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Scaling relations and the general effective-medium equation for isolator–conductor mixtures

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Abstract. The behaviour of the 'general effective-medium equation' near the percolation threshold of isolator–conductor mixtures has been analysed. A simple modification is proposed which renders the equation more consistent with fundamental scaling laws.

1. Introduction

In a series of papers McLachlan *et al* [1–12] have extensively discussed the electrical conductivity (and other transport properties) in percolating systems such as sintered nickel, carbon–polymer composites, microemulsions, sprayed metal films and model 2D media. Their aim is to describe the conductive behaviour over a wide range of isolator/conductor compositions, including the region around the percolation threshold. To match the existing effective-medium descriptions for such systems with modern percolation scaling laws, they have proposed the so-called 'general effective-medium equation' or 'GEM equation':

$$\frac{\Sigma_1 - \Sigma^*}{\Sigma_1 + A\Sigma^*} f_1 + \frac{\Sigma_2 - \Sigma^*}{\Sigma_2 + A\Sigma^*} f_2 = 0 \tag{1}$$

with

$$\Sigma \equiv \sigma^{1/t} \tag{2}$$

$$A \equiv f_c^{-1} - 1. \tag{3}$$

The symbols σ_i and f_i stand for the conductivities and volume fractions of the isolator ($i = 1$) and conductor ($i = 2$) phases ($f_1 + f_2 = 1$); f_c is the adjustable critical volume fraction for percolation of the conductor phase; the exponent t is treated as a second adjustable parameter. The asterisk denotes the effective property of the heterogeneous system.

For the parameter values $f_c = 1/3$, $t = 1$ the GEM equation reduces to the classical symmetric Bruggeman equation [13]. When applied to a mixture with $\sigma_1 \ll$

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σ_2, the latter equation predicts for the divergence of the effective conductivity just below the threshold:

$$\sigma^*_{\mathrm{Br}} = \sigma_1 |f_2 - f_c|^{-1} \qquad f_2 \uparrow f_c \tag{4}$$

and for the vanishing of this from above the threshold:

$$\sigma^*_{\mathrm{Br}} = \sigma_2 \left| \frac{f_2 - f_c}{1 - f_c} \right| \qquad f_2 \downarrow f_c. \tag{5}$$

In contrast, the GEM equation yields relations with an adjustable exponent:

$$\sigma^*_{\mathrm{GEM}} = \sigma_1 |f_2 - f_c|^{-t} \qquad f_2 \uparrow f_c \tag{6}$$

$$\sigma^*_{\mathrm{GEM}} = \sigma_2 \left| \frac{f_2 - f_c}{1 - f_c} \right|^{t} \qquad f_2 \downarrow f_c. \tag{7}$$

In practice, the GEM equation proves to be useful in correlating conductivity data with composition for a wide variety of percolating systems. Furthermore, McLachlan *et al* have emphasized how—by suitable parameter identification—the GEM equation also reproduces existing asymmetric effective-medium expressions for the conductivity in mixtures without a percolation threshold. However, from a fundamental point of view the GEM equation has its limitations. Although the connection of the parameter t with a true critical exponent is often stressed, the GEM relations (6) and (7) cannot generally hold simultaneously as critical scaling relations. In fact, modern percolation theory [14] states that:

$$\sigma^* \sim \sigma_1 |f_2 - f_c|^{-s} \qquad f_2 \uparrow f_c \tag{8}$$

$$\sigma^* \sim \sigma_2 |f_2 - f_c|^{t} \qquad f_2 \downarrow f_c \tag{9}$$

with, in principle, distinct exponents s and t, which should take universal values for a large class of percolating systems. For dimension $D = 2$ one can prove that s and t are indeed equal [15], with an estimated value

$$s = t \approx 1.30 \qquad D = 2 \tag{10}$$

but for dimension $D = 3$ estimates are:

$$s \approx 0.73 \qquad t \approx 1.9\text{–}2.0. \tag{11}$$

It is clear that if, for $D = 3$, the GEM equation is to reproduce the true scaling behaviour in an actual isolator–conductor mixture, it can only make separate fits of the regions $f_2 < f_c$ and $f_2 > f_c$. Moreover, the continuous interpolation that the equation provides between the two regions yields in particular for the effective conductivity at the threshold:

$$\sigma^*_{\mathrm{GEM,c}} \sim \sqrt{\sigma_1 \sigma_2} \qquad f_2 = f_c. \tag{12}$$

