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Tuning the elastic nonlinearities in composite nanomaterials

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Abstract

The possibility of tuning the nonlinear effective response of composite materials and structures is of great importance for developing new concepts such as soft metamaterials, acoustic diodes, nonlinear waveguides and phononic crystals. In this paper we develop a homogenization technique for dispersions of nonlinear particles in a soft matrix able to take account of second and third order elastic nonlinearities. Based on this method, we prove the possibility to strongly amplify a given particles nonlinearity (either the second or the third one) under specific conditions concerning the linear response of the two constituents (particles and matrix). We finally give a realistic example based on a population of porous polymer particles embedded in a PDMS matrix.

Keywords: nonlinear elastic materials, homogenization techniques, acoustic metamaterials, landau coefficients

1. Introduction

In recent years, non linear properties of composite materials have received a great deal of attention due to their potential applications in various fields. For example, the design of non-linear electromagnetic components based on photonic crystals allowed to realize the optical counterpart of the basic electronic devices such as diodes, transistors and so on [1, 2]. The idea of rectifying energy transport has been explored in terms of ratchet solitons as well [3]. Moreover, the enhancement of second order non-linear effects in photonic crystals paves the way of devising much more faster circuits for information treatment (all optical technologies) keeping reduced dimensions compatible with integration requirements [1, 2]. Also, the development of nonlinear electromagnetic metamaterials and plasmonic devices allowed to target electromagnetic properties with the possibility of boosting the magnitude of specific nonlinearities [4–7].

Similar effects were studied in acoustics and efficient acoustic diodes constituted of highly nonlinear elastic materials combined with a one-dimensional phononic crystal were designed [8, 9]. Acoustic diodes present many potential applications especially for thermal management at a microscopic scale [10]. Realization of such devices requires acoustic materials with precisely tuned strong nonlinearities. In [9] strong nonlinear acoustic materials were obtained through bubbly liquids (i.e. ultrasound contrast agents used in medical imaging) with optimized concentration of gas. Unfortunately, from the technological point of view, bubbly liquids are not easily handled materials and research efforts were focused on the replacement of the liquid matrix by a soft solid material such as PDMS [11], leading to the development of soft acoustic metamaterials [12]. Indeed, such composite materials with a low concentration of bubbles inserted in a soft polymer background are well known to exhibit strong acoustic nonlinearities [13, 14]. To summarize, designing heterogeneous solid materials exhibiting strong elastic nonlinearities is a point of crucial importance to realize acoustic diodes and other advanced devices. This goal requires the elaboration of a theoretical model able to predict the nonlinear behavior in solid composites in terms of components properties and micro(nano)scopic morphology. In particular, it is necessary to precisely define the optimal criteria defining the concentration of inclusions, the choice of the constituents

response and the geometry of the microstructure in order to obtain strong and controlled nonlinearities of the second or third order. Therefore, in the present paper, we propose a homogenization technique for nonlinear elastic composite materials constituted of solid inclusions in a solid matrix, which is able to consider the nonlinear response up to the third order. This technique allows us to derive the whole set of effective moduli (linear and nonlinear) for both two-dimensional and three-dimensional heterogeneous structures. Conversely, such a method enables us to tailor the composition, i.e. the concentration and properties of constituents, in order to control the nonlinearities of the composite. It appears that for soft material inclusions in a nearly incompressible matrix, a structure corresponding to soft acoustic metamaterials [12], giant amplifications of the effective nonlinearities with respect to those of the constitutive materials can be obtained. In particular, we show the possibility to separately intensify, correctly choosing the inclusions concentration, either the quadratic or the cubic elastic nonlinear response. Thus, we can expect to design soft materials with controlled nonlinearities well adapted for applications in acoustic diodes or metamaterials.

Homogenization procedures have been successfully developed for the linear properties of heterogeneous materials [15–18]. General results concern the existence of upper and lower bounds for the effective response [19, 20] and exact expressions based on the spatial correlation among constituents [21, 22]. In particular, dispersions of inclusions in a homogeneous matrix have been widely studied both from the electrical [23–26] and the elastic point of view [27–32]. One of the most important result useful to elaborate homogenization procedures and effective medium theories for particulate elastic composites is given by the Eshelby property, describing the internal elastic fields in a linear ellipsoidal particle embedded in a different matrix. Eshelby proved that the internal strain is uniform provided that the externally applied one is so [33–35]. Recently, this result has been generalized by showing that the elastic fields within a generic nonlinear and anisotropic inhomogeneity embedded in a (linear and anisotropic) matrix are uniform as well. This general property has been applied to the case of a dispersion of isotropic nonlinear inclusions and some universal mixing schemes for the Landau coefficients (second order nonlinear moduli) have been obtained [36–39]. Here we exploit these results to improve previous theories with respect to (i) the possibility to consider both second and third order terms in the nonlinear constitutive equations (a point not investigated before that is useful, e.g. for the acoustic diode development) and (ii) the optimization of the effective nonlinear response in terms of the mixture features (this is done independently for the second and third order response and for two- and three-dimensional structures).

The paper is organized as follows. In sections 2 and 3 we introduce the nonlinear elastic constitutive equations for two- and three-dimensional systems, respectively. Accordingly, in sections 4 and 5 we elaborate the homogenization scheme for two- and three-dimensional heterogeneous structures. We study dilute dispersions of nonlinear particles, with elastic response described in sections 2 and 3, embedded in a linear matrix. In section 6 we show the exact analytical criteria that can be adopted to obtain a desired strong amplification of the nonlinear response. Finally in section 7 we present an example of application of previous results concerning a population of porous polymer particles embedded in a PDMS matrix.

2. Three-dimensional nonlinear constitutive equation

We write the elastic energy density U stored inside a deformed material as a given function of the strain tensor $\hat{\epsilon}$ [40, 41]

$$U = U(\hat{\epsilon}), \tag{1}$$

and the stress tensor can be therefore derived as follows [40, 41]

$$T_{ij} = \frac{\partial U}{\partial \epsilon_{ij}}. \tag{2}$$

If the material is isotropic, then the energy depends only on the three strain invariants, i.e.

$$U = U(\mathrm{Tr}(\hat{\epsilon}), \mathrm{Tr}(\hat{\epsilon}^2), \mathrm{Tr}(\hat{\epsilon}^3)), \tag{3}$$

and its expression expanded up to the fourth order is

$$\begin{aligned} U = {} & \mu \mathrm{Tr}(\hat{\epsilon}^2) + \frac{\lambda}{2}\mathrm{Tr}^2(\hat{\epsilon}) + \frac{A}{3}\mathrm{Tr}(\hat{\epsilon}^3) + B\mathrm{Tr}(\hat{\epsilon})\mathrm{Tr}(\hat{\epsilon}^2) \\ & + \frac{C}{3}\mathrm{Tr}^3(\hat{\epsilon}) + E\mathrm{Tr}(\hat{\epsilon})\mathrm{Tr}(\hat{\epsilon}^3) + F\mathrm{Tr}^2(\hat{\epsilon})\mathrm{Tr}(\hat{\epsilon}^2) \\ & + G\mathrm{Tr}^2(\hat{\epsilon}^2) + H\mathrm{Tr}^4(\hat{\epsilon}). \end{aligned} \tag{4}$$

Here, λ and μ are the standard Lamé coefficients of the linear elasticity theory, A, B and C are the second order nonlinear moduli (the so-called Landau coefficients [42]) and E, F, G and H are the third order nonlinear moduli, here introduced to extend previous theories (Tr represents the trace of a linear operator). Nonlinearity can be introduced in the theory of elasticity by means of the exact relation for the Lagrangian strain (geometrical nonlinearity) or through its simplified version for small deformations [43]. Here, we adopt the physical nonlinearity standpoint, whereas the geometrical nonlinearity is everywhere neglected: therefore, the balance equations are based on the small-strain tensor and on the symmetric Cauchy stress [43]. Accordingly, we differentiate equation (4) by using equation (2) and we eventually obtain the stress tensor in the form

$$\begin{aligned} \hat{T} = {} & 2\mu\hat{\epsilon} + \lambda\mathrm{Tr}(\hat{\epsilon})\hat{I} \\ & + A\hat{\epsilon}^2 + B\mathrm{Tr}(\hat{\epsilon}^2)\hat{I} + 2B\hat{\epsilon}\mathrm{Tr}(\hat{\epsilon}) + C\mathrm{Tr}^2(\hat{\epsilon})\hat{I} \\ & + E\mathrm{Tr}(\hat{\epsilon}^3)\hat{I} + 3E\hat{\epsilon}^2\mathrm{Tr}(\hat{\epsilon}) + 2F\mathrm{Tr}(\hat{\epsilon})\mathrm{Tr}(\hat{\epsilon}^2)\hat{I} \\ & + 2F\hat{\epsilon}\mathrm{Tr}^2(\hat{\epsilon}) + 4G\hat{\epsilon}\mathrm{Tr}(\hat{\epsilon}^2) + 4H\mathrm{Tr}^3(\hat{\epsilon})\hat{I}. \end{aligned} \tag{5}$$

This is the final expression of the three-dimensional constitutive equation for a nonlinear isotropic elastic material, as adopted in the present work. It will be used to derive its two-dimensional counterpart and to describe the nonlinear behavior of heterogeneous structures as those represented in figure 1.

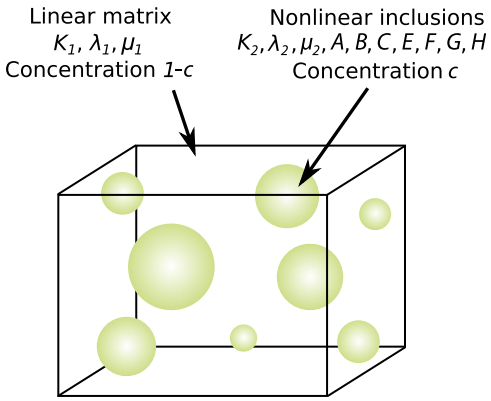

Figure 1. Geometry of a three-dimensional heterogeneous structure composed of a dispersion of nonlinear spheres embedded in a linear matrix.

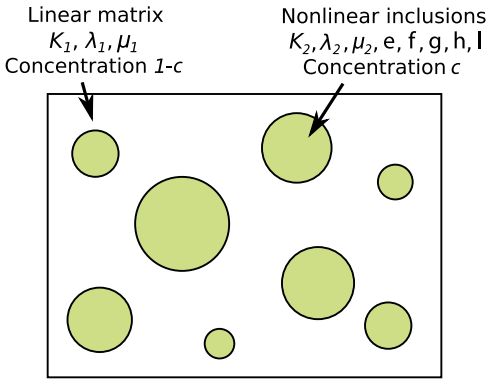

Figure 2. Top view of a two-dimensional heterogeneous structure composed of a dispersion of nonlinear cylinders embedded in a linear matrix.

