Non-linear electromagnetic properties of fractal metal clusters

1995 J. Phys.: Condens. Matter 7 3355

(http://iopscience.iop.org/0953-8984/7/17/017)

J. Phys.: Condens. Matter 7 (1995) 3355–3361. Printed in the UK

Non-linear electromagnetic properties of fractal metal clusters

K W Yu

Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Received 28 November 1995, in final form 3 March 1995

Abstract. We demonstrate that fractal clusters of small metal particles suspended in a dielectric host have a much larger absorption coefficient in the far-infrared region. The previous linear result is verified and generalized to the non-linear results. As a quasi-analytical model for the non-linear response of fractal clusters, we derive the non-linear differential effective-medium approximation in an attempt to understand the enhanced non-linear response.

1. Introduction

Recently, the physics of *non-linear* composite media has attracted much attention [1–8]. A typical system is that of a composite material in which a material with non-linear displacement–field ($\boldsymbol{D}$–$\boldsymbol{E}$) response is *randomly* embedded in a host medium which can be either linear or non-linear:

$$\boldsymbol{D} = \epsilon \boldsymbol{E} + \chi |\boldsymbol{E}|^2 \boldsymbol{E}$$

where ϵ and χ represent respectively the linear dielectric function and non-linear susceptibility of the medium. We denote ϵ_m and χ_m as the coefficients in the host and ϵ_i and χ_i as those in the inclusion.

When small metal particles are suspended in a dielectric host, the composite is found to have a long-wavelength absorption coefficient proportional to the frequency, which agrees with classical electromagnetic theory in the quasistatic limit. However, the strength of the observed absorption exceeds the theoretical prediction by several orders of magnitude [9–12]. A variety of methods have been proposed for the enhanced linear response [13]. Among these, it is suggested that non-random clustering may be a major factor in the enhancement [11, 12]. In this work, we extend the consideration to the non-linear response functions of a fractal cluster embedded in a host medium [14, 15]. Moreover, as a quasi-analytical model for the non-linear response of fractal clusters, we derive the non-linear differential effective-medium approximation [16] in an attempt to understand the enhanced non-linear response. It is our aim here to verify the previous linear result [17] and generalize to the non-linear results.

2. Dilute suspension of metal particles in a dielectric host

Consider a composite in two dimensions (2D), containing a small volume fraction p_i of metal particles embedded in a dielectric host. The metallic component has a frequency-dependent but field-independent *complex* dielectric function described by the Drude model:

$$\epsilon_i(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} = \epsilon_i' + i\epsilon_i'', \tag{1}$$

where $\epsilon_i' < 0, \epsilon_i'' > 0$, and $\epsilon_i'' \gg |\epsilon_i'|$. The dielectric host is assumed to have a purely real, frequency-independent but *field-dependent* dielectric function:

$$\epsilon_m^{NL}(E) = \epsilon_m + \chi_m |E|^2 \tag{2}$$

where $\chi_m |E|^2 \ll \epsilon_m$ is obeyed for weak non-linearity. In what follows, we are interested in the small-ω behaviour in the far-infrared regime. Let $\gamma \approx 0.1\omega_p$, and $\omega \approx 0.001\omega_p$, we may expand the ϵ_i-function as

$$\epsilon_i = -(\gamma^{-2} - 1) - \frac{1}{i\omega\gamma} + \cdots$$

where we have assumed $\omega_p = 1$. For convenience, let us define a permittivity ratio $h = \epsilon_m/\epsilon_i$ and express it in a small-frequency expansion

$$h = -i\omega\gamma\epsilon_m - \epsilon_m(1 - \gamma^2)\omega^2 + \cdots. \tag{3}$$

Throughout this work, the ratio h is treated as a small parameter. The metallic inclusion is assumed to be in the form of circular cylinders [6]. In the dilute limit, the effective linear response function is well described by the Maxwell–Garnett formula, valid in two spatial dimensions:

$$\epsilon_e = \epsilon_m(1 + 2p_i b_0) \tag{4}$$

$$b_0 = (\epsilon_i - \epsilon_m)/(\epsilon_i + \epsilon_m) \tag{5}$$

is the dipolar factor relating the inclusion and the host medium. The small-h expansion of b_0 is given by

$$b_0 = 1 - 2h + 2h^2 + \cdots. \tag{6}$$

We thus obtain the far-infrared absorption which is proportional to the imaginary part of the linear response:

$$\mathrm{Im}(\epsilon_e^{MG}) = 4p_i|h|\epsilon_m = 4p_i\omega\gamma\epsilon_m^2. \tag{7}$$

