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Homogenization-based constitutive models for porous elastomers and implications for macroscopic instabilities: I—Analysis

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Abstract

The purpose of this paper is to provide homogenization-based constitutive models for the overall, finite-deformation response of isotropic porous rubbers with *random* microstructures. The proposed model is generated by means of the "second-order" homogenization method, which makes use of suitably designed variational principles utilizing the idea of a "linear comparison composite." The constitutive model takes into account the evolution of the size, shape, orientation, and distribution of the underlying pores in the material, resulting from the finite changes in geometry that are induced by the applied loading. This point is key, as the evolution of the microstructure provides *geometric* softening/stiffening mechanisms that can have a very significant effect on the overall behavior and stability of porous rubbers. In this work, explicit results are generated for porous elastomers with isotropic, (in)compressible, strongly elliptic matrix phases. In spite of the strong ellipticity of the matrix phases, the derived constitutive model may lose strong ellipticity, indicating the possible development of shear/compaction band-type instabilities. The general model developed in this paper will be applied in Part II of this work to a special, but representative, class of isotropic porous elastomers with the objective of exploring the complex interplay between *geometric* and *constitutive* softening/stiffening in these materials.

Keywords: Constitutive behavior; Finite strain; Microstructures; Porous material; Soft matter

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1. Introduction

Porous elastomers are of considerable technological interest. They enjoy a wide range of applications which include packaging, cushioning, energy absorbtion, noise abatement, etc. In numerous situations, these materials are subjected to large deformations. It is, therefore, of practical interest to develop constitutive models for the mechanical behavior of porous elastomers under such loading conditions. Ideally, these models should be accurate and at the same time relatively simple, so that they are amenable to direct implementation into standard finite element packages for solving structural problems of interest. This presents a substantial challenge, as the mechanical behavior of porous elastomers is known to depend critically on their underlying microstructure, which is by and large rather complex. Indeed, more often than not, the distribution of pores in these materials is *random*. Also, depending on the specific application, porous elastomers may be open or closed cell, and may contain levels of porosity that range from very small to very large. In this connection, ever since the pioneering work of Gent and Thomas (1959), there have been numerous contributions concerning the modeling of the mechanical behavior of high-porosity elastomers (or low-density foams) under large deformations (see, for instance, the monograph by Gibson and Ashby, 1997). In contrast, the study of porous elastomers with low to moderate levels of porosity has not been pursued to nearly the same extent. The objective of this paper pertains precisely to the development of a constitutive model for this latter class of materials. More specifically, attention will focused on porous elastomers consisting of a *random* and *isotropic* distribution of polydisperse pores (in the undeformed configuration) in an isotropic, elastomeric matrix phase.

In terms of prior work, various attempts have been made using different methods. *Phenomenological* approaches include, for instance, the model of Blatz and Ko (1962), which was motivated by experimental work on polyurethane rubber with a random and isotropic distribution of pores of about 40 μm in diameter and an approximate volume fraction of about 50%. The predictive capabilities of this model for the response of actual porous elastomers is limited. However, the Blatz–Ko material does have a very appealing physical property: it loses strong ellipticity at sufficiently large compressive deformations (Knowles and Sternberg, 1975). This property is in agreement with physical evidence suggesting that porous elastomers can develop macroscopic bands of *strain localization* at sufficiently large deformations, which could correspond, for example, to buckling of the matrix ligaments at the micro-scale (see, e.g., Kinney et al., 2001; Gong and Kyriakides, 2005). *Homogenization-based* approaches include the microstructure-independent Voigt-type bound (Ogden, 1978), some rigorous estimates for special microstructures and loading conditions (Hashin, 1985), and various *ad hoc* approximations (Feng and Christensen, 1982). There is also a recently proposed estimate by Danielsson et al. (2004) for isotropic porous elastomers with incompressible, isotropic matrix phases. In fact, this estimate—as it will be discussed in Part II (Lopez-Pamies and Ponte Castañeda, 2007) of this work—can be shown to be a rigorous *upper bound* for porous elastomers with incompressible matrix phases and the *composite sphere assemblage* (CSA) microstructure (Hashin, 1962). Admittedly a very special class of microstructure, the CSA can be considered as a fair approximation to the type of microstructures of interest in this work, namely, random and isotropic distribution of polydisperse pores in an elastomeric matrix phase.

