Journal of Statistical Physics, Vol. 82, Nos. 5/6, 1996

Weakly Nonlinear Conductivity of Random Composites: A Series Expansion Approach

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Received June 14, 1995

We present a series expansion calculation of the bulk effective coefficient of weakly nonlinear behavior in some continuum composite conductors and in simple cubic random resistor networks. The expansion is in powers of the relative difference between the linear Ohmic conductivities of the components. It is carried up to third order for an independent random bond network and a diagrammatic scheme is used to aid in implementing the calculation. For continuum composites, only the first term of the expansion can be calculated explicitly without detailed information about the microgeometry. Such information is difficult to acquire and even more difficult to exploit.

KEY WORDS: Composite materials; nonlinear conductivity; series expansion.

1. INTRODUCTION

The phenomenon of weakly nonlinear electrical transport in a macroscopically inhomogeneous or composite medium has attracted increasing attention since 1985 (see ref. 1 for a recent review). In particular, much effort has centered around the problem of the bulk effective weakly nonlinear response in percolating metal–insulator or normal metal–superconductor composites, where the contrast between the properties of the two components (i.e., the ratio of conductivities) is infinite. The critical behavior of the weakly nonlinear response near percolation was also discussed for finite contrast composites.[2, 3] In this paper we are concerned with determining the effective nonlinear conductivity of a weakly nonlinear

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0022-4715/96/0300-1327$09.50/0

random composite far from the percolation threshold and with a finite contrast between the component properties. Stroud and Hui[4] showed that the bulk effective weak nonlinearity coefficient of a composite is proportional to the effective resistance fluctuations, $1/f$ noise,[5,6] in a linear composite that has the same linear conductivities and the same microgeometry. It can therefore be calculated, to first order in the nonlinearity, from an appropriate moment of the local field distribution in such a linear composite. Based on this perturbation approach, Zeng *et al.*[7,8] proposed an effective medium theory for the calculation of the effective nonlinear response. We present here a different approach, namely an expansion in powers of the relative difference between the Ohmic conductivities of the components.

In weakly nonlinear materials the local constitutive relation between the electric current density and the electric field is

$$J(r) = \sigma(r)\, E(r) + b(r)\, |E(r)|^2\, E(r) \tag{1.1}$$

where

$$b(r)\, |E(r)|^2 \ll \sigma(r) \tag{1.2}$$

The nonlinear term is the lowest order correction to Ohmic behavior in materials that have a centrosymmetric crystal structure. In a composite made of such weakly nonlinear conductors the Ohmic conductivity σ and the nonlinearity coefficient b may have different values in each component. The composite will exhibit a bulk behavior characterized by bulk effective coefficients σ_e and b_e,[1,4]

$$\langle J \rangle = \sigma_e \langle E \rangle + b_e\, |\langle E \rangle|^2 \langle E \rangle \tag{1.3}$$

where the angular brackets denote a volume average, $\langle E \rangle = E_0$ is the externally applied uniform electric field,

$$\sigma_e = \frac{1}{V} \int dV\, \sigma(r)\, \frac{|E_l(r)|^2}{|E_0|^2} \tag{1.4}$$

and

$$b_e = \frac{1}{V} \int dV\, b(r)\, \frac{|E_l(r)|^4}{|E_0|^4} \tag{1.5}$$

$E_l(r)$ is the local electric field in a corresponding linear composite of the same microgeometry and the same local Ohmic conductivities but with $b(r) = 0$ everywhere. An expression similar to (1.5) was previously obtained

for the lowest order nonlinear correction to the bulk effective superfluid density in HeII filled superleak as a function of the local superfluid velocity.[9]

The discrete analog of (1.1) for a two-component random resistor network (RRN) is

$$I = gV + b|V|^2 V \tag{1.6}$$

where g is the Ohmic conductivity and b is the nonlinear conductivity coefficient ($g = g_o$, $b = b_o$ in one component and $g = g_1$, $b = b_1$ in the second). The effective conductivities may be defined by the relation between the average current per bond I_0 and the average voltage per bond V_0,

$$I_0 = g_e V_0 + b_e |V_0|^2 V_0 \tag{1.7}$$

As in the continuum case, the effective nonlinear conductivity coefficient b_e can be calculated, to first order in the nonlinearity, from the fourth moment of the local voltage distribution in the corresponding linear network[4, 10, 11] weighted by the local values of b

$$b_e = \frac{1}{N} \sum_{\alpha} b_\alpha V_\alpha^4 \tag{1.8}$$

which is the discrete analog of (1.5). N is the total number of unit cells in the network and the sum is taken over all the bonds of the network. Here V_α is the voltage drop on the conductor α when all the b_α vanish and an external voltage is applied in the direction of one of the principal axes, such that $(1/N)\sum_\alpha V_\alpha = 1$. This sum may be taken either over all the bonds of the network or only over the bonds parallel to the external applied voltage. Clearly, b_e is sensitive to local fluctuations in V which are induced by the inhomogeneities of g. Our aim in this paper is to find a more explicit form of this dependence by expanding b_e as a power series in the local Ohmic conductance fluctuations.

