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# Dispersion theory of effective meromorphic nonlinear susceptibilities of nanocomposites

K-E Peiponen†, E M Vartiainen‡ and T Asakura§

† Väisälä Laboratory, Department of Physics, University of Joensuu, PO Box 111, Fin-80101 Joensuu, Finland
‡ Department of Information Technology, Lappeenranta University of Technology, PO Box 20, Fin-53851 Lappeenranta, Finland
§ Department of Electronics and Information Engineering, Hokkai-Gakuen University, Sapporo, Hokkaido 064, Japan

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**Abstract.** Dispersion theory of the nonlinear effective susceptibilities of layered and Maxwell-Garnett nanocomposites is considered. It is pointed out that in four-wave-mixing processes, where the nonlinear signal has the same angular frequency as the incident light wave, the effective nonlinear susceptibility is a complex meromorphic function. The special feature of such effective nonlinear susceptibilities is that they possess simultaneously poles and zeros in the upper half of the complex-angular-frequency plane. As a solution for the phase-retrieval problem, which cannot be treated by means of Kramers–Kronig relations, an analysis based on the maximum-entropy model is suggested.

At the beginning of this century, Maxwell-Garnett considered effective optical properties of media containing minute metal spheres [1, 2]. He was interested in the colours of metal glasses and of metallic films. Later, Brüggeman [3] devised a theoretical model for another type of system involving intermixed components. These two models have provided the basis for various standard interpretations of the linear optical properties of two-component materials [4]. In addition, Jarrett and Ward [5] have presented a relatively general model, dealing with ellipsoidal particles, that reproduces the major features of both of the classical models mentioned above.

Recently, the effective nonlinear susceptibilities of nanocomposite materials have attracted much attention due to the fact that the nonlinear susceptibility of a nanocomposite can exceed those of the materials from which it is constructed. In other words, it is possible to enhance the nonlinear signal by exposing a nanocomposite material to laser light. The main cause of this phenomenon is the enhanced local electric field in the vicinity of the nanostructure.

Models constructed for describing the effective nonlinear susceptibilities of various structures of nanocomposites have been given in the literature. Indeed, a model that describes the nonlinear response of ellipsoidal composites was furnished by Haus *et al* [6] (see also Zeng *et al* [7]). A model for the effective nonlinear susceptibility of Maxwell-Garnett materials was given by Sipe and Boyd [8] who studied two-phase composites with nonlinear inclusions and linear host materials and vice versa. Furthermore Boyd and Sipe [9] have investigated also the nonlinear optical properties of layered-geometry nanocomposites

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and considered mathematical models for the effective nonlinear susceptibility related to different nonlinear processes. We wish to emphasize here that layered constructions are important, for instance in modern laser technology. Fischer *et al* [10] were the first to give experimental evidence of the enhancement of the third-order nonlinear susceptibility of layered nanocomposite structure. Nonlinear susceptibilities of Brüggeman structures have also been considered in the case of porous-glass-based composite materials by Boyd *et al* [11] and by Gehr *et al* [12]. However, general dispersion theory which can be exploited in order to optimize the strength of the effective nonlinear susceptibility has, so far, not been considered in the literature. Nevertheless, it is of crucial importance to take into account the absorption–dispersion process, which is always present in the context of third-order nonlinear processes [13]. A first step towards dispersion–absorption studies was taken by Smith *et al* [14], who took into account photoinduced absorption in order to optimize the strength of the effective nonlinear susceptibility.

Here we concentrate on the dispersion theory of the degenerate, effective, third-order, nonlinear susceptibility $\chi^{(3)}_{eff}(\omega;\omega,\omega,-\omega)$. Such a theory has not been presented in the literature for nanocomposites. However, it has considerable importance in fundamental studies and in practical applications.

