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METHODOLOGICAL NOTES

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Did Maxwell know about the percolation threshold? (on the fiftieth anniversary of percolation theory)

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Abstract. **A new approximation obtained in terms of the Maxwell approach is proposed for the effective conductivity of a macroscopically disordered medium. In contrast to the standard Maxwell approximation, this approximation is valid over a much wider concentration range and can qualitatively describe the presence of the percolation threshold. The relation of the proposed approximation to the Padé approximant of the standard Maxwell approximation is also discussed.**

1. Introduction

Effective kinetic coefficients and, in particular, effective conductivity, are the main characteristics of macroscopically inhomogeneous media. These have been calculated in numerous monographs (see, e.g., Refs [1 – 9]) and boundless-in-number papers (inquire about, for example, *effective conductivity*, on the sites Arxiv.org or Elsevier). Although effective conductivity is now calculated by rather fine methods (such as the path-integral approach [10]), the Maxwell, Maxwell – Garnett, and Bruggeman (self-consistent field) approximations, which are simple and obtained from physically transparent considerations, have received wide acceptance, especially among experimentalists. These approximations cover a rather wide range of parameters, attract the attention of theorists up to the present day, and are still being generalized [11]. Of course, they cannot be used to describe the percolation threshold quantitatively, in particular, to describe the critical conductivity indices. The percolation theory, which was first formulated by Broadbent and Hammersley [12], is a geometrical analog for the theory of second-order phase transitions, and the quantitative determination of its characteristics, such as the critical indices, requires specific mathematical methods or numerical calculation [1 – 10, 12 – 14].

The Maxwell approximation, which is one of the first approximations, can only be applied to a low inclusion concentration and cannot be used even qualitatively near the percolation threshold. The Bruggeman self-consistent field approximation [15] (see also Ref. [16]) well describes virtually the entire concentration range and coincides with the numerical mesh computation, apart from a narrow region near the percolation threshold. In this region, the approximation only gives a qualitative description, and the critical indices evaluated with this approximation do not coincide with the numerically calculated or experimental indices.

The paper outline is as follows. In the second section, we present basic definitions and briefly derive the Maxwell approximation. In Section 3, we use the Maxwell approach, i.e., the solution to the problem of an individual inclusion, and obtain a new approximated expression for the effective conductivity that qualitatively describes the percolation transition.

2. Derivation of the standard Maxwell approximation

Let us at first formulate some definitions. A macroscopically inhomogeneous conducting medium is considered to be a medium that obeys locally Ohm's law

$$\mathbf{j}(\mathbf{r}) = \sigma(\mathbf{r})\,\mathbf{E}(\mathbf{r})\,, \tag{1}$$

and the effective conductivity relates volume-average fields to currents, namely

$$\langle \mathbf{j} \rangle = \sigma_{\text{eff}} \langle \mathbf{E} \rangle\,. \tag{2}$$

Next we will consider a two-phase medium consisting of a well-conducting phase with conductivity σ_1 (for brevity, a black phase) and poorly conducting phase with conductivity σ_2 (white phase). The main problem is to find the form of the $\sigma_{\text{eff}} = \sigma_{\text{eff}}(\sigma_1, \sigma_2, p)$ dependence, where p is the black-phase concentration.

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Maxwell was one of the first scientists to formulate the problem of the effective coefficient calculation, and he solved this problem using a certain approximation, which is now called the Maxwell approximation. Although the derivation of the Maxwell approximation is well known [17], we will briefly repeat it.

We now analyze well-conducting spherical inclusions embedded in a poorly conducting matrix and assume that the inclusion concentration is $p \ll 1$. To derive an expression for σ_{eff}, we have to solve two problems.

The first problem consists in finding the field in one inclusion at a given uniform field $\mathbf{E}_\infty$ set at infinity. Its solution has the form

$$\mathbf{E}_1 = \frac{3\sigma_2}{2\sigma_2 + \sigma_1}\, \mathbf{E}_\infty\,. \tag{3}$$

