ANALYTICAL CALCULATION OF THE CONDUCTIVITY OF HIGHLY HETEROGENEOUS MEDIA WITH ALLOWANCE FOR PERCOLATION PHENOMENA

A. M. Mandel'

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Purely analytical methods without employing any computer-empirical relations or parameters have been used to construct a simple model of the conductivity of a two-phase heterogeneous medium composed of grains in the form of oriented ellipsoids. The model is applicable at any, up to infinite, contrast of the conductivities of the phases and in the entire range of their possible concentrations. Moreover, it "automatically" predicts the existence of a percolation threshold, the value of which depends on the grain shape.

The problem of the conductivity (electrical conductivity, thermal conductivity, dielectric permittivity, and some other properties) of two-phase heterogeneous systems has a very long history of, apparently, about 150 years. By now by different methods a multitude of conductivity models of such media (e.g., [1-3] etc.) have been constructed that develop the underlying premises with one or another degree of consistency. A model usually results in an analytical expression relating the conductivity of a heterogeneous medium to the conductivities, concentrations, and (more rarely) the grain shape of the components.

However, none of the known systematically analytical models can be applied at a very large, up to infinite, contrast of the conductivities of components (as, for instance, in electrical-conductivity calculations of metal-dielectric or superconductor-dielectric systems). The reason for this limitation on permissible contrasts is well known: percolation phenomena [4-6], i.e., the influence of the changing topology of the conducting phase on the conductivity of a highly heterogeneous medium. Therefore, the conductivity of the mentioned systems is, as a rule, calculated by combining any of the traditional analytical models with computer-empirical relations of percolation theory [3, 6]. The form of the latter is borrowed from the theory of phase transitions, and a range of the possible values of the parameters is determined with the aid of modeling by the Monte Carlo method.

In our opinion, a correct model of the conductivity of a heterogeneous medium must take percolation phenomena into consideration in a natural way as a consequence of the initial premises and not be adjusted for the percolation relations. The present work provides such a model constructed by purely analytical methods without using any computer-empirical relations or parameters. It should be noted that in a comparison with experimental data these parameters (critical concentration, exponent, point of matching with an analytical relation) are used as fitting ones, so that in this sense our model possesses incomparably less arbitrariness.

Now consider a two-component heterogeneous medium, the grains of which are ellipsoids of revolution with their axis of symmetry oriented along the field. As usual, the shape of the ellipsoids will be characterized by the parameter F [7-9]. In a three-dimensional medium the range of values of F is $0 \le F \le 1/2$. At $F = 0$ the ellipsoids are transformed into plates located perpendicular to the flow, at $F < 1/3$ they are flattened, at $F = 1/3$ they degenerate into spheres, at $F > 1/3$ they are stretched along the axis of symmetry, and at $F = 1/2$ they are transformed into infinite cylinders with the generatrix along the flow. As in [7], we can consider the medium to consist of arbitrarily oriented ellipsoids but this will make the procedure more cumbersome and not lead to any radically new results. Furthermore, precisely the case of oriented ellipsoids will allow testing of the model on transitions to known exact results in the limit.

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Our goal is to obtain a simple closed expression for the effective conductivity of a heterogeneous medium $\sigma_e(\sigma_1, \sigma_2, F, \eta)$ applicable for any ratios $\sigma_1/\sigma_2 > 1$ and any values of η. In the numerous calculations of the conductivity of heterogeneous media it is important to single out reliable results that can be used for testing the constructed model. Such results are comparatively few.

First, it is known that the conductivity of a medium composed of plates located normal to the flow is determined as

$$\sigma_e = [\eta/\sigma_1 + (1-\eta)/\sigma_2]^{-1}, \tag{1}$$

while the conductivity of a medium consisting of cylinders parallel to the flow is equal to

$$\sigma_e = \eta\,\sigma_1 + (1-\eta)\,\sigma_2 . \tag{2}$$

Expressions (1) and (2) are exact solutions of the Laplace equation that correspond to a homogeneous flow and a homogeneous field, and they coincide with the known Wiener boundary-value estimates [10]. The formula for $\sigma_e(\sigma_1, \sigma_2, F, \eta)$ must pass into (1) in the limit $F \to 0$ and into (2) in the limit $F \to 1/2$.

