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1996 J. Phys.: Condens. Matter 8 11327

(http://iopscience.iop.org/0953-8984/8/50/053)

J. Phys.: Condens. Matter **8** (1996) 11327–11336. Printed in the UK

The microstructure and effective dielectric response of nonlinear composites: decoupling technique and variational method

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Received 25 March 1996, in final form 21 May 1996

Abstract. The decoupling technique has been applied to nonlinear composites of coated spherical inclusions. The method allows us to convert established results in linear composites to nonlinear ones with identical microstructure. Results are compared with those of the variational method and hence the quality of the approximation can be examined. For coated spheres with nonlinear shell embedded in a linear host, the results show that a relatively thin nonlinear coating may approach the enhancement effects of a solid nonlinear sphere of the same radius under appropriate conditions.

1. Introduction

Recently, the physics of nonlinear composites has attracted much attention because of their applications in engineering and physics [1, 2]. Over the past few years, much effort has been devoted to the calculations of the effective response of composites in which two or more isotropic dielectric materials are randomly mixed together. In these composites the constituent dielectric functions depend on the applied electric field. The effective response depends on the applied field as well as on the volume fractions of the constituents and microstructure. In the case of a three-component composite, large effective nonlinear response may be obtained for some microstructures in which the nonlinear component is placed consistently in the high-field regions of the composite.

Nonlinear composites made of coated spherical inclusions embedded in a host medium have been extensively studied [3–5] because the nonlinearity can be enhanced. For a coated spherical inclusion with a nonlinear shell, it was shown that a large enhancement can be achieved per unit volume of nonlinear material [6–8]. These interesting and useful cases are generally intractable analytically because one has to solve nonlinear boundary-value problems which involve the detailed microstructure of the composite [1].

The object of the present investigation is threefold. First, previous studies were restricted primarily to weakly nonlinear composites, in which the nonlinearity can be treated as a small perturbation [6, 7]. In this work, we want to extend the study to strongly nonlinear composites [9, 10] of coated spheres. In this case, the usual perturbative approach becomes invalid [7]. Alternative approaches were developed based on the variational method [10] and on the decoupling technique [11]. Second, these approaches are generally approximate [10, 11]. While both approaches are able to convert established results on linear composites to nonlinear ones with identical microstructure and provide reasonable estimates of the

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effective nonlinear response, we want to compare their results with each other and hence examine the quality of the approximations. Third, we want to extend the study to coated spheres with nonlinear shell embedded in a linear host and provide further evidence for the enhancement of nonlinearity.

The paper is organized as follows. In the next section, we review the established linear response of spherical inclusions and concentric spheres. Given these results, we shall generate approximate expressions for the effective response of strongly nonlinear composites via the decoupling technique. In section 3, we evaluate the strongly nonlinear response of spherical inclusions by the decoupling technique and compare the results with published variational calculations. In section 4, we perform similar calculations for the strongly nonlinear response of concentric spheres. In section 5, we consider some exactly solvable cases of strongly nonlinear spherical inclusions and concentric spheres with a nonlinear core embedded in a linear host. In these cases, we demonstrate that the decoupling technique indeed gives exact results. Lastly, in section 6, we consider concentric spheres with nonlinear shell embedded in a linear host. Since no available result exists for this case, we shall perform both the variational and decoupling calculations. Discussions on related problems will be given.

2. Linear response of spherical inclusions and concentric spheres

In this section, we consider the linear characteristic

$$\boldsymbol{D} = \epsilon \boldsymbol{E} \tag{1}$$

where the dielectric constant ϵ takes on different values in the inclusion and host regions. Let us consider a microstructure consisting of identical coated spheres with a spherical core of radius a_1 and dielectric constant ϵ_c, surrounded by a concentric spherical shell of radius $a_2 > a_1$ and dielectric constant ϵ_s, suspended in a host medium of ϵ_m, with the application of an external uniform field E_0. Without loss of generality, we let $a_2 = 1$ and $a_1 = y^{1/3} < 1$. The potential can be solved by standard electrostatics:

$$\varphi_c(r,\theta) = -cE_0 r\cos\theta \qquad r < a_1 \tag{2}$$

$$\varphi_s(r,\theta) = -E_0(fr - gyr^{-2})\cos\theta \qquad a_1 < r < a_2 \tag{3}$$