Generally speaking, in the linear regime, the effective permittivity of nanocomposites obeys the familiar Kramers–Kronig relations. In addition, in most cases in nonlinear optics, nanocomposites obey Kramers–Kronig relations (for more details see the review articles [15] and [16]). However, the assumption of holomorphicity of the effective nonlinear susceptibility of nanocomposites, crucial for the validity of the Kramers–Kronig relations, is no longer valid for $\chi^{(3)}_{eff}(\omega;\omega,\omega,-\omega)$. We have recently studied a simple model for the total meromorphic susceptibility of two-level atoms, and suggested the solving of the phase-retrieval problem by means of an analysis based on the maximum-entropy model [17]. It turns out that $\chi^{(3)}_{eff}(\omega;\omega,\omega,-\omega)$ is also a meromorphic function in the complex plane.

In this paper we present evidence that the maximum-entropy model is at the moment the only solution for the phase-retrieval problem of nanocomposites whose nonlinear optical signal is characterized by $\chi^{(3)}_{eff}(\omega;\omega,\omega,-\omega)$. We wish to emphasize that in most cases the only information that is available relating to the complex-valued function $\chi^{(3)}_{eff}$ is the intensity, which is proportional to $|\chi^{(3)}_{eff}|$.

As an example, let us consider the effective nonlinear susceptibilities of layered and Maxwell-Garnett two-phase nanocomposites. For layered nanocomposites it holds that, in the case where the incident electric field has a component perpendicular to the plane of the layers,

$$\chi^{(3)}_{eff}(\omega;\omega,\omega,-\omega) = \left(\frac{f_a\chi^{(3)}_a(\omega;\omega,\omega,-\omega)}{|\varepsilon_a(\omega)|^2\,\varepsilon_a^2(\omega)} + \frac{f_b\chi^{(3)}_b(\omega;\omega,\omega,-\omega)}{|\varepsilon_b(\omega)|^2\,\varepsilon_b^2(\omega)}\right) \times \left(\left|\frac{f_a}{\varepsilon_a(\omega)} + \frac{f_b}{\varepsilon_b(\omega)}\right|^2\left[\frac{f_a}{\varepsilon_a(\omega)} + \frac{f_b}{\varepsilon_b(\omega)}\right]^2\right)^{-1} \tag{1}$$

where $f_a$ and $f_b$ are the volume fractions of the two components $a$ and $b$, $\chi^{(3)}_a$ and $\chi^{(3)}_b$ are the corresponding nonlinear susceptibilities and, in addition, $\varepsilon_a$ and $\varepsilon_b$ are the permittivities of the two components. For Maxwell-Garnett nanocomposites, and for the sake of simplicity taking the inclusion particles $(a)$ to be nonlinear and the host material $(b)$ to be linear, we can write [8] this as follows:

$$\chi^{(3)}_{eff}(\omega;\omega,\omega,-\omega) = f_a\left|\frac{\varepsilon_{eff}+2\varepsilon_b}{\varepsilon_a+2\varepsilon_b}\right|^2\left[\frac{\varepsilon_{eff}+2\varepsilon_b}{\varepsilon_a+2\varepsilon_b}\right]^2\chi^{(3)}_a(\omega;\omega,\omega,-\omega) \tag{2}$$

where

$$f_a \frac{\varepsilon_a - \varepsilon_b}{\varepsilon_a + 2\varepsilon_b} = \frac{\varepsilon_{eff} - \varepsilon_b}{\varepsilon_{eff} + 2\varepsilon_b} \tag{3}$$

and $f_a$ is the filling fraction.