In this work, we make use of the second-order homogenization theory, originally developed by Ponte Castañeda (2002) for viscoplastic materials, and extended recently for general hyperelastic composites by Lopez-Pamies and Ponte Castañeda (2006a). This technique has the capability to incorporate statistical information about the microstructure beyond the volume fraction of the phases and can be applied to large classes of elastomeric composites (Lopez-Pamies and Ponte Castañeda, 2006a, b). In particular, Lopez-Pamies and Ponte Castañeda (2004) have previously developed second-order estimates for the effective stored-energy function of two-dimensional (2D) model porous systems consisting of elastomers weakened by an isotropic distribution (in the transverse plane) of aligned cylindrical pores with initially circular cross section, and subjected to in-plane loading. Interestingly, these estimates—which account approximately for the change in size, shape, and orientation of the pores that are induced by the finite deformations—admit loss of strong ellipticity at sufficiently large compressive deformations (even when specialized to *strongly elliptic* matrix phases). Furthermore, these analytical results were found to be in qualitative agreement with previous *numerical* results obtained by Abeyaratne and Triantafyllidis (1984) for 2D porous materials consisting of *periodically* arranged, aligned, cylindrical holes of initially circular cross section. Motivated by these findings, Michel et al. (2007) have recently conducted a combined *numerical* and *analytical* study of the influence of the underlying microstructure on the development of *microscopic* and *macroscopic* instabilities in 2D porous elastomers under finite deformations. These investigations have shown that the second-order theory can deliver accurate estimates not only for the macroscopic constitutive behavior, but also for the more sensitive information on the possible development of macroscopic instabilities in porous elastomers with periodic microstructures. These encouraging results for 2D microstructures strongly suggest that the second-order theory should also be able to deliver accurate estimates for the effective behavior, as well as for the onset of macroscopic instabilities, of porous elastomers with the three-dimensional (3D), random microstructures of interest in this work. In this connection, it should be remarked that while for 3D periodic microstructures estimates can be obtained *numerically*, for the random case this approach would be exceedingly intensive from a computational point of view, and the *analytical* approach proposed here—though approximate—is perhaps more appropriate.

This paper is organized as follows. Section 2 provides a review of basic results for the macroscopic and microscopic response of porous hyperelastic composites. Section 3 presents the specialization of the second-order theory to the above-defined general class of porous elastomers, including a subsection on evolution of microstructure for these systems. Section 4 describes the further specialization to porous elastomers with ‘‘generalized Neo-Hookean’’ behavior for the matrix phase, as defined by relation (22). The main results are contained in Eqs. (23) and (26) for compressible and incompressible matrix phases, respectively. The derivation of these results is provided in Appendices B and C. Finally, some general conclusions are drawn in Section 5.

2. Preliminaries on porous hyperelastic composites

Consider a porous material made up of initially *spherical* voids distributed *randomly* in an elastomeric matrix.[1] A specimen of this material is assumed to occupy a volume Ω_0, with boundary $\partial\Omega_0$, in the undeformed configuration and to be such that the characteristic

[1]These idealizations constitute a good approximation to the actual microstructures found in a wide range of porous elastomeric systems.

length of the underlying pores is much smaller than the size of the specimen and the scale of variation of the applied loading.

The constitutive behavior for the matrix phase is characterized by a stored-energy function $W^{(1)}$ that is a *non-convex* function of the deformation gradient tensor $\mathbf{F}$. The porous phase is characterized by the stored-energy function $W^{(2)}=0$. Thus, the *local* stored-energy function for the porous elastomer may be written as

$$W(\mathbf{X};\mathbf{F})=\chi_0^{(1)}(\mathbf{X})W^{(1)}(\mathbf{F})+\chi_0^{(2)}(\mathbf{X})W^{(2)}(\mathbf{F})=\chi_0^{(1)}(\mathbf{X})W^{(1)}(\mathbf{F}), \tag{1}$$

where the characteristic function $\chi_0^{(1)}$ $(\chi_0^{(2)})$, which takes the value of one if the position vector $\mathbf{X}$ is inside the matrix (porous) phase and zero otherwise, serves to characterize the microstructure of the material in the undeformed configuration. Note that, in view of the assumed random distribution of the pores, the dependence of $\chi_0^{(1)}$ on $\mathbf{X}$ is not known precisely, and the microstructure is only partially defined in terms of its n-point statistics. In this work, use will be made of one- and two-point statistics, as detailed further below. The stored-energy function $W^{(1)}$ is, of course, taken to be objective, in the sense that $W^{(1)}(\mathbf{QF})=W^{(1)}(\mathbf{F})$ for all proper orthogonal, second-order tensors $\mathbf{Q}$ and all deformation gradients $\mathbf{F}$. Making use of the right polar decomposition $\mathbf{F}=\mathbf{R}\,\mathbf{U}$, where $\mathbf{R}$ is the macroscopic rotation tensor and $\mathbf{U}$ denotes the right stretch tensor, it follows, in particular, that $W^{(1)}(\mathbf{F})=W^{(1)}(\mathbf{U})$. Moreover, to try to ensure material impenetrability, $W^{(1)}$ is assumed to satisfy the condition: $W^{(1)}(\mathbf{F})\to\infty$ as $\det\mathbf{F}\to 0+$. The local constitutive relation for the porous elastomer is given by

$$\mathbf{S}=\frac{\partial W}{\partial \mathbf{F}}(\mathbf{X};\mathbf{F}), \tag{2}$$

where $\mathbf{S}$ denotes the first Piola–Kirchhoff stress tensor and sufficient smoothness has been assumed for W on $\mathbf{F}$.