$$\varphi_m(r,\theta) = -E_0(r - br^{-2})\cos\theta \qquad r > a_2 \tag{4}$$

where the coefficients b, c, f and g are obtained from the boundary conditions:

$$b = \frac{(\epsilon_s - \epsilon_m) + (\epsilon_m + 2\epsilon_s)xy}{(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy} \tag{5}$$

$$c = \frac{3\epsilon_m(1-x)}{(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy} \tag{6}$$

$$f = \frac{3\epsilon_m}{(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy} \tag{7}$$

$$g = \frac{3\epsilon_m x}{(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy} \tag{8}$$

and

$$x = \frac{\epsilon_c - \epsilon_s}{\epsilon_c + 2\epsilon_s}. \tag{9}$$

In the dilute limit, the volume V_i of inclusion is much smaller than the volume V of the whole composite. Let $p = V_i/V$ be the volume fraction of inclusion, we obtain the effective linear response of a small volume fraction of coated spheres embedded in a host medium [7]:

$$\epsilon_e = \epsilon_m + p\frac{3\epsilon_m[(\epsilon_s - \epsilon_m) + (\epsilon_m + 2\epsilon_s)xy]}{(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy}. \tag{10}$$

In the limit of identical core and shell materials, i.e. $\epsilon_c = \epsilon_s = \epsilon_i$, or $x = 0$, we recover the well known results for a spherical inclusion of radius a and dielectric constant ϵ_i embedded in a host medium of ϵ_m:

$$\varphi_i(r, \theta) = -cE_0 r\cos\theta \qquad r < a \tag{11}$$

$$\varphi_m(r, \theta) = -E_0(r - br^{-2})\cos\theta \qquad r > a \tag{12}$$

where the coefficients b and c are

$$b = \frac{\epsilon_i - \epsilon_m}{\epsilon_i + 2\epsilon_m} \tag{13}$$

$$c = \frac{3\epsilon_m}{\epsilon_i + 2\epsilon_m}. \tag{14}$$

The effective linear response is given by

$$\epsilon_e = \epsilon_m + p\frac{3\epsilon_m(\epsilon_i - \epsilon_m)}{\epsilon_i + 2\epsilon_m}. \tag{15}$$

The same result can be obtained by letting $\epsilon_s = \epsilon_i$ and $y = 0$ (vanishing core) or $\epsilon_c = \epsilon_i$ and $y = 1$ (vanishing shell). Given the linear results, we shall generate approximate expressions for the effective nonlinear response of strongly nonlinear composites via the variational method [10] and the decoupling technique [11] in subsequent studies.

3. Strongly nonlinear response of spherical inclusions

In this section, we consider the strongly nonlinear characteristic

$$\boldsymbol{D} = \chi|\boldsymbol{E}|^2\boldsymbol{E} \tag{16}$$

where the nonlinear coefficient χ takes on different values in the inclusion and host regions. Although we discuss cubic nonlinearity [9–11] for illustration, generalization can readily be made to arbitrary nonlinearity. Let us consider a spherical inclusion of nonlinear coefficient χ_i, embedded in a host medium of χ_m, with the application of an external uniform field E_0. In the variational approach [10], we used equations (11) and (12) as trial potential functions and treated the as-yet undetermined coefficient b ($c = 1 - b$) as a variational parameter. We then minimized the energy functional:

$$W[\varphi] = \int_V \boldsymbol{D}\cdot\boldsymbol{E}\,\mathrm{d}V \tag{17}$$

with respect to b and obtained approximate results for the effective nonlinear response χ_e. In this work, we shall use the decoupling technique [11] by converting equation (15) to strongly nonlinear response through self-consistent equations. As shown in [10] and [11], the variational method gives the rigorous upper bound while the decoupling technique gives the rigorous lower bound for the effective nonlinear response, namely,

$$\chi_e(\text{decoupling}) \leqslant \chi_e(\text{exact}) \leqslant \chi_e(\text{variational}). \tag{18}$$

It is clear that the two methods are indispensable for estimating the effective nonlinear response of intractable boundary-value problems, such as those of strongly nonlinear composites. If the two bounds coincide, they both give the exact result. On the other hand, if the two bounds are tight, the estimates are indeed good approximations.