The second problem is the construction of the Maxwell approximation proper. To solve this problem, we will consider the integral $\langle \mathbf{j} - \sigma_2 \mathbf{E} \rangle$, where $\langle \ldots \rangle = V^{-1} \int_V \ldots \, \mathrm{d}V$ is the volume integral with a characteristic size much larger than the interinclusion distance. On the one hand, this integral equals

$$\begin{aligned}\langle \mathbf{j} - \sigma_2 \mathbf{E} \rangle &= \frac{1}{V}\int (\mathbf{j} - \sigma_2 \mathbf{E})\, \mathrm{d}V = \frac{1}{V}\int (\sigma \mathbf{E} - \sigma_2 \mathbf{E})\, \mathrm{d}V \\ &= \frac{V_1}{V}\,(\sigma_1 - \sigma_2)\, \mathbf{E}_1 = (\sigma_1 - \sigma_2)\, p \mathbf{E}_1\,,\end{aligned} \tag{4}$$

where V_1 is the first-phase volume, $\mathbf{E}_1 = 1/V_1 \int_{V_1} \mathbf{E}\, \mathrm{d}V$, and $p = V_1/V$. On the other hand, according to effective conductivity definition (2), we obtain

$$\langle \mathbf{j} - \sigma_2 \mathbf{E} \rangle = \langle \mathbf{j} \rangle - \langle \sigma_2 \mathbf{E} \rangle = (\sigma_{\text{eff}} - \sigma_2)\, \langle \mathbf{E} \rangle\,. \tag{5}$$

Since the first problem considered one inclusion in an infinite medium, we have $\mathbf{E}_\infty = \langle \mathbf{E} \rangle$. Substituting formula (3) into Eqn (4) and setting it equal to Eqn (5), we arrive at the effective conductivity in the Maxwell approximation:

$$\sigma_{\text{eff}}^{\text{BW}} = \sigma_2 \left(1 + 3p\, \frac{\sigma_1 - \sigma_2}{2\sigma_2 + \sigma_1} \right). \tag{6}$$

Here, the superscript BW (black in white) indicates that we analyze well-conducting (black) phase inclusions in the poorly conducting (white) phase.

Figure 1 depicts the concentration dependence of $\sigma_{\text{eff}}^{\text{BW}}$ in the Maxwell approximation (6). In the case of a strong inhomogeneity (for $\sigma_1 \gg \sigma_2$), a percolation transition takes place in a random medium: the behavior of the effective conductivity changes sharply near the percolation threshold, i.e., near a concentration $p = p_{\text{c}}$ at which a connected path (the so-called infinite cluster) first forms in the system along the well-conducting phase. It is generally accepted that the Maxwell approximation, which is based on the one-inclusion problem, cannot describe this transition even roughly. Indeed, the curve indicating the behavior of effective conductivity (6) near the percolation threshold passes by $p = p_{\text{c}}$, as if it overlooks the threshold. Based on the assumption that $\rho_{\text{eff}}^{\text{BW}} = 1/\sigma_{\text{eff}}^{\text{BW}}$, the effective resistivity expression

$$\begin{aligned}\rho_{\text{eff}}^{\text{BW}} &= \frac{1}{\sigma_{\text{eff}}^{\text{BW}}} = \left[\sigma_2 \left(1 + 3p\, \frac{\sigma_1 - \sigma_2}{2\sigma_2 + \sigma_1} \right) \right]^{-1} \\ &= \rho_2 \left[1 + 3p\, \frac{\rho_2 - \rho_1}{2\rho_1 + \rho_2} \right]^{-1}\end{aligned} \tag{7}$$

is also valid only at low concentrations.

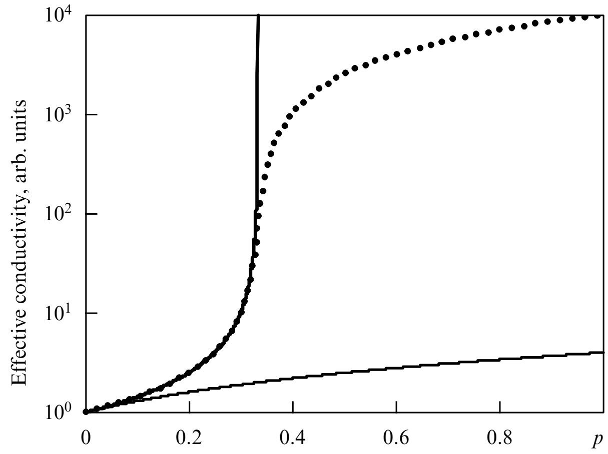

Figure 1. Concentration dependence of the effective conductivity: thin line conforms to Maxwell approximation (6), thick line to new approximation (17), and dashed line to Bruggeman approximation (9). The ordinate axis is represented on a logarithmic scale. As an example, the conductivity of the well-conducting phase is taken to be $\sigma_1 = 10^4$, and the conductivity of the poorly conducting phase $\sigma_1 = 1$ (arbitrary units). Up to the percolation threshold, approximation (17) is seen to virtually coincide with approximation (9).