Under the hypotheses of *statistical uniformity*, and the above-mentioned *separation of length scales*, it follows (Hill, 1972) that the *global* constitutive relation for the porous elastomer is given by

$$\overline{\mathbf{S}}=\frac{\partial \widetilde{W}}{\partial \overline{\mathbf{F}}}, \tag{3}$$

where $\overline{\mathbf{S}}=\langle\mathbf{S}\rangle$, $\overline{\mathbf{F}}=\langle\mathbf{F}\rangle$ are the *average stress* and *average deformation gradient*, respectively, and

$$\widetilde{W}(\overline{\mathbf{F}})=\min_{\mathbf{F}\in\mathscr{K}(\overline{\mathbf{F}})}\langle W(\mathbf{X};\mathbf{F})\rangle=\min_{\mathbf{F}\in\mathscr{K}(\overline{\mathbf{F}})} c_0^{(1)}\langle W^{(1)}(\mathbf{F})\rangle^{(1)} \tag{4}$$

is the *effective stored-energy function* of the composite. In the above expressions the triangular brackets $\langle\cdot\rangle$ and $\langle\cdot\rangle^{(1)}$ denote, respectively, volume averages—in the undeformed configuration—over the specimen (Ω_0) and the matrix phase $(\Omega_0^{(1)})$, so that the scalar $c_0^{(1)}=\langle\chi_0^{(1)}\rangle$ corresponds to the volume fraction of the elastomeric phase in the undeformed configuration. Furthermore, $\mathscr{K}$ denotes the set of kinematically admissible deformation gradients:

$$\mathscr{K}(\overline{\mathbf{F}})=\{\mathbf{F}\,|\,\exists\mathbf{x}=\mathbf{x}(\mathbf{X})\text{ with }\mathbf{F}=\text{Grad}\,\mathbf{x}\text{ in }\Omega_0,\ \mathbf{x}=\overline{\mathbf{F}}\mathbf{X}\text{ on }\partial\Omega_0\}. \tag{5}$$

Note that $\widetilde{W}$ represents the average elastic energy stored in the porous elastomer when subjected to an affine displacement boundary condition that is consistent with $\langle\mathbf{F}\rangle=\overline{\mathbf{F}}$.

Moreover, from definition (4) and the objectivity of $W^{(1)}$, it can be shown that $\widetilde{W}$ is an objective scalar function of $\overline{\mathbf{F}}$, and hence such that $\widetilde{W}(\overline{\mathbf{F}}) = \widetilde{W}(\overline{\mathbf{U}})$. Here, $\overline{\mathbf{U}}$ is the macroscopic right stretch tensor associated with the right polar decomposition $\overline{\mathbf{F}} = \overline{\mathbf{R}}\,\overline{\mathbf{U}}$, with $\overline{\mathbf{R}}$ denoting the macroscopic rotation tensor. (Note that $\overline{\mathbf{U}} \neq \langle \mathbf{U} \rangle$ and $\overline{\mathbf{R}} \neq \langle \mathbf{R} \rangle$.) In turn, the objectivity of $\widetilde{W}$ guarantees the macroscopic rotational equilibrium: $\overline{\mathbf{S}}\,\overline{\mathbf{F}}^{\mathrm{T}} = \overline{\mathbf{F}}\,\overline{\mathbf{S}}^{\mathrm{T}}$ (Hill, 1972).

Because of the non-convexity of W on $\mathbf{F}$, the solution (assuming that it exists) of the Euler–Lagrange equations associated with the variational problem (4) need not be unique. Physically, this corresponds to the possible development of *instabilities* in the porous elastomer under sufficiently large deformations. At this stage, following Triantafyllidis and coworkers (see, e.g., Geymonat et al., 1993; Triantafyllidis et al., 2006; Michel et al., 2007), it is useful to make the distinction between "microscopic" instabilities, that is, instabilities with wavelengths that are small compared to the size of the specimen, and "macroscopic" instabilities, that is, instabilities with wavelengths comparable to the size of the specimen. The computation of "microscopic" instabilities is a very difficult problem, especially for the type of porous elastomers with *random* microstructures of interest in this work. On the other hand, as explained in more detail further below, the computation of "macroscopic" instabilities is relatively simple, since it amounts to detecting the loss of *strong ellipticity* of the effective stored-energy function of the composite (Geymonat et al., 1993). Hence, in view of the difficulties associated with the computation of "microscopic" instabilities, we do not attempt here to solve the minimization problem (4), but instead, we adopt a more pragmatic approach. By assuming—for consistency with the classical theory of linear elasticity—that $W^{(1)} = \frac{1}{2}\boldsymbol{\varepsilon} \cdot \mathbf{L}_{\text{lin}}\boldsymbol{\varepsilon} + o(\boldsymbol{\varepsilon}^3)$ as $\mathbf{F} \to \mathbf{I}$, where $\boldsymbol{\varepsilon}$ denotes the infinitesimal strain tensor and $\mathbf{L}_{\text{lin}}$ is a positive-definite, constant, fourth-order tensor, it is expected that, at least in a neighborhood of $\overline{\mathbf{F}} = \mathbf{I}$, the solution of the Euler–Lagrange equations associated with the variational problem (4) is unique, and gives the minimum energy. As the deformation progresses into the finite deformation regime, the composite may reach a point at which this "principal" solution bifurcates into lower energy solutions. This point corresponds to the onset of an *instability*, beyond which the applicability of the "principal" solution becomes questionable. However, it is still possible to extract useful information from the principal solution by computing the associated macroscopic instabilities from the loss of strong ellipticity of the homogenized behavior. In practice, this means that we will estimate the effective stored-energy function (4) by means of the stationary variational statement:

$$\widehat{W}(\overline{\mathbf{F}}) = \underset{\mathbf{F} \in \mathscr{K}(\overline{\mathbf{F}})}{\text{stat}} \; c_0^{(1)} \langle W^{(1)}(\mathbf{F}) \rangle^{(1)}, \tag{6}$$

where it is emphasized that the energy is evaluated at the above-described "principal" solution of the relevant Euler–Lagrange equations. From its definition, it is clear that $\widetilde{W}(\overline{\mathbf{F}}) = \widehat{W}(\overline{\mathbf{F}})$ from $\overline{\mathbf{F}} = \mathbf{I}$ all the way up to the onset of the first microscopic instability. Beyond the first microscopic instability $\widetilde{W}(\overline{\mathbf{F}}) \leqslant \widehat{W}(\overline{\mathbf{F}})$. The point is that, as already mentioned, while the computation of microscopic instabilities is difficult, it is relatively simple to estimate the onset of macroscopic instabilities from $\widehat{W}(\overline{\mathbf{F}})$. Furthermore, it is often the case (Geymonat et al., 1993) that the first instability is indeed a long wavelength instability, in which case, $\widetilde{W}(\overline{\mathbf{F}}) = \widehat{W}(\overline{\mathbf{F}})$ all the way up to the development of a macroscopic instability, as characterized by the loss of strong ellipticity of $\widehat{W}(\overline{\mathbf{F}})$. More generally, the first instability is of finite wavelength (i.e., small compared to the size of the specimen), but it so happens that the loss of strong ellipticity of $\widehat{W}(\overline{\mathbf{F}})$ defines a "failure surface" that bounds all other types of instabilities (Geymonat et al., 1993). In this case, the porous elastomer would become unstable before reaching the deformations at which $\widehat{W}(\overline{\mathbf{F}})$ loses strong ellipticity. Finally, it is appropriate to mention that the recent work by Michel et al. (2007) suggests that the macroscopic instabilities may be the more relevant ones for random, porous systems, since many of the microscopic instabilities in periodic systems tend to disappear as the periodicity of the microstructure is broken down.

We conclude this section by spelling out the condition of strong ellipticity for the effective stored-energy function (6), which will be used in the sequel to detect the development of macroscopic instabilities in porous elastomers. Thus, the homogenized porous elastomer characterized by $\widehat{W}$ is said to be strongly elliptic if and only if its associated acoustic tensor is positive definite, namely, if and only if

$$\widehat{K}_{ik}m_i m_k = \widehat{\mathscr{L}}_{ijkl}N_j N_l m_i m_k > 0 \tag{7}$$

is satisfied for all $\mathbf{m} \otimes \mathbf{N} \neq \mathbf{0}$. Here, $\widehat{K}_{ik} = \widehat{\mathscr{L}}_{ijkl}N_j N_l$ is the effective acoustic tensor, and $\widehat{\mathscr{L}} = \partial^2 \widehat{W}/\partial \overline{\mathbf{F}}^2$ is the effective incremental elastic modulus characterizing the overall incremental response of the porous elastomer.

Note that, in general, the detection of loss of strong ellipticity requires a tedious, but straightforward, scanning process (i.e., a numerical search of unit vectors $\mathbf{N}$ and $\mathbf{m}$ for which condition (7) ceases to hold true). However, for certain special cases, it is possible to write *necessary* and *sufficient* conditions for the strong ellipticity of $\widehat{W}$ exclusively in terms of the material properties (i.e., in terms of the components of $\widehat{\mathscr{L}}$). This is the case, for instance, for the *isotropic* materials of interest in this paper. The corresponding conditions, first provided in three dimensions by Simpson and Spector (1983) (see also Zee and Sternberg, 1983; Dacorogna, 2001) are recalled in Appendix A for completeness.