To proceed, we compute the mean-square local fields in the inclusion and host regions [11]:

$$\langle E_i^2 \rangle = \frac{1}{p}\frac{\partial \epsilon_e}{\partial \epsilon_i} E_0^2 = \left(\frac{3\epsilon_m}{\epsilon_i + 2\epsilon_m} \right)^2 E_0^2 \tag{19}$$

$$\langle E_m^2 \rangle = \frac{1}{1-p}\frac{\partial \epsilon_e}{\partial \epsilon_m} E_0^2 = \left(1 + \frac{2p(\epsilon_i - \epsilon_m)(2\epsilon_i + \epsilon_m)}{(1-p)(\epsilon_i + 2\epsilon_m)^2} \right) E_0^2. \tag{20}$$

The local field in the host region is of order E_0 as it must be. We make the following substitutions:

$$\epsilon_i = \chi_i \langle E_i^2 \rangle \tag{21}$$

$$\epsilon_m = \chi_m \langle E_m^2 \rangle \tag{22}$$

and solve equations (19) and (20) self- consistently for the mean-square local fields. The effective nonlinear response can be calculated from equation (15). In figure 1, we plot the effective strongly nonlinear response χ_e/χ_m against χ_i/χ_m at a volume fraction $p = 0.08$. The parameters are chosen so as to compare with published variational calculations [10]. Results are presented for the variational method (dotted line) and the decoupling technique (solid line). The two approximations agree reasonably well especially at low contrast.

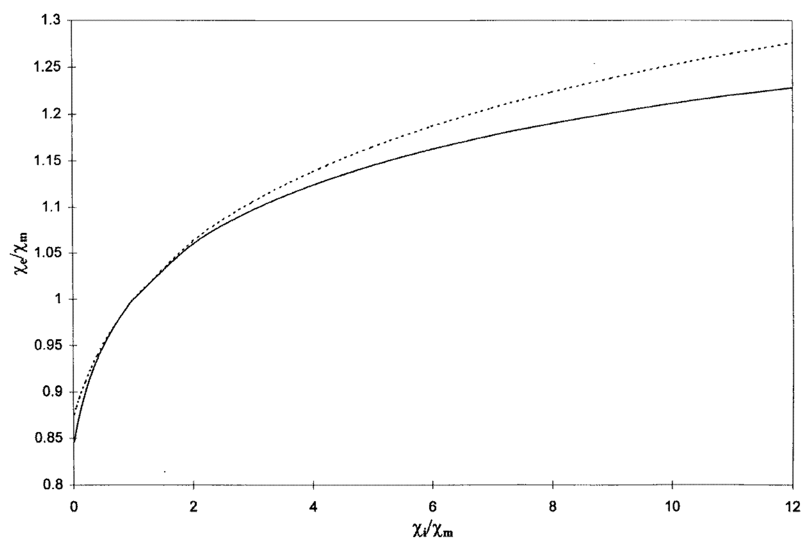

Figure 1. For spherical inclusions, the effective strongly nonlinear response χ_e/χ_m is plotted against χ_i/χ_m at a volume fraction $p = 0.08$. Results are presented for the variational method (dotted line) and the decoupling technique (solid line). The two approximations agree reasonably well especially at low contrast.

4. Strongly nonlinear response of concentric spheres

In this section, we consider coated spheres with nonlinear coefficients χ_c, χ_s and χ_m and calculate the effective strongly nonlinear response. In the variational approach [10], we used equations (2)–(4) as trial potential functions and treated the as-yet undetermined coefficients f and g ($b = 1 - f + gy$ while $c = f - g$) as variational parameters. We minimized the energy functional $W[\varphi]$ and obtained the effective nonlinear response. In this work, we use the decoupling technique [11] and compute the mean-square local fields in the core, shell and host regions [11]. Note that volume fraction of core = py while volume fraction of shell = $p(1 - y)$:

$$\langle E_c^2 \rangle = \frac{1}{py}\frac{\partial \epsilon_e}{\partial \epsilon_c} E_0^2 = \left(\frac{3\epsilon_m(1-x)}{(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy} \right)^2 E_0^2 \tag{23}$$

$$\langle E_s^2 \rangle = \frac{1}{p(1-y)}\frac{\partial \epsilon_e}{\partial \epsilon_s} E_0^2 = \frac{9\epsilon_m^2(1+2x^2y)}{[(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy]^2} E_0^2 \tag{24}$$

$$\begin{aligned} \langle E_m^2 \rangle &= \frac{1}{1-p}\frac{\partial \epsilon_e}{\partial \epsilon_m} E_0^2 = [1 + O(p)]E_0^2 \\ &= E_0^2 + \frac{2pE_0^2}{(1-p)[(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy]^2}[(\epsilon_s - \epsilon_m)(\epsilon_m + 2\epsilon_s) \\ &\quad + (8\epsilon_s^2 - \epsilon_s\epsilon_m + 2\epsilon_m^2)xy + (2\epsilon_s + \epsilon_m)(4\epsilon_s - \epsilon_m)x^2y^2]. \end{aligned} \tag{25}$$