The non-linear response is given by an analogous dilute-limit expression previously derived for random non-linear composites [6–8]:

$$\chi_e = \chi_m + p_i(g_i\chi_i + g_m\chi_m) \tag{8}$$

$$g_i = [2\epsilon_m/(\epsilon_i + \epsilon_m)]^4 \tag{9}$$

$$g_m = -1 + 4b_0 + 4b_0^2 + \frac{1}{3}b_0^4 \tag{10}$$

are local field factors in the inclusion and host regions. For linear metal inclusions, $\chi_i = 0$ and

$$g_m = \frac{22}{3} - \frac{80}{3}h + \cdots. \tag{11}$$

The effective non-linear susceptibility χ_e can also be obtained and the non-linear absorption is proportional to the imaginary part of the non-linear response:

$$\mathrm{Im}(\chi_e^{MG}) = \frac{80}{3}p_i|h|\chi_m = \frac{80}{3}p_i\omega\gamma\epsilon_m\chi_m. \tag{12}$$

3. The cluster response in the differential effective-medium approximation

In this section, we derive the differential effective-medium approximation (DEMA) [16] as a quasi-analytical model for the non-linear response of fractal clusters, generalizing a similar scheme developed previously for linear response. We shall restrict ourselves to two dimensions where analytic rather than merely numerical solutions can be obtained.

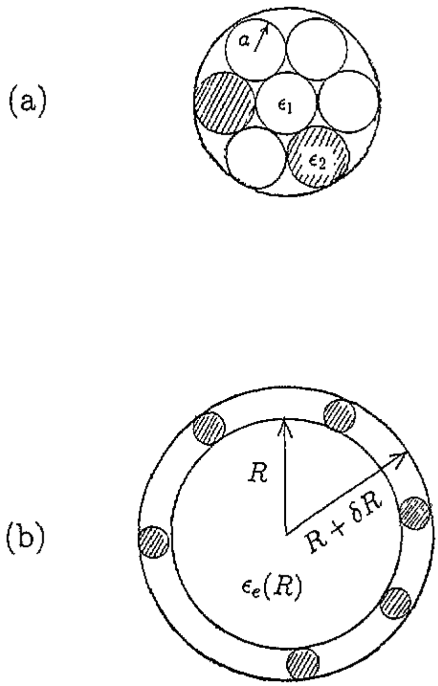

Figure 1. Formation of the effective-cluster response in the differential effective-medium approximation. (a) A pure type-1 (ϵ_1, χ_1) cylindrical inclusion has a radius a. The volume fraction of host medium (ϵ_2, χ_2) is increased by adding type-2 inclusions (shaded circles). (b) The effective-linear-cluster response at size R is $\epsilon_e(R)$. The size is increased to $R+\delta R$ while the change in the effective-linear-cluster response $\delta\epsilon_e$ can be determined. The change in the effective-non-linear-cluster response $\delta\chi_e$ can be determined in essentially the same way; see the text.

We shall use the results of random composites in the dilute limit (equations (4) and (8)) to obtain an approximate expression for the non-linear response of a cluster. In order to describe a fractal cluster of type 1 embedded in a host medium of type 2, we start with a pure type-1 cylinder of radius a as shown in figure 1(a), for which $p_1 = 1$ and $p_2 = 0$. The volume fraction of host medium is increased by adding type-2 material in the form of cylinders. As shown in figure 1(b), let the cluster at radius R have effective response $\epsilon_e(R)$ and $\chi_e(R)$. Now increase R by δR and the volume fraction by δp_2. Then from equations (4) and (8), we find

$$\delta\epsilon_e = \delta p_2\,[2\epsilon_e\tilde{b}] \tag{13}$$

$$\delta\chi_e = \delta p_2\,[g\chi_e + g_2\chi_2] \tag{14}$$

where $\tilde{b}$, g_2 and g have correspondingly similar forms as equations (5), (9) and (10) and are given by

