, \gamma, \delta$, and $\Delta$ hold for lattice and continuum percolation models satisfying our assumptions, and establish in general that the two-parameter scaling exhibited by phase transitions in statistical mechanics holds for transport as well. They are satisfied by the critical exponents in effective medium theory for the resistor network $t = 1, \gamma = 1, \delta = 2$, and $\Delta = 2$.[3,43] Unfortunately, it appears as if not enough is known numerically at this point about exponents other than $t$ for the models of interest to test their validity. Although for the $d = 2$ lattice, where $\delta = 2$, these relations imply $t = \gamma = \Delta/2$, so that with $t = 1.3$,[4] $\gamma = 1.3$ and $\Delta = 2.6$. For the $d = 2$ checkerboard, where it is believed that $\delta = 4$, these relations imply $t = \gamma/3 = \Delta/4$. The relation $\Delta = 2t$ for the $d = 2$ lattice was found in ref.[43] with a different argument. We note that the inequalities[44] $1 \leq t \leq 2$ in $d = 2, 3$ and $2 \leq t \leq 3$ in $d \geq 4$ can be combined with (5) to yield various inequalities on combinations of the other critical exponents.

We now briefly discuss the assumption that there is a gap $\theta_h$ in the support of $\mu$ in (2) around $h = 0$ or $s = 1$ for $p > p_c$, which has been investigated in[5] for the case of the random resistor network. It is believed that for any $p > p_c$ there is spectrum that extends all the way to the origin $h = 0$, corresponding to very large, but very rare connected regions of the insulating phase (Lifshitz phenomenon). However, even though this spectrum gives $m(h)$ an essential singularity at $h = 0$, its contribution to the asymptotics of $m$ is exponentially small (presumably due to the exponentially small probabilities of such regions much larger than a correlation length), and do not affect our investigation of power laws. Thus we have assumed a gap in the support of $\mu$ (or $\phi$). In fact, it is predicted in ref.[5] that in numerical simulations the "cut" of $m(h)$ for $p > p_c$ will appear to extend only to a negative crossover value of $h$ (our effective gap $\theta_h$), which tends to 0 as $p \to p_c^+$. Indeed, evidence for this behavior is found in the numerical simulations in ref.[43] For the Swiss cheese model, we expect similar behavior. In fact, for a modified Swiss cheese model where the insulating holes are separated by a minimal distance $\epsilon$ (or if there are separated, conducting inclusions in an insulating matrix) Bruno[33] has proven the existence of a spectral gap $\theta_h$ around $h = 0$ (and $h = \infty$), and studied how it vanishes as $\epsilon \to 0$. This result will play a key role in the bounds we discuss in the next section.

Finally, we have investigated the zeros of the conductivity partition function in the complex $p$–plane, which correspond to the poles of $F(p,s)$, by calculating Padé approximants to the perturbation expansion of (2) around $h = 1$,

$$F(p,s) = \frac{\mu_0(p)}{s} + \frac{\mu_1(p)}{s^2} + \frac{\mu_2(p)}{s^3} + \ldots, \tag{6}$$

where the $\mu_j(p)$ are the moments of $\mu$. They yield a sequence of approximants to the partition function. For the $d = 2$ random resistor network, where we have exact results for $\mu_0, \mu_1, \mu_2$ and $\mu_3$,[45] and precise numerical results for $\mu_4$ and $\mu_5$,[43,46] we have found strong evidence that the percolation threshold $p_c = \frac{1}{2}$ is an accumulation point of the zeros of these approximants (as more and more of the moments are used), and the real $p$–axis is "pinched" at $p_c$ as $h \to 0$. Furthermore, for $h > 0$ we have proven[25] the existence of a gap $\theta_p$ in the zeros in the $p$–plane around $p_c$, for a class of models Bruno has called "infinitely interchangeable media," (see ref.,[45] for example), which include the random resistor network and cell materials in the continuum such as the random checkerboard. We construct an explicit domain in the complex $p$–plane in which $\sigma^*(p)$ is analytic in $p$. Because of our explicit construction, assuming $\theta_p \sim (p - p_c)^{\Delta_p}$, our result establishes the general inequality $\Delta_p \leq 1$ for these media.

