Permittivity of composite percolation materials: similarity law and equations of state

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A numerical experiment has been carried out, confirming the self-similarity hypothesis in the case of the electrical conductivity of percolation systems. Phenomenological equations capable of yielding analytically the permittivity and the conductivity of a large class of disordered systems were derived for the first time.

We consider the behavior of the electrical conductivity and the permittivity of percolation composite systems near the percolation threshold. An example of such systems is a composite material consisting of a disordered mixture of metallic and insulating particles. A reduction in the concentration P of the metallic (conducting) component reduces the static conductivity of the composite, so that it vanishes at some critical concentration P_c known as the percolation threshold. In other words, composite metal–insulator mixtures with a concentration P of the conducting component equal to the percolation threshold P_c undergoes a composition-dependent metal–insulator transition.

The electrophysical characteristics of a composite exhibit a number of special features near P_c. The effective conductivity σ_{eff} vanishes in accordance with $\sigma_{\text{eff}} \propto \sigma_m \tau^t$, where σ_m is the conductivity of the metallic (conducting) component and $\tau = (P - P_c)/P_c$ is the dimensionless concentration. The effective permittivity ε_{eff} and the internal inductance l_{eff} diverge at the percolation threshold: $\varepsilon_{\text{eff}} \propto \varepsilon_i |\tau|^{-q}$, and $l_{\text{eff}} \propto a_0^2 \tau^{-\mu}$ (Refs. 1–3), where ε_i is the permittivity of the insulator and a_0 is the microscopic scale (size of the composite particles). The scaling invariance of percolation systems was used in Ref. 1 to put forward a similarity hypothesis: near P_c the effective complex conductivity σ_{eff} depends on the frequency ω and on the dimensionless concentration τ as follows:

$$\hat{\sigma}_{\text{eff}} = \sigma_{\text{eff}} - i\omega\varepsilon_{\text{eff}}/4\pi = \sigma_m \tau^t f(\tau/h^{1/(t+q)}), \tag{1}$$

where $h = \hat{\sigma}_i/\sigma_m = i\omega\varepsilon_i/4\pi\sigma_m/\ \hat{\sigma}_i = -i\omega\varepsilon_i/4\pi$ is the complex conductivity of the insulator; $f(x)$ is a universal function which is independent of the microstructure of the composite.

We use numerical experiments to confirm the similarity hypothesis of Eq. (1) and then we shall apply this hypothesis to obtain a phenomenological equation of state for $\hat{\sigma}_{\text{eff}}$:

$$F(\sigma_{\text{eff}}, \tau, h) = 0. \tag{2}$$

In our numerical experiments we determined $\hat{\sigma}_{\text{eff}}$ by modeling a composite material with the aid of a cubic lattice with edges in the form of resistors or capacitors. The concentration of the resistors was assumed to be P and that of the capacitors $1 - P$. We then solved the Kirchhoff equations and found the effective complex conductivity $\hat{\sigma}_{\text{eff}}$ as a function of the frequency ω and the dimensionless concentration τ (for details see Ref. 4).

It follows from the scaling hypothesis [Eq. (1)] that the loss-angle tangent $\tan\delta = 4\pi\sigma_{\text{eff}}/\omega\varepsilon_{\text{eff}}$ should depend only on the parameter $x = \tau/h^{1/(t+q)}$. This consequence of the similarity hypothesis was checked in a numerical experiment. It was found that all the points obtained fitted a single smooth curve $\tan\delta = \varphi(x)$, as shown in Fig. 1. The critical exponents t and q were selected so that $t + q = 3.0 \pm 0.1$, in satisfactory agreement with the known values $t = 2.0 \pm 0.2$ and $q = 0.8 \pm 0.1$ (see Refs. 4–7 and the literature cited there). The fact that $\tan\delta$ depends only on the parameter x is a confirmation of the similarity hypothesis in the three-dimensional case (for $d = 2$ cm—see Refs. 8 and 9).