The same result is predicted by the original Bruggeman equation. In practice, however, this result should read [14]:

$$\sigma^*_c \sim \sigma_1^u \sigma_2^{1-u} \qquad f_2 = f_c \tag{13}$$

with

$$u = \frac{t}{s+t} \qquad \begin{cases} = \frac{1}{2} & D=2 \\ \approx 0.7 & D=3. \end{cases} \tag{14}$$

The difference between (12) and (13) is relevant, for example, for the critical scaling with frequency in a three-dimensional mixture of a dielectric and a conductor. In fact, substitution of $\sigma_1 = i\omega\varepsilon_1$ yields a complex critical effective permittivity

$$\varepsilon_c^* \sim \varepsilon_1^u \sigma_2^{1-u} \frac{e^{-i(1-u)\pi/2}}{\omega^{1-u}}. \tag{15}$$

The exponent u may in particular be evaluated from the frequency-independent critical loss angle:

$$\delta_c = \operatorname{arctg}\left[(1-u)\frac{\pi}{2}\right]. \tag{16}$$

The critical scaling with frequency and the critical loss angle have been investigated experimentally on various systems [16–18], and found to be essentially in accordance with (14)–(16). As explained, such behaviour cannot be described with the GEM equation.

2. Generalization of the GEM equation

The purpose of the present communication is to show that the shortcomings of the GEM equation indicated here, i.e., formally equal exponents s and t, and the inherently incorrect critical scaling with frequency, can be repaired in a very simple way. The subcritical GEM scaling relation (6) comes about by putting in (1) $\Sigma_1, \Sigma^* \ll \Sigma_2$, as a result of which the exponent t drops from the second term in (1). Conversely, the supercritical GEM scaling relation (7) is found by putting $\Sigma_1 \ll \Sigma^*, \Sigma_2$, which eliminates t from the first term. So it is obvious that equation (1) should be generalized to:

$$\frac{\Sigma_1 - \Sigma^*}{\Sigma_1 + A\Sigma^*} f_1 + \frac{T_2 - T^*}{T_2 + AT^*} f_2 = 0 \tag{17}$$

with

$$\Sigma = \sigma^{1/s} \tag{18}$$

$$T = \sigma^{1/t} \tag{19}$$

and again equation (3). Eliminating the denominators from (17) we obtain:

$$(\Sigma_1 T_2 - \Sigma_1 T^*) + (\Sigma^* T_2 - \Sigma_1 T^*)[(A+1)f_2 - 1] - (\Sigma^* T^* - \Sigma_1 T^*)A = 0. \tag{20}$$

We are interested in the scaling region, i.e. in effective conductivities satisfying $\sigma_1 \ll \sigma^* \ll \sigma_2$, so that the terms involving the products $\Sigma_1 T^*$ can always be neglected. Introducing

$$\Delta \equiv (A+1)f_2 - 1 = f_2/f_c - 1 \tag{21}$$

we then get, in this region:

$$\Sigma_1 T_2 + \Sigma^* T_2 \Delta - \Sigma^* T^* A = 0. \tag{22}$$

The subcritical region ($T^* A \ll T_2 \Delta$) is governed by the first two terms in this equation, and yields the scaling law (8), as envisaged. In the supercritical region ($\Sigma_1 \ll \Sigma^* \Delta$) the last two terms are retained, and similarly give the scaling law (9). The scaling behaviour at the threshold has not been envisaged, but follows by putting $\Delta = 0$. The first and third terms of (22) then lead to:

$$A(\sigma_c^*)^{1/s+1/t} = \sigma_1^{1/s} \sigma_2^{1/t} \qquad f_2 = f_c \tag{23}$$

and hence, with (3) and (14):

$$\sigma_c^* = (f_c^{-1} - 1)^{-su} \sigma_1^u \sigma_2^{1-u} \qquad f_2 = f_c. \tag{24}$$