3. Second-order estimates for isotropic porous elastomers

Following up on the preceding formulation, the main purpose of the present work is to generate an estimate for the effective stored-energy function (6) for isotropic porous elastomers consisting of a random and isotropic distribution of initially spherical pores in an isotropic, elastomeric matrix phase. A second aim is to provide estimates for the evolution of suitably identified microstructural variables, as well as to establish the development of macroscopic instabilities in these materials. This is accomplished here by means of the second-order homogenization method (Lopez-Pamies and Ponte Castañeda, 2006a). The main concept behind this method is the construction of suitable variational principles making use of the idea of a "linear comparison composite" (LCC) with the same microstructure as the hyperelastic composite (i.e., the same $\chi_0^{(1)}$). This homogenization technique has the distinguishing feature of being exact to second order in the heterogeneity contrast, and, as already remarked, can be applied to a large class of hyperelastic composites. In this section, we provide the key components of the theory needed to generate estimates for the type of porous elastomers of interest in this work. Furthermore, we identify the relevant microstructural variables and write down their evolution laws.

Thus, making use of the general results of Lopez-Pamies and Ponte Castañeda (2006a) for two-phase composites, an estimate for the effective stored-energy function $\widehat{W}$ for porous elastomers consisting of vacuous inclusions (i.e., $W^{(2)} = 0$), with given initial porosity $f_0(=1-c_0^{(1)})$, in a compressible isotropic matrix with stored-energy function $W^{(1)}=W$, may be generated in terms of a porous LCC with matrix phase characterized by

$$W_T(\mathbf{F}) = W(\overline{\mathbf{F}}) + \mathscr{S}(\overline{\mathbf{F}})\cdot(\mathbf{F}-\overline{\mathbf{F}}) + \tfrac{1}{2}(\mathbf{F}-\overline{\mathbf{F}})\cdot\mathbf{L}(\mathbf{F}-\overline{\mathbf{F}}), \tag{8}$$

and the same microstructure as the actual porous elastomer. In expression (8), $\mathscr{S}(\cdot)=\partial W(\cdot)/\partial\mathbf{F}$ and $\mathbf{L}$ is a constant, fourth-order tensor with major symmetry (but with no minor symmetry) to be specified further below. The corresponding effective stored-energy function for such LCC is given by (see, e.g., Lopez-Pamies and Ponte Castañeda, 2004):

$$\widehat{W}_T(\overline{\mathbf{F}}) = (1-f_0)W(\overline{\mathbf{F}}) + \tfrac{1}{2}\mathscr{S}(\overline{\mathbf{F}})\cdot\mathbf{M}[\widetilde{\mathbf{L}}-(1-f_0)\mathbf{L}]\mathbf{M}\mathscr{S}(\overline{\mathbf{F}}), \tag{9}$$

where $\mathbf{M}=\mathbf{L}^{-1}$, and $\widetilde{\mathbf{L}}$ is the effective modulus tensor of the LCC. After some simplification, the second-order estimate for the effective stored-energy function $\widehat{W}$ may finally be written as

$$\widehat{W}(\overline{\mathbf{F}}) = (1-f_0)[W(\hat{\mathbf{F}}^{(1)}) - \mathscr{S}(\overline{\mathbf{F}})\cdot(\hat{\mathbf{F}}^{(1)}-\overline{\mathbf{F}}^{(1)})], \tag{10}$$

where the variables $\hat{\mathbf{F}}^{(1)}$ and $\overline{\mathbf{F}}^{(1)}$ are functions—of the applied loading $\overline{\mathbf{F}}$, the material properties of the matrix phase, and the initial microstructure—that must be determined from the above-defined LCC. More specifically, $\overline{\mathbf{F}}^{(1)}$ corresponds to the average deformation gradient in the matrix phase of the LCC, and is given *explicitly* in terms of $\mathbf{L}$ by the expression:

$$\overline{\mathbf{F}}^{(1)} \equiv \langle\mathbf{F}\rangle^{(1)} = \overline{\mathbf{F}} + \frac{1}{1-f_0}\mathbf{M}(\widetilde{\mathbf{L}}-(1-f_0)\mathbf{L})\mathbf{M}\mathscr{S}(\overline{\mathbf{F}}). \tag{11}$$

On the other hand, the variable $\hat{\mathbf{F}}^{(1)}$ is defined by the "generalized secant" condition:

$$\mathscr{S}(\hat{\mathbf{F}}^{(1)}) - \mathscr{S}(\overline{\mathbf{F}}) = \mathbf{L}(\hat{\mathbf{F}}^{(1)}-\overline{\mathbf{F}}). \tag{12}$$

Note that estimate (10) for $\widehat{W}$ is now completely specified in terms of the modulus tensor $\mathbf{L}$ of the matrix phase of the LCC. From the general theory, this modulus tensor is obtained from a variational approximation for $\widehat{W}$, where the tensor $\mathbf{L}$ plays the role of trial field. The corresponding optimization with respect to $\mathbf{L}$ leads to conditions that involve the covariance tensor $\mathbf{C}_{\mathbf{F}}^{(1)} = \langle(\mathbf{F}-\langle\mathbf{F}\rangle^{(1)})\otimes(\mathbf{F}-\langle\mathbf{F}\rangle^{(1)})\rangle^{(1)}$ of the deformation field in the matrix phase of the LCC, as outlined next.