We now use the similarity hypothesis to obtain a phenomenological equation for σ_{eff}. We introduce an analog of the susceptibility $\chi(\tau,h)$ (Ref. 1):

$$\chi = \frac{\partial(\hat{\sigma}_{\text{eff}}/\sigma_m)}{\partial h} = -\frac{x^{t+q+1}\tau^{-q}}{t+q} f'(x). \tag{3}$$

If we had been able to express f in terms of χ on the right-hand side of Eq. (3), Eq. (3) would have become a differential equation for χ. However, the function $f(x)$ is very inconvenient in practice because, as deduced from Eq. (1), there is a singularity of $f(x)$ at $x = 0$. Therefore, following Ref. 10, we derive the dependence of f on χ with the aid of auxiliary functions $u(x)$ and $v(x)$, which are finite for all values of x:

$$u(x) = (\hat{\sigma}_{\text{eff}}/\sigma_m)\chi^{t/q} = [-1/(t+q)]^{t/q} x^{t(t+q+1)/q} f(x) [f'(x)]^{t/q},$$
$$\tag{4}$$
$$v(x) = h\chi^{(t+q)/t} = [-1/(t+q)]^{(t+q)/q} x^{(t+q)(t+1)/q} [f'(x)]^{(t+q)/q}.$$

The relationships given by Eq. (4) define parametrical-

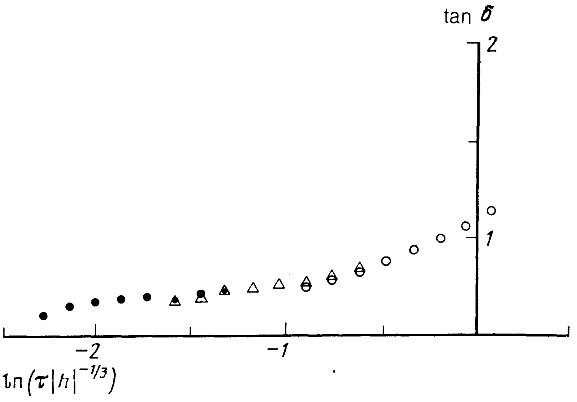

FIG. 1. Dependence of the loss-angle tangent $\tan\sigma = 4\pi\sigma_{\text{eff}}/\omega\varepsilon_{\text{eff}}$ on the parameter $\tau|h|^{-1/3}$; $h = -i\omega\varepsilon_i/4\pi\sigma_m$, $\tau = (P - P_c)/P_c$, $P_c = 0.25$; ●) $\tau = 0.08$; △) $\tau = 0.16$; ○) $\tau = 0.32$.

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ly the functional dependence $v(u)$. Our aim is to determine the explicit form of this dependence because this makes it possible to reduce the problem of finding $\hat{\sigma}_{\text{eff}}$ to solution of the differential equation for the function $\tilde{\chi} = \tau^q \chi$:

$$d(u\tilde{\chi}^{-t/q}(u))/d[v(u)\tilde{\chi}^{-(t+q)/q}(u)] = \tilde{\chi}(u). \qquad (5)$$

In an analysis of the dependence $v(u)$ it is convenient to consider real values of h, which corresponds to a percolation composite consisting of a mixture of powders of highly conducting and poorly conducting particles with the conductivities σ_m and σ_i, respectively ($h = \sigma_i/\sigma_m$). In this case the parameter x is a real variable which ranges from $-\infty$ to $+\infty$.

We consider the asymptotic behavior of the functions $v(x)$ and $u(x)$ in the limit $x \to \pm\infty$. The case $x \to -\infty$ corresponds to a system which is below the percolation threshold ($\tau < 0$) and $h \to 0$. According to the theory of Efros and Shklovskii,[1] in this limit we have

$$\sigma_{\text{eff}}/\sigma_m \propto h(-\tau)^{-q},$$
$$\chi = \partial(\sigma_{\text{eff}}/\sigma_m)/\partial h \propto (-\tau)^{-q},$$

which consequently leads to

$$v(x) = h\chi^{(t+q)/q} \propto h(-\tau)^{-(t+q)} \propto (-x)^{-(t+q)},$$
$$u(x) = (\sigma_{\text{eff}}/\sigma_m)\chi^{t/q} \propto (-x)^{-(t+q)}. \qquad (6)$$

