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Effective medium approximation for two-component nonlinear composites with shape distribution

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Abstract

The effective medium approximation (EMA) is derived to investigate the effective linear and nonlinear responses of two-component composites in which one component is nonspherical and distributed in shape. Both components with the volume fractions p and q are assumed to obey a current–field $\boldsymbol{J}$–$\boldsymbol{E}$ relation of the form $\boldsymbol{J} = \sigma_i \boldsymbol{E} + \chi_i |\boldsymbol{E}|^2 \boldsymbol{E}$, where σ_i and χ_i are the linear conductivity and nonlinear response of the component i ($i = 1, 2$) respectively. As the percolation threshold p_c (or q_c) is approached from above (or below), the effective linear conductivity σ_e and effective nonlinear response χ_e behave as $\sigma_e \sim [p - p_c(\Delta)]^t$ and $\chi_e \sim [p - p_c(\Delta)]^{t_2}$ in the conductor/insulator (C/I) limit, and $\sigma_e \sim [q_c(\Delta) - q]^{-s}$ and $\chi_e \sim [q_c(\Delta) - q]^{-s_2}$ in the superconductor/conductor (S/C) limit, where the exponents are found to be $t = s = 1$ and $t_2 = s_2 = 2$, independent of the shape variance parameter Δ, and $p_c(\Delta)$ (or $q_c(\Delta)$) is a monotonically decreasing (or increasing) function with Δ. For a finite-conductivity ratio $h = \sigma_1/\sigma_2$, numerical results show that σ_e may be increased or decreased with increasing Δ, dependent on whether the first component is a good or a poor conductor, while χ_e can exhibit a monotonic increase, monotonic decrease and nonmonotonic behaviour. Therefore, χ_e can be greatly enhanced by the adjustment of the shape variance parameter, and thereby provides an alternative way to achieve large enhancement of effective nonlinear response. The results of EMA with shape distribution are also compared with exact solutions in the dilute limit and reasonable agreement is found.

1. Introduction

The linear and nonlinear responses of inhomogeneous media have received much attention in recent years because of their potential applications in engineering and technology [1, 2]. The simultaneous presence of both inhomogeneity and nonlinearity in a system is an interesting and important problem [3]. A weakly nonlinear composite consists of one material with a

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nonlinear current–field characteristic of the form $\boldsymbol{J} = \sigma_1 \boldsymbol{E} + \chi_1 |\boldsymbol{E}|^2 \boldsymbol{E}$ and the other material with a linear or nonlinear response. One of the basic questions concerning such a random system is the calculation of the effective linear conductivity σ_e and the effective nonlinear response χ_e.

To calculate the effective linear conductivity, two important theories such as the Maxwell-Garnett approximation [4] and the Bruggeman effective medium approximation (EMA) [5] can be adopted. As we know, the derivations of both approximations were based on the assumption that the granular inclusions are spherical in shape. Later, the generalizations of these two approximations for all ellipsoidal inclusions having a fixed shape were done in various works [6–11].

In order to investigate the effective nonlinear response, the scientists developed the T-matrix method [12], decoupling approximation [13], perturbative method [14], numerical simulations in random resistor network [15] and so on [16–18]. All of these methods employed the spherical or cylindrical shape concept.

In a realistic composite system, the granular inclusions are usually nonspherical and even shape-distributed. In [19] and [20], we derived two different Maxwell-Garnett type approximations to investigate how the shape, and shape distribution of the granular inclusions affect the optical nonlinearity enhancement, when the alternating-current (ac) electric field was applied. As the two-component materials were considered to have asymmetrical microstructures (the granular inclusions of one component are embedded in the host medium), no percolation effect takes place. In this paper, we would like to investigate the effective linear and nonlinear responses of the conducting composite media of zero frequency in which two nonlinear components with shape distribution are randomly mixed. For simplicity, we assume that one component is spherical with the volume fraction q, while the other component with the volume fraction p (note that $p+q = 1$) is ellipsoidal in shape with a shape distribution function characterized by $f(L_x, L_y) = 2/\Delta^2\theta(L_x - 1/3 + \Delta/3)\theta(L_y - 1/3 + \Delta/3)\theta(2/3 + \Delta/3 - L_x - L_y)$, where $\theta(\cdots)$ is the Heaviside function, $L_{x,(y)}$ is the depolarization factor along the $x(y)$-symmetric axis and Δ is the shape variance parameter. This kind of distribution function has already been applied to study the effective absorption and scattering cross section [21, 22] for a system of small non-interacting ellipsoids distributed in shape. Here, based on the self-consistent condition of zero net polarization, we derive EMA by including the shape distribution in the calculation. In conjunction with the decoupling approximation [13], we are able to investigate the effects of shape variance parameter Δ on the percolation thresholds p_c and q_c, the critical exponents of σ_e and χ_e near the percolation thresholds in conductor/insulator (C/I) and superconductor/conductor (S/C) limits. Furthermore, for more realistic composites in which both components have finite linear conductivities, the effective linear conductivity and nonlinear response are also numerically examined.

Our paper is organized as follows. In section 2, EMA is derived by taking into account the shape distribution of components, and the effective nonlinear response is then solved within the decoupling approximation. In section 3, two important cases including C/I and S/C limits are carefully examined. In section 4, the effects of shape variance parameter Δ on the effective linear and nonlinear responses are numerically calculated. In section 5, our theoretical results are compared with exact solutions. Finally, a summary of our results and discussions will be given in section 6.