$$\tilde{b} = (\epsilon_2 - \epsilon_e)/(\epsilon_2 + \epsilon_e) \tag{15}$$

$$g_2 = [2\epsilon_e/(\epsilon_2 + \epsilon_e)]^4 \tag{16}$$

$$g = -1 + 4\tilde{b} + 4\tilde{b}^2 + \frac{1}{3}\tilde{b}^4. \tag{17}$$

Equations (13) and (14) are ordinary differential equations for the effective linear and non-linear response of clusters as functions of p_2 in 2D. They can usually be solved numerically. However, analytic solutions can be obtained in 2D. For the linear response, we find

$$\frac{\epsilon_e}{\epsilon_1}\left(\frac{\epsilon_2-\epsilon_1}{\epsilon_2-\epsilon_e}\right)^2 = f^{-2} \tag{18}$$

where $f = 1 - p_2$ is the volume fraction of the cluster; f decreases from unity towards zero and ϵ_e varies from ϵ_1 to ϵ_2 as the cluster size increases. Accordingly, the dipolar factor $\tilde{b}$ varies from

$$\tilde{b}_0 = (\epsilon_2 - \epsilon_1)/(\epsilon_2 + \epsilon_1) \tag{19}$$

towards 0^- in the same limit. If $\epsilon_2 \ll \epsilon_1$, then $\tilde{b}_0 \approx -1$. The non-linear response is readily integrated from equation (14):

$$\chi_e = (-1+\tilde{b})^{11/3}\tilde{b}(1+\tilde{b})^{-1/3}\exp(\tilde{b}^2/6)\left[C + \chi_2\int_{\tilde{b}_0}^{\tilde{b}} \frac{\exp(-z^2/6)\,dz}{(-1+z)^{2/3}z^2(1+z)^{2/3}}\right]. \tag{20}$$

Equations (18) and (20) are the central results for the linear and non-linear response functions for clustering of a non-linear material in a host medium, which remain general within DEMA. We should remark that the present approach *does* not necessarily assume that the cluster is fractal. If, however, the cluster is indeed a fractal of fractal dimension d_f, then the volume fraction of non-linear fractal inclusion is related to the cluster size as

$$f \approx (R/a)^{-(2-d_f)} \tag{21}$$

and simple analytic results can be obtained. If the theory is applied to non-fractal clusters, then the calculations will not only be more complicated but they also provide no simple analytic result. The results are readily applied to a linear fractal embedded in a non-linear host. We invoke the initial condition $\chi_e = \chi_1 = 0$ at $R = a$; the constant of integration is determined to be $C = 0$. We find

$$\chi_e = \chi_2(-1+\tilde{b})^{11/3}\tilde{b}(1+\tilde{b})^{-1/3}e^{\tilde{b}^2/6}\int_{\tilde{b}_0}^{\tilde{b}} \frac{e^{-z^2/6}\,dz}{(-1+z)^{2/3}z^2(1+z)^{2/3}}. \tag{22}$$

For a large cluster size R, however, $\epsilon_e \to \epsilon_2$ and $\tilde{b} \to 0^-$ and we find $\chi_e \to \chi_2$ as it should. We are now in a position to obtain analytic expressions for the effective response of clustering metal particles in a dielectric host. We take $\epsilon_1 = \epsilon_i$, $\epsilon_2 = \epsilon_m$ and $h = \epsilon_m/\epsilon_i$. The quadratic equation (18) can be readily solved to give

$$\epsilon_e^{cl}(h, f) = \frac{\epsilon_i}{2}\left[f^2(1-h)^2 + 2h + f(1-h)\sqrt{f^2(1-h)^2 + 4h}\right]. \tag{23}$$

In the limit of simultaneously small h and f (i.e. large sizes), we find

$$\epsilon_e^{cl} = \epsilon_i h(1 + 2y + \sqrt{1+4y})/2y \tag{24}$$

where $y = hf^{-2}$. The result shows that $y = hf^{-2}$ is the relevant scaling variable. For convenience of subsequent studies, the dipolar factor b between the cluster and the dielectric host is defined:

$$b = (\epsilon_e^{cl} - \epsilon_m)/(\epsilon_e^{cl} + \epsilon_m) \tag{25}$$

which attains a limiting value b_0 at small sizes while it obeys the following scaling form in the limit of small h and f:

$$b = (1+4y)^{-1/2} \tag{26}$$

and $0 < b < 1$. In terms of b, the non-linear response is given by

$$\chi_e^{cl} = \chi_m (1+b)^{11/3} b (1-b)^{-1/3} e^{b^2/6} \int_b^{b_0} \frac{e^{-z^2/6}\,dz}{(1-z)^{2/3} z^2 (1+z)^{2/3}}. \qquad (27)$$