It follows from the relationships in the system (6) that in the limit $u \to 0$, we have the asymptotic relationship

$$v(u) = u + o(u). \qquad (7)$$

In the other limiting case when $x \to +\infty$ (when the system is above the percolation threshold $\tau > 0$) and $h \to 0$, the values of σ_{eff} and χ are described by the asymptotic expressions

$$\sigma_{\text{eff}} \propto \sigma_m \tau^t (1 + ah\tau^{-(q+t)} + {}^1/_2 bh^2\tau^{-2(q+t)}),$$
$$\chi \propto (a\tau^{-q} + bh\tau^{-t-2q}),$$

which lead to

$$v(x) = h\chi^{(t+q)/q} \propto a^{(t+q)/q} x^{-(t+q)}, \qquad (8a)$$
$$u(x) = (\sigma_{\text{eff}}/\sigma_m)\chi^{t/q} \propto a^{t/q}[1 + (a + bt/aq)x^{-(t+q)}] \to u^*, \qquad (8b)$$
$$v(u) = (u - u^*)/(1 + bt/a^2 q) + o(u - u^*). \qquad (9)$$

Since we do not know the values of a and b, it follows that $(dv/du)_{x \to +\infty}$ remains unknown.

The similarity invariance hypothesis postulates that the only characteristic length of the problem is the correlation length ε (see, for example, Ref. 2). For a fixed value of τ and h approaching zero (which corresponds to $x \to \pm\infty$), the quantity ξ is a function of just the dimensionless concentration τ:

$$\xi \sim \xi_\tau \propto |\tau|^{-\nu}, \qquad (10)$$

where ν is a critical exponent which is $\nu = 0.88 \pm 0.02$ for the three-dimensional case.[2,11] If h is fixed and $\tau \to 0$ (which corresponds to $x \to 0$), then

$$\xi \sim \xi_h \propto h^{-\nu/(t+q)}. \qquad (11)$$

The crossover from Eq. (10) to Eq. (11) occurs at $\xi_h/\xi_\tau \equiv |x|^\nu \sim 1$. Consequently, the functions $u(x)$ and $v(x)$ change from the asymptotic behavior described by Eq. (6) ($x \to -\infty$) to the asymptotic behavior described by Eq. (8) ($x \to +\infty$) in the interval $-1 \lesssim x \lesssim 1$. In this interval the only characteristic scale of the problem is the quantity ξ_h so that it is natural to assume that the functions $v(x)$ and $u(x)$ have no more than one extremum and if it exists, it must lie in this interval. According to Eqs. (6) and (8), we find that $v(x) \to 0$ in the limit $|x| \to \infty$, and since $v(x) > 0$, it is obvious that this function has a maximum. We can easily show also that the function $u(x)$ is either monotonic or has one maximum.

Depending on the presence of a maximum in the case of a function $u(x)$ and its position relative to the maximum of the function $v(x)$, we can have three qualitatively different forms of the function $v(u)$. According to hypothesis A the function $u(x)$ is monotonic, ranging from 0 to u^* as x is varied from $-\infty$ to $+\infty$. It then follows from Eqs. (8) and (9) that $(dv/du)_{u=u^*} < 0$. Figure 2a shows qualitatively the function $v(u)$ corresponding to hypothesis A. Hypotheses B and C postulate that the function $u(x)$ has a maximum. It then follows from Eqs. (8) and (9) that $(dv/du)_{u=u^*} > 0$. In case B, the function $v(x)$ reaches its maximum earlier than does the function $u(x)$, whereas in case C the function $u(x)$ reaches a maximum before the function $v(x)$. Figures 2b and 2c show qualitatively the form of the functions $v(u)$ corresponding to the hypotheses B and C.

In the effective medium approximation, which is used widely to calculate the effective parameters of composite materials,[12] hypothesis A applies and the function $v(u)$ then has a very simple form:

$$v(u) = u - u^2. \qquad (12)$$

Another method for approximate analysis of percolation systems is the method of renormalization groups in real space,[13,14] which has become popular recently. In this method an analysis of a real system is replaced with an analysis of a certain hierarchical structure with its parameters selected so as to reproduce the real system. We shall consider a fairly simple hierarchical fractal, which is constructed as demonstrated in Fig. 3. As in the case of a regular lattice, assuming

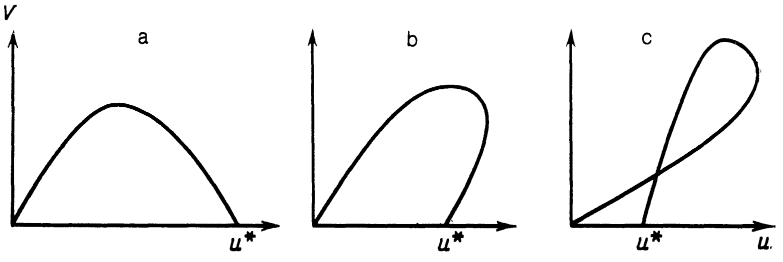

FIG. 2. Qualitative form of the function $v(u)$ corresponding to the hypotheses A (a), B (b), and C (c).