2. Effective medium approximation with shape distribution (SDEMA)

We consider a two-constituent, three-dimensional granular composite material, in which the ellipsoidal component 1 with volume fraction p and the spherical component 2 with volume fraction $q = 1 - p$ are randomly distributed. Both components are assumed to be nonlinear and obey a current–field ($\boldsymbol{J}$–$\boldsymbol{E}$) characteristic of the form

$$\boldsymbol{J} = \sigma_i \boldsymbol{E} + \chi_i |\boldsymbol{E}|^2 \boldsymbol{E} \qquad (i = 1, 2), \tag{1}$$

where σ_i is the linear conductivity and χ_i is the nonlinear response of the ith component. Due to the weak nonlinearity term in equation (1), the effective linear conductivity σ_e and nonlinear response χ_e of the whole system can be defined as follows:

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

where $\langle \boldsymbol{J} \rangle$ and $\langle \boldsymbol{E} \rangle \equiv \boldsymbol{E}_0$ represent the spatial average of the current density and the electric field.

In order to construct the EMA, let us consider the embeddings of both component 1 and 2 in the composite media, replaced by a fictitious homogeneous one with conductivity equal to the effective conductivity σ_e [23]. The polarization factor produced in the granular inclusions made of component i with σ_i can be written as

$$P_i = \frac{\sigma_i - \sigma_e}{3} \left[\frac{1}{L_x \sigma_i + (1 - L_x)\sigma_e} + \frac{1}{L_y \sigma_i + (1 - L_y)\sigma_e} + \frac{1}{L_z \sigma_i + (1 - L_z)\sigma_e} \right], \tag{3}$$

where L_j is the depolarization factor of an ellipsoid along three-symmetric axes and can be used to describe the shape of the ellipsoids [24]. Note that the sum rule $L_x + L_y + L_z = 1$ must be satisfied.

The effective linear conductivity σ_e can then be determined by imposing the consistency requirement that the arithmetic average of the polarization over different types of granular inclusions must vanish, i.e.

$$p P_1 + q P_2 = 0. \tag{4}$$

When both components are perfectly spherical in shape (i.e. $L_x = L_y = L_z = 1/3$), equation (4) reduces to

$$p \frac{\sigma_1 - \sigma_e}{\sigma_1 + 2\sigma_e} + (1 - p) \frac{\sigma_2 - \sigma_e}{\sigma_2 + 2\sigma_e} = 0. \tag{5}$$

Equation (5) is a quadratic equation for σ_e and is known as the original EMA [5].

When granular inclusions made of component 1 are randomly oriented ellipsoids and those of component 2 are spherical in shape, from equation (4) we obtain

$$p \frac{1}{3} \sum_{j=1}^{3} \frac{\sigma_1 - \sigma_e}{\sigma_e + L_j(\sigma_1 - \sigma_e)} + 3(1 - p) \frac{\sigma_2 - \sigma_e}{\sigma_2 + 2\sigma_e} = 0, \tag{6}$$

which is an effective medium approximation with dipole–dipole interaction (EMADD) in [8].

For an assembly of component 1 having different ellipsoidal shapes, P_1 should take the form

$$P_1 = \frac{\sigma_1 - \sigma_e}{3} \int\int \left[\frac{1}{L_x \sigma_1 + (1 - L_x)\sigma_e} + \frac{1}{L_y \sigma_1 + (1 - L_y)\sigma_e} + \frac{1}{(1 - L_x - L_y)\sigma_1 + (L_x + L_y)\sigma_e} \right] f(L_x, L_y)\, \mathrm{d}L_x\, \mathrm{d}L_y, \tag{7}$$

where $f(L_x, L_y)$ is the distribution function of the depolarization factor, which can, in principle, be used to describe the shape distribution.

Here we assume the shape distribution function to be [21, 22]

$$f(L_x, L_y) = C\theta\left(L_x - \frac{1}{3} + \frac{\Delta}{3}\right)\theta\left(L_y - \frac{1}{3} + \frac{\Delta}{3}\right)\theta\left(\frac{2}{3} + \frac{\Delta}{3} - L_x - L_y\right), \tag{8}$$

where $C \equiv 2/\Delta^2$ is the normalized constant and Δ is the shape variance parameter of the granular inclusions made of component 1, which defines both the domain of nonzero values and the half-width of the $f(L_x, L_y)$ function. Actually, Δ can change from zero to unity. Physically, for $\Delta = 0$, all granular inclusions are spherical ($L_j = 1/3$ for $j = 1, 3$); for $\Delta = 1$, all possible ellipsoidal shapes are equiprobable [20].

Introducing equation (8) into (7) leads to

$$P_1\left(\frac{\sigma_e}{\sigma_1}\right) = \frac{2}{\Delta^2}\left[\left(\frac{\sigma_e}{\sigma_1-\sigma_e} + \frac{1+2\Delta}{3}\right)\ln\left(\frac{\sigma_e/(\sigma_1-\sigma_e)+(1+2\Delta)/3}{\sigma_e/(\sigma_1-\sigma_e)+(1-\Delta)/3}\right) - \Delta\right]. \tag{9}$$

As $\Delta \to 0$, $P_1(\sigma_e/\sigma_1)$ in equation (9) is nothing but $3p(\sigma_1-\sigma_e)/(\sigma_1+2\sigma_e)$.