## 3. BOUNDS ON THE COMPLEX PERMITTIVITY OF MATRIX-PARTICLE COMPOSITES

In this section, we first briefly review the analytic continuation method for obtaining bounds on the complex permittivity of two component random media, and then describe the new bounds for matrix-particle composites. We formulate our problem exactly as above, except we assume that our medium consists of two materials of complex permittivities $\epsilon_1$ and $\epsilon_2$, in the volume fractions $p_1$ and $p_2$. Then the effective complex permittivity $\epsilon^*$ is defined via $< D >= \epsilon^* < E >$, where $D = \epsilon E$ is the displacement field, $\epsilon = \epsilon_1 \chi_1 + \epsilon_2 \chi_2$, $\nabla \cdot D = 0$ and $\nabla \times E = 0$. As we have discussed, the key step in the method is obtaining the integral representation (2) for the effective complex permittivity,

$$F(s) = 1 - \frac{\epsilon^*}{\epsilon_2} = \int_0^1 \frac{d\mu(z)}{s - z}\,, \tag{7}$$

where $s = 1/(1-h), h = \epsilon_1/\epsilon_2$ and $\mu$ is a positive measure on $[0,1]$. One of the most important features of (7) is that it separates the parameter information in $s = 1/(1 - \epsilon_1/\epsilon_2)$ from information about the geometry of the mixture, which is all contained in $\mu$. Again, $\mu$ is the spectral measure associated with the operator $\Gamma\chi_1$.

Statistical assumptions about the geometry are incorporated into $\mu$ through its moments $\mu_n = \int_0^1 z^n d\mu(z)$. Comparison of the perturbation expansion (6) around a homogeneous medium ($s = \infty$, or $\epsilon_1 = \epsilon_2$) with a similar expansion of a resolvent representation for $F(s)$,[31] yields $\mu_n = (-1)^n < \chi_1[(\Gamma\chi_1)^n e_k] \cdot e_k >$. Then

$$\mu_0 = p_1 \tag{8}$$

if only the volume fractions are known, and

$$\mu_1 = \frac{p_1 p_2}{d} \tag{9}$$

if the material is statistically isotropic, where $d$ is the dimension of the system. In general, knowledge of the $(n+1)$–point correlation function of the medium allows calculation of $\mu_n$ (in principle).

Bounds on $\epsilon^*$, or $F(s)$, are obtained by fixing $s$ in (7), varying over admissible measures $\mu$ (or admissible geometries), such as those that satisfy only (8), and finding the corresponding range of values of $F(s)$ in the complex plane. Two types of bounds on $\epsilon^*$ are readily obtained. The first bound $R_1$ assumes only that the relative volume fractions $p_1$ and $p_2 = 1 - p_1$ are known, so that (8) is satisfied. In this case, the admissible set of measures forms a compact, convex set. Since (7) is a linear functional of $\mu$, the extreme values of $F$ are attained by extreme points of the set of admissible measures, which are the Dirac point measures of the form $p_1\delta_z$. The values of $F$ must lie inside the circle $p_1/(s-z), -\infty \le z \le \infty$, and the region $R_1$ is bounded by circular arcs, one of which is parametrized in the $F$-plane by

$$C_1(z) = \frac{p_1}{s-z}, \qquad 0 \le z \le p_2. \tag{10}$$

To display the other arc, it is convenient to use the auxiliary function[47]

$$E(s) = 1 - \frac{\epsilon_1}{\epsilon^*} = \frac{1 - sF(s)}{s(1-F(s))}, \tag{11}$$