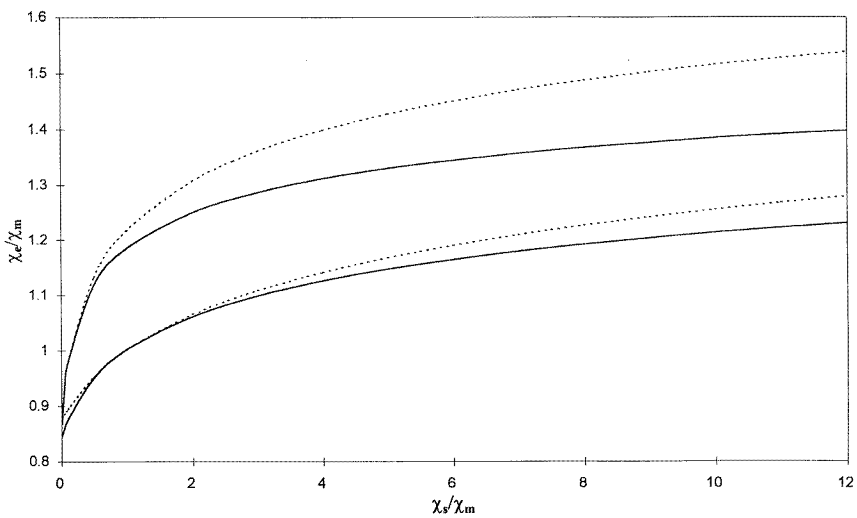

Figure 2. For coated spheres, the effective strongly nonlinear response χ_e/χ_m is plotted against χ_s/χ_m for $\chi_c/\chi_s = 8$ at a volume fraction $p = 0.08$. Results are displayed into two separate groups: $y = (0.99)^3$ (upper curves) and $y = (0.2)^3$ (lower curves). In each group, results are presented for the variational method (dotted lines) and the decoupling technique (solid lines).

Again the local field in the host region is of order E_0. We further make the following substitutions:

$$\epsilon_c = \chi_c \langle E_c^2 \rangle \tag{26}$$

$$\epsilon_s = \chi_s \langle E_s^2 \rangle \tag{27}$$

$$\epsilon_m = \chi_m \langle E_m^2 \rangle \tag{28}$$

and solve equations (23)–(25) self-consistently for the local fields. The effective nonlinear response can be calculated from equation (10). In figure 2, we plot the effective strongly nonlinear response χ_e/χ_m against χ_s/χ_m for $\chi_c/\chi_s = 8$ at a volume fraction $p = 0.08$. The results are displayed in two separate groups: $y = (0.99)^3$ (upper curves) and $y = (0.2)^3$ (lower curves). The parameters are chosen so as to compare with published variational calculations [10]. As evident from figure 2, the two approximations agree reasonably well especially at low contrast. In figure 3, for $\chi_c/\chi_s = 1/8$, the results are displayed into two separate groups: $y = (0.2)^3$ (upper curves) and $y = (0.99)^3$ (lower curves). Again the two approximations agree reasonably well.