Following Lopez-Pamies and Ponte Castañeda (2006a), $\mathbf{L}$ can be shown to be of the form:

$$L_{ijkl} = \overline{Q}_{rm}\overline{Q}_{jn}\overline{Q}_{sp}\overline{Q}_{lq}\overline{R}_{ir}\overline{R}_{ks}L^*_{mnpq}, \tag{13}$$

where indicial notation has been used for clarity. (In the absence of explicit statements to the contrary, Latin indices range from 1 to 3, and the usual summation convention is employed.) In expression (13), $\overline{\mathbf{R}}$ is the rotation tensor in the polar decomposition of $\overline{\mathbf{F}}=\overline{\mathbf{R}}\,\overline{\mathbf{U}}$, and $\overline{\mathbf{Q}}$ is the proper-orthogonal, second-order tensor describing the orientation of the macroscopic Lagrangian principal axes (i.e., the principal axes of $\overline{\mathbf{U}}$) via the relation $\overline{\mathbf{U}}=\overline{\mathbf{Q}}\,\overline{\mathbf{D}}\,\overline{\mathbf{Q}}^{\mathrm{T}}$, where $\overline{\mathbf{D}}=\mathrm{diag}(\overline{\lambda}_1,\overline{\lambda}_2,\overline{\lambda}_3)$ relative to the frame of reference of choice and $\overline{\lambda}_i$ $(i=1,2,3)$ denote the principal stretches of $\overline{\mathbf{U}}$. Assuming that $\mathbf{L}^*$ is orthotropic relative to the laboratory frame of reference with *at most* nine independent principal components, denoted by ℓ^*_α $(\alpha=1,2,\ldots,9)$, the above-mentioned optimization procedure for determining $\mathbf{L}$ leads (Lopez-Pamies and Ponte Castañeda, 2006a) to the following conditions:

$$(\hat{\mathbf{F}}^{(1)} - \overline{\mathbf{F}}) \cdot \frac{\partial \mathbf{L}}{\partial \ell_\alpha^*} (\hat{\mathbf{F}}^{(1)} - \overline{\mathbf{F}}) = \frac{2}{1 - f_0} \frac{\partial \widehat{W}_T}{\partial \ell_\alpha^*} \quad (\alpha = 1, 2, \ldots, 9). \tag{14}$$

It is noted that this set of conditions for the parameters ℓ_α^* $(\alpha = 1, 2, \ldots, 9)$ involve the fluctuations of the deformation-gradient fields in the matrix phase of the LCC, as discussed in more detail in Lopez-Pamies and Ponte Castañeda (2006a).

In summary, Eqs. (12) and (14) reduce to a system of 18 nonlinear, coupled, algebraic equations for the 18 scalar unknowns formed by the nine components of $\hat{\mathbf{F}}^{(1)}$ and the nine components of $\mathbf{L}$ (i.e., the nine independent components ℓ_α^*). Upon computing the values of the variables ℓ_α^* and the components of $\hat{\mathbf{F}}^{(1)}$ for a given initial porosity f_0, given stored-energy function W, and given applied loading $\overline{\mathbf{F}}$, the values of the components of $\overline{\mathbf{F}}^{(1)}$ can be readily determined from (11). In turn, the second-order estimate (10) for the effective stored-energy function of porous elastomers may be computed from these results.

To conclude this section, it is expedient to point out that the above-defined second-order estimate (10) for the effective stored-energy function $\widehat{W}$ can be shown to be an *objective* and *isotropic* scalar function of the macroscopic deformation gradient $\overline{\mathbf{F}}$, in agreement with the exact result (see Lopez-Pamies and Ponte Castañeda, 2006a, for details). To be precise, estimate (10) is such that $\widehat{W}(\overline{\mathbf{K}}\,\overline{\mathbf{F}}\,\overline{\mathbf{K}}') = \widehat{W}(\overline{\mathbf{F}})$ for all proper orthogonal tensors $\overline{\mathbf{K}}$ and $\overline{\mathbf{K}}'$. Making contact with the decompositions $\overline{\mathbf{F}} = \overline{\mathbf{R}}\,\overline{\mathbf{U}}$ and $\overline{\mathbf{U}} = \overline{\mathbf{Q}}\,\overline{\mathbf{D}}\,\overline{\mathbf{Q}}^{\mathrm{T}}$ used in the context of expression (13), this implies that:

$$\widehat{W}(\overline{\mathbf{F}}) = \widehat{W}(\overline{\mathbf{R}}\,\overline{\mathbf{Q}}\,\overline{\mathbf{D}}\,\overline{\mathbf{Q}}^{\mathrm{T}}) = \widehat{W}(\overline{\mathbf{D}}) = \widehat{\Phi}(\overline{\lambda}_1, \overline{\lambda}_2, \overline{\lambda}_3), \tag{15}$$

where $\widehat{\Phi}$ is symmetric. A practical implication of (15) is that it suffices to restrict attention to *diagonal* pure stretch loadings in the above formulation. Namely, it suffices to consider:

$$\overline{\mathbf{F}} = \overline{\mathbf{D}} = \mathrm{diag}(\overline{\lambda}_1, \overline{\lambda}_2, \overline{\lambda}_3) \quad \text{and} \quad \overline{\mathbf{R}} = \overline{\mathbf{Q}} = \mathbf{I}. \tag{16}$$

3.1. Estimates for the LCC

The above framework allows the determination of $\widehat{W}$ in terms of the effective modulus tensor $\tilde{\mathbf{L}}$ of the LCC with the same microstructure as the actual nonlinear composite. In this work, as already stated, we are interested in porous elastomers where the pores are assumed to be initially spherical in shape, polydisperse, and to be randomly distributed with isotropic symmetry in the undeformed configuration. For this type of "particulate" microstructure, we make use of the following isotropic Hashin–Shtrikman (HS) estimate for the effective modulus tensor due to Willis (1977) (see also Walpole, 1966):

$$\widetilde{\mathbf{L}} = \mathbf{L} + f_0[(1 - f_0)\mathbf{P} - \mathbf{M}]^{-1}, \tag{17}$$

where the microstructural tensor $\mathbf{P}$ is given (in component form) by

$$P_{ijkl} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} (L_{imkn} \xi_m \xi_n)^{-1} \xi_j \xi_l \sin \Phi \, \mathrm{d}\Phi \, \mathrm{d}\Theta, \tag{18}$$

with $\xi_1 = \cos \Theta \sin \Phi$, $\xi_2 = \sin \Theta \sin \Phi$, $\xi_3 = \cos \Phi$. It is important to recall that for the special subclass of linear elastic composites with isotropic phases and the CSA microstructure, the HS-type estimate (17) is very accurate for all values of initial porosity

f_0. Further, for more general classes of microstructures, estimate (17) is known to be accurate for small to moderate initial porosities, and it may become inaccurate for large values of f_0, when the interactions among the pores become especially strong. Since the porosity, as well as the shape, orientation, and distribution of the voids, of a porous material can evolve as a function of finite loading histories, this has the practical implication that—in general—the second-order estimates of the HS type may become inaccurate once the porosity, or other relevant microstructural variables reach values approaching the percolation limit, as explained in detail in Lopez-Pamies (2006). However, it should be emphasized that the second-order estimates (10) could still be used in the high-porosity range, provided that a more refined estimate was used for the LCC.

3.2. The evolution of microstructure

The above-outlined characterization of the behavior of porous elastomers has been carried out in the context of a Lagrangian description of the kinematics. This means that the stationary solution in expression (6) for the effective stored-energy function of porous elastomers contains implicitly all the necessary information to characterize how every single material point in the specimen moves, and therefore, also how the microstructure evolves, with the applied loading. In this subsection, we outline how to extract information from the above formulation in order to characterize the evolution of suitably selected microstructural variables. Knowledge of the evolution of such variables will provide us with the means to develop a better understanding of the mechanical behavior of porous elastomers.

First, there is the notion that the evolution of the size, shape, and orientation of the pores should be governed—on average—by the average deformation gradient in the porous phase $\overline{\mathbf{F}}^{(2)}$. Thus, the relevant microstructural variables characterizing the size, shape, and orientation of the pores are identified here as the volume fraction, f, the average aspect ratios, ω_1, ω_2, and the average orientation of the pores, ϕ_1, ϕ_2, ϕ_3, as determined by $\overline{\mathbf{F}}^{(2)}$. In this regard, it is important to note that within the context of the second-order estimates (10), with the HS-type approximation (17) for the effective behavior of the associated LCC, the deformation gradient field $\mathbf{F}(\mathbf{X})$ inside the pores turns out to be constant, and therefore, such that $\mathbf{F} = \langle \mathbf{F} \rangle^{(2)} \equiv \overline{\mathbf{F}}^{(2)}$ for $\mathbf{X} \in \Omega_0^{(2)}$ (with $\langle \cdot \rangle^{(2)}$ denoting the volume average over the porous phase $\Omega_0^{(2)}$ in the reference configuration). As a result, a spherical pore of radius R^i centered at $\mathbf{X}^i$ in the undeformed configuration, defined by