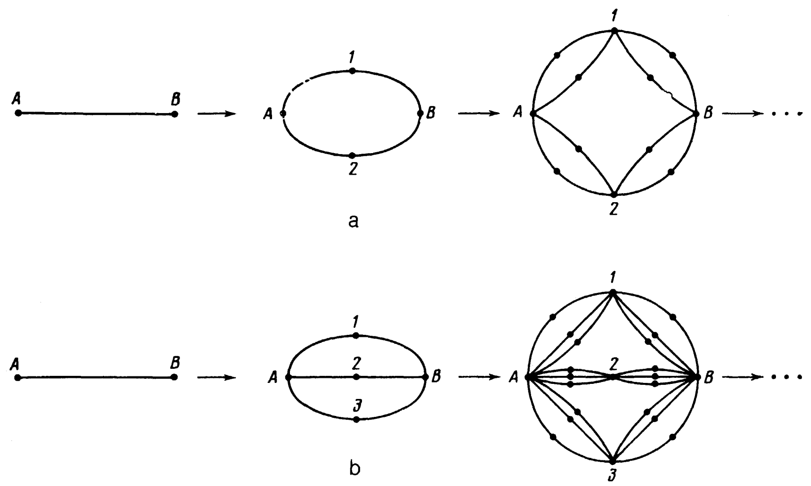

FIG. 3. Three successive stages of construction of a hierarchical fractal for the cases when $n = 2$ (a) and $n = 3$ (b). In case a, each stage gives rise to an edge (for example, AB), which then changes to a combination of four edges A 1, 1B, A 2, 2B, etc. In case b at each stage an edge (for example, B) is replaced by a combination of six edges A 1, 1B, A 2, 2B, A 3, 3B, etc. A fractal with an arbitrary value of n is constructed in a similar manner.

that each edge of a fractal can have the conductivity σ_m with the probability P and the conductivity σ_i with the probability $1 - P$, and also, as in a regular lattice, we shall assume that this fractal is characterized by a percolation threshold P_c. The conductivity of the fractal σ_{eff} vanishes in accordance with the law $\sigma_{\text{eff}} \propto \tau^t$, whereas the permittivity diverges at the percolation threshold as $\varepsilon_{\text{eff}} \propto |\tau|^{-q}$. The properties of this fractal depend on the parameter n (Fig. 3) and for $n = 2$ the problem of percolation on a fractal is similar to the problem of percolation on a square lattice, whereas for $n = 4$ it is similar to percolation on a cubic lattice. The conductivity of such a fractal considered as a function of the quantities τ and $h = \sigma_i/\sigma_m$ can be found exactly by successive application of a "decimation" procedure (see, for example, Ref. 14). Consequently, we can calculate the function $v(u)$. Plots of the dependences $v(u)$ for the cases $n = 2$, 3, and 4 are shown in Fig. 4. We can see that, as in the effective medium approximation, the function $v(u)$ corresponds to hypothesis A.

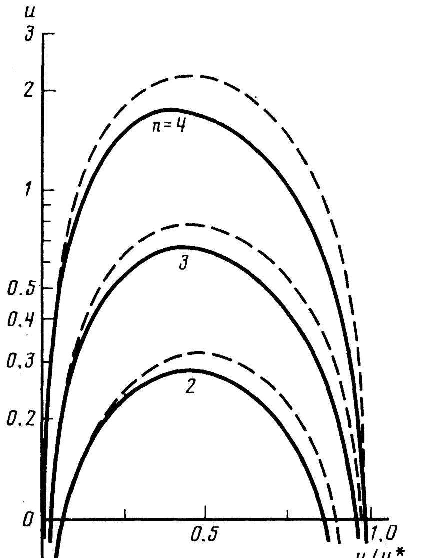

FIG. 4. Form of the function $v(u)$ for hierarchical fractals plotted for different values of the parameter n: the continuous curves represent the exact calculations and the dashed curves are calculated on the basis of Eq. (14).