which is a Herglotz function like $F(s)$, analytic off $[0,1]$. Then in the $E$-plane, we can parametrize the other circular boundary of $R_1$ by

$$\hat{C}_1(z) = \frac{p_2}{s-z}, \qquad 0 \le z \le p_1. \tag{12}$$

In the $\epsilon^*$-plane, $R_1$ has vertices $V_1 = \epsilon_1/(1-\hat{C}_1(0)) = (p_1/\epsilon_1 + p_2/\epsilon_2)^{-1}$ and $W_1 = \epsilon_2(1 - C_1(0)) = p_1\epsilon_1 + p_2\epsilon_2$, and collapses to the interval

$$(p_1/\epsilon_1 + p_2/\epsilon_2)^{-1} \le \epsilon^* \le p_1\epsilon_1 + p_2\epsilon_2 \tag{13}$$

when $\epsilon_1$ and $\epsilon_2$ are real, which are the classical arithmetic (upper) and harmonic (lower) mean bounds, also called the elementary bounds. The complex elementary bounds (10) and (12) are optimal and can be attained by a composite of uniformly aligned spheroids of material 1 in all sizes coated with confocal shells of material 2, and vice versa. These arcs are traced out as the aspect ratio varies.

If the material is further assumed to be statistically isotropic, i.e., $\epsilon^*_{ik} = \epsilon^*\delta_{ik}$, then (9) must be satisfied as well. A convenient way of including this information is to use the following transformation,[47,48]

$$F_1(s) = \frac{1}{p_1} - \frac{1}{sF(s)}. \tag{14}$$

The function $F_1(s)$ is, again, a Herglotz function which has the representation

$$F_1(s) = \int_0^1 \frac{d\mu^1(z)}{s-z}. \tag{15}$$

The constraint (9) on $F(s)$ is then transformed to a restriction of only the mass, or zeroth moment $\mu_0^1$ of $\mu^1$, with $\mu_0^1 = p_2/p_1 d$. Applying the same procedure as for $R_1$ yields a region $R_2$, whose boundaries are again circular arcs. In the $F$-plane, one of these arcs is parametrized by

$$C_2(z) = \frac{p_1(s-z)}{s(s-z-p_2/d)}, \qquad 0 \le z \le (d-1)/d. \tag{16}$$

In the $E$-plane, the other arc is parametrized by

$$\hat{C}_2(z) = \frac{p_2(s-z)}{s(s-z-p_1(d-1)/d)}, \qquad 0 \le z \le 1/d. \tag{17}$$

In the $\epsilon^*$-plane, $R_2$ has vertices $V_2 = \epsilon_2(1 - C_2(0))$ and $W_2 = \epsilon_1/(1-\hat{C}_2(0))$, and collapses to the interval

$$\epsilon_2 + p_1 \Big/ \left(\frac{1}{\epsilon_1 - \epsilon_2} + \frac{p_2}{d\epsilon_2}\right) \le \epsilon^* \le \epsilon_1 + p_2 \Big/ \left(\frac{1}{\epsilon_2 - \epsilon_1} + \frac{p_1}{d\epsilon_1}\right), \tag{18}$$

when $\epsilon_1$ and $\epsilon_2$ are real with $\epsilon_1 \ge \epsilon_2$, which are the Hashin–Shtrikman bounds.[32] When $\epsilon_1 \le \epsilon_2$, the sequence of inequalities is reversed. The vertices $V_2$ and $W_2$ (which correspond to the expressions in (18)), are attained by the Hashin–Shtrikman coated sphere geometries (spheres of all sizes of material 1 in the volume fraction $p_1$ coated with spherical shells of material 2 in the volume fraction $p_2$, and vice versa), and lie on the arcs which bound $R_1$. We remark that higher-order correlation information can be conveniently incorporated by iterating (14), as in ref.[48]