In the limit of small y, i.e. $hf^{-2} \ll 1, b \approx 1 - 2y, b_0 \approx 1 - 2h$, the non-linear response of a cluster is given by

$$\chi_e^{cl} = 24\chi_m (1 - f^{2/3})(1 - 5y + \cdots). \qquad (28)$$

One can see that there is a substantial enhancement in the non-linear response. In the following, we shall consider a dilute suspension of fractal clusters and calculate the composite response. The enhancement of the non-linear response is revealed by a comparison with that obtained from a random mixture of an *identical* fraction of metallic particles where the Maxwell–Garnett formula is valid.

4. The composite response for a dilute suspension of fractal clusters

Let us consider a dilute suspension of volume fraction p of circular clusters of radius R embedded in a dielectric host; the composite response is given by the dilute-limit expressions in section 2. For the linear response,

$$\epsilon_e = \epsilon_m (1 + 2pb) \qquad (29)$$

where b is the dipolar factor between the cluster and the host as given by equation (25). For small $y = hf^{-2}$, we find

$$\mathrm{Im}(\epsilon_e) = 4pf^{-2}|h|\epsilon_m. \qquad (30)$$

Comparing the result with the Maxwell–Garnett formula (equation (4)) with a volume fraction $p_i = pf$, $\mathrm{Im}(\epsilon_e^{MG}) = 4pf|h|\epsilon_m$, we find an enhancement factor

$$\frac{\mathrm{Im}(\epsilon_e)}{\mathrm{Im}(\epsilon_e^{MG})} = f^{-3} \approx (R/a)^{3(2-d_f)}. \qquad (31)$$

Note that equation (31) agrees with previous linear result [17]. For the non-linear response, the composite response can be calculated from equation (8). One can show that the contribution from the local field factor of the embedding clusters is of higher order in y, i.e. $g\chi_e^{cl} \approx 384\chi_m y^4 + \cdots$. Retaining the leading contribution, we find

$$\mathrm{Im}(\chi_e) = \frac{80}{3} pf^{-2}|h|\chi_m. \qquad (32)$$

We therefore obtain an enhancement factor for the non-linear response:

$$\frac{\mathrm{Im}(\chi_e)}{\mathrm{Im}(\chi_e^{MG})} = f^{-3} \approx (R/a)^{3(2-d_f)}. \qquad (33)$$

With slight modifications, the results are readily generalized to three dimensions. Note that the dipolar factor still obeys a scaling form $b = \Phi(y)$ in three dimensions, where $\Phi(y)$ is given by one of the solutions of the cubic equation:

$$(2 - 27y^2)b^3 - 3b^2 + 1 = 0$$

but the relevant scaling variable is changed to $y = hf^{-3/2}$. Following essentially the same arguments as in 2D, the enhancement factors in three dimensions are given by

$$\frac{\mathrm{Im}(\epsilon_e)}{\mathrm{Im}(\epsilon_e^{MG})} = f^{-5/2} \approx (R/a)^{5(3-d_f)/2} \qquad (34)$$

$$\frac{\mathrm{Im}(\chi_e)}{\mathrm{Im}(\chi_e^{MG})} = f^{-5/2} \approx (R/a)^{5(3-d_f)/2}. \qquad (35)$$

5. Discussion

Equations (33) and (35) are the central results of our present work. The DEMA results are expected to give a reasonable estimate of the enhancement factor. While the present investigation accounts only for the effect of clustering on the enhanced non-linear response, which we believe is the important one, other methods of enhancement are certainly viable [13]. Also, the results can naturally be generalized to the non-linear response of realistic fractals, generated in various aggregation processes [18–20]. The fractal geometry should have an observable effect on the non-linear as well as the linear properties [21]. The non-linear response may be analysed by the non-linear differential effective-medium approximation presented here. In realistic composites, typically there are clusters of various sizes randomly distributed in a host medium. The dilute-limit expressions (equations (4) and (8)) can be used to calculate the composite response of a dilute suspension of clusters. Moreover, in order to take into account clusters of various sizes, an integration over a specified distribution of cluster sizes is needed [16]. The predicted enhancement may be observed in experiments on non-linear fractal cluster dispersions, on which, to our knowledge, it has never been reported. Finally, if one is interested in a higher-order non-linear response, the perturbative scheme [6, 7] can be used. We expect even larger enhancement will occur in higher-order susceptibilities.