In an analysis of real systems we shall concentrate our attention on hypothesis A and ignore hypotheses B and C. The function $v(u)$ defined in a finite interval $0 < u < u^*$ carries all the information on the conductivity of the percolation system for all the parameters of τ and h. In accordance with hypothesis A and on the basis of Eqs. (7) and (9) we find that the function $v(u)$ has one maximum and vanishes at $u = u^*$, and also that we have $v(u) \sim u + o(u)$ in the limit $u \to 0$. Clearly, such a function can be approximated as accurately as we please by the following series:

$$v(u) = u + \sum_i g_i u^{\alpha_i}, \quad \alpha_i > 1. \tag{13}$$

We shall make the simplest assumption and limit Eq. (13) to two terms:

$$v(u) = u - g u^{\alpha}, \quad \alpha > 1, \quad g > 0. \tag{14}$$

The quantity α can be found by considering the behavior of $u(x)$ and $v(x)$ at $x = 0$. In fact, following Ref. 10, we can easily show that $f(x) \propto x^{-t}(1 + Ax)$ in the limit $x \to 0$. Using Eq. (4), we find that

$$\frac{v(0)}{u(0)} = \frac{t}{t+q}, \quad \left.\frac{dv}{du}\right|_{u=0} = \frac{t-1}{t+q-1}. \tag{15}$$

Substituting Eq. (14) into the left-hand sides of Eq. (15), we obtain

$$\alpha = (t+q)/(t+q-1). \tag{16}$$

The function $v(u)$ expressed in the form of Eq. (14) is in satisfactory agreement with the exact function $v(u)$ deduced for a hierarchical fractal (Fig. 4) and makes it possible, as shown below, to reproduce well the results of numerical experiments. Substituting Eq. (14) into Eq. (5) and solving the latter, we obtain

$$\chi = c\tau^{-q}\left[-1 + \left(\frac{t+q}{q}\right) g u^{1/(t+q-1)}\right]^q. \tag{17}$$

If we now introduce new variables $\theta = g u^{1/(t+q-1)}$ and $R = (\chi/c)^{-1/q}$, we find that the relationships (4) and (17) are converted into a system of parametric equations for the determination of the complex conductivity $\hat{\sigma}_{\text{eff}}$:

$$\tau = R[\theta(t+q)/q - 1], \quad h = A R^{t+q} \theta^{t+q-1}(1-\theta),$$

$$\hat{\sigma}_{\text{eff}}/\sigma_m = B\theta^{t+q-1} R^t, \tag{18}$$

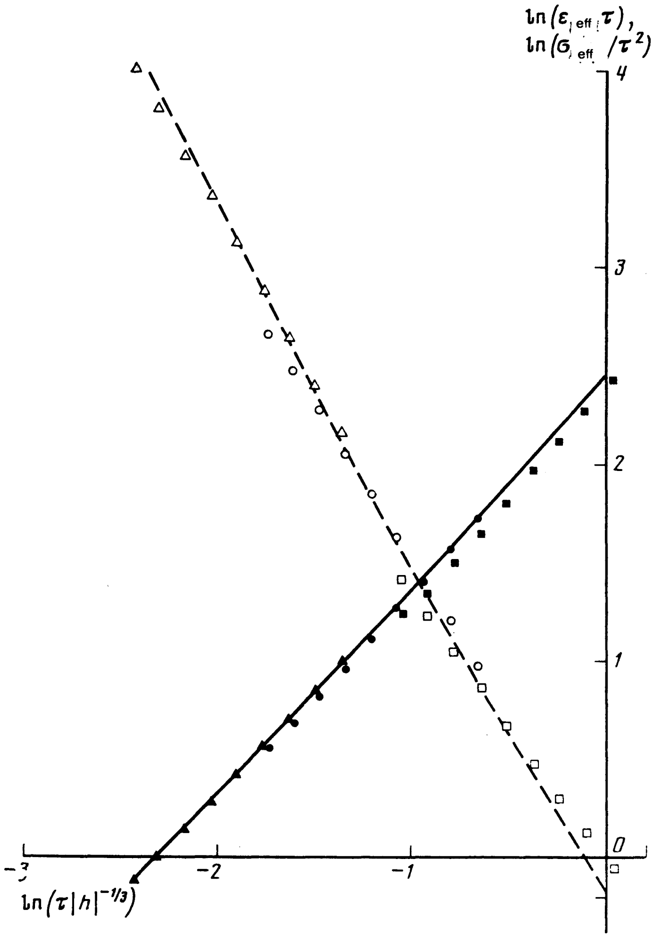

FIG. 5. Dependences of the effective conductivity $\sigma_{\rm eff}$ and of the permittivity $\varepsilon_{\rm eff}$ on the parameter $\tau|h|^{-1/3}$. The results of numerical experiments ($P_c = 0.25$, open circles represent $\sigma_{\rm eff}/\tau^2$ and the black dots represent $\varepsilon_{\rm eff}\tau$): ▲), △) $\tau = 0.08$; ●), ○) $\tau = 0.16$; ■), □) $\tau = 0.32$. The solution of Eq. (19) was obtained for $a = 0.516$ and $b = 1.12$; the dashed curve represents $\sigma_{\rm eff}/\tau^2$ and the continuous curve gives $\varepsilon_{\rm eff}\tau$.

where A and B are certain real constants governed by the geometric structure on a microscopic scale. A comparison of the results of a numerical experiment reported in Ref. 4 with the solutions of the system of equations (18) in the case $h = i\omega\varepsilon_i/4\pi\sigma_m$ is made in Fig. 5. The solution is selected by analytic continuation of h from the real axis.[1)] The solution of the system of equations (18) agrees well with the results of this numerical experiment if we assume that the critical exponents are $t = 2$ and $q = 1$. For $q = 1$, the system (18) simplifies to

$$h + a(\hat{\sigma}_{\rm eff}/\sigma_m)\tau = b(\hat{\sigma}_{\rm eff}/\sigma_m)^{(t+1)/t}. \qquad (19)$$

In particular, when the critical exponent is $t = 2$, which corresponds to the dimensionality $d = 3$, the problem of calculating the conductivity of three-dimensional percolation systems reduces to the solution of the cubic equation (19).

Figure 6 shows the dependences of the permittivity $\varepsilon_{\rm eff}$ and of the conductivity $\sigma_{\rm eff}$ on the dimensionless concentration τ found on the basis of Eq. (18). It is interesting to note that, in contrast to the generally accepted view (see, for example, Ref. 1), the value of $\varepsilon_{\rm eff}$ reaches its maximum not at the percolation threshold but at a certain concentration $P^*(\omega)$ that depends on the electric field frequency ω.

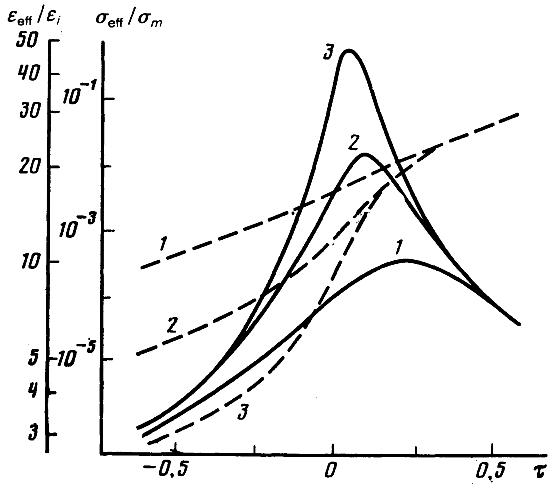

FIG. 6. Dependences of the permittivity $\varepsilon_{\rm eff}$ (continuous curves) and of the conductivity $\sigma_{\rm eff}$ (dashed curves) of a percolation composite system on the dimensionless concentration τ for different values of the dimensionless frequency: $|h| = \omega\varepsilon_i/4\pi\sigma_m$: 1) $|h| = 10^{-3}$; 2) $|h| = 10^{-4}$; 3) $|h| = 10^{-5}$.

It should be stressed that the accuracy of the above procedure for the determination of $\hat{\sigma}_{\rm eff}(\tau, h)$ depends on the precision of the approximation of the function $v(u)$ and is independent of the functional form of the approximation itself. However, the nature of the parametric equations (18) may generally depend on the method of approximation of the function $v(u)$. This ambiguity can be removed by applying field-theoretic methods.[15] However, at present considerable difficulties are encountered in the application of such methods to the problem in question, even in the space of dimensionality $d = 6 - \varepsilon$. Nevertheless, we may assume that the approximation of $v(u)$ by Eq. (14) proposed above should give the simplest form of the similarity equations (18) and (19) that reproduce satisfactorily the results of numerical experiments.

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1)The values of h lie only in the first and fourth quadrants of the complex plane.

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