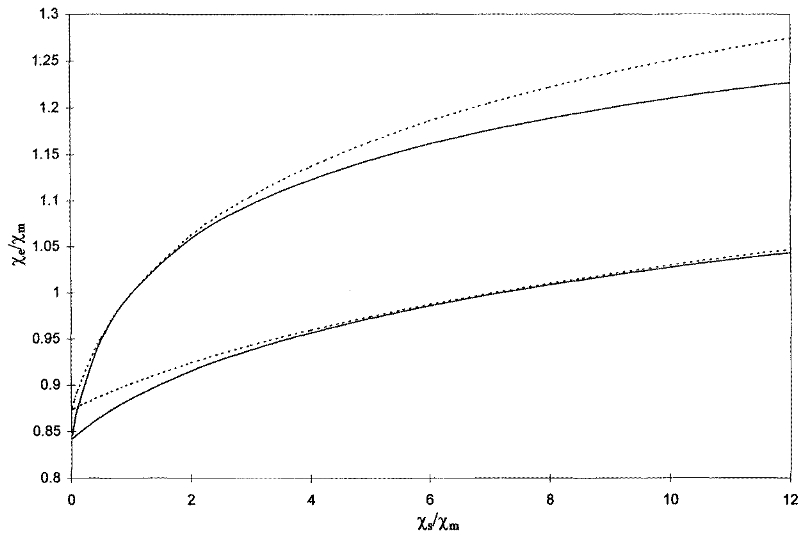

Figure 3. Similar to figure 2 but for $\chi_c/\chi_s = 1/8$. Results are displayed into two separate groups: $y = (0.2)^3$ (upper curves) and $y = (0.99)^3$ (lower curves). In each group, results are presented for the variational method (dotted lines) and the decoupling technique (solid lines).

5. Some exactly solvable cases

In this section, we consider some exactly solvable microstructures [12]. First we consider strongly nonlinear spheres embedded in a linear host with a uniform applied field E_0. Since the host medium is linear, the effective nonlinear response is weakly nonlinear [13, 14]. In this case, we let $\epsilon_i = \chi_i\langle E_i^2\rangle$, where $\langle E_i^2\rangle$ will be solved from the following self-consistent equation [11]:

$$\langle E_i^2\rangle = \frac{1}{p}\frac{\partial\epsilon_e}{\partial\epsilon_i}E_0^2 = \left(\frac{3\epsilon_m}{\chi_i\langle E_i^2\rangle + 2\epsilon_m}\right)^2 E_0^2. \tag{29}$$

As the local field E_i is uniform in the inclusion, the decoupling scheme [11] is indeed exact. As a result, equation (29) gives the exact local field $\langle E_i^2\rangle$. Solving $\langle E_i^2\rangle$ numerically and putting $\epsilon_i = \chi_i\langle E_i^2\rangle$ into equation (15), we obtain the field-dependent effective response $\epsilon_e(E_0)$. In figure 4, we plot $\epsilon_e(E_0)$ against E_0 for $\chi_i = 1$, $\epsilon_m = 3$ at volume fraction $p = 0.08$. It is observed that $\epsilon_e(E_0)$ increases monotonically with E_0 and saturates at both low fields ($E_0 \leqslant 0.1$) and high fields ($E_0 \geqslant 200$). The limiting values of ϵ_e agree with those calculated directly from equation (15); we find $\epsilon_e(E_0 \to 0) = 2.64$ and $\epsilon_e(E_0 \to \infty) = 3.72$ respectively. The effective nonlinear response is strongly field

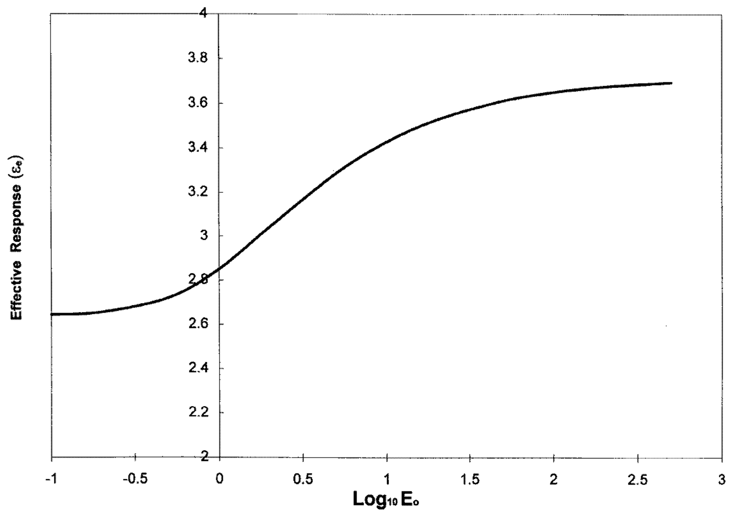

Figure 4. For strongly nonlinear spheres embedded in a linear host, the field-dependent effective response $\epsilon_e(E_0)$ is plotted against E_0 for $\chi_i = 1$, $\epsilon_m = 3$ at volume fraction $p = 0.08$.

dependent. It is also interesting to note that when $E_0 = \sqrt{3}$, $\chi_i E_0^2 = \epsilon_m$, the contrast between inclusion and host vanishes identically and hence $\epsilon_e = \epsilon_m$.