Acknowledgments

This work was supported by the Research Grants Council of the Hong Kong Government under Project Number CUHK 78/93E (221-600-130). I thank P M Hui for clarifying discussions.

References

[1] For a recent review of both electrical and optical properties, see, e.g.,
Bergman D J and Stroud D 1992 *Solid State Physics* vol 46, ed H Ehrenreich and D Turnbull (New York: Academic) p 147
[2] Stroud D and Hui P M 1988 *Phys. Rev.* B **37** 8719
[3] For recent reviews, see, e.g., the articles in
J. Opt. Soc. Am. 1989 B **6** No 4
and see also
Flytzanis C 1992 *Prog. Opt.* **29** 2539
[4] Stroud D and Wood V E 1989 *J. Opt. Soc. Am.* B **6** 778
Neeves A E and Birnboim M H 1989 *J. Opt. Soc. Am.* B **6** 787
Li Y Q, Sung C C, Inguva R and Bowden C M 1989 *J. Opt. Soc. Am.* B **6** 814
[5] Haus J W, Kalyaniwalla N, Inguva R, Bloemer M and Bowden C M 1989 *J. Opt. Soc. Am.* B **6** 797
Haus J W, Inguva R and Bowden C M 1990 *Phys. Rev.* A **40** 5729
Bloemer M J, Ashley P R, Haus J W, Kalyaniwalla N and Christensen C R 1990 *IEEE J. Quantum Electron.* **QE-26** 1075
[6] Gu G Q and Yu K W 1992 *Phys. Rev.* B **46** 4502
Yu K W and Gu G Q 1992 *Phys. Lett.* **168A** 313
[7] Yu K W, Hui P M and Stroud D 1993 *Phys. Rev.* B **47** 14 150
[8] Bergman D J 1989 *Phys. Rev.* B **39** 4598
[9] Tanner D B, Sievers A J and Buhrman R A 1975 *Phys. Rev.* B **11** 1330
[10] Devaty R P and Sievers A J 1984 *Phys. Rev. Lett.* **52** 1344
[11] Lee S I, Noh T W, Cummings K and Gaines J R 1985 *Phys. Rev. Lett.* **55** 1626
[12] Curtin W A, Spitzer R C, Ashcroft N W and Sievers A J 1985 *Phys. Rev. Lett.* **54** 1971
[13] Zhang X and Stroud D 1994 *Phys. Rev.* B **49** 944
[14] Butenko A V, Shalaev V M, Stockman M I 1988 *Sov. Phys.–JETP* **67** 60

Butenko A V, Shalaev V M and Stockman M I 1988 *Z. Phys.* D **10** 71
Rautian S G, Safonov V P, Chubakov P A, Shalaev V M and Stockman M I 1988 *JETP Lett.* 47 243
Shalaev V M, Stockman M I and Botet R 1992 *Physica* A **185** 181
[15] Yu K W 1994 *Phys. Rev.* B **49** 9989
Yu K W, Chan E M Y, Chu Y C and Gu G Q 1995 *Phys. Rev.* B at press
[16] Hui P M and Stroud D 1994 *Phys. Rev.* B **49** 11 729
[17] Hoffmann I and Stroud D 1991 *Phys. Rev.* B **43** 9965
[18] Chang C Y, Kuo L C and Hui P M 1992 *Phys. Rev.* B **46** 14 505
[19] Meakin P 1988 *Phase Transitions and Critical Phenomena* vol 12, ed C Domb and J L Lebowitz (New York: Academic) p 355
[20] See the articles in
Stanley H E and Ostrowsky N (ed) 1986 *On Growth and Form: Fractal and Non-Fractal Patterns in Physics* (Amsterdam: Martinus Nijhoff)
[21] Alexander S and Orbach R 1982 *J. Physique Lett.* **43** L625
For a recent review, see
Nakayama T, Yakubo K and Orbach R 1994 *Rev. Mod. Phys.* **66** 381