So our—admittedly semi-empirical—modification of the equally semi-empirical GEM equation also naturally repairs the incorrect GEM prediction (12) at the threshold.

In the spirit of the present paper s and t are well-known critical exponents, and no ambiguity is introduced by extending the GEM equation by an additional parameter. However, in the original papers [1–12] the single exponent t is often treated as a component-specific morphology parameter, and related to the depolarization factor L that enters the asymmetric effective-medium equations [3]. Since the latter equations coincide in form with the scaling relations (8) or (9) it is always clear whether s or t should be related to L, and again no ambiguity occurs.

3. The scaling function

The separate scaling relations (8), (9) and (13) with (14), have been cast into one 'scaling *ansatz*' by Straley [15, 19] and others [20, 21]:

$$\sigma_\pm^* = \sigma_2 |f_2 - f_c|^t F_\pm(x) \tag{25}$$

$$x = \frac{\sigma_1 / \sigma_2}{|f_2 - f_c|^{s+t}} \tag{26}$$

where the $\pm$ sign refers to $f_2 \gtrless f_c$. The scaling functions $F_\pm(x)$ should both be regular near the origin, with $F_+(0) > F_-(0) = 0$ and $F'_\pm(0) > 0$. For asymptotically large x the two functions should be equal, positive and proportional to x^u. With these restrictions, the *ansatz* (25) with (26) guarantees the correct scaling behaviour below, at, and above the percolation threshold. We now want to analyse the new equation (17) in the light of this *ansatz*. To this end we write for the solution of (22):

$$T^* = T_2 |\Delta| G^{1/t} A^{-1}. \tag{27}$$

With $G = 1$, equation (27) would be the scaling law (9). The correction factor G specifying the deviation from that scaling law is determined by substituting (27) into (22) and using (18) and (19). This gives after some algebra:

$$G(G^{1/t} - \delta)^s = y \tag{28}$$

where

$$\delta = \mathrm{sgn}(\Delta) \tag{29}$$

and

$$y = A^{t}\frac{\sigma_1/\sigma_2}{|\Delta|^{s+t}}. \tag{30}$$

So G is a function of y which furthermore only depends on the sign δ. In fact, we have from (28):

$$G_+(y) = 1 + ty^{1/s} + \ldots \quad y \to 0 \tag{31}$$

$$G_-(y) = y - sy^{1+1/t} + \ldots \quad y \to 0 \tag{32}$$

$$G_\pm(y) = y^u + \ldots \quad y \to \infty. \tag{33}$$

Comparison of (27) and (30) with (25) and (26) shows that G and y differ from F and x only by trivial factors. From equations (31)–(33) we then conclude that in lowest order the solution (27) of the modified GEM equation obeys the scaling *ansatz*. Higher-order terms near the origin are non-analytic, as are the corresponding terms in the original GEM equation. However, these corrections to the dominant scaling behaviour are anyway difficult to access experimentally.

4. Conclusion

We have pointed out that the 'general effective-medium equation' or GEM equation (1)–(3), although very useful in fitting conductivity data of isolator–conductor mixtures, does not provide the correct conductivity scaling laws simultaneously below, at, and above the percolation threshold. This shortcoming is easily remedied by modifying the GEM equation into equation (17)–(19) of this paper. The modified equation obeys Straley's scaling *ansatz*, however, with a scaling function that has non-analytic higher-order terms near the origin.

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