Equation (9) admits the following asymptotic behaviour:

$$P_1(x) = \begin{cases} \dfrac{2}{\Delta^2}\left[\dfrac{1+2\Delta}{3}\ln\left(\dfrac{1+2\Delta}{1-\Delta}\right) - \Delta\right] + \dfrac{2}{\Delta^2}\left[\ln\left(\dfrac{1+2\Delta}{1-\Delta}\right) - \dfrac{3\Delta}{1-\Delta}\right]x \\ x \ll 1 \\ \dfrac{2}{\Delta^2}\left[\dfrac{2(\Delta-1)}{3}\ln\left(\dfrac{2-2\Delta}{2+\Delta}\right) - \Delta\right] - \dfrac{2}{\Delta^2}\left[\ln\left(\dfrac{2-2\Delta}{2+\Delta}\right) + \dfrac{3\Delta}{2+\Delta}\right]\Big/ x \\ x \gg 1. \end{cases} \tag{10}$$

Thus, the self-consistency equation becomes

$$\frac{2p}{\Delta^2}\left[\left(\frac{\sigma_e}{\sigma_1-\sigma_e} + \frac{1+2\Delta}{3}\right)\ln\left(\frac{\sigma_e/(\sigma_1-\sigma_e)+(1+2\Delta)/3}{\sigma_e/(\sigma_1-\sigma_e)+(1-\Delta)/3}\right) - \Delta\right] + 3q\frac{\sigma_2-\sigma_e}{\sigma_2+2\sigma_e} = 0. \tag{11}$$

Equation (11) is a linear EMA with shape distribution, which allows us to estimate the effective linear conductivity of the random mixture in which the first component possesses the shape distribution form, described by equation (8).

Within the mean field approximation [13], the effective nonlinear response χ_e of the two-component random composite media can be expressed as

$$\chi_e \boldsymbol{E}_0^4 = p\chi_1\langle \boldsymbol{E}^4\rangle_1 + q\chi_2\langle \boldsymbol{E}^4\rangle_2 \approx p\chi_1\langle \boldsymbol{E}^2\rangle_1^2 + q\chi_2\langle \boldsymbol{E}^2\rangle_2^2. \tag{12}$$

In the above equation, the decoupling technique $\langle \boldsymbol{E}^4\rangle_i \approx \langle \boldsymbol{E}^2\rangle_i^2$ has been adopted.

It is well known that $\langle \boldsymbol{E}^2\rangle_i$ can be expressed as

$$\langle \boldsymbol{E}^2\rangle_1 = \frac{1}{p}\frac{\partial\sigma_e}{\partial\sigma_1}\boldsymbol{E}_0^2, \qquad \text{and} \qquad \langle \boldsymbol{E}^2\rangle_2 = \frac{1}{q}\frac{\partial\sigma_e}{\partial\sigma_2}\boldsymbol{E}_0^2. \tag{13}$$

Equation (13) follows from an established formula in a linear random composite giving σ_e in terms of the local fields:

$$\sigma_e = p\sigma_1\frac{\langle \boldsymbol{E}\rangle_1^2}{\boldsymbol{E}_0^2} + (1-p)\sigma_2\frac{\langle \boldsymbol{E}^2\rangle_2}{\boldsymbol{E}_0^2}. \tag{14}$$

Substituting equation (13) into (12), we have

$$\chi_e = \frac{\chi_1}{p}\left(\frac{\partial\sigma_e}{\partial\sigma_1}\right)^2 + \frac{\chi_2}{q}\left(\frac{\partial\sigma_e}{\partial\sigma_2}\right)^2. \tag{15}$$

With equation (10), $\partial\sigma_e/\partial\sigma_1$ and $\partial\sigma_e/\partial\sigma_2$ can be obtained from

$$\left\{\ln\left[\frac{\sigma_e/(\sigma_1-\sigma_e)+(1+2\Delta)/3}{\sigma_e/(\sigma_1-\sigma_e)+(1-\Delta)/3}\right] - \frac{\Delta}{\sigma_e/(\sigma_1-\sigma_e)+(1-\Delta)/3}\right\} \times \frac{2p}{\Delta^2}\left[\frac{\partial\sigma_e/\partial\sigma_1\cdot\sigma_1-\sigma_e}{(\sigma_1-\sigma_e)^2}\right] - \frac{9q\sigma_2\partial\sigma_e/\partial\sigma_1}{(\sigma_2+2\sigma_e)^2} = 0 \tag{16}$$

$$\left\{\ln\left[\frac{\sigma_e/(\sigma_1-\sigma_e)+(1+2\Delta)/3}{\sigma_e/(\sigma_1-\sigma_e)+(1-\Delta)/3}\right]-\frac{\Delta}{\sigma_e/(\sigma_1-\sigma_e)+(1-\Delta)/3}\right\}$$
$$\times\frac{2p}{\Delta^2}\left[\frac{\partial\sigma_e/\partial\sigma_2\cdot\sigma_1}{(\sigma_1-\sigma_e)^2}\right]+\frac{9q(\sigma_e-\partial\sigma_e/\partial\sigma_2\cdot\sigma_2)}{(\sigma_2+2\sigma_e)^2}=0. \tag{17}$$

So far, we have formulated an effective medium approximation with shape distribution (SDEMA) made of equations (11) and (15)–(17) to investigate the effective linear conductivity σ_e and nonlinear response χ_e of the two-component nonlinear composites.