In both cases the functions $\chi_{eff}^{(3)}$ are meromorphic, since $\chi_a^{(3)}$ and $\chi_b^{(3)}$ are meromorphic, i.e. they possess poles in both half-planes. For qualitative purposes they can be described for instance by the model for the third-order nonlinear susceptibility of two-level atoms of Yariv [18]. Nevertheless, meromorphism has already arisen, due to the squared moduli given by the permittivities, in equations (1) and (2). In addition to the poles that now appear in the upper and lower half-planes, one can find complex zeros in the upper half-plane. In the case of equation (2), the number of zeros depends on the spectral features of $\varepsilon_a$. Due to the existence of zeros and poles in the upper half-plane we have a function that is meromorphic but can be termed holomorphic almost everywhere. Logical foundations of the dispersion theory in linear optics, developed in order to treat problems where a function has zeros in the upper half-plane, and is holomorphic in the upper half-plane, but in addition possesses poles in the lower half-plane, were given by Toll [19]. However, in his treatment, poles and zeros were located in the opposite half-planes in a symmetric manner; therefore the phase retrieval could be managed by introducing a Blaschke product [19, 20]. The case of the effective meromorphic nonlinear susceptibility of nanocomposites is totally different, as described above. We are in trouble in the phase-retrieval problem if poles and zeros appear simultaneously in the upper half-plane, since the zeros and poles of the logarithm function, $\ln|\chi_{eff}^{(3)}|$, are essential singularities.

One attempt at solving the problem of phase retrieval from the modulus of the effective, degenerate, meromorphic, nonlinear susceptibility is based on the application of the maximum-entropy model (MEM). In this model the measured data are fitted by the model [21]

$$|\chi_{eff}^{(3)}(\nu)| = |\beta| \Big/ \left| 1 + \sum_{k=1}^{M} c_k \exp(-\mathrm{i}\, 2\pi k \nu) \right| \tag{4}$$

using a so-called squeezing procedure (with the squeezing parameter $K \geqslant 1$). The unknown MEM coefficients $c_k$ and $|\beta|$ are obtained from a set of linear Yule–Walker equations (the detailed procedure is explained in [21]). The variable $\nu$ is a normalized frequency $\nu = (\omega - \omega_1)/(\omega - \omega_2)$, where $[\omega_1, \omega_2]$ is a finite measurement range. Thus, unlike in Kramers–Kronig analysis, no data extrapolations are carried out in the MEM procedure. However, since $\chi_{eff}^{(3)}(\omega; \omega, \omega, -\omega)$ is to be retrieved from its ME model

$$\chi_{eff}^{(3)}(\nu) = |\beta| \exp\left[-\mathrm{i}\theta_{err}(\nu)\right] \Big/ \left( 1 + \sum_{k=1}^{M} c_k \exp(-\mathrm{i}\, 2\pi k \nu) \right) \tag{5}$$

where the unknown error phase $\theta_{err}$ is estimated by a polynomial

$$\widehat{\theta}_{err}(\nu) = B_0 + B_1\nu + \cdots + B_L \nu^L = \sum_{l=0}^{L} B_l \nu^l \tag{6}$$

we need $L+1$ ellipsometric measurements (i.e. measurements of the phase of $\chi_{eff}^{(3)}$) in the range $[\omega_1, \omega_2]$ to get the coefficients $B_l$. The squeezing procedure makes $\theta_{err}$ more linear (i.e. reduces $L$). As an example, we show in figure 1 the results of MEM calculations (with $K = 1$) where the real and imaginary parts of $\chi_{eff}^{(3)}$ were resolved from the modulus of the