For coated spherical inclusions with nonlinear core, we let $\epsilon_c = \chi_c \langle E_c^2 \rangle$, where $\langle E_c^2 \rangle$ can be solved from the following self-consistent equation [11]:

$$\langle E_c^2 \rangle = \frac{1}{py} \frac{\partial \epsilon_e}{\partial \epsilon_c} E_0^2 = \left(\frac{3\epsilon_m(1-x)}{(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy} \right)^2 E_0^2. \tag{30}$$

Again, as the core field E_c is uniform, the decoupling scheme is exact. Moreover, it can be shown that the problem of a multi-coated sphere with nonlinear core can be solved exactly [15]. Solving $\langle E_c^2 \rangle$ numerically and putting $\epsilon_c = \chi_c \langle E_c^2 \rangle$ into equation (10), we obtain the field-dependent effective response $\epsilon_e(E_0)$. In figure 5, we plot $\epsilon_e(E_0)$ against the thickness parameter y for $\chi_c = 1$, $\epsilon_s = 2$, $\epsilon_m = 3$ at volume fraction $p = 0.08$. Results are presented for $E_0 = 0.1$ and $E_0 = 200$. The results for nonlinear spherical inclusions are plotted for comparison. As y increases, i.e. from small to large core, ϵ_e changes monotonically from the linear result towards the results of nonlinear spheres in both low and high fields.

6. Concentric spheres with nonlinear shell embedded in linear host

In this section, we consider coated spheres with a linear core and a strongly nonlinear shell, embedded in a linear host with a uniform applied field E_0. In this case, the variational approach has to be modified slightly to take care of mixed characteristics [16]:

$$\delta W[\varphi] = \int_V \boldsymbol{D} \cdot \delta \boldsymbol{E} \, \mathrm{d}V = 0. \tag{31}$$

The energy functional is of the form [16]

$$W[\varphi] = \frac{1}{2} \int_V \epsilon |\boldsymbol{E}|^2 \, \mathrm{d}V + \frac{1}{4} \int_V \chi |\boldsymbol{E}|^4 \, \mathrm{d}V \tag{32}$$

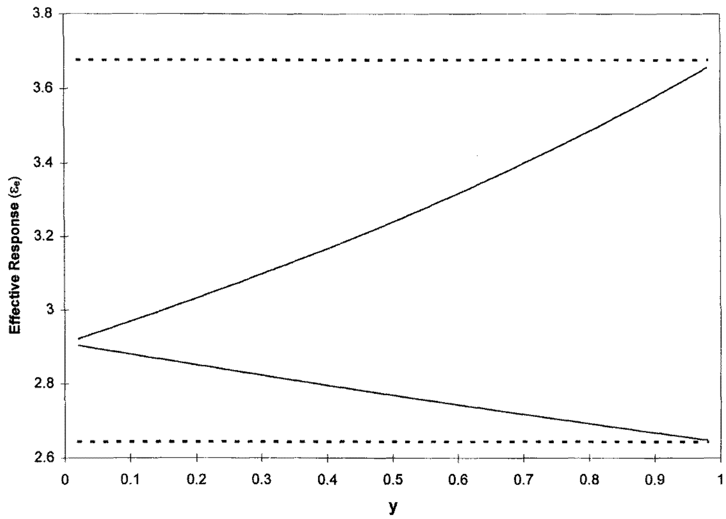

Figure 5. For coated spheres with strongly nonlinear core, the field-dependent effective response $\epsilon_e(E_0)$ is plotted against the thickness parameter y for $\epsilon_m = 3$ at volume fraction $p = 0.08$. Results are displayed into two separate groups: $E_0 = 200$ (upper curves) and $E_0 = 0.1$ (lower curves). The exact results for nonlinear spheres (dashed lines) are plotted for comparison.