3. Nonlinear conductor/insulator (C/I) and superconductor/nonlinear conductor (S/C) limits

In this section, we discuss two important limits, i.e. the conductor/insulator (C/I) and superconductor/conductor (S/C) cases. In these limits, percolation phenomena will take place, and thus it is necessary to study the percolation thresholds for both components 1 and 2 first.

In the C/I limit, where $\sigma_2 = 0$ and $\chi_2 = 0$, we identify the percolation threshold of component 1 below which the effective conductivity becomes zero and have [23]

$$p_c(\Delta)\equiv\frac{P_2\left(\frac{\sigma_e}{\sigma_2}\to\infty\right)}{P_2\left(\frac{\sigma_e}{\sigma_2}\to\infty\right)-P_1\left(\frac{\sigma_e}{\sigma_1}\to 0\right)}=\frac{3}{3+4/\Delta^2\left[(1+2\Delta)/3\ln\left(\frac{(1+2\Delta)}{(1-\Delta)}\right)-\Delta\right]}. \tag{18}$$

Clearly, the percolation threshold $p_c(\Delta)$ is dependent on the shape variance. That is to say, p_c is determined by all possible depolarization factors in the range $[1/3-\Delta, 1/3+\Delta]$. In this connection, for a two-phase medium composed of randomly oriented spheroids with a fixed principal depolarization factor L and a spherical insulating component [8], the percolation threshold $p_c(L)$ admits the form

$$p_c(L)=\frac{9L(1-L)}{-9L^2+15L+2}. \tag{19}$$

Note that equation (19) yields a L-dependent percolation threshold, which is quite different from equation (18).

As the percolation threshold $p_c(\Delta)$ is approached from above, we expect $\sigma_e \ll \sigma_1$. By substituting equation (10) into (4), the effective linear response is found to be

$$\sigma_e=\frac{p-p_c(\Delta)}{2/\Delta^2[3\Delta/(1-\Delta)-\ln((1+2\Delta)/(1-\Delta))]p_c(\Delta)}\sigma_1$$
$$\sim\sigma_1[p-p_c(\Delta)]^t=\sigma_1[p-p_c(\Delta)]^1. \tag{20}$$

Introducing equation (20) into (15), we have

$$\chi_e\sim[p-p_c(\Delta)]^{t_2}=[p-p_c(\Delta)]^2. \tag{21}$$

In the S/C limit, where $\sigma_2 = \infty$, we identify the percolation threshold of the superconducting component 2, above which the whole composite will become superconducting and have

$$q_c(\Delta)=\frac{P_1(\frac{\sigma_e}{\sigma_1}\to\infty)}{P_1(\frac{\sigma_e}{\sigma_1}\to\infty)-P_2(\frac{\sigma_e}{\sigma_2}\to 0)}$$
$$=\frac{2/\Delta^2\{\Delta+2(1-\Delta)/3\ln[2(1-\Delta)/(2+\Delta)]\}}{3+2/\Delta^2\{\Delta+2(1-\Delta)/3\ln[2(1-\Delta)/(2+\Delta)]\}}. \tag{22}$$

Again, the percolation threshold q_c is dependent on Δ.

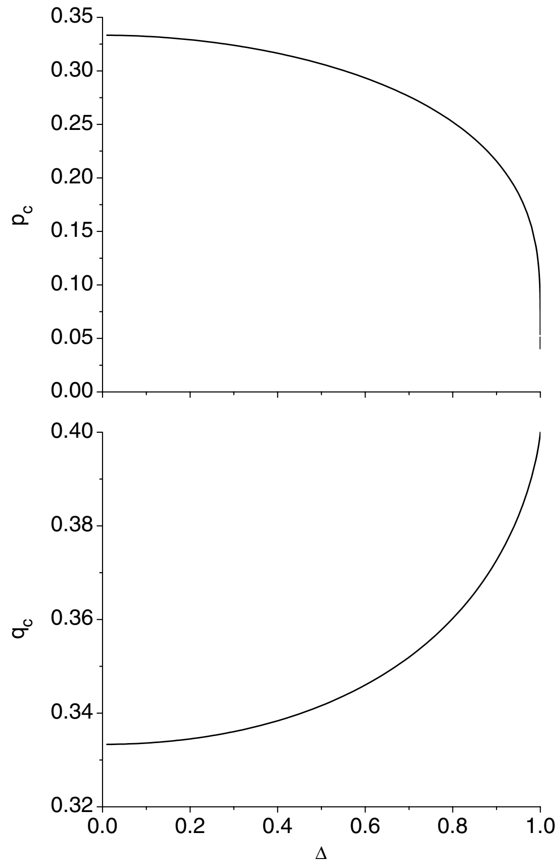

Figure 1. The percolation thresholds p_c and q_c as a function of Δ.