3. Two-dimensional nonlinear constitutive equation

We suppose now to deal with a nonlinear material described by the constitutive relation given in equation (5) and subjected to plane strain conditions. We consider a Cartesian coordinate system identified by the axes (x, y, z). If, to fix the ideas, the plane strain conditions are applied to the plane (x, y), then we have $u_1 = u_1(x, y)$, $u_2 = u_2(x, y)$ and $u_3 = 0$, where u_i represents the i-th component of the displacement vector. Correspondingly, the non-zero components of the strain tensor are $\epsilon_{11}, \epsilon_{12}$ and ϵ_{22} [40, 41]. They can be used to define a two-by-two matrix representation of the strain on the plane. In this two-dimensional case, the tensor $\hat{\epsilon}$ has only two invariants given by $\mathrm{Tr}(\hat{\epsilon})$ and $\mathrm{Tr}(\hat{\epsilon}^2)$. We use the Cayley–Hamilton theorem and the following procedure to express $\hat{\epsilon}^2$ and $\mathrm{Tr}(\hat{\epsilon}^3)$ as a function of $\mathrm{Tr}(\hat{\epsilon})$ and $\mathrm{Tr}(\hat{\epsilon}^2)$. We define, as usual, the characteristic polynomial of $\hat{\epsilon}$ as

$$P_{\hat{\epsilon}}(\lambda) = \det(\hat{\epsilon} - \lambda \hat{I}) \tag{6}$$

and we obtain the explicit two-dimensional form given by

$$P_{\hat{\epsilon}}(\lambda) = \det(\hat{\epsilon}) - \lambda \mathrm{Tr}(\hat{\epsilon}) + \lambda^2. \tag{7}$$

Since the Cayley–Hamilton theorem affirms that $P_{\hat{\epsilon}}(\hat{\epsilon}) = 0$, we have

$$\det(\hat{\epsilon})\hat{I} - \hat{\epsilon}\mathrm{Tr}(\hat{\epsilon}) + \hat{\epsilon}^2 = \hat{0}. \tag{8}$$

The trace of the left hand side of equation (8) gives

$$2\det(\hat{\epsilon}) - \mathrm{Tr}^2(\hat{\epsilon}) + \mathrm{Tr}(\hat{\epsilon}^2) = 0, \tag{9}$$

and, by replacing $\det(\hat{\epsilon})$ obtained from equation (9) into equation (8) itself, we eventually get

$$\hat{\epsilon}^2 = \hat{\epsilon}\mathrm{Tr}(\hat{\epsilon}) - \tfrac{1}{2}\left[\mathrm{Tr}^2(\hat{\epsilon}) - \mathrm{Tr}(\hat{\epsilon}^2)\right]\hat{I}. \tag{10}$$

Moreover, from equation (10) we easily prove that

$$\mathrm{Tr}(\hat{\epsilon}^3) = \tfrac{3}{2}\mathrm{Tr}(\hat{\epsilon})\mathrm{Tr}(\hat{\epsilon}^2) - \tfrac{1}{2}\mathrm{Tr}^3(\hat{\epsilon}). \tag{11}$$

To do this, we multiply equation (10) by $\hat{\epsilon}$ and we apply the trace operator. Now, since we are dealing with a two-dimensional system, also the stress tensor can be represented by a two-by-two matrix (composed of T_{11}, T_{12} and T_{22}) and equation (5) remains still valid with both two-dimensional stress and strain tensors. We then replace $\hat{\epsilon}^2$ and $\mathrm{Tr}(\hat{\epsilon}^3)$ in equation (5) and we regroup the terms by introducing the following parameters

$$e = B + \frac{A}{2}, \tag{12}$$

$$3f = C - \frac{A}{2}, \tag{13}$$

$$g = G, \tag{14}$$

$$h = 4H - 2E, \tag{15}$$

$$\ell = 2F + 3E. \tag{16}$$

The final two-dimensional constitutive equation is therefore given by

$$\begin{aligned}\hat{T} = {} & 2\mu\hat{\epsilon} + \lambda\mathrm{Tr}(\hat{\epsilon})\hat{I} + e\mathrm{Tr}(\hat{\epsilon}^2)\hat{I} + 2e\hat{\epsilon}\mathrm{Tr}(\hat{\epsilon}) \\ & + 3f\mathrm{Tr}^2(\hat{\epsilon})\hat{I} + 4g\hat{\epsilon}\mathrm{Tr}(\hat{\epsilon}^2) + h\mathrm{Tr}^3(\hat{\epsilon})\hat{I} \\ & + \ell\hat{\epsilon}\mathrm{Tr}^2(\hat{\epsilon}) + \ell\mathrm{Tr}(\hat{\epsilon})\mathrm{Tr}(\hat{\epsilon}^2)\hat{I}.\end{aligned} \tag{17}$$

Please note that the coefficient 3 in the expression for f (see equation (13)) has been introduced in order to be coherent with existing literature about two-dimensional second order nonlinear parameters [44]. This constitutive equation will be used to study the effective properties of composite structures as in figure 2.

4. Two-dimensional nonlinear homogenization

The homogenization procedure for determining the effective properties of a dispersion of nonlinear particles in a linear matrix is composed of two steps: in the first one we analyse the distribution of the elastic fields generated by the presence of a single particle; then, in the second one we study the collective behavior of a population of particles through an ad hoc averaging process of the pertinent elastic fields.

To begin we consider a cylindrical nonlinear particle described by equation (17), embedded in a linear matrix and subjected to a remote load identified by the strain tensor $\hat{\epsilon}^\infty$. To be consistent with previous section we suppose to work

under plane strain conditions on the planes perpendicular to the circular cylinder. As discussed in the Introduction, the analysis of a linear particle embedded in a linear matrix is a classical subject in the mechanics of solids [27, 33, 34]. Moreover, the perturbations of the elastic fields generated by the presence of a nonlinear particle can be studied by means of the recent generalization of the Eshelby theory [36–39]. If $\hat{S}$ is the Eshelby tensor, $\hat{T}_d$ and $\hat{\epsilon}_d$ the stress and strain tensors inside the nonlinear inclusions (which are always uniform), then we can write the following relation between the applied strain and the internal one [36–39]

$$\hat{\epsilon}^{\infty} = \hat{\epsilon}_d + \hat{S}\left(\hat{C}_1^{-1}\hat{T}_d - \hat{\epsilon}_d\right), \tag{18}$$

where $\hat{T}_d = \hat{C}_2(\hat{\epsilon}_d)\hat{\epsilon}_d$ is the nonlinear constitutive equation of the particle, $\hat{C}_2(\hat{\epsilon}_d)$ is the strain dependent stiffness of the particle and $\hat{C}_1$ is the constant stiffness tensor of the linear matrix [36–39]. The Eshelby tensor acts as an operator on the strain tensors and its effects can be summed up through the following expression (two-dimensional case) [35]

$$\hat{S}\hat{\epsilon}_d = \frac{K_1 + 2\mu_1}{2\,(K_1 + \mu_1)}\hat{\epsilon}_d + \frac{K_1 - 2\mu_1}{4\,(K_1 + \mu_1)}\mathrm{Tr}(\hat{\epsilon}_d)\hat{I}, \tag{19}$$

where the bulk modulus K_1 corresponds to the two-dimensional version $K_1 = \lambda_1 + \mu_1$, being λ_1 and μ_1 the Lamé coefficients of the matrix (we will use the standard three-dimensional version $K_1 = \lambda_1 + 2\mu_1/3$ within the three-dimensional homogenization procedure). On the other hand, λ_2 and μ_2 represent the Lamé coefficients of the particle. The stress-strain relation inside the linear matrix is therefore written as

$$\hat{T}_1 = \hat{C}_1\hat{\epsilon}_1 = 2\mu_1\hat{\epsilon}_1 + (K_1 - \mu_1)\,\mathrm{Tr}(\hat{\epsilon}_1)\hat{I}. \tag{20}$$

We easily invert this relation eventually obtaining

$$\hat{\epsilon}_1 = \hat{C}_1^{-1}\hat{T}_1 = \frac{\hat{T}_1}{2\mu_1} - \frac{K_1 - \mu_1}{4K_1\mu_1}\mathrm{Tr}(\hat{T}_1)\hat{I}. \tag{21}$$

By using equation (19), we can replace the Eshelby operator in equation (18) and we get

$$\begin{aligned}\hat{\epsilon}^{\infty} = \hat{\epsilon}_d &+ \frac{K_1 + 2\mu_1}{2\,(K_1 + \mu_1)}\left(\hat{C}_1^{-1}\hat{T}_d - \hat{\epsilon}_d\right)\\ &+ \frac{K_1 - 2\mu_1}{4\,(K_1 + \mu_1)}\mathrm{Tr}\left(\hat{C}_1^{-1}\hat{T}_d - \hat{\epsilon}_d\right)\hat{I}.\end{aligned} \tag{22}$$

We may now expand $\hat{C}_1^{-1}\hat{T}_d$ and $\mathrm{Tr}(\hat{C}_1^{-1}\hat{T}_d)$ by exploiting equation (21); the result is

$$\begin{aligned}\hat{\epsilon}^{\infty} = &\left(1 - \frac{K_1 + 2\mu_1}{2\,(K_1 + \mu_1)}\right)\hat{\epsilon}_d - \frac{K_1 - 2\mu_1}{4\,(K_1 + \mu_1)}\mathrm{Tr}(\hat{\epsilon}_d)\hat{I}\\ &+ \frac{K_1 + 2\mu_1}{4\,(K_1 + \mu_1)\,\mu_1}\hat{T}_d - \frac{K_1}{8\,(K_1 + \mu_1)\,\mu_1}\mathrm{Tr}(\hat{T}_d)\hat{I}.\end{aligned} \tag{23}$$

Then, we can determine the internal stress $\hat{T}_d$ through equation (17) (where λ and μ are replaced by λ_2 and μ_2 to represent the particle response) and we calculate its trace

$$\begin{aligned}\mathrm{Tr}(\hat{T}_d) = &\,2K_2\mathrm{Tr}(\hat{\epsilon}_d) + 2e\mathrm{Tr}(\hat{\epsilon}_d^2) + (2e + 6f)\mathrm{Tr}^2(\hat{\epsilon}_d)\\ &+ (2\ell + 4g)\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2)\\ &+ (2h + \ell)\mathrm{Tr}^3(\hat{\epsilon}_d),\end{aligned} \tag{24}$$

where $K_2 = \lambda_2 + \mu_2$. After a long but straightforward calculation, we therefore obtain from equation (23)

$$\begin{aligned}\hat{\epsilon}^{\infty} = &\,L\hat{\epsilon}_d + M\mathrm{Tr}(\hat{\epsilon}_d)\hat{I} + N\hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d) + O\mathrm{Tr}(\hat{\epsilon}_d^2)\hat{I}\\ &+ P\mathrm{Tr}^2(\hat{\epsilon}_d)\hat{I} + Q\hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d^2) + R\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2)\\ &+ S\hat{\epsilon}_d\mathrm{Tr}^2(\hat{\epsilon}_d) + T\mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I},\end{aligned} \tag{25}$$

with

$$L = 1 + \frac{1}{2}\frac{K_1 + 2\mu_1}{K_1 + \mu_1}\left(\frac{\mu_2}{\mu_1} - 1\right), \tag{26}$$

$$M = \frac{2K_2 - K_1\left(1 + \frac{\mu_2}{\mu_1}\right) - 2(\mu_2 - \mu_1)}{4(K_1 + \mu_1)}, \tag{27}$$