Now we consider the implications on the above bounding procedure when one assumes further that composite geometry has a matrix-particle structure, i.e., separated inclusions of $\epsilon_1$ embedded in a matrix of $\epsilon_2$. We refer the reader elsewhere[33,35,34] for precise definitions of the class of materials, and for proofs of the results we will use below. The key result which allows us to obtain tighter bounds on $\epsilon^*$ than those above is that for matrix-particle composites, the support of $\mu$ is contained in an interval $[s_m, s_M] \subset [0,1]$, so that (7) takes the form

$$F(s) = \int_{s_m}^{s_M} \frac{d\mu(z)}{s-z}\,. \tag{19}$$

We will describe later how these values of $s_m$ and $s_M$ are chosen for relevant microgeometries. A convenient way of incorporating the support restriction is to first consider a new variable $t$, defined by

$$s = (s_M - s_m)t + s_m. \tag{20}$$

Then the interval $[s_m, s_M]$ in the $s-$plane gets mapped to $[0,1]$ in the $t-$plane, and the function

$$H(t) = F(s) = F((s_M - s_m)t + s_m) \tag{21}$$

is analytic off $[0,1]$ in the complex $t-$plane. It can be shown that there is a positive Borel measure $\nu$ on $[0,1]$ such that

$$H(t) = \int_0^1 \frac{d\nu(z)}{t-z}\,. \tag{22}$$

Letting $\lambda = s_M - s_m$ be the spectral width, it can be shown using (8) and (9) that

$$\nu_0 = \frac{p_1}{\lambda} \tag{23}$$

if only the volume fractions are known, and

$$\nu_1 = \frac{p_1}{\lambda^2}\left(\frac{p_2}{d} - s_m\right) \tag{24}$$

if the material is statistically isotropic.

Now let us assume only that (23) is satisfied, and we apply the same extremal procedure described above to see that the values of $H$ lie inside the circle

$$K_1(z) = \frac{p_1/\lambda}{t-z}\,, \qquad -\infty \le z \le \infty. \tag{25}$$

In the $F-$plane this translates via (20) and (21) into the circle

$$K_1'(z) = \frac{p_1}{s-(\lambda z + s_m)}\,, \qquad -\infty \le z \le \infty, \tag{26}$$

which happens to coincide with the circle $C_1(z), -\infty \le z \le \infty$, so that the matrix-particle assumption in this case provides no improvement over the standard complex elementary bound. Now we consider the analog $G(t)$ of $E(s)$ defined by

$$G(t) = \frac{1 - tH(t)}{t(1-H(t))}. \tag{27}$$

Then $G(t)$ has an integral representation

$$G(t) = \int_0^1 \frac{d\rho(z)}{t-z}\,, \tag{28}$$

where the mass of $\rho$ is $\rho_0 = 1 - p_1/\lambda$. We then obtain a circle in the $G-$plane analogous to $\hat{C}_1(z)$ in (12),

$$\hat{K}_1(z) = \frac{1-p_1/\lambda}{t-z}\,, \qquad -\infty \le z \le \infty. \tag{29}$$

In the $F$−plane this becomes via (27) and (21)

$$\hat{K}_1'(z) = \frac{p_1(s - s_m) - \lambda^2 z}{(s - s_m)(p_1 - \lambda + s - s_m) - \lambda^2 z}, \quad -\infty \leq z \leq \infty, \tag{30}$$

which is an improvement over (12). Back in the $\epsilon^*$−plane, the intersection of the two circles (26) and (30) yields a region $R_1^{mp}$ which has vertices $V_1^{mp} = \epsilon_2(1 - \hat{K}_1'(0))$ and $W_1^{mp} = \epsilon_2(1 - K_1'(0))$. When $\epsilon_1$ and $\epsilon_2$ are real and positive, $R_1^{mp}$ collapses to the interval with endpoints $V_1^{mp}$ and $W_1^{mp}$,

$$\epsilon_2 \frac{\epsilon_2 - s_M(\epsilon_2 - \epsilon_1)}{\epsilon_2 - (s_M - p_1)(\epsilon_2 - \epsilon_1)} \leq \epsilon^* \leq \epsilon_2 \frac{\epsilon_2 - (s_m + p_1)(\epsilon_2 - \epsilon_1)}{\epsilon_2 - s_m(\epsilon_2 - \epsilon_1)}. \tag{31}$$