Similarly, as the percolation threshold q_c is approached from below, σ_e and χ_e diverge as

$$\sigma_e \sim \sigma_1[q_c(\Delta) - q]^{-s} = \sigma_1[q_c(\Delta) - q]^{-1}$$

and (23)

$$\chi_e \sim [q_c(\Delta) - q]^{-s_2} = [q_c(\Delta) - q]^{-2}.$$

Thus within SDEMA, for a three-dimensional composite system, although p_c and q_c are found to be dependent on Δ, the critical exponents $t = s = 1$ and $t_2 = s_2 = 2$, which describe the vanishing or divergence of σ_e and χ_e near the percolation thresholds, are indeed independent of Δ. In fact, in the two-dimensional case, we have $p_c(\Delta) = 2\Delta/\{2\Delta + \ln[(1+\Delta)/(1-\Delta)]\}$ and $q_c(\Delta) = \ln[(1+\Delta)/(1-\Delta)]/\{2\Delta + \ln[(1+\Delta)/(1-\Delta)]\}$, while the critical exponents still remain unchanged. It is well known that EMA may give the critical behaviour near the percolation threshold qualitatively, but usually predicts the incorrect exponents, because the full complexity of the spatial fluctuations of the local field is not taken into account [25, 26].

In figure 1, we plot the percolation thresholds p_c and q_c as a function of Δ in the three-dimensional case.

It is evident that p_c is a monotonically decreasing function of Δ, but q_c increases with increasing Δ. Such dependences on Δ can be easily understood as follows: the depolarization factor of component 1 along the j-symmetric axis can take a value from $1/3 - \Delta/3 \leqslant L_j \leqslant$

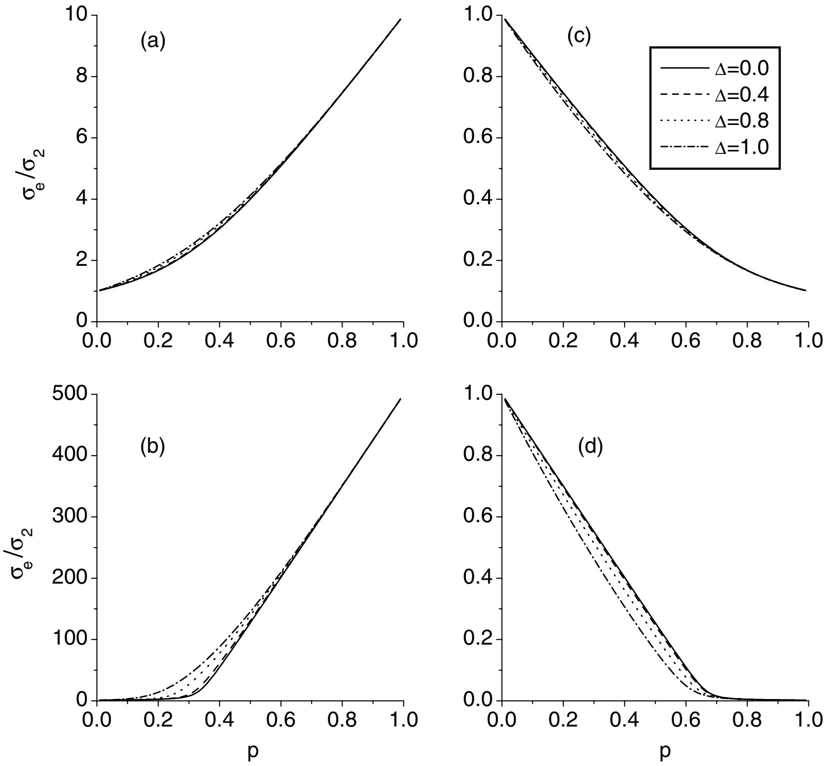

Figure 2. The effective linear conductivity σ_e/σ_1 as a function of the volume fraction p for various Δ and $h = \sigma_1/\sigma_2$. (a) $h = 10$, (b) $h = 500$, (c) $h = 0.1$ and (d) $h = 0.002$.

$1/3 + \Delta/3$. Thus there is the possibility for the first component 1 to be needle-like along the applied field and it is easy to form an infinite connected cluster throughout the whole composite, resulting in a small percolation threshold $p_c(\Delta)$ with increasing Δ; on the other hand, there is also the possibility for the first component's shape to be plate-like in shape, which keeps the superconducting phase (the second component) from connecting one with another, leading to a large percolation threshold for component 2.

4. Numerical results for finite ratio of conductivity σ_1/σ_2

We are now in a position to study the effective linear and nonlinear responses of the composite media with finite ratio of conductivity. The dependence of the effective linear and nonlinear responses on the shape variance parameter Δ are examined numerically.