2. THE CONTINUUM CASE: NONLINEAR COMPOSITE MATERIALS

The local Ohmic conductivity of a continuum composite will be written as

$$\sigma(r) = \sigma_0 + \delta\sigma(r) \tag{2.1}$$

where σ_0 is some constant value, most conveniently chosen equal to the Ohmic conductivity of one of the components. $\delta\sigma(r)$ is the local variation

of the Ohmic conductivity, which assumes a different value in each component. It can be written as

$$\delta\sigma(r) = \sum_i \theta_i(r)\, \delta\sigma_i \tag{2.2}$$

where the sum is over all the components and $\theta_i(r)$ is the characteristic function of the component i, equal to 1 inside it and to 0 in the other components. The nonlinear conductivity coefficient can be similarly expressed as

$$b(r) = \sum_i \theta_i(r)\, b_i \tag{2.3}$$

It is clear that the effective nonlinear conductivity b_e of Eq. (1.5) is sensitive to local fluctuations in the electric field. These fluctuations are induced by the inhomogeneity of the Ohmic conductivity $\delta\sigma(r)$, since b_e depends only on the Ohmic fields. The explicit form of this dependence can be found by expanding b_e as a power series in the linear conductivity variations $\delta\sigma(r)$. This expansion can be symbolically written as

$$b_e = \langle b(r) \rangle + \delta b_e + \delta^2 b_e + \cdots \tag{2.4}$$

The zeroth-order term of this expansion is simply the volume average of $b(r)$ over the whole composite. It would be the exact result in a system where $\sigma(r) = \sigma_0 = \text{const}$ is uniform, in which case also $E(r) = E_0$ will be uniform. When $\sigma(r)$ is not a constant, then the Ohmic electric field can also be formally expanded as a power series in $\delta\sigma(r)$,

$$E(r) = E_0 + \delta E(r) + \delta^2 E(r) + \cdots \tag{2.5}$$

where E_0 is the volume-averaged electric field applied on the composite. A similar expansion can be written for the electrostatic potential

$$\Phi(r) = \Phi_0 + \delta\Phi(r) + \delta^2\Phi(r) + \cdots \tag{2.6}$$

where $E_0 = -\nabla\Phi_0$ and $\delta^n E = -\nabla\delta^n\Phi$.

In inhomogeneous materials $\delta\sigma(r) \neq 0$ in parts of the volume. This gives rise to local fluctuations of the electric field and to additional contributions to the effective nonlinear conductivity coefficient. The first- and second-order contributions are

$$\delta b_e = \frac{4}{V} \int dV\, b(r)\, \frac{E_0 \cdot \delta E(r)}{E_0^2} \tag{2.7}$$

and

$$\delta^2 b_e = \frac{12}{V}\int dV\, b(r)\frac{(E_0\cdot\delta E(r))^2}{E_0^4} + \frac{4}{V}\int dV\, b(r)\frac{E_0\cdot\delta^2 E(r)}{E_0^2} \tag{2.8}$$

If we assume that the volume-averaged electric field is applied along the x-axis and its magnitude is equal to unity, $E_0 = \hat{e}_x$, then the expansion terms of (2.7) and (2.8) can be simplified,

$$\delta b_e = \frac{4}{V}\int dV\, b(r)\,\hat{e}_x\cdot\delta E(r) \tag{2.9}$$

and

$$\delta^2 b_e = \frac{12}{V}\int dV\, b(r)(\hat{e}_x\cdot\delta E(r))^2 + \frac{4}{V}\int dV\, b(r)\,\hat{e}_x\cdot\delta^2 E(r) \tag{2.10}$$

To calculate the first-order contribution (2.9), we have to find an explicit expression for δE. This can be done by applying the differential operator δ to the divergence equation of the electric current

$$\nabla\cdot J = 0 \tag{2.11}$$

where the Ohmic current is given by $J(r) = \sigma(r)\,E(r)$. From this we find

$$\nabla\cdot\delta J = \nabla\cdot(\delta\sigma E_0 + \sigma_0\,\delta E) = 0 \tag{2.12}$$

This gives a first-order differential equation for δE,

$$\nabla\cdot\delta E = -\frac{E_0}{\sigma_0}\nabla\cdot\delta\sigma = -\frac{\hat{e}_x\cdot\nabla\delta\sigma}{\sigma_0} = -\frac{\partial\delta\sigma/\partial x}{\sigma_0} \tag{2.13}$$