$$N = \frac{e(K_1 + 2\mu_1)}{2\mu_1(K_1 + \mu_1)}, \tag{28}$$

$$O = \frac{e}{2(K_1 + \mu_1)}, \tag{29}$$

$$P = \frac{3f}{2(K_1 + \mu_1)} - \frac{eK_1}{4\mu_1(K_1 + \mu_1)}, \tag{30}$$

$$Q = \frac{g(K_1 + 2\mu_1)}{\mu_1(K_1 + \mu_1)}, \tag{31}$$

$$R = \frac{\ell\mu_1 - gK_1}{2\,(K_1 + \mu_1)\,\mu_1}, \tag{32}$$

$$S = \frac{\ell(K_1 + 2\mu_1)}{4\mu_1(K_1 + \mu_1)}, \tag{33}$$

$$T = \frac{4h\mu_1 - \ell K_1}{8\,(K_1 + \mu_1)\,\mu_1}. \tag{34}$$

Finally, equation (25) represents the nonlinear relation between the applied strain and the internal one for a single nonlinear particle embedded in a linear matrix. This result, expanded up to the third order in the strain, can be used to develop a nonlinear homogenization technique for a dispersion of nonlinear particles. We consider the heterogeneous system in the plane region Ω_t, which is separated into two domains: the matrix sub-region Ω_m and the particles sub-region Ω_p. We therefore define the volume fraction of the dispersed particles as

$$c = \frac{V_\mathrm{p}}{V_t} \quad \text{with } 0 \leqslant c \ll 1, \tag{35}$$

where $V_\mathrm{p} = \mathrm{mes}(\Omega_\mathrm{p})$ and $V_t = \mathrm{mes}(\Omega_t)$. We write the exact expression of the average stress in the inhomogeneous medium

$$\begin{aligned}\langle\hat{T}\rangle &= \frac{1}{V_t}\int_{\Omega_t}\hat{T}\,\mathrm{d}\vec{r}\\ &= \frac{1}{V_t}\left[\int_{\Omega_\mathrm{p}}\hat{T}_d\,\mathrm{d}\vec{r} + \int_{\Omega_\mathrm{m}}\hat{C}_1\hat{\epsilon}\,\mathrm{d}\vec{r}\right]\\ &= \frac{V_\mathrm{p}}{V_t}\frac{1}{V_\mathrm{p}}\int_{\Omega_\mathrm{p}}\hat{T}\,\mathrm{d}\vec{r} + \frac{1}{V_t}\int_{\Omega_\mathrm{m}}\hat{C}_1\hat{\epsilon}\,\mathrm{d}\vec{r}\\ &= c\langle\hat{T}_d\rangle + \frac{\hat{C}_1}{V_t}\left[\int_{\Omega_\mathrm{m}}\hat{\epsilon}\,\mathrm{d}\vec{r} + \int_{\Omega_\mathrm{p}}\hat{\epsilon}\,\mathrm{d}\vec{r} - \int_{\Omega_\mathrm{p}}\hat{\epsilon}\,\mathrm{d}\vec{r}\right]\\ &= c\langle\hat{T}_d\rangle + \hat{C}_1\left[\frac{1}{V_t}\int_{\Omega_t}\hat{\epsilon}\,\mathrm{d}\vec{r} - \frac{V_\mathrm{p}}{V_t}\frac{1}{V_\mathrm{p}}\int_{\Omega_\mathrm{p}}\hat{\epsilon}\,\mathrm{d}\vec{r}\right]\\ &= c\langle\hat{T}_d\rangle + \hat{C}_1\left[\langle\hat{\epsilon}\rangle - c\langle\hat{\epsilon}_d\rangle\right]\end{aligned} \tag{36}$$

This is an exact expression, which can be used as follows. Since we assume a strongly dilute mixture, $c \ll 1$, we make

the approximation that $\langle \hat{T}_d \rangle \approx \hat{T}_d$ and $\langle \hat{\epsilon}_d \rangle \approx \hat{\epsilon}_d$. It means that the elastic fields inside the particles can be considered uniform and given by the Eshelby theory. This is coherent with the assumption of weak interaction (small volume fraction) among the inhomogeneities. Hence, we simply obtain

$$\langle \hat{T} \rangle = c\hat{T}_d + \hat{C}_1 \left[\langle \hat{\epsilon} \rangle - c\hat{\epsilon}_d \right]. \tag{37}$$

From the point of view of the strain averaging we adopt the following approximation

$$\langle \hat{\epsilon} \rangle = c\hat{\epsilon}_d + (1-c)\hat{\epsilon}^{\infty}, \tag{38}$$

which is largely used within the homogenization procedures for elastic, electric and thermal properties [23–25, 45–48]. By using equations (25) and (38), we obtain

$$\begin{aligned}\langle \hat{\epsilon} \rangle = {} & L'\hat{\epsilon}_d + M'\mathrm{Tr}(\hat{\epsilon}_d)\hat{I} + N'\hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d) + O'\mathrm{Tr}(\hat{\epsilon}_d^2)\hat{I} \\ & + P'\mathrm{Tr}^2(\hat{\epsilon}_d)\hat{I} + Q'\hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d^2) + R'\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2) \\ & + S'\hat{\epsilon}_d\mathrm{Tr}^2(\hat{\epsilon}_d) + T'\mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I},\end{aligned} \tag{39}$$

where

$$L' = c + (1-c)L, \tag{40}$$

$$M' = (1-c)M, \tag{41}$$

$$N' = (1-c)N, \tag{42}$$

$$O' = (1-c)O, \tag{43}$$

$$P' = (1-c)P, \tag{44}$$

$$Q' = (1-c)Q, \tag{45}$$

$$R' = (1-c)R, \tag{46}$$

$$S' = (1-c)S, \tag{47}$$

$$T' = (1-c)T. \tag{48}$$

The problem consists now in inverting equation (39) in order to find the internal strain in terms of the average one. To do this, by means of equation (39), we elaborate the following expressions

$$\begin{aligned}\mathrm{Tr}\langle \hat{\epsilon} \rangle = {} & (L' + 2M')\mathrm{Tr}(\hat{\epsilon}_d) + (2P' + N')\mathrm{Tr}^2(\hat{\epsilon}_d) \\ & + 2O'\mathrm{Tr}(\hat{\epsilon}_d^2) + (Q' + 2R')\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2) \\ & + (S' + 2T')\mathrm{Tr}^3(\hat{\epsilon}_d),\end{aligned} \tag{49}$$

$$\begin{aligned}\langle \hat{\epsilon} \rangle \mathrm{Tr}\langle \hat{\epsilon} \rangle = {} & L'(L' + 2M')\hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d) \\ & + 2(N'L' + L'P' + N'M')\hat{\epsilon}_d\mathrm{Tr}^2(\hat{\epsilon}_d) \\ & + 2O'L'\hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d^2) + M'(L' + 2M')\mathrm{Tr}^2(\hat{\epsilon}_d)\hat{I} \\ & + (4P'M' + P'L' + M'N')\mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I} \\ & + (4O'M' + O'L')\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2)\hat{I},\end{aligned} \tag{50}$$

$$\begin{aligned}\langle \hat{\epsilon} \rangle^2 = {} & L'^2\hat{\epsilon}_d^2 + 2L'M'\hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d) + 2L'N'\hat{\epsilon}_d^2\mathrm{Tr}(\hat{\epsilon}_d) \\ & + 2L'O'\hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d^2) + 2(L'P' + M'N')\hat{\epsilon}_d\mathrm{Tr}^2(\hat{\epsilon}_d) \\ & + M'^2\mathrm{Tr}^2(\hat{\epsilon}_d)\hat{I} + 2M'O'\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2)\hat{I} \\ & + 2M'P'\mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I},\end{aligned} \tag{51}$$

$$\begin{aligned}\mathrm{Tr}\langle \hat{\epsilon} \rangle^2 = {} & L'^2\mathrm{Tr}(\hat{\epsilon}_d^2) + 2M'(L' + M')\mathrm{Tr}^2(\hat{\epsilon}_d) \\ & + 2(L'N' + L'O' + 2M'O')\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2) \\ & + 2(L'P' + M'N' + 2M'P')\mathrm{Tr}^3(\hat{\epsilon}_d),\end{aligned} \tag{52}$$

$$\begin{aligned}\mathrm{Tr}^2\langle \hat{\epsilon} \rangle = {} & (L' + 2M')^2\mathrm{Tr}^2(\hat{\epsilon}_d) \\ & + 2(L' + 2M')(2P' + N')\mathrm{Tr}^3(\hat{\epsilon}_d) \\ & + 4O'(L' + 2M')\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2),\end{aligned} \tag{53}$$

$$\begin{aligned}\langle \hat{\epsilon} \rangle \mathrm{Tr}\langle \hat{\epsilon} \rangle^2 = {} & L'^3\hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d^2) + 2L'(L'M' + M'^2)\hat{\epsilon}_d\mathrm{Tr}^2(\hat{\epsilon}_d) \\ & + M'L'^2\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2)\hat{I} \\ & + 2M'^2(L' + M')\mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I},\end{aligned} \tag{54}$$

$$\begin{aligned}\langle \hat{\epsilon} \rangle \mathrm{Tr}^2\langle \hat{\epsilon} \rangle = {} & L'(L' + 2M')^2\hat{\epsilon}_d\mathrm{Tr}^2(\hat{\epsilon}_d) \\ & + M'(L' + 2M')\mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I},\end{aligned} \tag{55}$$

$$\begin{aligned}\mathrm{Tr}\langle \hat{\epsilon} \rangle \mathrm{Tr}\langle \hat{\epsilon} \rangle^2 = {} & L'^2(L' + 2M')\mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2) \\ & + 2M'(L' + M')(L' + 2M')\mathrm{Tr}^3(\hat{\epsilon}_d),\end{aligned} \tag{56}$$

$$\mathrm{Tr}^3\langle \hat{\epsilon} \rangle = (L' + 2M')^3\mathrm{Tr}^3(\hat{\epsilon}_d). \tag{57}$$

These results have been written by taking into consideration only the terms up to the third degree of the average strain. We can further write previous expressions in the following matrix form

$$\hat{\mathcal{U}} \begin{bmatrix} \hat{\epsilon}_d \\ \mathrm{Tr}(\hat{\epsilon}_d)\hat{I} \\ \hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d) \\ \mathrm{Tr}(\hat{\epsilon}_d^2)\hat{I} \\ \mathrm{Tr}^2(\hat{\epsilon}_d)\hat{I} \\ \hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d^2) \\ \mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2)\hat{I} \\ \hat{\epsilon}_d\mathrm{Tr}^2(\hat{\epsilon}_d) \\ \mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I} \end{bmatrix} = \begin{bmatrix} \langle \hat{\epsilon} \rangle \\ \mathrm{Tr}\langle \hat{\epsilon} \rangle \hat{I} \\ \langle \hat{\epsilon} \rangle \mathrm{Tr}\langle \hat{\epsilon} \rangle \\ \mathrm{Tr}\langle \hat{\epsilon} \rangle^2 \hat{I} \\ \mathrm{Tr}^2\langle \hat{\epsilon} \rangle \hat{I} \\ \langle \hat{\epsilon} \rangle \mathrm{Tr}\langle \hat{\epsilon} \rangle^2 \\ \mathrm{Tr}\langle \hat{\epsilon} \rangle \mathrm{Tr}\langle \hat{\epsilon} \rangle^2 \hat{I} \\ \langle \hat{\epsilon} \rangle \mathrm{Tr}^2\langle \hat{\epsilon} \rangle \\ \mathrm{Tr}^3\langle \hat{\epsilon} \rangle \hat{I} \end{bmatrix}, \tag{58}$$

where the matrix $\hat{\mathcal{U}}$ is defined as follows and depends on the parameters listed in equations (40)–(48)

$$\hat{\mathcal{U}} = \begin{bmatrix} L' & M' & N' & O' & P' \\ 0 & L' + 2M' & 0 & 2O' & 2P' + N' \\ 0 & 0 & L'(L' + 2M') & 0 & M'(L' + 2M') \\ 0 & 0 & 0 & L'^2 & 2M'(L' + M') \\ 0 & 0 & 0 & 0 & (L' + 2M')^2 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\begin{bmatrix} Q' & R' & S' & T' \\ 0 & Q' + 2R' & 0 & S' + 2T' \\ 2O'L' & 4O'M' + O'L' & 2(N'L' + L'P' + N'M') & 4P'M' + P'L' + M'N' \\ 0 & 2(L'N' + L'O' + 2M'O') & 0 & 2(L'P' + M'N' + 2M'P') \\ 0 & 4O'(L' + 2M') & 0 & 2(L' + 2M') \times (2P' + N') \\ L'^3 & M'L'^2 & 2L'(L'M' + M'^2) & 2M'^2(L' + M') \\ 0 & L'^2(L' + 2M') & 0 & 2M'(L' + M') \times (L' + 2M') \\ 0 & 0 & L'(L' + 2M')^2 & M'(L' + 2M')^2 \\ 0 & 0 & 0 & (L' + 2M')^3 \end{bmatrix}. \tag{59}$$