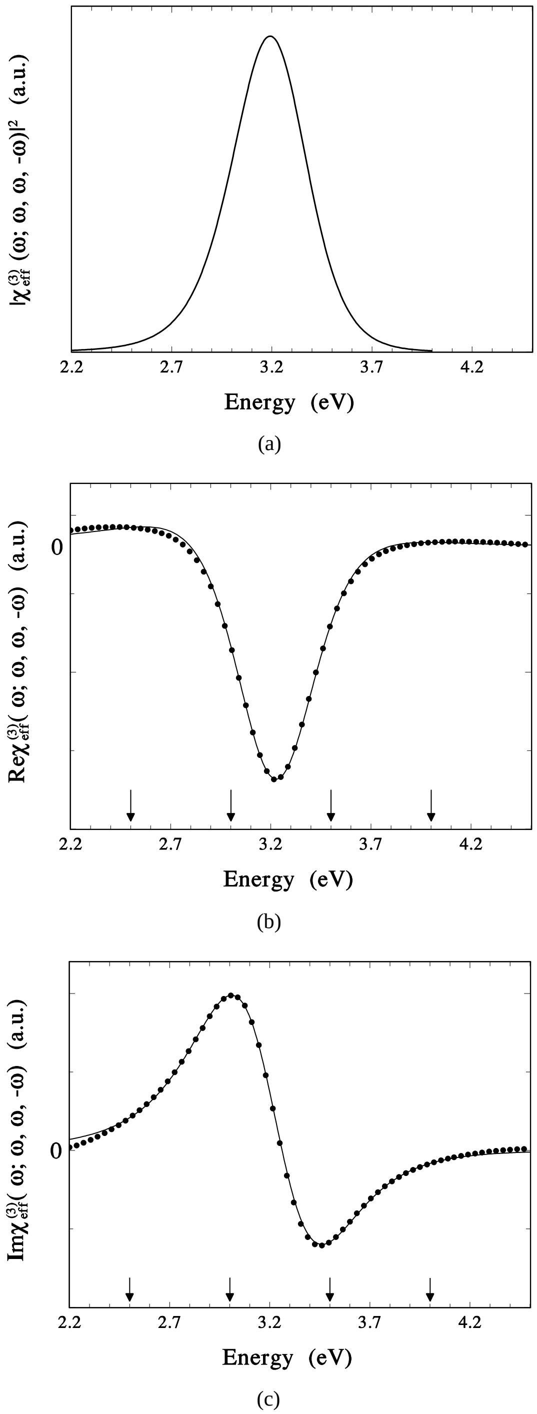


**Figure 1.** (a) The square of the modulus of the effective nonlinear susceptibility of a Maxwell-Garnett nanocomposite, and (b) the real part and (c) the imaginary part. The arrows denote the energies at which the phase is assumed to be known. The parameters used in calculation were $f_a = 0.2$, $A_a = 30$, $A_b = 50$, $\omega_a = 3.0$, $\omega_b = 4.5$, $\Gamma_a = 1.0$, $\Gamma_b = 1.0$, $B = 0.5$, $\omega_r = 3.0$ and $\Gamma_r = 1.0$.

effective, meromorphic, nonlinear susceptibility of the Maxwell-Garnett nanocomposite of equation (2). In the Maxwell-Garnett model we used the Lorentzian permittivities

$$\varepsilon_j = 1 + \frac{A_j}{\omega_j^2 - \omega^2 - \mathrm{i}\Gamma_j \omega} \tag{7}$$

where $j = a$ or $b$. The degenerate third-order nonlinear susceptibility of the inclusion particles was chosen to be

$$\chi_a^{(3)}(\omega; \omega, \omega, -\omega) = \frac{B}{|D(\omega)|^2 \, D(\omega)^2} \tag{8}$$

where $D(\omega) = \omega_r^2 - \omega^2 - \mathrm{i}\Gamma_r \omega$. This model has been used for the qualitative description of semiconductors [22]. The squared modulus of the degenerate nonlinear susceptibility is presented in figure 1(a). We observe from figures 1(b) and 1(c) that the real and imaginary parts are quite well estimated by the MEM when additional phase data are known for four angular frequencies (i.e. $L = 3$ in equation (6)) denoted by arrows in figures 1(b) and 1(c). Compared with our earlier MEM calculations [21], it seems that a successful phase retrieval requires more additional information in the case of a meromorphic susceptibility than in the case of a holomorphic susceptibility.