Substituting (2.2), we get a Poisson equation for the first-order term of the electrostatic potential

$$\nabla^2\delta\Phi = \frac{1}{\sigma_0}\nabla_x\sum_i \theta_i(r)\,\delta\sigma_i \tag{2.14}$$

The boundary conditions satisfied by $\delta\Phi$ are $\delta\Phi = 0$ at the two condenser plates and $\partial\delta\Phi/\partial x = 0$ at the walls. This is just Poisson's equation for the potential produced by an electric polarization field,

$$P = \frac{\hat{e}_x}{4\pi\sigma_0}\sum_i \theta_i(r)\,\delta\sigma_i \tag{2.15}$$

Equation (2.14) can be formally solved using a method introduced by Bergman.[12] In this approach, each pure component of the composite is divided into a large number of small grains and an index μ is assigned to every grain. A θ-function can be defined for every grain, such that $\theta_\mu(r)$ is 1 when r is inside the grain μ, and 0 otherwise. The first-order term in the expansion of Φ can be written as a sum of the contributions of all the individual grains

$$\delta\Phi = \sum_\mu \Phi_\mu \, \delta\sigma_\mu \tag{2.16}$$

where

$$\nabla^2 \Phi_\mu = \frac{1}{\sigma_0} \nabla_x \theta_\mu(r) \tag{2.17}$$

A solution to Eq. (2.17) is given by

$$\Phi_\mu = -\frac{1}{4\pi\sigma_0} \int \frac{\nabla'_x \theta_\mu(r')}{|r - r'|} \, dV' \tag{2.18}$$

This solution does not satisfy the boundary conditions of the exact solution $\delta\Phi$ of Eq. (2.14), but the correction that should be added to it in order to repair this fault would be $\mathcal{O}(1/V)$ if both r and r' are well away from the surface.[12] Consequently, this solution can be used to represent Φ_μ inside the grain μ and in its vicinity, but not over the entire system. We will use it to calculate $\delta\Phi$ within a certain grain μ only by evaluating the self-field of that grain and the fields produced in it by other grains within a finite volume V_μ surrounding it. This is the "near-field contribution." The field produced by the other, faraway grains can be calculated if the composite is assumed to be macroscopically homogeneous. In this case, the actual polarization P can be replaced by its average value $\langle P \rangle$ given by

$$\langle P \rangle = \frac{\hat{e}_x}{4\pi\sigma_0} \sum_i p_i \, \delta\sigma_i \tag{2.19}$$

where p_i is the volume fraction of the component i. We will call the field produced in this way the "far-field contribution."

We will now evaluate the near field contribution to the first-order term in the expansion of b_e by substituting the solution (2.18) into Eq. (2.9). This gives

$$[\delta b_e]_{\text{near}} = \frac{4}{V} \int dV \, b(r) \, \nabla_x \frac{1}{4\pi\sigma_0} \sum_\mu \delta\sigma_\mu \int dV' \, \frac{\nabla'_x \theta_\mu(r')}{|r - r'|} \tag{2.20}$$

Substituting

$$b(r) = \sum_{\nu} \theta_\nu b_\nu \tag{2.21}$$

we can now use the near-field restriction $\mu \in V_\nu$ to perform a partial integration over x', which finally gives

$$[\delta b_e]_{\text{near}} = \frac{4}{V} \int dV \frac{1}{4\pi\sigma_0} \int dV' \sum_{\nu} \sum_{\mu \in V_\nu} b_\nu \delta\sigma_\nu \theta_\nu(r)\, \theta_\mu(r') (\nabla'_x)^2 \frac{1}{|r-r'|} \tag{2.22}$$

If we restrict the sums on μ and ν to a particular component or pair of components i and j, then since b_ν and $\delta\sigma_\mu$ are constant, we have to sum first over the product of θ-functions

$$g_{ij}(r, r') \equiv \sum_{\nu \in i} \sum_{\mu \in V_\nu, j} \theta_\nu(r)\, \theta_\mu(r') \tag{2.23}$$

The function $g_{ij}(r, r')$ is a truncated correlation function, which is equal to 0 for large separations $|r-r'|$. For separations somewhat smaller than the smallest radius of V_ν, this function tends to the probability of finding r in the component i and r' in the component j. For $r = r'$ it satisfies

$$g_{ij}(r, r) = p_i \delta_{ij} \tag{2.24}$$

If the composite system has a rotational symmetry that is either isotropic or cubic, and if we choose V_ν to be a large, but finite sphere (i.e., much larger than the grain ν, but much smaller than the composite system itself) centered around the grain ν, then $g_{ij}(r, r')$ will have the same symmetry. In this case, the double integral

$$\frac{1}{V} \int dV \int dV'\, g_{ij}(r, r')\, \nabla_x^2 \frac{1}{|r-r'|} \tag{2.25}$$

will be independent of the axis along which the double derivative is taken, and we can rewrite it as

$$\frac{1}{V} \int dV \int dV'\, g_{ij}(r, r') \frac{1}{3} \nabla^2 \frac{1}{|r-r'|} = -\frac{4\pi}{3} p_i \delta_{ij} \tag{2.26}$$