Figure 2 shows the effective linear conductivity σ_e as a function of the volume fraction p for various Δ and different conductivity ratio $h = \sigma_1/\sigma_2$. When component 1, which possesses the shape distribution, is a good conductor and component 2 with spherical shape is a poor conductor, i.e. $h > 0$, the effective linear conductivity σ_e increases with increasing Δ, and such a tendency is clearly observed, especially for larger h (see figure 2(b)). In contrast, when $h < 1$ (i.e. the second component is a good conductor), increasing Δ yields decreasing σ_e, and the smaller h is, the more distinct the effect becomes. For larger volume fraction $p > 0.7$, the prevailing component is component 2, whose shape is spherical and is independent of Δ. Thus the change in Δ does not affect σ_e significantly, as predicted. From figure 2, we conclude

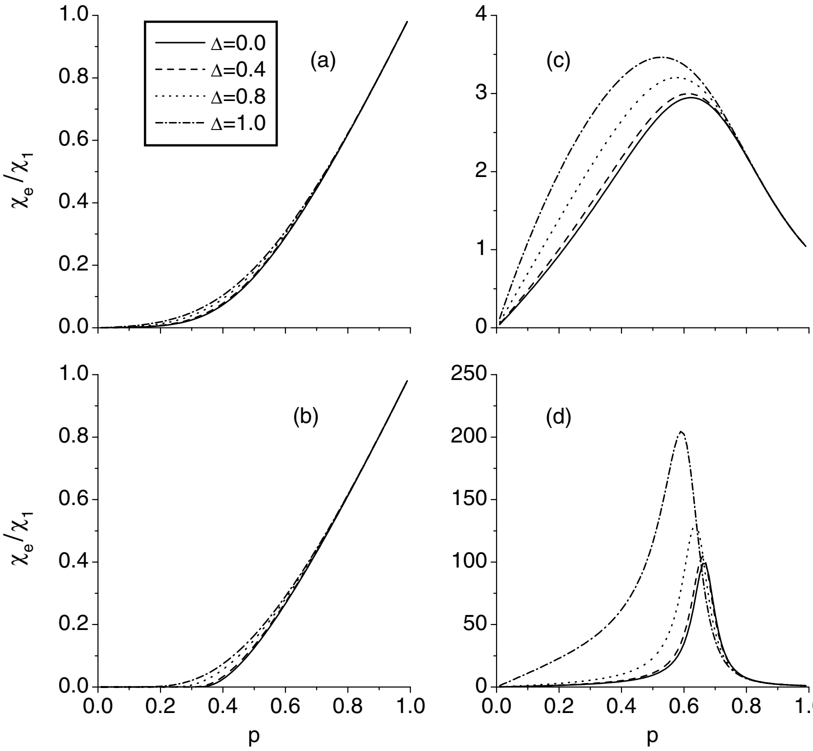

Figure 3. The effective nonlinear response χ_e/χ_1 of the composites in which $\chi_2 = 0$ as a function of p. Other parameters are the same as in figure 2.

that the effective linear conductivity σ_e predicted by our SDEMA is, in most cases, slightly different from the original EMA [5].

Then, we speculate on how the shape variance parameter Δ affects the effective nonlinear response.

Figure 3 show the results for effective nonlinear response χ_e/χ_1 of the composite media in which only component 1 is assumed to be nonlinear (i.e. $\chi_2 = 0$).

When the conductivity ratio h is larger than 1, χ_e increases monotonically with increasing p for all given Δ, which is similar to that reported in [15, 27]. For larger h, say $h = 500$ (see figure 3(b)), it was suggested that the rapid increase of χ_e/χ_1 around $0.2 < p < 0.4$ reflects the percolation threshold above which component 1 forms an infinite cluster throughout the whole composite [15, 28]. We also find that, for $h > 1$, increasing Δ always leads to increasing χ_e, in accord with that observed for σ_e. This is a new result. In this situation, however, the effective nonlinear response is still less than that of the component, which limits possible applications.

The enhancement of χ_e can be found in the composite in which nonlinear component 1 has the poor conductivity $\sigma_1 < \sigma_2$ (see figures 3(c) and (d)). In this case, χ_e/χ_1 can be enhanced and exhibits a peak. Such phenomena have been previously observed in numerical calculations on a two-dimensional random resistor network [15, 27, 28] and in analytical scaling calculations [27]. The peak, arising near the percolation threshold of component 2, demonstrates the fact that χ_e diverges as q_c is approached in S/C random mixtures. Interestingly, as Δ increases, the effective nonlinearity increases monotonically for $h = 0.1$; while for $h = 0.002$, χ_e can take on quite different behaviours, dependent on the volume fractions. Thus, the adjustment of the shape variance Δ in this case is useful to achieve a