Second, it is established that the field in a solitary oriented ellipsoid located in a medium with conductivity σ_e and in an external (self-consistent) field E_0 is expressed as [8]

$$E_i = E_0\,\sigma_e\,[(1-2F)\,\sigma_i + 2F\sigma_e]^{-1}; \tag{3}$$

by virtue of the scalar character of conductivity the sign of the vector of the field and the flow can be omitted henceforth. As is seen from this relation, a cylindrical grain does not change the external field:

$$F = 1/2, \quad E_i = E_0 ,$$

and a plate retains the external field:

$$F = 0, \quad E_i = E_0\,\sigma_e/\sigma_i, \quad j_i = \sigma_i\,E_i = \sigma_e\,E_0 = j_0 .$$

Formula (3) is also the exact solution of the Laplace equation with continuity conditions for the normal component of the flow and the tangential component of the field at the grain boundary.

Third, if the concentration of inclusion grains with conductivity σ_2 in a medium (matrix) with conductivity σ_1 is low so that they can be considered to be solitary, then

$$\sigma_e = \sigma_1 - \sigma_1\,(\sigma_1 - \sigma_2)\,(1-\eta)\,[(1-2F)\,\sigma_2 + 2F\sigma_1]^{-1}, \tag{4}$$

where $1-\eta \to 0$. This expression follows directly from (3), and for the particular case of spherical grains ($F = 1/3$) it corresponds to the Wagner model [8, 11]. The relationship $\sigma_e(\sigma_1, \sigma_2, F, \eta)$ must reduce to (4) in the asymptotics $\eta \to 1$ for any F.

Below, in constructing the model we will lean upon the three exact results given above.

As mentioned, a correct model of the conductivity of a heterogeneous medium must naturally predict percolation phenomena and, in particular, provide a nonzero value of the critical concentration. The only known expression of this kind follows from the symmetric Bruggeman model [7], more often called the EMA (effective-medium approximation) model [9] or the "effective-medium" model [3]. For the considered case of oriented-ellipsoid grains, σ_e is determined, according to this model, from the equation

$$\eta\,(\sigma_1 - \sigma_e)\,[(1-2F)\,\sigma_1 + 2F\,\sigma_e]^{-1} + (1-\eta)\,(\sigma_2 - \sigma_e)\,[(1-2F)\,\sigma_2 + 2F\,\sigma_e]^{-1} = 0,$$

which can be written in the somewhat different form

$$\sigma_e \eta \, [(1 - 2F)\sigma_1 + 2F\sigma_e]^{-1} + \sigma_e (1 - \eta) \, [(1 - 2F)\sigma_2 + 2F\sigma_e]^{-1} = 1 . \tag{5}$$

If we now multiply (5) by E_0 and use (3), the relation of the EMA model will acquire the form

$$\eta \, E_1 + (1 - \eta) \, E_2 = \langle E \rangle = E_0 . \tag{6}$$

Thus, the physical meaning of the model described is quite clear: the effective conductivity of the medium is chosen from the condition of equality of the volume-averaged $\langle E \rangle$ and self-consistent E_0 values of the field. Here, it is assumed that each grain with conductivity $\sigma_{1,2}$ is solitary in a medium with conductivity σ_e.

In the limit of a highly heterogeneous medium $\sigma_2/\sigma_1 \to 0$ the EMA model of the effective conductivity has the linear dependence

$$\sigma_e = \sigma_1 \, (\eta - 1 + 2F)/2F ; \tag{7}$$

in essence, this is the asymptotics of (4) at $\sigma_2 = 0$ extended to the entire range of η. In particular, for spherical grains we obtain the following formula from (7):

$$\sigma_e = \sigma_1 \, (3\eta - 1)/2 ,$$

which for the critical concentration gives $\eta_c = 1/3$, considerably exceeding the correct value. Therefore, as a rule, it is considered that the EMA model is valid for the limited contrasts of conductivity $\sigma_1/\sigma_2 < 30-100$ (according to the data of various authors) in the entire range of η and for the unlimited contrasts $\sigma_1/\sigma_2 \to \infty$ in the concentration range $\eta \geq 0.4-0.5$ [3, 4, 6].