Using this result in Eq. (2.22), and summing over the phases i and j, we find for the near-field contribution

$$[\delta b_e]_{\text{near}} = -\frac{4}{3\sigma_0} \sum_i p_i b_i \delta\sigma_i \tag{2.27}$$

The far-field contribution to the electric field δE at the center of the sphere V_ν is just the Lorentz local field calculated with zero average field and with a polarization given by Eq. (2.19),

$$\delta E = \frac{\hat{e}_x}{3\sigma_0} \sum_i p_i \delta\sigma_i \tag{2.28}$$

Therefore, the far-field contribution to Eq. (2.9) is

$$[\delta b_e]_{\text{far}} = \frac{4}{3\sigma_0} \left(\sum_i p_i b_i \right) \left(\sum_i p_i \delta\sigma_i \right) \tag{2.29}$$

From Eqs. (2.27) and (2.29) we finally get the first-order term in the expansion of b_e,

$$\delta b_e = \frac{4}{3\sigma_0} \left(\left(\sum_i p_i b_i \right) \left(\sum_i p_i \delta\sigma_i \right) - \sum_i p_i b_i \delta\sigma_i \right) \tag{2.30}$$

For the special case of a two-component composite with components denoted by 0 and 1 we find the simple result

$$\delta b_e = -\frac{4}{3\sigma_0} p_1 p_0 (\sigma_1 - \sigma_0)(b_1 - b_0) \tag{2.31}$$

A similar calculation of the second-order contribution $\delta^2 b_e$ is impossible without detailed knowledge about the microgeometry of the composite. This can be seen if we try to calculate the first term of (2.10). Substituting the near-field and far-field contributions to δE into this expression from (2.18) and (2.28), respectively, we find

$$\frac{12}{V} \int dV\, b(r) (\hat{e}_x \cdot \delta E(r))^2$$

$$= \frac{12}{V} \int dV\, b(r) \left(\nabla_x \sum_\mu \frac{\delta\sigma_\mu}{4\pi\sigma_0} \int \frac{\nabla'_x \theta_\mu(r')}{|r - r'|} dV' + \frac{1}{3\sigma_0} \sum_i p_i \delta\sigma_i \right)^2 \tag{2.32}$$

There are three parts to this expression; one is quadratic in the far-field contribution, another is quadratic in the near-field contribution, and the third is mixed. The calculation of the far-field term is straightforward. It gives

$$\frac{12}{V} \int dV\, b(r) \left(\frac{1}{3\sigma_0} \sum_i p_i \delta\sigma_i \right)^2 = \frac{12}{9\sigma_0^2} \left(\sum_i p_i b_i \right) \left(\sum_i p_i \delta\sigma_i \right)^2 \tag{2.33}$$

The mixed term includes an integral that is identical to the one obtained in the calculation of the first order-term. It can be solved by the same method, for a system of an isotropic or cubic rotational symmetry,

$$\frac{8}{\sigma_0^2}\left(\sum_i p_i \delta\sigma_i\right)\frac{1}{V}\int dV \int \frac{dV'}{4\pi}\sum_\nu \sum_{\mu\in V_\nu} b_\nu \delta\sigma_\mu \theta_\nu(r)\,\theta_\mu(r')\,\nabla_x^2 \frac{1}{|r-r'|}$$
$$= -\frac{8}{\sigma_0^2}\left(\sum_i p_i \delta\sigma_i\right)\left(\sum_i p_i b_i \delta\sigma_i\right) \tag{2.34}$$

The near-field term cannot be calculated in the same way. After substitution of Eq. (2.21) and the use of the near-field restriction $\mu \in V_\nu$ to perform a partial integration over x', we obtain

$$\frac{12}{V}\int dV\, b(r)\left(\sum_\mu \frac{\delta\sigma_\mu}{4\pi\sigma_0}\nabla_x \int \frac{\nabla_x' \theta_\mu(r')}{|r-r'|}\,dV'\right)^2$$
$$= \frac{12}{V}\int dV \sum_\nu b_\nu \left(\frac{1}{4\pi\sigma_0}\int dV' \sum_{\mu\in V_\nu} \theta_\nu(r)\,\theta_\mu(r')\,\delta\sigma_\mu \nabla_x^2 \frac{1}{|r-r'|}\right)^2 \tag{2.35}$$

Inside the triple integral there appears a three-point correlation function

$$\theta_\nu(r) \sum_{\mu\in V_\nu} \theta_\mu(r') \sum_{\lambda\in V_\nu} \theta_\lambda(r'') \tag{2.36}$$

In contrast with the two-point correlation function $g_{ij}(r, r')$ which appeared in the first-order term, this function cannot be easily simplified in a way similar to (2.24). Therefore, it is impossible to calculate the near-field contribution to (2.32), and to the other term of (2.10), without a more detailed knowledge of the microstructure. Explicit information is required about the three-point correlation function of the composite material. Calculation of higher order terms in this expansion involves yet higher order correlation functions.