By inverting the above matrix $\hat{\mathcal{U}}$ (it is immediate since $\hat{\mathcal{U}}$ is upper triangular) we can simply find $\hat{\epsilon}_d$ in terms of $\langle\hat{\epsilon}\rangle$. Then, we can also obtain $\hat{T}_d$ through the constitutive equation of nonlinear particles. By substituting the obtained results $\hat{\epsilon}_d = \hat{\epsilon}_d(\langle\hat{\epsilon}\rangle)$ and $\hat{T}_d = \hat{T}_d(\langle\hat{\epsilon}\rangle)$ in equation (37), we finally obtain the effective nonlinear constitutive equation of the composite structure in the form $\langle\hat{T}\rangle = \langle\hat{T}\rangle(\langle\hat{\epsilon}\rangle)$, as follows

$$\begin{aligned}\langle\hat{T}\rangle &= c\left(\hat{T}_d - \hat{C}_1\hat{\epsilon}_d\right) + \hat{C}_1\langle\hat{\epsilon}\rangle \\ &= c\begin{bmatrix} 2\mu_2 - 2\mu_1 \\ K_2 - \mu_2 - K_1 + \mu_1 \\ 2e \\ e \\ 3f \\ 4g \\ \ell \\ \ell \\ h \end{bmatrix}^T \begin{bmatrix} \hat{\epsilon}_d \\ \mathrm{Tr}(\hat{\epsilon}_d)\hat{I} \\ \hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d) \\ \mathrm{Tr}(\hat{\epsilon}_d^2)\hat{I} \\ \mathrm{Tr}^2(\hat{\epsilon}_d)\hat{I} \\ \hat{\epsilon}_d\mathrm{Tr}(\hat{\epsilon}_d^2) \\ \mathrm{Tr}(\hat{\epsilon}_d)\mathrm{Tr}(\hat{\epsilon}_d^2)\hat{I} \\ \hat{\epsilon}_d\mathrm{Tr}^2(\hat{\epsilon}_d) \\ \mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I} \end{bmatrix} \\ &\quad + \begin{bmatrix} 2\mu_1 \\ K_1 - \mu_1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}^T \begin{bmatrix} \langle\hat{\epsilon}\rangle \\ \mathrm{Tr}\langle\hat{\epsilon}\rangle\hat{I} \\ \langle\hat{\epsilon}\rangle\mathrm{Tr}\langle\hat{\epsilon}\rangle \\ \mathrm{Tr}\langle\hat{\epsilon}\rangle^2\hat{I} \\ \mathrm{Tr}^2\langle\hat{\epsilon}\rangle\hat{I} \\ \langle\hat{\epsilon}\rangle\mathrm{Tr}\langle\hat{\epsilon}\rangle^2 \\ \mathrm{Tr}\langle\hat{\epsilon}\rangle\mathrm{Tr}\langle\hat{\epsilon}\rangle^2\hat{I} \\ \langle\hat{\epsilon}\rangle\mathrm{Tr}^2\langle\hat{\epsilon}\rangle \\ \mathrm{Tr}^3\langle\hat{\epsilon}\rangle\hat{I} \end{bmatrix}. \end{aligned} \tag{60}$$

We can finally use equation (58) in equation (60) and, therefore, we identify all the effective linear and nonlinear parameters

$$\begin{aligned}\begin{bmatrix} 2\mu_{\mathrm{eff}} \\ K_{\mathrm{eff}} - \mu_{\mathrm{eff}} \\ 2e_{\mathrm{eff}} \\ e_{\mathrm{eff}} \\ 3f_{\mathrm{eff}} \\ 4g_{\mathrm{eff}} \\ \ell_{\mathrm{eff}} \\ \ell_{\mathrm{eff}} \\ h_{\mathrm{eff}} \end{bmatrix}^T &= \begin{bmatrix} 2\mu_1 \\ K_1 - \mu_1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}^T \\ &\quad + c\begin{bmatrix} 2\mu_2 - 2\mu_1 \\ K_2 - \mu_2 - K_1 + \mu_1 \\ 2e \\ e \\ 3f \\ 4g \\ \ell \\ \ell \\ h \end{bmatrix}^T \hat{\mathcal{U}}^{-1}. \end{aligned} \tag{61}$$

This completes the characterization of the composite material: as result, we have determined the linear properties K_{eff} and μ_{eff}, the second order nonlinearities e_{eff} and f_{eff} and the third order nonlinearities g_{eff}, ℓ_{eff} and h_{eff}. These effective parameters have been written in terms of the properties of the matrix, the properties of the particles and the volume fraction c. The importance of this procedure for practical exploitation resides in the fact that we can consider third order nonlinearities, an aspect always neglected in previous literature.

This general homogenization theory can be specialized to analyse a particular case of broad interest for the applications. We consider a population of particles with only the two nonlinear coefficients f and h different from zero. Therefore, in this case we have $e = 0$, $\ell = 0$ and $g = 0$. From the physical point of view, it means that the nonlinear behavior of the particles is limited to the compressive mechanical response. Indeed, from equation (24) we obtain

$$\mathrm{Tr}(\hat{T}_d) = 2K_2\mathrm{Tr}(\hat{\epsilon}_d) + 6f\mathrm{Tr}^2(\hat{\epsilon}_d) + 2h\mathrm{Tr}^3(\hat{\epsilon}_d), \tag{62}$$

which represents a nonlinear relation between the pressure and the specific volume change. In this specific case the homogenization procedure reduces to the following expression

$$\begin{aligned}\begin{bmatrix} 2\mu_{\mathrm{eff}} \\ K_{\mathrm{eff}} - \mu_{\mathrm{eff}} \\ 3f_{\mathrm{eff}} \\ h_{\mathrm{eff}} \end{bmatrix}^T &= \begin{bmatrix} 2\mu_1 \\ K_1 - \mu_1 \\ 0 \\ 0 \end{bmatrix}^T \\ &\quad + c\begin{bmatrix} 2\mu_2 - 2\mu_1 \\ K_2 - \mu_2 - K_1 + \mu_1 \\ 3f \\ h \end{bmatrix}^T \hat{\mathcal{M}}_{2D}^{-1} \end{aligned} \tag{63}$$

where we have defined the matrix

$$\hat{\mathcal{M}}_{2D} = \begin{bmatrix} L' & M' & P' & T' \\ 0 & L' + 2M' & 2P' & 2T' \\ 0 & 0 & (L' + 2M')^2 & 4P'(L' + 2M') \\ 0 & 0 & 0 & (L' + 2M')^3 \end{bmatrix}, \tag{64}$$

which represent the reduced counterpart of $\hat{\mathcal{U}}$.

5. Three-dimensional nonlinear homogenization

A similar procedure can be also elaborated for a dispersion of nonlinear spherical particles (three-dimensional case). Here, for the sake of brevity, we only describe the simple homogenization scheme for particle having the nonlinear behavior limited to the compressive mechanical response. We use, therefore, the following expression for the stress-strain relation of the particles

$$\begin{aligned}\hat{T}_d &= 2\mu_2\hat{\epsilon}_d + \lambda_2\mathrm{Tr}(\hat{\epsilon}_d)\hat{I} \\ &\quad + C\mathrm{Tr}^2(\hat{\epsilon}_d)\hat{I} + 4H\mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I}, \end{aligned} \tag{65}$$

which can be simply obtained from equation (5) by setting $A = 0$, $B = 0$, $E = 0$, $F = 0$ and $G = 0$. By calculating the trace of equation (65) we get

$$\mathrm{Tr}(\hat{T}_d) = 3K_2\mathrm{Tr}(\hat{\epsilon}_d) + 3C\mathrm{Tr}^2(\hat{\epsilon}_d) + 12H\mathrm{Tr}^3(\hat{\epsilon}_d), \tag{66}$$

where the three-dimensional bulk modulus is defined as $K_2 = \lambda_2 + \frac{2}{3}\mu_2$. Equation (66), similarly to equation (62), represents a direct relation between pressure and specific volume change. On the other hand, the matrix is linear and isotropic and therefore is described by the standard constitutive equation

$$\hat{T}_1 = \hat{C}_1\hat{\epsilon}_1 = 2\mu_1\hat{\epsilon}_1 + \left(K_1 - \frac{2}{3}\mu_1\right)\mathrm{Tr}(\hat{\epsilon}_1)\hat{I}, \tag{67}$$

where $K_1 = \lambda_1 + \frac{2}{3}\mu_1$ is the matrix bulk modulus. This expression can be straightforwardly inverted getting

$$\hat{\epsilon}_1 = \hat{C}_1^{-1}\hat{T}_1 = \frac{1}{2\mu_1}\hat{T}_1 - \frac{3K_1 - 2\mu_1}{18\mu_1 K_1}\mathrm{Tr}(\hat{T}_1)\hat{I}. \tag{68}$$

For spherical particles the Eshelby tensor effect on a given deformation is [35]

$$\hat{S}\hat{\epsilon}_d = \frac{6}{5}\frac{K_1 + 2\mu_1}{3K_1 + 4\mu_1}\hat{\epsilon}_d + \frac{1}{5}\frac{3K_1 - 4\mu_1}{3K_1 + 4\mu_1}\mathrm{Tr}\left(\hat{\epsilon}_d\right)\hat{I}. \tag{69}$$