As already mentioned, formulas (3), (4) are exact and applicable at any ratios σ_i/σ_e and σ_1/σ_2. The reason for restrictions on the applicability of the EMA model in the region of near-critical concentrations lies in the following. The infinitesimal change $d\sigma_e$ in the region $\eta \to 1$, when all grains with σ_1 enter the conducting matrix, can be obtained by differentiating (4) and passing to the limit as $\sigma_2/\sigma_1 \to 0$:

$$d\sigma_e = \sigma_1/2F \, d\eta .$$

According to (7), $d\sigma_e$ must be exactly such $\forall\eta > \eta_c$. But for η close to η_c some of the conducting grains do not belong to a conducting cluster. Their removal from the medium will decrease η without influencing σ_e in any way. Consequently, the infinitesimal change in the conductivity of the medium $d\sigma_e$ must decrease with decreasing η, which is not taken into account in the EMA model. However, the independence of $d\sigma_e$ from η in (7) inevitably follows from (5), (6), i.e., in essence, from the additivity of the field E_i in these expressions.

Therefore, it can be assumed (this is the main idea of the article) that the field in (6) is "additive to the power $f(F, \eta)$" – a monotonically decreasing function of the concentration of the high-conductivity component:

$$\eta \, (E_1)^f + (1 - \eta) \, (E_2)^f = (E_0)^f . \tag{8}$$

Using (3), from (8) we obtain the following equation for σ_e:

$$\eta \, [\sigma_e \, [(1 - 2F)\sigma_1 + 2F\sigma_e]^{-1}]^f + (1 - \eta) \, [\sigma_e \, [(1 - 2F)\sigma_2 + 2F\sigma_e]^{-1}]^f = 1 . \tag{9}$$

As calculations show, the arbitrariness in $f(F, \eta)$ does not influence the value of σ_e considerably. We recover the behavior of the function $f(F, \eta)$ by comparing (9) to the exact formulas (1)-(4) given earlier. In the limit as $F \to 0$, we obtain from (9)

$$\sigma_e^f \, [\eta/\sigma_1^f + (1 - \eta)/\sigma_2^f] = 1 ;$$

for agreement with (1), it is necessary to take

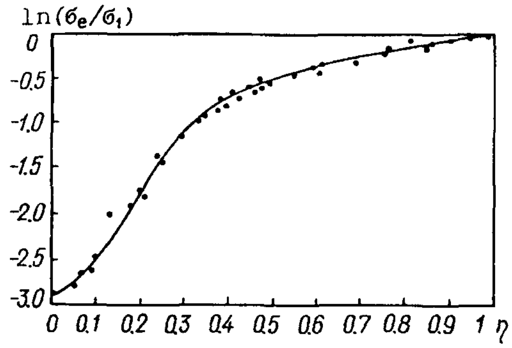

Fig. 1. Relative conductivity of a highly heterogeneous medium ln (σ_2/σ_1) versus the volume concentration of the component with a high conductivity η (both quantities are dimensionless): curve, calculation by formulas (9), (13) for $\sigma_2/\sigma_1 = 1.2 \cdot 10^{-3}$ and $F = 1/3$; points, experimental data on the electrical conductivity of lithium-ammonium solutions [6].

$$f(0, \eta) = 1 \quad \forall \eta . \tag{10}$$

In the limit as $F \to 1/2$, expression (9) turns into the identity

$$\eta + (1 - \eta) \equiv 1 ,$$

and therefore, for comparison with (2) it is necessary to investigate the behavior of (9) in the vicinity of this point. Assuming that $F = 1/2 - \varepsilon$, $\varepsilon \to 0$, we reduce the equation considered to the form

$$2f(1/2, \eta) \; [\eta\sigma_1 - (1 - \eta) \, \sigma_2 - \sigma_e] = 0$$

to the order of $\sim \varepsilon$ and to the form

$$(\sigma_1 - \sigma_e) \, (\sigma_2 - \sigma_e) \; [\eta - f(1/2, \eta)] = 0$$

to the order of $\sim \varepsilon^2$. It is seen that the first of these relations together with (2) is fulfilled independently of the value of $f(1/2, \eta)$, and according to the second relation

$$f(1/2, \eta) = \eta . \tag{11}$$

For comparison with (4), we will consider Eq. (9) in the limit as $\eta \to 1$. With accuracy to small quantities of the first order we have

$$\sigma_e \approx \sigma_1 - \sigma_1 (1 - \eta) \; [[\sigma_1 \; [(1 - 2F) \, \sigma_2 + 2F \sigma_1]^{-1}]^{f(F,1)} -$$