In summary, the series expansion for the nonlinear conductivity of a weakly nonlinear continuum composite with either isotropic or cubic symmetry can be carried out explicitly to first order in the conductivity variations. The result to this order is

$$b_e = \langle b\rangle + \frac{4}{3\sigma_0}\left(\left(\sum_i p_i b_i\right)\left(\sum_i p_i \delta\sigma_i\right) - \sum_i p_i b_i \delta\sigma_i\right) \tag{2.37}$$

Calculation of higher order terms requires detailed knowledge of the microgeometry of the composite.

3. THE DISCRETE CASE: NONLINEAR RANDOM RESISTOR NETWORKS

The series expansion approach introduced in the previous section can be applied to random resistor networks (RRN). These networks provide the simplest type of model for a randomly inhomogeneous conductor. In this section, we try to exploit that simplicity in order to develop a systematic expansion for the macroscopic nonlinear conductivity coefficient of a random cubic network of conductors g_1, g_2 as a function of g_1/g_2 and for arbitrary values of p_1, the probability for any conductor to be g_1. It is hoped that the simplicity of the model will allow us to carry this expansion to higher orders than was possible in the more complicated case of a continuum composite.

We consider a three-dimensional cubic RRN where every bond between nearest neighbor sites independently assumes one of the two

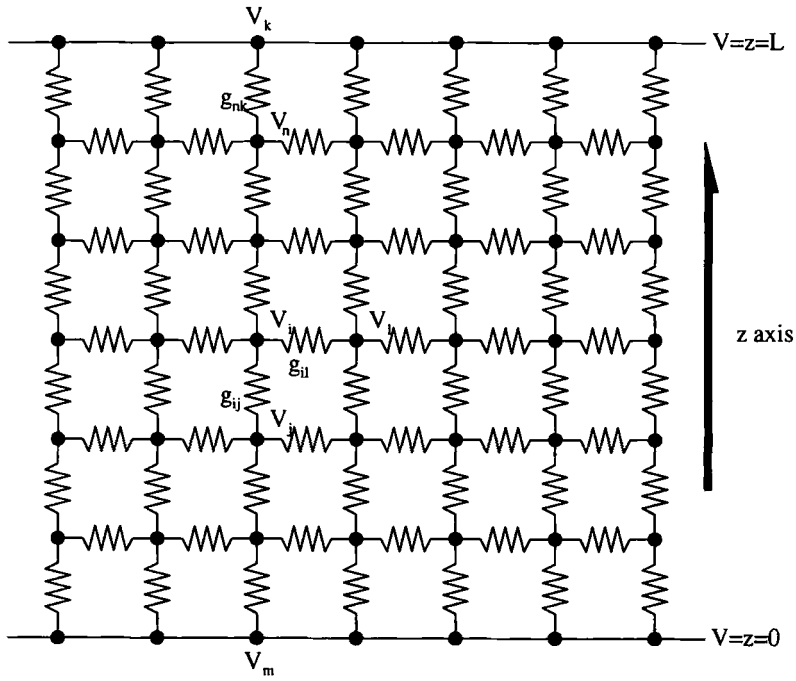

Fig. 1. Schematic representation of the RRN between the parallel plates of an infinite condenser. In this drawing, the distance between the plates is $L = 6$. The sites m and k are surface sites.

conductances g_1, g_2 with probability $p_1, 1-p_1$, respectively. A series expansion for the Ohmic conductivity of such an RRN was developed by Bergman and Kantor.[13] We adopt their notation and use a method which is based on this discrete model to develop a similar expansion for the weakly nonlinear conductivity. The network we consider is assumed to fill the space between the infinitely large plates of a parallel plate condenser at a distance L from each other and is subjected to a potential difference also equal to L (see Fig. 1). Kirchhoff's equations for the potentials V_j at all the lattice sites are given by

$$\sum_j g_{ij}(V_i - V_j) = 0 \tag{3.1}$$

where the sum is over all the nearest neighbors to the site i, and where i is any internal site (surface sites are excluded—there the potential is either 0 or L). The conductance g_{ij} which is either g_1 or g_2, can be represented in the form

$$g_{ij} = g_2 \varepsilon_{ij}(1 - u\theta_{ij}) \tag{3.2}$$

where

$$u \equiv 1 - \frac{g_1}{g_2} \tag{3.3}$$

$$\theta_{ij} = \begin{cases} 1 & \text{if } g_{ij} = g_1 \\ 0 & \text{if } g_{ij} = g_2 \end{cases} \tag{3.4}$$

and

$$\varepsilon_{ij} = \begin{cases} 1 & \text{if } i, j \text{ are nearest neighbors} \\ 0 & \text{otherwise} \end{cases} \tag{3.5}$$