These bounds are tighter than the classical arithmetic and harmonic mean bounds and reduce to them for $s_m = 0$ and $s_M = 1$. (Eq. (3.34) in ref.[34] is an incorrect version of (30), and the corresponding region in Figure 2 in ref.[34] is incorrect as well.)

Finally, we consider the case where the material is further assumed to be statistically isotropic. Let

$$H_1(t) = \frac{1}{\nu_0} - \frac{1}{tH(t)} = \frac{\lambda}{p_1} - \frac{1}{tH(t)}. \tag{32}$$

Then $H_1$ is a Herglotz function which is analytic off $[0, 1]$ and has the standard integral representation in terms of a measure $\nu^1$, which can be shown to have mass

$$\nu_0^1 = \frac{\nu_1}{(\nu_0)^2} = \frac{\frac{p_2}{d} - s_m}{p_1}. \tag{33}$$

Then the allowed values of $H_1(t)$ are contained inside the circle $\nu_0^1/(t - z)$, $-\infty \leq z \leq \infty$, which becomes in the $H$−plane

$$K_2(z) = \frac{\nu_0^2(t - z)}{t(\nu_0(t - z) - \nu_1)}, \qquad -\infty \leq z \leq \infty, \tag{34}$$

or in the $F$−plane,

$$K_2'(z) = \frac{p_1(s - s_m - z\lambda)}{(s - s_m)(s - p_2/d - z\lambda)}, \qquad -\infty \leq z \leq \infty. \tag{35}$$

For $s_m = 0$ and $s_M = 1$ ($\lambda = 1$) the above circle is identical with the full circle containing the arc (16).

To obtain the other circle, we apply a similar transformation to $G(t)$, obtaining a function

$$G_1(t) = \frac{1}{\rho_0} - \frac{1}{tH(t)} = \frac{\lambda}{\lambda - p_1} - \frac{1}{tH(t)}, \tag{36}$$

which, again, is a Herglotz function analytic off $[0, 1]$ with representing measure $\rho^1$ of mass $\rho_0^1 = \frac{\nu_0(1-\nu_0)-\nu_1}{(1-\nu_0)^2}$. Then in the $G_1$−plane, the allowed values are contained inside the circle $\rho_0^1/(t - z)$, $-\infty \leq z \leq \infty$, which becomes in the $G$−plane

$$\hat{K}_2(z) = \frac{(1 - \nu_0)(t - z)}{t(t - z - \nu_0 + \nu_1/(1 - \nu_0))}, \quad -\infty \leq z \leq \infty. \tag{37}$$

The intersection of the two circles (35) and (37) (in a common plane) yields a region $R_2^{mp}$ which in the $\epsilon^*$− plane has vertices $V_2^{mp} = \epsilon_2(1 - K_2'(0))$ and $W_2^{mp}$, which is the image of $\hat{K}_2(0)$ in the $\epsilon^*$− plane. The region $R_2^{mp}$ is an improvement over the complex Hashin-Shtrikman bounds under the matrix-particle assumption. When $\epsilon_1$ and $\epsilon_2$ are real and positive, with $\epsilon_1 \geq \epsilon_2$, $R_2^{mp}$ collapses to the interval with endpoints $V_2^{mp}$ and $W_2^{mp}$,

$$1 - \frac{p_1}{s - p_2/d} \leq \frac{\epsilon^*}{\epsilon_2} \leq \frac{s - s_M}{s - s_m}\left(1 + \frac{1 - \nu_0^2}{(1 - \nu_0)t + \nu_1}\right). \tag{38}$$