An approximation that is sensitive to the percolation threshold is the Bruggeman self-consistent field approximation [15]. Although this approximation is also based on the one-inclusion problem, it takes into account the 'parity' between inclusions of different phases. First, the field E_1 in a black inclusion that is embedded into a medium with a conductivity equal to the desired effective conductivity σ_{eff} is found, and then the same procedure is performed for the field $\mathbf{E}_2$ in a white inclusion:

$$\mathbf{E}_1 = \frac{3\sigma_{\text{eff}}}{2\sigma_{\text{eff}} + \sigma_1}\, \mathbf{E}_\infty\,, \quad \mathbf{E}_2 = \frac{3\sigma_{\text{eff}}}{2\sigma_{\text{eff}} + \sigma_2}\, \mathbf{E}_\infty\,. \tag{8}$$

The self-consistency condition consists in the fact that, in a medium with a black-phase concentration p and a white-phase concentration $1 - p$, the average field represents the sum $p\mathbf{E}_1 + (1 - p)\, \mathbf{E}_2$, so that

$$p\mathbf{E}_1 + (1 - p)\, \mathbf{E}_2 = \langle \mathbf{E} \rangle\,, \quad \mathbf{E}_\infty = \langle \mathbf{E} \rangle\,. \tag{9}$$

Substituting Eqn (7) into self-consistency condition (8), we arrive at a quadratic equation for σ_{eff}, and its solution is given by

$$\begin{aligned}\sigma_{\text{eff}} = \frac{1}{4} \Big[&(3p - 1)\, \sigma_1 + (2 - 3p)\, \sigma_2 \\ &+ \sqrt{\big[(3p - 1)\, \sigma_1 + (2 - 3p)\, \sigma_2\big]^2 + 8\sigma_1 \sigma_2} \Big]\,.\end{aligned} \tag{10}$$

As is seen in the figure, the concentration dependence in the Bruggeman approximation for $\sigma_1 \gg \sigma_2$ does abruptly change its behavior at the percolation threshold, which is equal to $p_{\text{c}} = 1/3$ in this case. Of course, the critical indices of the effective conductivity that can be obtained from Eqn (10) do not coincide with the indices that are calculated using the percolation theory or numerical simulation.

Thus, at first glance (which is reflected in numerous monographs), the Maxwell approximation well describes the concentration behavior of the effective conductivity at a low inclusion concentration (being coincided with the Bruggeman approximation), is invalid at high inclusion concentrations, and can in no way describe the percolation threshold at all events.

3. New approximation

Let us demonstrate that the Maxwell approach contains much more than Eqn (6) can reflect. To this end, we again calculate the effective conductivity of the macroscopically inhomogeneous medium.

As earlier, the first problem is to calculate the field and current in an inclusion. In contrast to the standard Maxwell approximation, we specify a current rather than a field at infinity: $\mathbf{j}_\infty = \langle \mathbf{j} \rangle$. An individual inclusion cannot affect fields and currents at infinity. Therefore, taking into account that the medium conductivity is σ_2, for $\mathbf{j}_\infty$ we can write down the expression

$$\mathbf{E}_\infty = \rho_2 \mathbf{j}_\infty \,, \tag{11}$$

whence it follows, with allowance for formula (3), that

$$\mathbf{j}_1 = \sigma_1 \mathbf{E}_1 = \frac{3\sigma_2}{2\sigma_2 + \sigma_1} \frac{\sigma_1}{\sigma_2} \sigma_2 \mathbf{E}_\infty = \frac{3\rho_2}{2\rho_1 + \rho_2} \langle \mathbf{j} \rangle \,. \tag{12}$$

Note that, at first glance, the current $\mathbf{j}_1$ should be determined from formula (3) as

$$\mathbf{j}_1 = \sigma_1 \mathbf{E}_1 = \frac{3\sigma_2}{2\sigma_2 + \sigma_1} \sigma_1 \mathbf{E}_\infty = \frac{3\sigma_2}{2\sigma_2 + \sigma_1} \sigma_1 \langle \mathbf{E} \rangle \,, \tag{13}$$

and we then should move from $\langle \mathbf{E} \rangle$ to $\langle \mathbf{j} \rangle$ using the relationship $\langle \mathbf{E} \rangle = \rho_{\text{eff}} \langle \mathbf{j} \rangle$ for the effective values.