θ_{ij} is a random bond-variable that is analogous to the characteristic function $\theta_i(r)$ which appears in the continuum composite case. Using this representation, Kirchhoff's equations become

$$\sum_j \varepsilon_{ij}(V_i - V_j) = u \sum_j \varepsilon_{ij}\theta_{ij}(V_i - V_j) \tag{3.6}$$

Bergman and Kantor introduced the discrete lattice Green's function γ_i^l to solve this set of equations[13]. It is defined by

$$\sum_i \varepsilon_{ij}(\gamma_i^l - \gamma_j^l) = \delta_{il} \tag{3.7}$$

together with the requirement that γ_i^l vanishes when i is a surface site. The quantity γ_i^l is the discrete analog of the potential created at i by a point charge at l. Using it, Eq. (3.6) and the accompanying boundary condition can be transformed into a set of equations for the voltages across the individual conductors[13]

$$V_\alpha = z_\alpha + u \sum_\beta \Gamma_{\alpha\beta} \theta_\beta V_\beta \tag{3.8}$$

The indices α and β are bond indices, i.e.,

$$V_\alpha \equiv V_{ij} = V_i - V_j, \qquad z_\alpha \equiv z_i - z_j, \qquad \theta_\alpha \equiv \theta_{ij} \tag{3.9}$$

where z_i is the z coordinate of the site i and z_α is equal to unity if the bond α is parallel to the applied voltage and is zero otherwise. Here

$$\Gamma_{\alpha\beta} \equiv \Gamma_{il,jm} \equiv \gamma_i^l - \gamma_i^m - \gamma_j^l + \gamma_j^m \tag{3.10}$$

is a Hermitian matrix which is the discrete analog of a dipole–dipole interaction between the bonds (ij) and (lm)[13]

Equation (3.8) can be written more compactly in a symbolic notation as

$$V = z + u\Gamma\theta V \tag{3.11}$$

This equation can be formally solved and the solution expanded in powers of u,

$$V = \frac{1}{1 - u\Gamma\theta} z = (1 + u\Gamma\theta + u^2\Gamma\theta\Gamma\theta + \ldots) z \tag{3.12}$$

from which we get

$$\delta V_\alpha = u(\Gamma\theta z)_\alpha = u \sum_\beta \Gamma_{\alpha\beta} \theta_\beta z_\beta \tag{3.13}$$

$$\delta^2 V_\alpha = u^2 (\Gamma\theta\Gamma\theta z)_\alpha = u^2 \sum_\beta \Gamma_{\alpha\beta} \theta_\beta \sum_\gamma \Gamma_{\beta\gamma} \theta_\gamma z_\gamma \tag{3.14}$$

etc.

The effective weakly nonlinear conductance per bond of the RRN is given by Eq. (1.8),

$$b_e = \frac{1}{N} \sum_\alpha b_\alpha V_\alpha^4$$

where V_α is given by Eq. (3.8) and N is the total number of unit cells in the network. Its expansion as a power series in u can be formally written as

$$b_e = \langle b_\alpha \rangle + \delta b_e + \delta^2 b_e + \delta^3 b_e \ldots \tag{3.15}$$

As in the continuum case, the first term in this expansion (the zeroth-order term) is simply the volume average of b_α over the entire system. The next three terms in this expansion are

$$\delta b_e = \frac{4}{N} \sum_\alpha b_\alpha z_\alpha \delta V_\alpha \tag{3.16}$$

$$\delta^2 b_e = \frac{12}{N} \sum_\alpha b_\alpha z_\alpha (\delta V_\alpha)^2 + \frac{4}{N} \sum_\alpha b_\alpha z_\alpha \delta^2 V_\alpha \tag{3.17}$$

and

$$\delta^3 b_e = \frac{24}{N} \sum_\alpha b_\alpha z_\alpha (\delta V_\alpha)^3 + \frac{36}{N} \sum_\alpha b_\alpha z_\alpha \delta V_\alpha \delta^2 V_\alpha + \frac{4}{N} \sum_\alpha b_\alpha z_\alpha \delta^3 V_\alpha \tag{3.18}$$