Note that the left endpoint $V_2^{mp}$ is the lower Hashin-Shtrikman expression, so that it coincides with the same vertex from the region $R_2$. When $\epsilon_1 \leq \epsilon_2$ the sequence of inequalities is reversed. (We point out that in eqs. (3.44) and

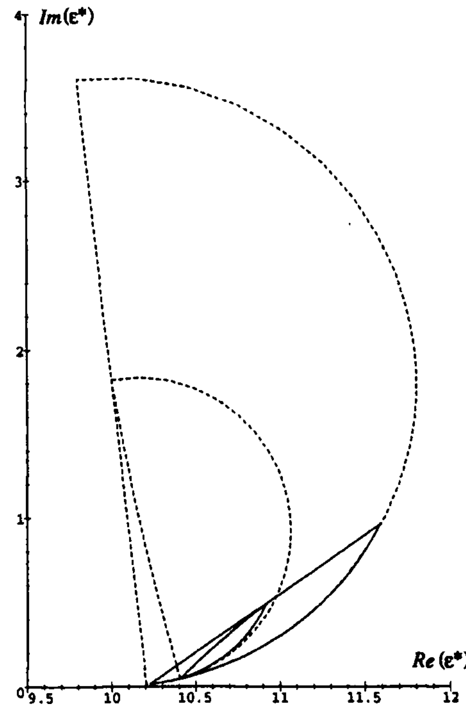


**Figure 1.** Bounds $R_1$ (outer, dotted), $R_2$ (inner, dotted), $R_1^{mp}$ (outer, solid), and $R_2^{mp}$ (inner, solid) on the complex permittivity of a PEO-PPY insulator-conductor composite. $R_1$ assumes only knowledge of the volume fractions and $R_2$ assumes statistical isotropy as well. $R_1^{mp}$ and $R_2^{mp}$ further assume the material is a matrix-particle composite with $q = 0.9$ and $p_1 = 0.02$. The complex permittivities of the components are $\epsilon_1 = 0 + i180$ and $\epsilon_2 = 10 + i0.00018$

(3.47) of ref.[34] which correspond to (38) here, there is a typographical error that also appeared in ref.[33] Furthermore, the inner regions $R_2^{mp}$ of Figures 3 and 4 in ref.[34] have been plotted incorrectly.) We note that the positivity of the moments of the measures $\nu$ and $\rho$ imply that the spectrum cannot be too small,[33] $s_m \leq p_2/d$ and $s_M \geq p_2/d + p_1$.

Finally, we wish to apply our bounds to a reasonable model of an insulator-conductor composite. For simplicity we take a two dimensional medium, and assume that we have conducting discs randomly embedded in a dielectric, insulating matrix. Then we may take advantage of Bruno's explicit calculations of $s_m$ and $s_M$, given a separation parameter $q$, defined as follows. We assume that our conducting discs of complex permittivity $\epsilon_1$ and radius $r_1$ are surrounded by a "corona" of the insulator $\epsilon_2$ of outer radius $r_2$, so that $q = r_1/r_2$ (the radii of different discs need not be the same). For such a medium, Bruno[33] has calculated $s_m = \frac{1}{2}(1 - q^2)$ and $s_M = \frac{1}{2}(1 + q^2)$. Smaller $q$ values indicate well separated inclusions, and $q = 1$ corresponds to $s_m = 0, s_M = 1$, in which case $R_1^{mp}$ and $R_2^{mp}$ reduce to $R_1$ and $R_2$. In Figure 1 we have plotted all the bounds for permittivities representing a PEO(polyethyleneoxide)-PPY(polypyrrole) composite[2] (with $p_1 = 0.02$) at 0.1 GHz. Even for the $q$ value of 0.9 in the figure, the matrix-particle bounds yield a dramatic improvement over the complex elementary and Hashin-Shtrikman bounds.

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