However, the use of the relationship $\langle \mathbf{E} \rangle = \rho_{\text{eff}} \langle \mathbf{j} \rangle$ in the first problem is invalid, since the first problem, namely, the determination of the fields and currents in an individual inclusion with conductivity σ_1 in a medium with conductivity σ_2, is quite independent and is in no way related to the second problem, namely, to the determination of the effective conductivity.

We can derive an expression for current $\mathbf{j}_1$ in the inclusion, without using the considerations given above, as the solution to the mathematical physics problem if we assume $\mathbf{j}(\mathbf{r} \to \infty) = \langle \mathbf{j} \rangle$ at infinity and a continuous potential and continuous normal current components at the inclusion boundary.

The second problem is the Maxwell approximation proper. On the one hand, we have

$$\langle \mathbf{E} - \rho_2 \mathbf{j} \rangle = \frac{V_1}{V} \frac{1}{V_1} \int_{V_1} (\rho_1 - \rho_2)\, \mathbf{j}\, \mathrm{d}V = p(\rho_1 - \rho_2)\, \mathbf{j}_1 \,, \tag{14}$$

and, on the other, one finds

$$\langle \mathbf{E} - \rho_2 \mathbf{j} \rangle = \langle \mathbf{E} \rangle - \langle \rho_2 \mathbf{j} \rangle = \rho_{\text{eff}} \langle \mathbf{j} \rangle - \rho_2 \langle \mathbf{j} \rangle \,. \tag{15}$$

We equate the right-hand sides of formulas (14) and (15), take into account formula (13), and obtain

$$\rho_{\text{eff}} = \rho_2 \left(1 - 3p \, \frac{\rho_2 - \rho_1}{2\rho_1 + \rho_2} \right), \tag{16}$$

or

$$\sigma_{\text{eff}} = \sigma_2 \left(1 - 3p \, \frac{\sigma_1 - \sigma_2}{2\sigma_2 + \sigma_1} \right)^{-1} . \tag{17}$$

Equation (17) is seen to differ radically from Eqn (6): the concentration dependence of the effective conductivity σ_{eff} in the case of a high inhomogeneity $\sigma_1 \gg \sigma_2$ ($\sigma_1 \to \infty$) has a singularity for $p \to p_c = 1/3$, where the effective conductivity diverges. Up to $p_c = 1/3$, the concentration dependence of the effective conductivity coincides with the Bruggeman approximation and, thus, with numerical mesh simulation. At low concentrations, Eqn (17) coincides with Eqn (6).

Thus, it is surprising that new approximation (17), which is based on the Maxwell approach, qualitatively describes the percolation threshold. [1]

Of course, the fact that the Maxwell approximation can be utilized to detect the percolation threshold does not minimize the importance of the percolation theory, which can be used to describe and calculate new concepts in the field of kinetic phenomena in disordered media, such as critical behavior, critical indices, and scaling, to name but a few.

In conclusion, note that a Maxwell approximation analogous to Eqn (17) can also be obtained for poorly conducting inclusions embedded in a well-conducting matrix:

$$\sigma_{\text{eff}} = \frac{\sigma_1(\sigma_2 + 2\sigma_1)}{5\sigma_1 - 2\sigma_2 + 3p\,(\sigma_2 - \sigma_1)} \,. \tag{18}$$

4. Conclusion. Small addition regarding the Padé approximants

To describe critical phenomena, researchers often employ the Padé approximant technique (see, e.g., monograph [18]). The Padé approximant of an $f(x)$ function is the ratio of two polynomials whose coefficients are found from a comparison of the power series expansions of the Padé approximant and the $f(x)$ function in smallness x. The Padé approximants give an analytic continuation of a power series outside the radius of convergence. In terms of the Padé approximant, effective conductivity $\sigma_{\text{eff}}^{\text{BW}}$ (6) is the power series expansion of a certain function, which can comprise a singularity, in concentration. It is readily seen that representing the Padé approximant in the form

$$\sigma_{\text{eff}}(p) = \frac{a}{1 - bp} \,, \tag{19}$$

expanding it as a power series in concentration to the first order, and equating the multipliers before concentrations p having the same powers we will arrive, as a result, at $a = \sigma_2$ and $b = 3\,(\sigma_1 - \sigma_2)/(2\sigma_2 + \sigma_1)$.

Thus, effective conductivity (17) represents nothing but Padé approximant (6).

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[1] It is pertinent to note that it is not the only example where the Maxwell theory 'runs ahead'. The system of electrodynamic equations is known to have been written out by Maxwell in a relativistically invariant form almost half a century before the concepts of the relativistic theory were formulated.

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