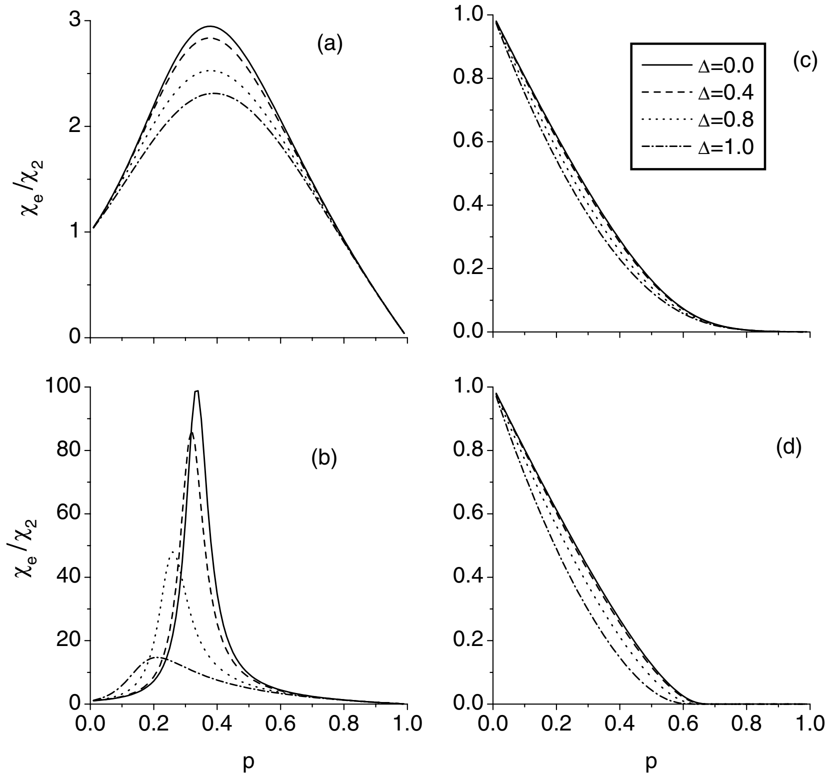

Figure 4. χ_e/χ_2 as a function of p. Other parameters are the same as in figure 2.

large effective nonlinear response near the percolation threshold. Such an enhancement is analysed to be a geometrical effect. Near q_c, there exist some disconnected regions composed of conductors with good linear conductivity σ_2, separated by regions of nonlinear conductors with poor linear conductivity σ_1. For this restricted geometry, the current must pass through the nonlinear conductors with poor linear conductivity, leading to the enhancement in the effective nonlinear response [15]. Meanwhile, as the regions of the nonlinear conductors are related to the shape variance parameter, the effective nonlinear response depends on Δ accordingly.

Next, we investigate χ_e in the composite media in which the spherical component 2 is weakly nonlinear and the component 1 is linear. The results are shown in figure 4. Generally (see figures 4(a), (c) and (d)), increasing Δ leads to a decrease of χ_e, which should be in contrast to that observed in figure 3. More interesting results are those in figure 4(b), in which a large enhancement of χ_e is again found [15, 28], and with increasing Δ, the enhancement peak decreases accompanied by the shift to small volume fractions due to the dependence of p_c on Δ.

In order to show the influence of Δ on χ_e clearly, we plot χ_e/χ_1 or χ_e/χ_2 as a function of Δ in figure 5. As can be seen from figure 5, for large conductivity contrast (σ_1/σ_2 or σ_2/σ_1), the effective nonlinear response may exhibit monotonic increase, monotonic decrease and even nonmonotonical behaviour, depending on the volume fractions. Moreover, for small Δ, χ_e is generally slightly dependent on Δ, which indicates that a slight deviation of particle shape from spherical does not affect χ_e significantly and the original EMA can be used as a first step to estimate the effective response of the random mixtures with shape distribution. However,

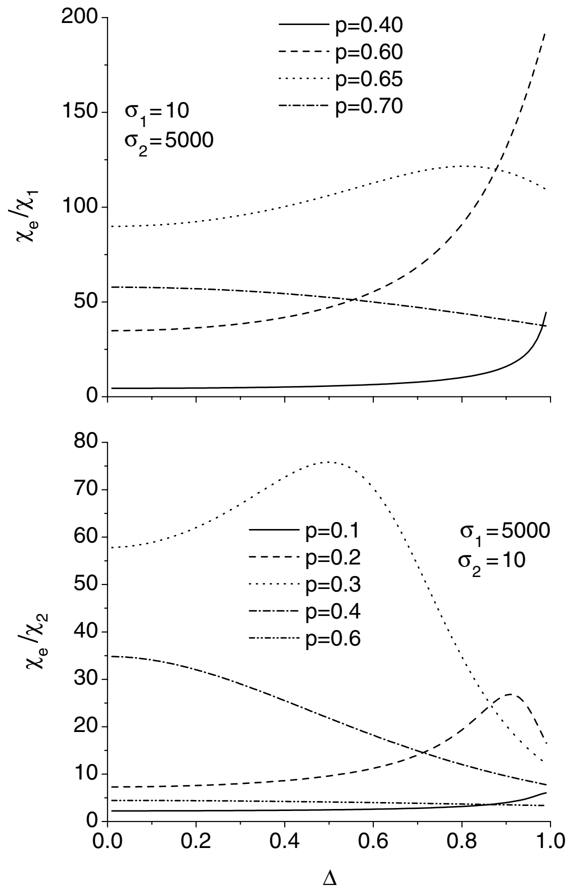

Figure 5. The effective nonlinear response as a function of Δ for various p.

for larger Δ, the effective nonlinear response is heavily dependent on Δ, the use of the original EMA will become rough and the shape distribution must be taken into account by means of our SDEMA.

5. Exact results in the dilute limit

In this section, we discuss the effective nonlinear response of a dilute suspension of nonlinear randomly oriented ellipsoidal particles with shape distribution embedded in a linear medium. In the dilute limit, the average of the mean fourth power of the linear local field within the ellipsoidal particles of component 1 can first be calculated according to the rule

$$\langle f(\theta,\phi)\rangle = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} f(\theta,\phi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi, \tag{24}$$

and is found to be

$$\frac{\langle \boldsymbol{E}^4\rangle_1}{\boldsymbol{E}_0^4} = \frac{1}{15}[3\beta_x^4 + 3\beta_y^4 + 3\beta_z^4 + 2\beta_x^2\beta_y^2 + 2\beta_y^2\beta_z^2 + 2\beta_z^2\beta_x^2], \tag{25}$$

where $\beta_j = \sigma_2/[L_j\sigma_1 + (1 - L_j)\sigma_2]$ $(j = x, y, z)$.