These results can be used in equation (18), which remains valid independently of the dimensionality of the system. As result we obtain, as in the previous section, the relation between the applied strain and the internal one for a single nonlinear sphere

$$L\hat{\epsilon}_d + M\mathrm{Tr}\hat{\epsilon}_d I + Q\mathrm{Tr}^2\hat{\epsilon}_d I + W\mathrm{Tr}^3\hat{\epsilon}_d I = \hat{\epsilon}^\infty, \tag{70}$$

with

$$L = 1 + \frac{6}{5}\frac{K_1 + 2\mu_1}{3K_1 + 4\mu_1}\left(\frac{\mu_2}{\mu_1} - 1\right), \tag{71}$$

$$M = \frac{5K_2 - K_1\left(3 + 2\frac{\mu_2}{\mu_1}\right) - 4(\mu_2 - \mu_1)}{5(3K_1 + 4\mu_1)}, \tag{72}$$

$$Q = \frac{C}{3K_1 + 4\mu_1}, \tag{73}$$

$$W = \frac{4H}{3K_1 + 4\mu_1}. \tag{74}$$

This completes the first step of the homogenization procedure concerning a single spherical particle. To elaborate the second one, we observe that averaging results given in equations (37) and (38) of previous section are still valid and we eventually obtain the following relation between the internal and the average strain

$$\hat{\mathcal{M}}_{3D}\begin{bmatrix}\hat{\epsilon}_d\\ \mathrm{Tr}(\hat{\epsilon}_d)\hat{I}\\ \mathrm{Tr}^2(\hat{\epsilon}_d)\hat{I}\\ \mathrm{Tr}^3(\hat{\epsilon}_d)\hat{I}\end{bmatrix} = \begin{bmatrix}\langle\hat{\epsilon}\rangle\\ \mathrm{Tr}\langle\hat{\epsilon}\rangle\hat{I}\\ \mathrm{Tr}^2\langle\hat{\epsilon}\rangle\hat{I}\\ \mathrm{Tr}^3\langle\hat{\epsilon}\rangle\hat{I}\end{bmatrix}, \tag{75}$$

where we introduced the matrix

$$\hat{\mathcal{M}}_{3D} = \begin{bmatrix}L' & M' & Q' & W'\\ 0 & (L'+3M') & 3Q' & 3W'\\ 0 & 0 & (L'+3M')^2 & 6Q'(L'+3M')\\ 0 & 0 & 0 & (L'+3M')^3\end{bmatrix}, \tag{76}$$

which is the three-dimensional counterpart of equation (64). Here we defined $L' = c + (1-c)L$, $M' = (1-c)M$, $Q' = (1-c)Q$ and $W' = (1-c)W$. To conclude, we can identify all the linear and nonlinear effective parameters as follows

$$\begin{bmatrix}2\mu_{\mathrm{eff}}\\ K_{\mathrm{eff}} - \frac{2}{3}\mu_{\mathrm{eff}}\\ C_{\mathrm{eff}}\\ 4H_{\mathrm{eff}}\end{bmatrix}^T = \begin{bmatrix}2\mu_1\\ K_1 - \frac{2}{3}\mu_1\\ 0\\ 0\end{bmatrix}^T + c\begin{bmatrix}2\mu_2 - 2\mu_1\\ K_2 - \frac{2}{3}\mu_2 - K_1 + \frac{2}{3}\mu_1\\ C\\ 4H\end{bmatrix}^T \hat{\mathcal{M}}_{3D}^{-1}. \tag{77}$$

This is the final result concerning the homogenization of a dispersion of elastic spheres with a nonlinear behavior limited to the compressive response. We underline that, if necessary, a complete procedure taking into account all the nonlinear parameters appearing in equation (5) can be elaborated as in the 2D case, previously discussed.

6. Intensification of nonlinear properties

We use now the results concerning the two- and three-dimensional homogenization procedures (see equations (63) and (77)) to study the possibility to strongly amplify the nonlinear properties of a composite material with respect to the nonlinear response of its components.

To begin we analyse the paradigmatic cases where the cylinders (2D structures) or the spheres (3D structures) have only one nonlinear coefficients different from zero. More specifically, in the 2D case we suppose either $f \neq 0$, $h = 0$ or $f = 0$, $h \neq 0$; on the other hand, in the 3D case we suppose either $C \neq 0$, $H = 0$ or $C = 0$, $H \neq 0$. In a following section we will describe the combined effects of both second and third order nonlinearities.

The measure of nonlinearity for a single arbitrary material can be defined as the ratio between the pertinent nonlinear coefficient divided by a linear elastic modulus. For example, in the first 2D case with $f \neq 0$ we measure the nonlinearity of the cylinders with the ratio f/K_2 and the nonlinearity of the overall composite with $f_{\mathrm{eff}}/K_{\mathrm{eff}}$. It is important to remark that we chose here the bulk linear modulus K_2 or K_{eff} since it describes the compressive behavior, coherently with the meaning of the nonlinear parameter f or f_{eff} (see equation (62) for details). Based on the previous discussion, we can define the amplification of the nonlinearity introduced by the composite structure as the ratio $\mathcal{A} = (f_{\mathrm{eff}}/K_{\mathrm{eff}})/(f/K_2)$. This definition is valid for the case $f \neq 0$, $h = 0$ (amplification of the second order nonlinearity in 2D geometry). Similarly, for the third order nonlinerity in 2D geometry ($f = 0$, $h \neq 0$) we have $\mathcal{A} = (h_{\mathrm{eff}}/K_{\mathrm{eff}})/(h/K_2)$. The same definitions can be adopted for the 3D geometry: $\mathcal{A} = (C_{\mathrm{eff}}/K_{\mathrm{eff}})/(C/K_2)$ for the case with $C \neq 0$, $H = 0$ (second order nonlinearity); $\mathcal{A} = (H_{\mathrm{eff}}/K_{\mathrm{eff}})/(H/K_2)$ for the case with $C = 0$, $H \neq 0$ (third order nonlinearity).

We start by summing up the results for the linear properties of the composite structures. For the dispersion of parallel cylinders the above procedure leads to the results

$$\mu_{\mathrm{eff}} = \mu_1 + \frac{c(\mu_2 - \mu_1)}{c + (1-c)\left[1 + \frac{1}{2}\left(\frac{\mu_2}{\mu_1} - 1\right)\frac{K_1 + 2\mu_1}{K_1 + \mu_1}\right]}, \tag{78}$$

$$K_{\mathrm{eff}} = K_1 + \frac{c(K_2 - K_1)}{c + (1-c)\frac{\mu_1 + K_2}{\mu_1 + K_1}}, \tag{79}$$

and for the dispersion of spheres we obtain

$$\mu_{\mathrm{eff}} = \mu_1 + c\frac{\mu_2 - \mu_1}{c + (1-c)\left[1 + \frac{6}{5}\left(\frac{\mu_2}{\mu_1} - 1\right)\frac{K_1 + 2\mu_1}{3K_1 + 4\mu_1}\right]}, \tag{80}$$

$$K_{\mathrm{eff}} = K_1 + \frac{c\,(K_2 - K_1)}{c + (1-c)\frac{3K_2 + 4\mu_1}{3K_1 + 4\mu_1}}. \tag{81}$$

Table 1. Optimal volume fractions and correponding nonlinearity amplifications for the four cases defined by $g = 2, 3$ and $d = 2, 3$ ($x = \mu_1/K_1$ and $y = K_1/K_2$).

	$d = 2$	$d = 3$
$g = 2$	$c_{\text{opt}} = \dfrac{1+xy}{4x(y-1)}\left(1-\sqrt{1-8x}\right),\ x < \dfrac{1}{8}$	$c_{\text{opt}} = \dfrac{1+\frac{4}{3}xy}{\frac{16}{3}x(y-1)}\left(1-\sqrt{1-\dfrac{32}{3}x}\right),\ x < \dfrac{3}{32}$
	$\mathcal{A}_{\text{opt}} = \dfrac{64(1+x)^3xy^2}{(1+xy)^2(y-1)\left(1-\sqrt{1-8x}\right)\left(3+\sqrt{1-8x}\right)^3}$	$\mathcal{A}_{\text{opt}} = \dfrac{256\left(1+\frac{4}{3}x\right)^3xy^2}{3(1+\frac{4}{3}xy)^2(y-1)\left(1-\sqrt{1-\frac{32}{3}x}\right)\left(3+\sqrt{1-\frac{32}{3}x}\right)^3}$
$g = 3$	$c_{\text{opt}} = \dfrac{1+xy}{3x(y-1)}\left(1-\sqrt{1-3x}\right),\ x < \dfrac{1}{3}$	$c_{\text{opt}} = \dfrac{1+\frac{4}{3}xy}{4x(y-1)}\left(1-\sqrt{1-4x}\right),\ x < \dfrac{1}{4}$
	$\mathcal{A}_{\text{opt}} = \dfrac{27(1+x)^4x^2y^3}{(1+xy)^3(y-1)\left(1-\sqrt{1-3x}\right)^2\left(2+\sqrt{1-3x}\right)^4}$	$\mathcal{A}_{\text{opt}} = \dfrac{48(1+\frac{4}{3}x)^4x^2y^3}{(1+\frac{4}{3}xy)^3(y-1)\left(1-\sqrt{1-4x}\right)^2\left(2+\sqrt{1-4x}\right)^4}$

These results are in perfect agreement with previous linear theories [30] and they represent a first check of our developments. Of course, the effective linear moduli are not affected by the presence of nonlinear behaviors of the constituents.

Concerning the nonlinear properties we obtained the following results for the four cases under investigations (we define g as the degree on nonlinearity involved and d as the dimensionality of the system): if $f \neq 0, h = 0$ $(g = 2, d = 2)$ we get

$$f_{\text{eff}} = \frac{cf(K_1+\mu_1)^3}{[c(K_1-K_2)+K_2+\mu_1]^3}, \tag{82}$$

if $f = 0, h \neq 0$ $(g = 3, d = 2)$ we get

$$h_{\text{eff}} = \frac{ch(K_1+\mu_1)^4}{[c\,(K_1-K_2)+K_2+\mu_1]^4}, \tag{83}$$

if $C \neq 0, H = 0$ $(g = 2, d = 3)$ we get

$$C_{\text{eff}} = \frac{cC(3K_1+4\mu_1)^3}{[3c(K_1-K_2)+3K_2+4\mu_1]^3}, \tag{84}$$

and, finally, if $C = 0, H \neq 0$ $(g = 3, d = 3)$ we get

$$H_{\text{eff}} = \frac{cH(3K_1+4\mu_1)^4}{[3c\,(K_1-K_2)+3K_2+4\mu_1]^4}. \tag{85}$$

By means of previous linear and nonlinear results we can evaluate the amplification $\mathcal{A}$ above defined for all the four cases analysed. For practical applications it is interesting to observe that the quantity $\mathcal{A}$ shows a maximum point for a given value of the volume fraction c of the nonlinear constituent. It is therefore important to calculate this optimal value c_{opt} of c and the corresponding value of the amplification $\mathcal{A}_{\text{opt}}$. The results are reported in table 1 for all the cases with $g = 2, 3$ and $d = 2, 3$. We observe that these expressions can be written in terms of $x = \mu_1/K_1$, characterizing the response of the matrix and $y = K_1/K_2$, defining the compressibility contrast between particles and matrix. Some limitations on the values of x are reported in order to assure the existence of the optimal solution. In general, we must have $0 < x < 3$ for $d = 2$ and $x > 0$ for $d = 3$ to fulfil standard energetic constraints and therefore the limitations indicated belong to the admissibility domains of the linear elastic constants.