The case where the host material is nonlinear and inclusion particles linear calls for slightly more complicated meromorphic functions than that of equation (2). As regards their detailed expressions, here we merely refer the reader to the paper of Sipe and Boyd [8]. Nevertheless, zeros and poles in the upper half-plane can also be found for such materials and dispersion analysis by the MEM procedure can be carried out. Detailed MEM calculations for the effective, meromorphic, nonlinear susceptibility of layered nanocomposites will be considered elsewhere.

Finally we remark that, in principle, the existence of both poles and zeros can be established and their numbers can be estimated using the argument theory of complex analysis. Another method would be to apply Jensen's formula for meromorphic functions [17].

In conclusion, we state that the meromorphic, nonlinear susceptibility of two- (or multi-) phase nanocomposites has special features and differs drastically from a one-phase system in the context of dispersion theory. One can find poles located in the upper plane and half-planes—we deal with either a meromorphic two-phase or one-phase system (described e.g. by equation (8)). However, with the meromorphic, nonlinear, two-phase system there appear complex zeros that are due to the permittivity of the composition, in both half-planes, whereas the meromorphic, nonlinear susceptibility of the constituent is in that sense 'well behaved' because its expression has the property of introducing poles not zeros (see equation (8)).

The MEM procedure was shown to be applicable to the phase-retrieval problem of two-phase nanocomposites.

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## References

[1] Maxwell-Garnett J C 1904 *Phil. Trans. R. Soc.* **203** 386
[2] Maxwell-Garnett J C 1906 *Phil. Trans. R. Soc.* **205** 237

[3] Brüggeman D A G 1935 *Ann. Phys., Lpz.* **24** 636
[4] Ward L 1988 *The Optical Constants of Bulk Materials and Films* (Bristol: Hilger)
[5] Jarrett D N and Ward L 1976 *J. Phys. D: Appl. Phys.* **46** 1515
[6] Haus J R, Inguva R and Bowden C M 1989 *Phys. Rev.* A **40** 5729
[7] Zeng X C, Bergman D J, Hui P M and Stroud D 1988 *Phys. Rev.* B **38** 10 970
[8] Sipe J E and Boyd R W 1992 *Phys. Rev.* A **46** 1614
[9] Boyd R W and Sipe J E 1994 *J. Opt. Soc. Am.* B **11** 297
[10] Fischer G L, Boyd R W, Gehr R J, Jenekhe S A, Osaheni J A, Sipe J E and Weller-Brophy L A 1995 *Phys. Rev. Lett.* **74** 1871
[11] Boyd R W, Gehr R J, Fischer G L and Sipe J E 1996 *Pure Appl. Opt.* **5** 505
[12] Gehr R J, Fischer G L and Boyd W B 1997 *J. Opt. Soc. Am.* B **14** 2310
[13] Bassani F and Scandolo S 1991 *Phys. Rev.* B **44** 8446
[14] Smith D D, Fischer G, Boyd R W and Gregory D A 1997 *J. Opt. Soc. Am.* B **14** 1625
[15] Peiponen K-E, Vartiainen E M and Asakura T 1997 Dispersion relations and phase retrieval in optical spectroscopy *Progress in Optics* vol 37, ed E Wolf (Amsterdam: North-Holland) pp 57–94
[16] Peiponen K-E, Vartiainen E M and Asakura T 1997 *Opt. Rev.* **4** 433
[17] Peiponen K-E, Vartiainen E M and Asakura T 1997 *J. Phys.: Condens. Matter* **9** 8937
[18] Yariv A 1988 *Quantum Electronics* 3rd edn (New York: Wiley)
[19] Toll J S 1956 *Phys. Rev.* **104** 1760
[20] Nussenzveig H M 1972 *Causality and Dispersion Relations* (New York: Academic)
[21] Vartiainen E M, Peiponen K-E and Asakura T 1996 *Appl. Spectrosc.* **50** 1283
[22] Hopf F A and Stegeman G I 1986 *Applied Classical Electrodynamics, vol II Nonlinear Optics* (New York: Wiley)