The nonlinear conductance of the bonds b_α can be written in a way analogous to Eq. (2.3), using the characteristic θ-function (3.4),

$$b_\alpha = (b_1 - b_0)\, \theta_\alpha + b_0 \tag{3.19}$$

With this representation, the expansion terms can be calculated following the approach of ref. 13 using three identities satisfied by the matrix elements of Γ:

$$\sum_\beta \Gamma_{\alpha\beta} z_\beta = 0; \qquad \sum_\beta \Gamma_{\alpha\beta} \Gamma_{\beta\gamma} = \Gamma_{\alpha\gamma}; \qquad \Gamma_{\alpha\alpha} = 1/3 \tag{3.20}$$

In order to calculate the expansion terms in the case of a random network, we must average over the distribution of θ_α. This averaging is necessary in order to get an expansion for the ensemble average of b_e. We discuss infinitely large networks, in which γ_i' depends only upon the vector separation between the network sites $\mathbf{i} - \mathbf{l}$ and $\Gamma_{\alpha\beta}$ depends only on the vector separation of the bonds α and β and on their relative orientations, and not on their absolute locations. Consequently, the ensemble average of each of the terms (3.16)–(3.18) also depends only on the orientations and vector separations of the bonds and we can omit the sum on one of the bond indices, at the same time omitting also the $1/N$ factor. Thus, in each of the above expansion terms we have to evaluate correlation functions of the

independent random variables θ_α. Each term will include a correlation function of the type

$$\langle \theta_\alpha \theta_\beta \theta_\gamma \cdots \rangle$$

For independently distributed bonds, each of these correlation functions may be decomposed into a sum of δ-functions multiplied by polynomials of p_1, e.g.,[13]

$$\begin{aligned} \langle \theta_0 \rangle &= p_1 \\ \langle \theta_0 \theta_1 \rangle &= p_1^2 + p_1(1-p_1)\delta_{01} \\ \langle \theta_0 \theta_1 \theta_2 \rangle &= p_1^3 + p_1^2(1-p_1)(\delta_{01}+\delta_{02}+\delta_{12}) + p_1(1-p_1)(1-2p_1)\delta_{012} \end{aligned} \tag{3.21}$$

where a symbol such as δ_{01} is equal to 1 if the bonds 0,1 are equal, and to 0 otherwise.

Given these considerations, the first-order term (3.16) is

$$\begin{aligned} \delta b_e &= \frac{4u}{N} \sum_\alpha b_\alpha z_\alpha \sum_\beta \Gamma_{\alpha\beta} \theta_\beta z_\beta \\ &= \frac{4u}{N}(b_1 - b_0) \sum_{\alpha\beta} z_\alpha \theta_\alpha \Gamma_{\alpha\beta} \theta_\beta z_\beta + \frac{4u}{N} b_0 \sum_{\alpha\beta} z_\alpha \Gamma_{\alpha\beta} \theta_\beta z_\beta \end{aligned} \tag{3.22}$$

Applying the first relation of (3.20), we find that the second term in this sum is equal to 0. The first term includes a second-order correlation of θ-functions, which we substitute from (3.21). This gives

$$\begin{aligned} \delta b_e &= 4u(b_1 - b_0) \sum_\beta z_\alpha \Gamma_{\alpha\beta} z_\beta p_1(1-p_1)\delta_{\alpha\beta} \\ &= 4u(b_1 - b_0)\, p_1(1-p_1)\, z_\alpha \Gamma_{\alpha\alpha} z_\alpha \\ &= \tfrac{4}{3} u p_1(1-p_1)(b_1 - b_0) \end{aligned} \tag{3.23}$$

This result is identical to (2.31), which was obtained for a two-component continuum composite.

Using this method, we calculated the first three terms in the expansion $b_e - \langle b_\alpha \rangle = \sum_{n=1}^{\infty} a_n u^n$. Every correlation function which appears in this calculation is multiplied by a set of Γ matrices of equal or lower order. This gives various products of Γ matrices which have to be evaluated. Many of these products are found to vanish due to (3.20). To simplify the calculation of the coefficients a_n, it is useful to characterize each contribution by an appropriate graph (see Fig. 2): We assign a vertex to every independent bond index α, a line segment joining two vertices represents the matrix element $\Gamma_{\alpha\beta}$ and the factor z_α is represented by a dangling segment connected