$$- 1]/[(1 - 2F) \, f(F, 1)] + O \; [(1 - \eta)^2] .$$

As is seen, the relation obtained gives the asymptotics of (4) only at

$$f(F, 1) = 1 \quad \forall F . \tag{12}$$

The simplest expression for the function $f(F, \eta)$ that explains the behavior of the effective conductivity and is compatible with conditions (10)-(12) is as follows:

$$f(F, \eta) = 1 - 2F(1 - \eta) . \tag{13}$$

Then, with account for (13) the effective conductivity of the medium σ_e is uniquely determined from Eq. (9). No semiempirical or computer-empirical parameters are contained in this relation.

Now we enumerate the main features of the constructed model (9), (13). First, at small contrasts of the conductivities of the components the values of σ_e calculated by the mentioned formulas are practically the same as those given by the EMA model. Deviations from it become perceptible only at contrasts exceeding several tens, precisely in the concentration domain prescribed in [6]. Second, the values of σ_e calculated by model (9), (13) for the case $\sigma_2/\sigma_1 = 1.2\cdot 10^{-3}$ are comparable to the results of the classical percolation experiment on the electrical conductivity of lithium-ammonium solutions (see Fig. 1). The constructed curve illustrates the quality of the coincidence for all values of η.

Third, the suggested model is applicable for any contrasts of the conductivity of the components σ_1/σ_2 and any depolarization coefficients of the grains $0 \le F \le 1/2$. In the limits as $F \to 0$ and $F \to 1/2$ the dependence $\sigma_e(\sigma_1, \sigma_2, F, \eta)$ is reduced to exact solutions (1), (2) of the Laplace equation. However, in [9], a medium is described in which the grain shape cannot be characterized by a value of F from the mentioned range, but this is obviously a rather exotic situation.

Fourth, the model described makes it possible to naturally obtain, "on a pen's tip," the critical concentration η_c, moreover as a function of the grain shape. In the limit as $\sigma_2/\sigma_1 \to 0$ Eq. (9) provides analytical solutions for σ_e:

$$\sigma_e = \sigma_1 (1 - 2F)(2F)^{-1} [[\eta (\eta + (2F)^f - 1)^{-1}]^{1/f} - 1]^{-1}, \tag{14}$$

where $f(F, \eta)$ is determined from (13). In the asymptotics $\eta \to 1$ expression (14) coincides with (4) for $\sigma_2 = 0$, and σ_e vanishes for η_c determined from the condition

$$\eta + (2F)^f - 1 = 0 .$$

Thus, the value of the critical concentration η_c is a solution of the transcendental equation

$$2F(1 - \eta_c) + \ln(1 - \eta_c)/\ln(2F) = 1 . \tag{15}$$

As should be expected, for cylinders arranged along the flow ($F = 1/2$) we obtain $\eta_c = 0$, and for plates located across the flow ($F = 0$) $\eta_c = 1$. For the most "popular" case of isometric grains ($F = 1/3$) $\eta_c \approx 0.1644$ ..., which is rather close to computer-aided calculations of a number of authors ([5, 6] etc.).

In conclusion, it should be noted that by virtue of the statistical character of formation of an infinite conducting cluster the version of the function $f(F, \eta)$ in (13) is only one of the possible ones. It is also clear that the behavior of $f(F, \eta)$ must be associated with the special features of the topology of this cluster. An investigation of this relation is a "properly percolation problem" and is beyond the scope of the present work.

NOTATION

F, depolarization coefficient of a grain (an oriented ellipsoid) in the direction normal to the axis of symmetry of the ellipsoid; σ_1 (σ_2), conductivity of the first (second) component of the two-phase heterogenous system, $\sigma_1 > \sigma_2$; η, volume concentration of the first component with a higher conductivity; σ_e, effective conductivity of the heterogeneous medium; E_i, intensity modulus of the field inside the i-th grain; σ_i, conductivity of the i-th grain; E_0, intensity modulus of the external (self-consistent) field in which all grains of the heterogeneous system are located; j_0, volume-averaged (self-consistent) modulus of the flow; j_i, modulus of the flow in the i-th grain; $\langle ... \rangle$, symbol of averaging over a representative volume of the heterogeneous medium; $\langle E \rangle$, volume-averaged field; η_c, critical concentration (percolation threshold).

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