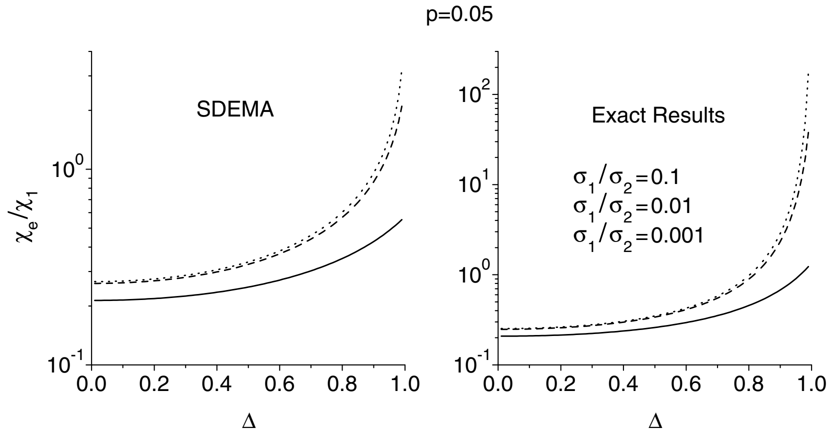

Figure 6. χ_e/χ_1 via Δ in the dilute limit $p = 0.05$. (a) Results from SDEMA and (b) exact results from equation (26).

If we choose χ_2 to be zero, from symmetry considerations, the effective nonlinear response of the composites with a shape variance distribution can be expressed as

$$\chi_e = p\chi_1 \int\int P(L_x, L_y)\frac{\langle \boldsymbol{E}^4\rangle_1}{\boldsymbol{E}_0^4}\,\mathrm{d}L_x\,\mathrm{d}L_y$$

$$= \frac{2}{5\Delta^2}p\chi_1 \int_{\frac{1}{3}(1-\Delta)}^{\frac{1}{3}(1+2\Delta)}\int_{\frac{1}{3}(1-\Delta)}^{\frac{1}{3}(2+\Delta)-L_x}(3\beta_x^2+\beta_y^2+\beta_z^2)\beta_x^2\,\mathrm{d}L_x\,\mathrm{d}L_y. \qquad (26)$$

Equation (26) does not require the decoupling treatment and thus represents an exact formula to calculate the effective nonlinear response χ_e.

In figure 6, we plot χ_e/χ_1 as a function of Δ in the dilute volume fraction $p = 0.05$. The predictions of the shape variance dependence of the effective nonlinear response given by an exact expression equation (26) are quite similar to those by our SDEMA, i.e. both of them yield the monotonic increase with Δ. However, by using the exact expression, we obtain a larger magnitude of the effective nonlinear response than those obtained from SDEMA. The reason is that the decoupling approximation $\langle \boldsymbol{E}^4\rangle_i \approx \langle \boldsymbol{E}^2\rangle_i^2$ has been adopted in SDEMA, which gives the rigorous lower bounds of the exact results.

6. Conclusions and discussions

In this paper, based on the self-consistent condition of zero net polarization and mean field approximation, we have formulated SDEMA to study the effective linear and nonlinear responses of two-component nonlinear composites with shape distribution. We have obtained the knowledge that, in C/I and S/C limits, the percolation thresholds p_c and q_c are significantly dependent on the shape variance parameter, while the critical exponents, which describe the vanishing (or divergence) of σ_e and χ_e near p_c (or q_c), are unchanged with increasing Δ. The dependence of the percolation thresholds on Δ suggests that the percolating system can be formed by adjusting the shape distribution of the components. Furthermore, we show that, for the finite-conductivity ratio $h = \sigma_1/\sigma_2$, the effective nonlinear response can be enlarged throughout the adjustment of Δ, and thus provides an alternative freedom to achieve large enhancement of the effective nonlinear response.

Here we add a few comments. In order to check the validity of our SDEMA, we can take a further step to extract the scaling forms of the effective nonlinear response in the vicinity of the percolation threshold and small h, and to compare it with a general scaling theory [27, 29]. Our method is applied to nonlinear transport properties of conducting composites of zero frequency. For dielectric composites with relaxation, the dielectric loss becomes important. With the spectral representation theory [30], we can derive the spectral density function to investigate the effective nonlinear optical properties. In this connection, both the collective phenomena and percolation effects will take place. For strongly nonlinear composites with shape distribution, it would also be of great interest to investigate the critical behaviour and scaling forms of the effective strongly nonlinear coefficient. More recently, we note an experimental work [31], in which the effect of particle shape distribution on the surface plasmon resonance of Ag/SiO_2 nanocomposite thin films was reported. By using the theoretical formula for the effective linear dielectric constant in our previous work [32], in which the Maxwell-Garnett approximation and EMA with shape distribution were derived, they accounted quite faithfully for inhomogeneous broadening of the plasmon band of the nanocomposite films. The effect of shape distribution on the effective nonlinear response shown here should be compared to systematic experiments on the nonlinear composites, and we hope our analysis may help to stimulate an experimental investigation of the composite media with shape variance distribution.

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