Order in u	Contributing graphs	Total contribution of the graphs
$n=1$		$4p_1(1-p_1)(b_1-b_0)\,\Gamma_{00}$
$n=2$		$4p_1^2(1-p_1)(b_1-b_0)\,\Gamma_{00}$
		$16p_1(1-p_1)(1-2p_1)(b_1-b_0)\,\Gamma_{00}^2$
		$12p_1(1-p_1)[b_0+p_1(b_1-b_0)]\sum_1 z_0\,\Gamma_{01}^2\,z_1$
$n=3$		$(24[b_0+p_1(b_1-b_0)](1-2p_1)+40p_1(1-p_1)(b_1-b_0))$ $\times p_1(1-p_1)\sum_1 z_0\Gamma_{01}^3\,z_1$
		$64p_1(1-p_1)(1-6p_1+6p_1^2)(b_1-b_0)\,\Gamma_{00}^3$
		$[44(1-2p_1)+4(1-p_1)]p_1^2(1-p_1)(b_1-b_0)\,\Gamma_{00}^2$
		$108p_1^2(1-p_1)^2(b_1-b_0)\,\Gamma_{00}\sum_1 z_0\Gamma_{01}^2\,z_1$
		$36[b_0+p_1(b_1-b_0)]p_1(1-p_1)(1-2p_1)\,\Gamma_{00}\sum_1 z_0\Gamma_{01}^2\,z_1$
		$36[b_0+p_1(b_1-b_0)]p_1^2(1-p_1)\sum_1 z_0\Gamma_{01}^2\,z_1$
		$4p_1^3(1-p_1)(b_1-b_0)\,\Gamma_{00}$

Fig. 2. All nonzero graphs and their contributions to the coefficient of u^n, $1 \leqslant n \leqslant 3$, in the series for b_e.

to the vertex α. All these graphs are multiconnected, i.e, they cannot be separated into disconnected parts by removing a single line. This rule follows from the fact that such an isolated line would be associated with a single sum of the form of the first relation of (3.20), which vanishes.[13] Another rule is that any vertex that has only two lines attached to it can

be ignored, and a line that includes any number of such vertices can be represented by a single factor $\Gamma_{\alpha\beta}$. This follows from the idempotency property of the matrix Γ [the second relation of (3.20)].

The first three coefficients are obtained by summing the appropriate graphs from Fig. 2. The first-order term includes a single contribution which was explicitly calculated above. To calculate the second- and third-order terms, we need to evaluate non trivial sums involving matrix elements of Γ. The quadratic sum which appears in the second-order term is the discrete analog of the three-point correlation function integral, which we were unable to calculate in the continuum case. The third-order term includes, in addition to such terms, also a cubic sum which is the discrete analog of the four-point correlation function integral. Due to the simple geometry of the cubic RRN model, these sums can be evaluated numerically using series expansions for the matrix elements $\Gamma_{\alpha\beta}$, developed in ref. 13. The results obtained are

$$\sum_{\alpha} z_\alpha \Gamma_{\alpha\beta}^2 z_\alpha = 0.1648 \pm 10^{-4}, \qquad \sum_{\alpha} z_\alpha \Gamma_{\alpha\beta}^3 z_\alpha = 0.03422 \pm 10^{-5} \quad (3.24)$$

The expansion presented here can in principle be improved by calculating more terms, although, beyond third order the number of graphs proliferates to such an extent that it becomes very difficult to keep track of them all.

4. DISCUSSION

In the preceding sections we presented a series expansion approach to the calculation of the nonlinear conductivity coefficient b_e of weakly nonlinear composites. An effective medium theory was previously devised to deal with this problem.[7,8] Both of these methods are based on a perturbation calculation to first order in the nonlinearity,[4] which gives b_e as the fourth moment of the local field distribution in a linear composite with the same Ohmic conductivities and the same microgeometry. They are thus both valid to first order in the nonlinearity coefficients of the components. The effective medium theory is a one-shot approximation which is quite poor in high contrast composites far from the dilute limit.[3] By contrast, the approach presented here is a systematic expansion that can in principle be improved by calculating more terms in the power series.

The calculation of the first term in this expansion does not require any specific information about the microstructure of the material other than overall isotropy (or cubic symmetry) and the values of component volume fractions. However, the calculation of additional terms requires detailed information about the microstructure. The information needed is of a more

complicated nature the further we proceed in the expansion. This microscopic information appears in the calculation in the form of multipoint microgeometric correlation functions. Thus, a knowledge of the three-point correlation function is needed for the calculation of the second-order term, the four-point correlation function is needed for the third-order term, and so on. This information is usually not available for continuum composites, but can, in principle, be extracted from micrographs and be used in carrying the expansion to higher order.

The independent-bond, simple cubic, random resistor network is a simple model on which higher order terms of this expansion can be calculated explicitly: The correlation functions can be evaluated in any order, and the expansion coefficients can then be calculated numerically using the discrete dipole–dipole interaction matrix Γ. The development of the expansion for the weakly nonlinear conductivity coefficient of such a network was presented in Section 3 and its first three terms were calculated. The calculation of higher order terms may prove cumbersome, although it should be quite straightforward.

ACKNOWLEDGMENTS

This research was supported in part by grants from the U.S.–Israel Binational Science Foundation and the Israel Science Foundation.

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