A first application of the results shown in table 1 can be envisaged by considering the case with $x \to 0$, which means gels, biological materials or organic liquids. In this case the matrix shear modulus μ_1 is very small with respect to the matrix bulk modulus K_1. The simplified results for this case are reported in table 2, which contains the first order expansions for $x \to 0$ of all results presented in table 1. It is interesting to draw a comparison between these results and those published in literature concerning the mixing laws of the nonlinear parameters of biological fluids. Typically, these results are important in the field of ultrasound acoustic imaging where the measurement of nonlinear parameters is useful to infer the tissue composition and to reconstruct the heterogeneous geometry of complex bio-structures [49, 50]. Since the involved phases are usually liquids, the shear modulus is zero in all previously published calculations. Therefore, the nonlinear constitutive equation relating the applied pressure to the local density variation is written in the following form [51–55]

$$p - p_0 = \mathbb{A}\left(\frac{\rho-\rho_0}{\rho_0}\right) + \frac{\mathbb{B}}{2}\left(\frac{\rho-\rho_0}{\rho_0}\right)^2 + \frac{\mathbb{C}}{6}\left(\frac{\rho-\rho_0}{\rho_0}\right)^3, \tag{86}$$

where ρ_0 and p_0 are the equilibrium density and pressure, ρ and p their perturbed values and $\mathbb{A}$, $\mathbb{B}$, $\mathbb{C}$ the constitutive parameters. The form of this equation can be conveniently compared with our results given in equations (62) and (66). The detailed relation between equation (86) and the complete elastic response given in equation (5) can be found in literature [56, 57]. The effects of the second order nonlinearity can be taken into account through the definition

$$\beta = \frac{\mathbb{B}}{2\mathbb{A}} + 1, \tag{87}$$

and those of the third order nonlinearity through

$$\gamma = \frac{\mathbb{C}}{6\mathbb{A}} - 1. \tag{88}$$

We remark that both the ratios $\frac{\mathbb{B}}{\mathbb{A}}$ and $\frac{\mathbb{C}}{\mathbb{A}}$ can be measured with standard ultrasound techniques [51, 52]. The already

Table 2. Results of the optimization for small values of x (gels or biological materials with negligible shear response) and for high values of y (large matrix to particles compressibility contrast).

$x \to 0$	$d = 2$	$d = 3$
$g = 2$	$c_{\text{opt}} \underset{x\to 0}{\sim} \dfrac{1}{y-1} + \dfrac{y+2}{y-1}x \underset{y\to\infty}{\sim} \dfrac{1}{y}(1+xy)$	$c_{\text{opt}} \underset{x\to 0}{\sim} \dfrac{1}{y-1} + \dfrac{4(y+2)}{3(y-1)}x \underset{y\to\infty}{\sim} \dfrac{1}{y}\left(1+\dfrac{4}{3}xy\right)$
	$\mathcal{A}_{\text{opt}} \underset{x\to 0}{\sim} \dfrac{y^2}{4(y-1)} - \dfrac{y^2(y-2)}{2(y-1)}x \underset{y\to\infty}{\sim} \dfrac{y}{4}(1-2xy)$	$\mathcal{A}_{\text{opt}} \underset{x\to 0}{\sim} \dfrac{y^2}{4(y-1)} - \dfrac{2y^2(y-2)}{3(y-1)}x \underset{y\to\infty}{\sim} \dfrac{y}{4}\left(1-\dfrac{8}{3}xy\right)$
$g = 3$	$c_{\text{opt}} \underset{x\to 0}{\sim} \dfrac{1}{2(y-1)} + \dfrac{3+4y}{8(y-1)}x \underset{y\to\infty}{\sim} \dfrac{1}{2y}(1+xy)$	$c_{\text{opt}} \underset{x\to 0}{\sim} \dfrac{1}{2(y-1)} + \dfrac{3+4y}{6(y-1)}x \underset{y\to\infty}{\sim} \dfrac{1}{2y}\left(1+\dfrac{4}{3}xy\right)$
	$\mathcal{A}_{\text{opt}} \underset{x\to 0}{\sim} \dfrac{4y^3}{27(y-1)} - \dfrac{2y^3(2y-3)}{9(y-1)}x \underset{y\to\infty}{\sim} \dfrac{4}{27}y^2(1-3xy)$	$\mathcal{A}_{\text{opt}} \underset{x\to 0}{\sim} \dfrac{4y^3}{27(y-1)} - \dfrac{8y^3(2y-3)}{27(y-1)}x \underset{y\to\infty}{\sim} \dfrac{4}{27}y^2(1-4xy)$

Note: We performed the first order expansions of expressions in table 1 for $x \to 0$ and $y \to \infty$ ($x = \mu_1/K_1$ and $y = K_1/K_2$).

published mixing laws can be summed up as follows for a mixture of N phases having parameters K_i, β_i and γ_i and volume fractions c_i ($i = 1...N$) [53–55]

$$\frac{1}{K_{\text{eff}}} = \sum_{i=1}^{N} \frac{c_i}{K_i}, \tag{89}$$

$$\beta_{\text{eff}} = \sum_{i=1}^{N} c_i \frac{K_{\text{eff}}^2}{K_i^2}\beta_i, \tag{90}$$

$$\gamma_{\text{eff}} - 2\beta_{\text{eff}}\left(\beta_{\text{eff}} - 1\right) = \sum_{i=1}^{N} c_i \frac{K_{\text{eff}}^3}{K_i^3}\left[\gamma_i - 2\beta_i\left(\beta_i - 1\right)\right]. \tag{91}$$

Here, K_{eff}, β_{eff} and γ_{eff} are the requested effective parameters of the heterogeneous system. Firstly, we observe that equation (89), when written for two constituents, is perfectly coherent with equations (79) and (81) with $\mu_1 = 0$. Moreover, we prove that also the nonlinear results stated in equations (90) and (91) are coherent with our achievements when $x \to 0$. To do this we consider in equations (90) and (91) two phases ($N = 2$) with the assumptions $c_1 = 1 - c$ (matrix), $c_2 = c$ (inclusions), $\mathbb{B}_1 = 0$ and $\mathbb{C}_1 = 0$ (linear matrix). To directly check the expressions in table 2, we consider two separate cases: in the first one we have $\mathbb{B}_2 \neq 0$ and $\mathbb{C}_2 = 0$ and in second one we have $\mathbb{B}_2 = 0$ and $\mathbb{C}_2 \neq 0$. In the first case we may evaluate the second order amplification $\mathcal{A} = \beta_{\text{eff}}/\beta_2$ and we may search for the critical volume fraction defined by $\mathrm{d}\mathcal{A}/\mathrm{d}c = 0$. The explicit calculation allows us to obtain

$$c_{\text{opt}} = \frac{1}{y-1} \;\Rightarrow\; \mathcal{A}_{\text{opt}} = \frac{y^2}{4(y-1)}, \tag{92}$$

where $y = K_1/K_2$. Similarly, in the second case we determine the third order amplification $\mathcal{A} = \gamma_{\text{eff}}/\gamma_2$ and we evaluate for the critical volume fraction defined by $\mathrm{d}\mathcal{A}/\mathrm{d}c = 0$. As before, the explicit calculation allows us to obtain

$$c_{\text{opt}} = \frac{1}{2(y-1)} \;\Rightarrow\; \mathcal{A}_{\text{opt}} = \frac{4y^3}{27(y-1)}, \tag{93}$$

where, again, $y = K_1/K_2$. It is evident that equations (92) and (93) are in perfect agreement with results in table 2: equation (92) exactly corresponds to the case $g = 2$ with $x = 0$; equation (93) to the case $g = 3$ with $x = 0$. Under this respect, our achievements represent a generalization of earlier investigation, allowing for the possibility to take into account small values of x (see table 2) and also arbitrary values of x (see table 1). It is important to observe that the structures with $x = 0$, exhibiting a pure compressive behavior (without shear response) have the same effective parameters independently of the dimensionality d. Indeed, equations (92) and (93) are valid both for the dispersion of cylinders ($d = 2$) and for the dispersion of spheres ($d = 3$), as one can find in table 2. Another interesting comparison can be made between our results and others obtained to explain the anomalous elastic nonlinearity of microinhomogeneous media with a composite nonlinear spring [58]. This paradigmatic unidimensional model is indeed able to exactly and quantitatively reproduce the observed amplification phenomena for both the second and the third order of nonlinearity [58].

In table 2 we also reported the limiting results obtained for a large contrast y. This situation is important for the applications because it leads to the largest amplifications of the nonlinear properties. If we consider the pure compressive case ($x = 0$) with large y we can state the following general rules of broad interest for designing nonlinear materials with desired properties: given a large y, if we set the volume fraction $c_{\text{opt}} = 1/y$ we optimize the second order nonlinearity, obtaining an amplification $\mathcal{A}_{\text{opt}} = y/4$. Conversely, given a large y, if we set the volume fraction $c_{\text{opt}} = 1/(2y)$ we optimize the third order nonlinearity, obtaining an amplification $\mathcal{A}_{\text{opt}} = 4y^2/27$. In both cases, the optimal volume fraction is inversely proportional to y, being therefore very small and perfectly coherent with our initial assumption of dilute systems. Moreover, the nonlinear second order and third order amplifications are proportional to y and y^2, respectively, yielding strong intensifications of the nonlinearity when $K_1 \gg K_2$. In figure 3 one can find the summary of the main results reported in table 2: the typical amplification curves are shown for $x = 0$. The critical volume fractions and the largest nonlinearity intensifications are reported for both the second order and third order nonlinear response. Finally, the results for a small x ($x \neq 0$) and a large y are reported in table 2 in order to consider organic materials where the shear behavior is weak but not completely negligible.

Another application of the results in table 1 deals with actual elastic materials where both the shear and the bulk

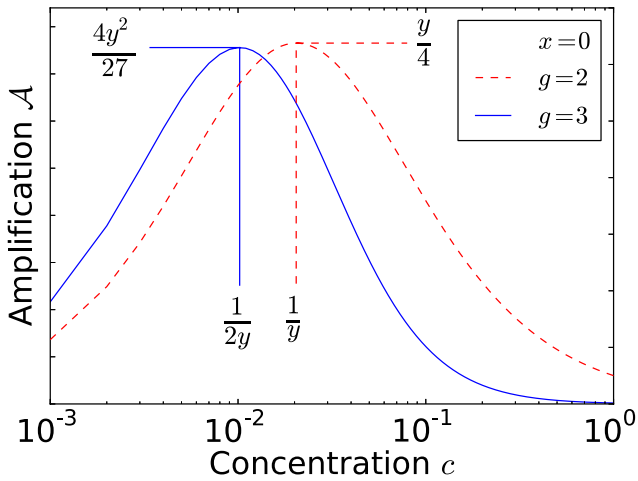

Figure 3. Typical curves showing the behavior of the amplification versus the volume fraction for the case with $x = 0$, as described in table 2 (continuous line for $g = 3$ and dashed line for $g = 2$). The critical concentrations and the corresponding amplification peaks are shown for large values of the contrast y. Since $x = 0$, the results are valid for both the two-dimensional and the three-dimensional structures.

behavior can be controlled. In this case we may try to further optimize the expressions of $\mathcal{A}_{\rm opt}(x, y)$ by identifying a relation between x and y leading to the largest nonlinearity intensification. It means that we can study the equation $\partial\mathcal{A}_{\rm opt}(x, y)/\partial y = 0$, where the amplification $\mathcal{A}_{\rm opt}(x, y)$ is taken from table 1. The results of this additional optimization are reported in table 3. It is interesting to note that the optimal value x^* of x, characterizing the linear response of the matrix, can be directly linked to the compressibility contrast y. Moreover these relations are very simple for large contrast y, allowing for easy practical applications. Once the value of x^* is determined, we can also evaluate the corresponding value of volume fraction and nonlinearity amplification, as shown in table 3. As in the case with $x = 0$ previously studied, the optimal volume fraction is inversely proportional to y, being again coherent with the assumption of dilute mixtures. In addition, the nonlinear second order and third order amplifications are proportional, as before, to y and y^2, respectively. This procedure is useful when the matrix elastic response or the linear elasticity of the particles can be arbitrarily modulated (we can think to a composite material for the matrix or the particles, leading to a hierarchical heterogeneous structure analysed through a multiscale homogenization scheme). In figure 4 one can find the summary of the main results reported in table 3: the amplification curves are shown for the case of the optimized value x^* of x. The critical volume fractions and the largest nonlinearity intensifications are reported for both the second order and third order nonlinear response.