and the variational parameters f and g will become field dependent. The field-dependent effective response can be calculated from $\epsilon_e(E_0) = \epsilon_e + \chi_e E_0^2$. In figure 6, we plot $\epsilon_e(E_0)$ against the thickness parameter y for $\chi_s = 1$, $\epsilon_c = 2$, $\epsilon_m = 3$ at volume fraction $p = 0.08$. Results are presented for $E_0 = 0.1$ and $E_0 = 200$. For $E_0 = 200$, as y increases, i.e. from thick to thin shell, $\epsilon_e(E_0)$ decreases only slightly from the exact nonlinear sphere result ($y \to 0$). When $y \to 1$ and the shell becomes thin, $\epsilon_e(E_0)$ decreases drastically towards the linear result. The results indicate that a relatively thin nonlinear shell may approach the effects of a solid nonlinear sphere of the same radius, consistent with the fact that a large enhancement can be achieved per unit volume of nonlinear coating material [6–8]. A similar conclusion is obtained for lower fields, but at a somewhat thicker coating. For $E_0 = 0.1$, as y increases, i.e. from thick to thin shell, $\epsilon_e(E_0)$ increases only slightly from the nonlinear sphere result ($y \to 0$). When $y \to 1$ and the shell becomes thin, $\epsilon_e(E_0)$ increases less rapidly towards the linear result.

We are now in a position to convert the effective linear response (equation (10)) to the field-dependent effective response of a nonlinear shell via the decoupling technique [11]. Let $\epsilon_s = \chi_s \langle E_s^2 \rangle$, where $\langle E_s^2 \rangle$ can be solved from the following self-consistent equation [11]:

$$\langle E_s^2 \rangle = \frac{1}{p(1-y)} \frac{\partial \epsilon_e}{\partial \epsilon_s} E_0^2 = \frac{9\epsilon_m^2 (1 + 2x^2 y)}{[(\epsilon_s + 2\epsilon_m) + 2(\epsilon_s - \epsilon_m)xy]^2} E_0^2. \tag{33}$$

In figure 6, we also plot the result of $\epsilon_e(E_0)$ from the decoupling technique for comparison. As evident from figure 6, the two approximations agree quite well.

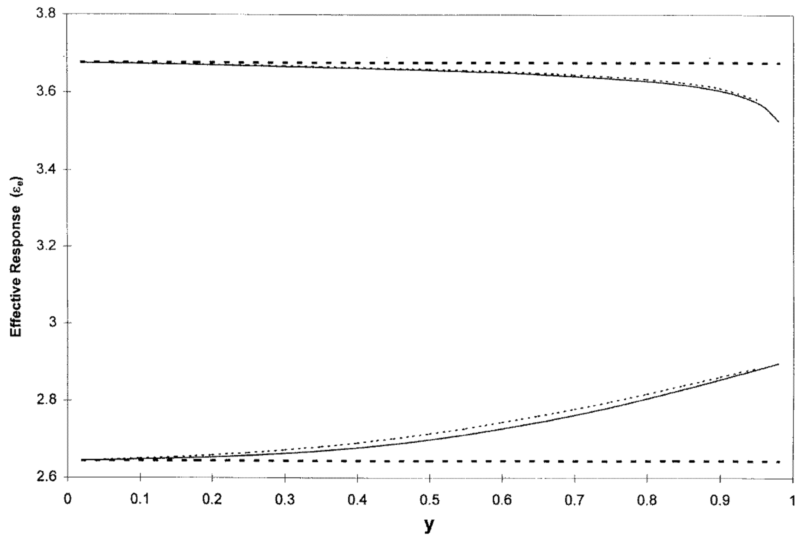

Figure 6. For coated spheres with strongly nonlinear shell, the field-dependent effective response $\epsilon_e(E_0)$ is plotted against the thickness parameter y for $\epsilon_m = 3$ at volume fraction $p = 0.08$. Results are displayed into two separate groups: $E_0 = 200$ (upper curves) and $E_0 = 0.1$ (lower curves). In each group, results are presented for the variational method (dotted lines) and the decoupling technique (solid lines) and the exact results for nonlinear spheres (dashed lines) are plotted for comparison.

7. Discussions and conclusions

Although the present investigation deals with static $\boldsymbol{D}$–$\boldsymbol{E}$ response, with slight modifications the treatments can be readily generalized to finite frequencies. We expect even larger enhancement of nonlinearity to occur in composites of metallic particles coated with nonlinear dielectric materials, due to surface-plasmon resonance [3, 6]. If the nonlinear materials are consistently placed in regions of high field, the nonlinear effect should be enormously enhanced.

In conclusion, the decoupling technique has been applied to nonlinear composites of coated spherical inclusions. The method allows us to convert effective response in linear composites to nonlinear ones with identical microstructure. Results are compared with those of the variational method and good agreements between the two methods are found.

Acknowledgments

This work was supported by the research grants council of the Hong Kong government under project number CUHK 461/95P. We acknowledge correspondence with Professor G Q Gu.

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