7. An example of application

We consider in this section an example of application of the optimization procedures previously described. We propose a composite structure based on a PDMS (polydimethylsiloxane or dimethicone) matrix with a population of porous polymer particles. The PDMS matrix is characterized by a density $\rho = 970\,\mathrm{Kg\,m^{-3}}$, an acoustic longitudinal velocity $v_l = 1100\,\mathrm{m\,s^{-1}}$ and a transversal velocity $v_t = 110\,\mathrm{m\,s^{-1}}$. We can therefore obtain the linear elastic constants $K_1 = 1.15\,\mathrm{GPa}$ and $\mu_1 = 11.7\,\mathrm{MPa}$ [59, 60]. We underline that the acoustic transverse velocity in PDMS varies in literature in a quite large spectrum of values. Nevertheless, the important point is that the relation $v_t \ll v_l$ is always satisfied [11, 61]. Importantly, we observe that previous moduli correspond to $x \simeq 1/100$, a sufficiently small value, precisely as requested by the above optimization procedures. On the other hand, we need for the particles a material which allows the possibility of tuning their linear properties, in order to fulfil the optimal criteria summed up in table 3. In particular, we need to control the bulk modulus K_2 in order to have $K_2 \simeq K_1/100$ (or $y \simeq 100$). More specifically, we should obtain $y = 1/x$ for $d = 2$ and $g = 2$, $y = 2/x$ for $d = 2$ and $g = 3$, $y = 3/(4x)$ for $d = 3$ and $g = 2$ and, finally $y = 3/(2x)$ for $d = 3$ and $g = 3$, as reported in table 3. For these reasons, we could exploit the properties offered by silica aerogels [62], exhibiting a very low sound speed $<100\,\mathrm{m\,s^{-1}}$, or porous polymer materials [63–65], which can be synthesized with a varying volume fraction of pores. These materials have been recently proposed for realizing soft acoustic metamaterials with negative-valued effective parameters [12]. Here, we choose to work with highly porous polymers since, with these microstructures, it is possible to fabricate micrometer-sized particles of both spherical and rod-like shape, matching perfectly our theoretical analysis (see figure 5 for details). In table 4 one can find the properties of the PDMS matrix compared with the acoustic response of some bulk polymers [67]. We suppose to fabricate highly porous polymeric particles by means of an ideal bulk polymer characterized by $\rho_{\rm m} = 1000\,\mathrm{Kg\,m^{-3}}$, $v_{l,m} = 2000\,\mathrm{m\,s^{-1}}$ and $v_{t,m} = 1000\,\mathrm{m\,s^{-1}}$, a set of parameters paradigmatically representing the real polymers shown in table 4. The corresponding elastic properties are $K_{\rm m} = 2.6\,\mathrm{GPa}$ and $\mu_{\rm m} = 1\,\mathrm{GPa}$ (or $E_{\rm m} = 2.6\,\mathrm{GPa}$ and $\nu_{\rm m} = 0.33$ in terms of Young modulus and Poisson ratio). Since we deal with highly porous polymers fabricated through the high internal phase emulsion (HIPE) technique [63–65], for analysing their elastic properties we need an homogenization scheme able to consider not diluted mixtures with high volume fractions of the dispersed phase. To this aim, one of the most used methodology is the differential effective medium theory [31], which provides the following results for the case of a porous structure with spherical voids

$$1-\phi = \left(\frac{1-5\nu_2}{1-5\nu_{\rm m}}\right)^{\frac{5}{6}}\left(\frac{1-5\nu_{\rm m}}{1-5\nu_2}\right)^{\frac{1}{6}}\left(\frac{1+\nu_{\rm m}}{1-\nu_2}\right)^{\frac{2}{3}}, \quad (94)$$

$$E_2 = E_{\rm m}\left(\frac{1-5\nu_2}{1-5\nu_{\rm m}}\right)^{\frac{5}{3}}\left(\frac{1+\nu_{\rm m}}{1-\nu_2}\right)^{\frac{2}{3}}. \quad (95)$$

Here $E_{\rm m}$ and $\nu_{\rm m}$ are the Young modulus and Poisson ratio of the bulk polymer, E_2 and ν_2 are the Young modulus and Poisson ratio of the final porous polymer and ϕ is the porosity (volume fraction of pores) varying in the entire range $0 < \phi < 1$. The application of this scheme to our case yields the results reported

Table 3. Optimization of results shown in table 1 with respect to the linear matrix response x.

$x>0$	$d=2$	$d=3$
	$\frac{\partial \mathcal{A}_{\rm opt}}{\partial y}=0 \Rightarrow x^*=\frac{y-2}{y^2} \underset{y\to\infty}{\sim} \frac{1}{y}$	$\frac{\partial \mathcal{A}_{\rm opt}}{\partial y}=0 \Rightarrow x^*=\frac{3(y-2)}{4y^2} \underset{y\to\infty}{\sim} \frac{3}{4y}$
$g=2$	$c_{\rm opt}(x^*) \underset{y\to\infty}{\sim} \frac{2}{y}$	$c_{\rm opt}(x^*) \underset{y\to\infty}{\sim} \frac{2}{y}$
	$\mathcal{A}_{\rm opt}(x^*) \underset{y\to\infty}{\sim} \frac{1}{16}y$	$\mathcal{A}_{\rm opt}(x^*) \underset{y\to\infty}{\sim} \frac{1}{16}y$
	$\frac{\partial \mathcal{A}_{\rm opt}}{\partial y}=0 \Rightarrow x^*=\frac{2y-3}{y^2} \underset{y\to\infty}{\sim} \frac{2}{y}$	$\frac{\partial \mathcal{A}_{\rm opt}}{\partial y}=0 \Rightarrow x^*=\frac{3(2y-3)}{4y^2} \underset{y\to\infty}{\sim} \frac{3}{2y}$
$g=3$	$c_{\rm opt}(x^*) \underset{y\to\infty}{\sim} \frac{3}{2y}$	$c_{\rm opt}(x^*) \underset{y\to\infty}{\sim} \frac{3}{2y}$
	$\mathcal{A}_{\rm opt}(x^*) \underset{y\to\infty}{\sim} \frac{4}{729}y^2$	$\mathcal{A}_{\rm opt}(x^*) \underset{y\to\infty}{\sim} \frac{4}{729}y^2$

Note: Once determined the critical value x^*, we calculated the corresponding volume fraction and nonlinear amplification for all the cases with $g=2,3$ and $d=2,3$ ($x=\mu_1/K_1$ and $y=K_1/K_2$).

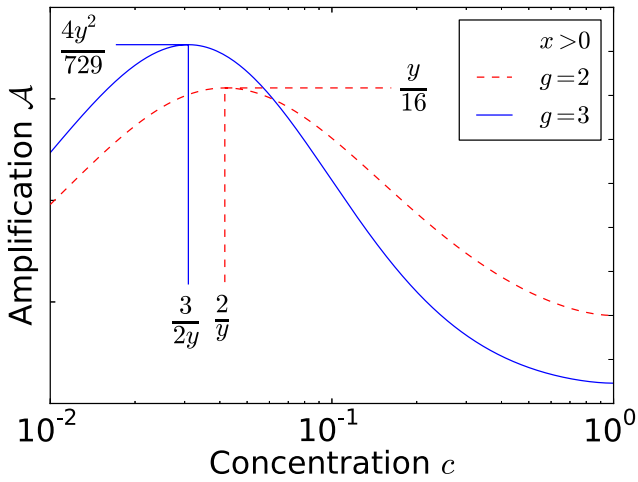

Figure 4. Typical curves showing the behavior of the amplification versus the volume fraction for the case with the optimized value of x, as described in table 3 (continuous line for $g=3$ and dashed line for $g=2$). The critical concentrations and the corresponding amplification peaks are shown for large values of the contrast y. For two-dimensional structures we considered $x^*=1/y$ for the second order nonlinearity and $x^*=2/y$ for the third order nonlinearity. On the other hand, for three-dimensional structures we considered $x^*=3/(4y)$ for the second order nonlinearity and $x^*=3/(2y)$ for the third order nonlinearity.

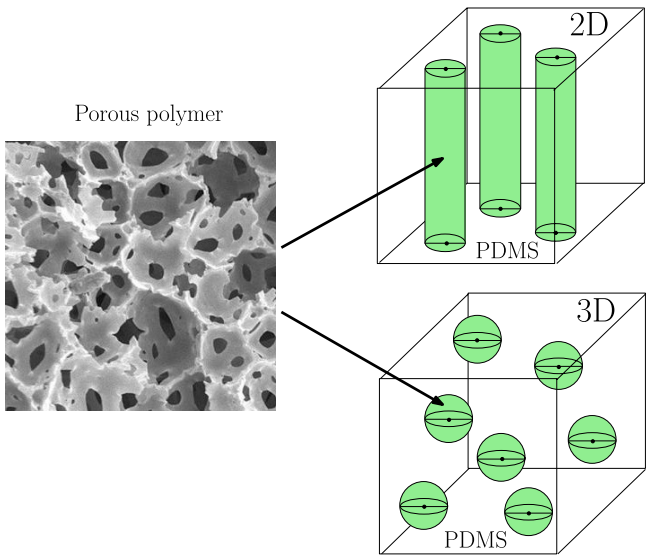

Figure 5. Composite structures analysed with the proposed homogenization schemes. The porous polymer image is adapted from http://matwww.technion.ac.il/Silverstein/HIPE.html and [66].

Table 4. Acoustic properties of the PDMS (which is a largely used silicon-based organic polymer, here adopted as matrix in our composite structure) and of several bulk polymers [67] (which can be used to fabricate highly porous polymeric particles).

Bulk polymer	ρ (Kg m^{-3})	v_l (m s^{-1})	v_t (m s^{-1})
PDMS	970	1100	110
Polystyrene	1052	2400	1150
Polypropylene	913	2650	1300
Polymethylmethacrylate	1191	2690	1344
Polyethylene	957	2430	946
Polyoxymethylene	1425	2440	1000

in figure 6, where $\log_{10} K_2$ and $\log_{10} \mu_2$ (corresponding to E_2 and ν_2 calculated through equations (94) and (95)) are shown versus the porosity ϕ. Importantly, we observe that we get $K_2 \simeq 11.5$ MPa or, equivalently, $y \simeq 100$ when ϕ is in the range $0.85 < \phi < 0.95$, a value of porosity in perfect agreement with the HIPE technique [63–65].

We now consider the whole system composed of inclusions of a porous polymer in the PDMS matrix. To begin, we suppose to work with the 3D geometry. We use the general result stated in equation (77) to prove that we can obtain the nonlinear amplifications described in table 3. In order to optimize the second order nonlinearity (described by C) we have to impose $y=3/(4x) \simeq 74$; the above analysis yields therefore a porosity $\phi \simeq 0.89$ for the porous polymer. The final result is represented by the dashed (red) curve in figure 7.

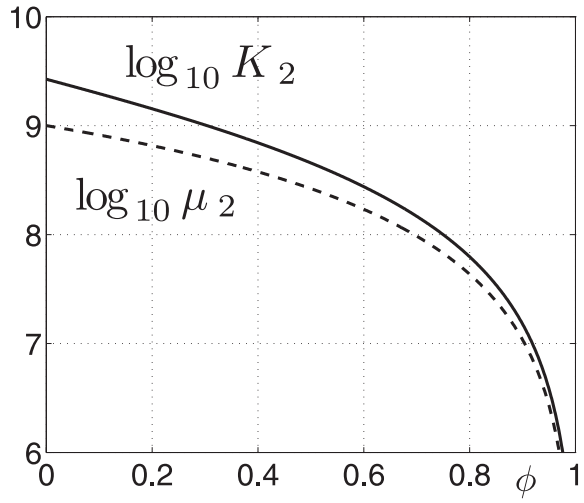

Figure 6. Linear elastic constants μ_2 and K_2 of the porous polymer versus the polymer porosity ϕ obtained through equations (94) and (95).

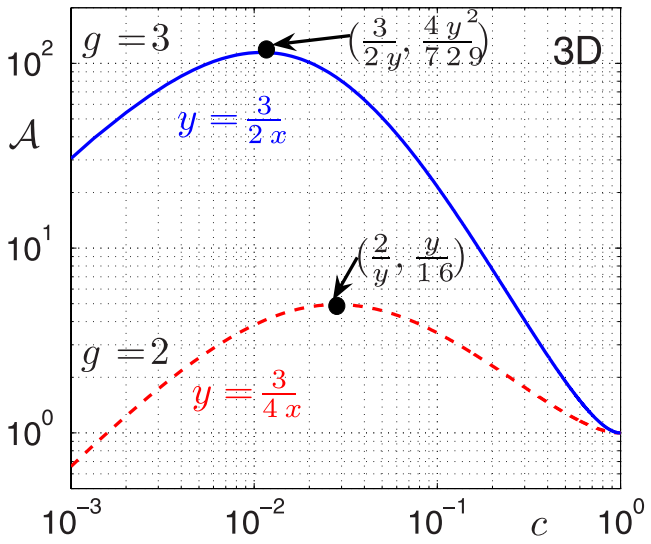

Figure 7. Amplification of the nonlinear elastic constants versus the volume fraction c for the three-dimensional structure.

On the other hand, to optimize the third order nonlinearity (H) we need $y = 3/(2x) \simeq 148$, leading to $\phi \simeq 0.92$. In this situation, the intensification is represented in figure 7 by the continuous (blue) curve. In both cases, it is not difficult to identify the maximum points, exactly corresponding to the results reported in table 3.

We consider now the two-dimensional geometry described by the general result stated in equation (63). For optimizing the second order nonlinearity (described by f) we impose $y = 1/x \simeq 97$ corresponding to a porosity $\phi \simeq 0.92$ for the porous polymer. The result is represented by the dashed (red) curve in figure 8. Conversely, to optimize the third order nonlinearity (h) we need $y = 2/x \simeq 196$, leading to $\phi \simeq 0.94$. Accordingly, the intensification is shown in figure 8 by the continuous (blue) curve. As before, in both cases, it is not difficult to identify the maximum points which exactly correspond to the results in table 3.

We underline that the amplification results for the second order nonlinearities C and f (red dashed lines in figures 7 and 8) are not influenced by the presence of a third order nonlinearity (H or h, respectively) within the particles. Therefore, the corresponding results are always correct, independently on the values of H and h adopted for the porous polymer. Differently, the amplification of the third order nonlinearities H or h may be influenced by the values of C and f within the particles. The results for the third order amplifications (blue continuous lines) in figures 7 and 8 have been obtained when $C = 0$ and $f = 0$, coherently with the conclusions in table 3. Nevertheless, it is important to further analyse the possible effects of C or f on the third order amplifications. Based on the complete homogenization scheme summed up in equation (63) (2D geometry) or in equation (77) (3D geometry), we can study the combined effects of the two nonlinearities. In figure 9 (3D geometry) and figure 10 (2D geometry) we show the third order amplification for an increasing value of the second order nonlinearity. More specifically, for the 3D geometry we fixed $H = 100K_2$ and we considered $C = 5jK_2$, where j varies from 1 to 10. Since typical values of C and H are given by $C \simeq 10K_2$ and $H \simeq 100K_2$, it follows from figure 9 that the nonlinear third order amplification is only slightly modified by the standard (rather small) values of the second order nonlinearity. However, we remark that larger values of C completely modify the nonlinear scenario, leading to a significant negative amplification of H, which can be exploited when $C \gtrsim 40K_2$. With regard to the 2D geometry, in figure 10 we fixed $h = 100K_2$ and we considered $f = jK_2$, where j varies from 1 to 10. In this case, the results given by the continuous blue curves in figures 8 and 10 (response with $f = 0$) may be sensibly modified also for small values of f and, as before, we can obtain a negative amplification for increasing values of f. To conclude, we can affirm that the third order amplification in two-dimensional structures is much more sensible to the second order nonlinearities than the three-dimensional geometry. This point should be thoroughly taken into consideration to properly design composite structures with a tuned nonlinear response.

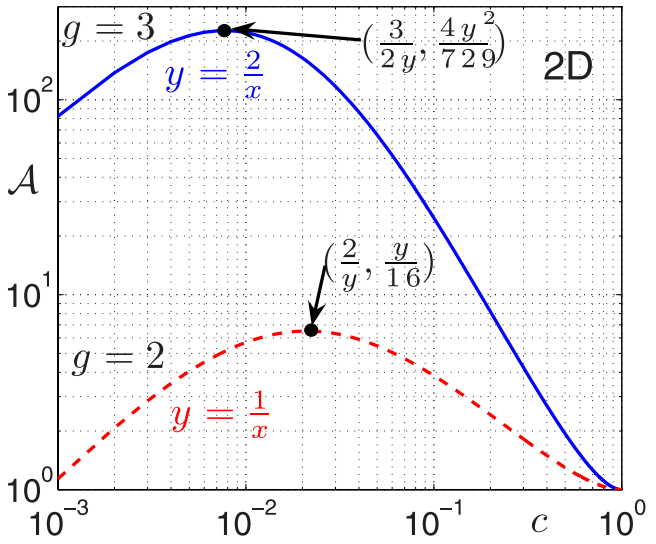

Figure 8. Amplification of the nonlinear elastic constants versus the volume fraction c for the two-dimensional structure.

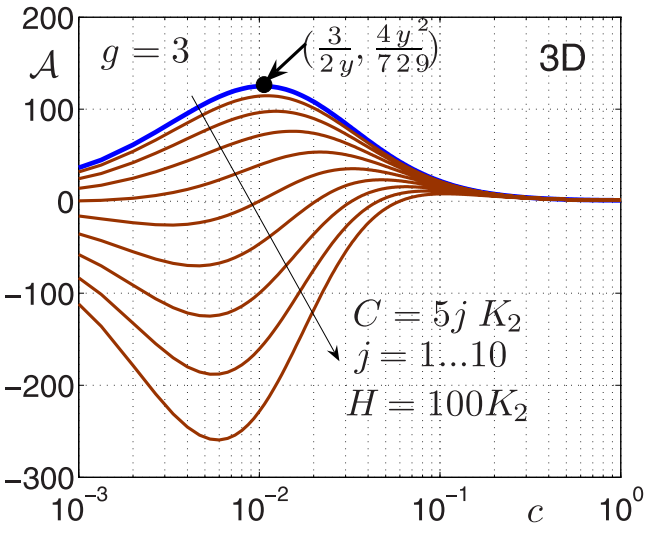

Figure 9. Effects of the second order nonlinear modulus C on the third order nonlinear amplification $\mathcal{A}$ of H. We obtain the result of figure 7 for small values of C (blue line) and a progressive deviation for larger values of C (brown lines).

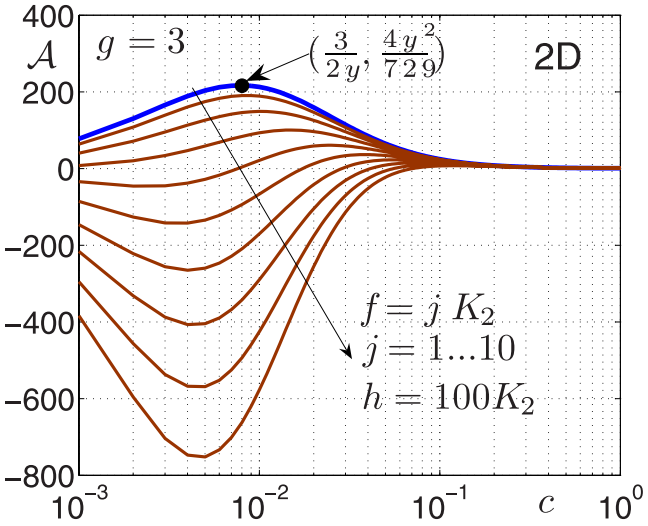

Figure 10. Effects of the second order nonlinear modulus f on the third order nonlinear amplification $\mathcal{A}$ of h. We obtain the result of figure 8 for small values of f (blue line) and a progressive deviation for larger values of f (brown lines).

8. Conclusions

Motivated by the necessity of nonlinear acoustic materials for developing acoustic diodes and other functionalities that can be implemented in specific nonlinear metamaterials, we elaborated a homogenization theory for linear and nonlinear elastic properties of heterogeneous particulate materials. In particular, we analysed dilute dispersions of nonlinear particles with constitutive equations expanded up to the third order in the elastic strain. Firstly, we obtained a general procedure for determining both the second and the third order nonlinear response of the overall composite structure. Secondly, we used these results to optimize a desired nonlinear response in terms of the mixture features, i.e. the volume fraction of the dispersed particles and the elastic/acoustic moduli of the constituents. We proved that, for a matrix composed of gels or biological materials with negligible shear response and for a large matrix to particles compressibility contrast, we can optimize the volume fraction in order to obtain a large amplification of the nonlinear response (see table 2 for details). Moreover, we also proved that a further optimization can be performed when the shear response of the matrix is finite (solid matrix) and we obtained simple relations allowing for the precise tailoring of the effective nonlinear properties of the mixture (see table 3 for details). The optimal criterion involves the linear properties of the matrix and the particles and, therefore, it can be fulfilled, e.g. by introducing a composite structure for the matrix or the particles themselves. An example of application is proposed concerning a dilute dispersion of porous polymer particles embedded in a PDMS matrix. In order to fulfil the optimal criterion above, we can modulate the linear response of the porous polymer particles through the porosity, a parameter that can be accurately controlled during the synthesis.

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