$$E_0^i = \{\mathbf{X} | (\mathbf{X} - \mathbf{X}^i) \cdot (\mathbf{X} - \mathbf{X}^i) \leqslant (R^i)^2\}, \tag{19}$$

will deform according to: $\mathbf{x} - \mathbf{x}^i = \overline{\mathbf{F}}^{(2)}(\mathbf{X} - \mathbf{X}^i)$, with $\mathbf{x}^i$ denoting the center of the pore in the deformed configuration. Thus, the spherical pore defined by (19) evolves into the ellipsoid:

$$E^i = \{\mathbf{x} | (\mathbf{x} - \mathbf{x}^i) \cdot \mathbf{Z}^{\mathrm{T}}\mathbf{Z}(\mathbf{x} - \mathbf{x}^i) \leqslant (R^i)^2\}, \tag{20}$$

in the deformed configuration, where $\mathbf{Z} = (\overline{\mathbf{F}}^{(2)})^{-1}$. The eigenvalues $1/z_1^2$, $1/z_2^2$, and $1/z_3^2$ of the symmetric second-order tensor $\mathbf{Z}^{\mathrm{T}}\mathbf{Z}$ define the *current* aspect ratios $\omega_1 = z_1/z_3$, $\omega_2 = z_2/z_3$ of the pore in the deformed configuration. Similarly, the principal directions of $\mathbf{Z}^{\mathrm{T}}\mathbf{Z}$, denoted here by the rectangular Cartesian basis $\{\mathbf{e}'_i\}$, characterize the principal directions of the pore in the deformed configuration. Note that the orientation of $\{\mathbf{e}'_i\}$ relative to the frame of reference of choice $\{\mathbf{e}_i\}$ can be conveniently characterized by the three Euler angles ϕ_1, ϕ_2, ϕ_3. Moreover, by making use of the fact that $\langle \det \mathbf{F} \rangle^{(2)} = \det \overline{\mathbf{F}}^{(2)}$ (recall that $\mathbf{F}$ is constant in the porous phase within the context of the HS-type approximation), the *current* volume fraction of the pores in the deformed configuration may be simply obtained via:

$$f = \frac{\det \overline{\mathbf{F}}^{(2)}}{\det \overline{\mathbf{F}}} f_0. \tag{21}$$

In short, the evolution of the size, shape, and orientation of the pores is completely characterized by $\overline{\mathbf{F}}^{(2)}$, via expressions (20) and (21), which can be readily computed by making use of the overall condition $\overline{\mathbf{F}} = (1 - f_0)\overline{\mathbf{F}}^{(1)} + f_0 \overline{\mathbf{F}}^{(2)}$, together with estimate (11) for the average deformation gradient $\overline{\mathbf{F}}^{(1)}$ in the matrix phase of the LCC.

Concerning the evolution of the *distribution* of the pores (i.e., the relative motion of the center of the underlying vacuous inclusions), it will be assumed here that center of the pores evolve with the macroscopic deformation gradient $\overline{\mathbf{F}}$. That is, a pore centered at $\mathbf{X}^i$ in the undeformed configuration will move according to: $\mathbf{x}^i = \overline{\mathbf{F}}\mathbf{X}^i$. This is known to be the exact result for periodic microstructures with simple unit cells.

4. Overall behavior of isotropic porous elastomers

The results presented in the previous sections are valid for any choice of the isotropic, elastomeric matrix phase. In this section, in an attempt to generate a constitutive model that is sufficiently general but as simple as possible, we will restrict attention to isotropic matrix phases characterized by stored-energy functions of the form:

$$W(\mathbf{F}) = \Phi(\lambda_1, \lambda_2, \lambda_3) = g(I) + h(J) + \frac{\kappa}{2}(J-1)^2, \tag{22}$$

where $I \equiv I_1 = \mathrm{tr}\,\mathbf{C} = \mathbf{F} \cdot \mathbf{F} = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$, $J = \sqrt{\det \mathbf{C}} = \det \mathbf{F} = \lambda_1\lambda_2\lambda_3$ are, respectively, the first and third fundamental invariants of the right Cauchy–Green deformation tensor $\mathbf{C} = \mathbf{F}^{\mathrm{T}}\mathbf{F}$, with λ_i $(i = 1, 2, 3)$ denoting the principal stretches associated with $\mathbf{F}$. The parameter κ corresponds to the bulk modulus of the material at zero strain, and g and h are twice-differentiable, material functions that satisfy the conditions: $g(3) = h(1) = 0$, $g_I(3) = \mu/2$, $h_J(1) = -\mu$, and $4g_{II}(3) + h_{JJ}(1) = \mu/3$. Here, μ denotes the shear modulus of the material at zero strain, and the subscripts I and J indicate differentiation with respect to these invariants. Note that when these conditions are satisfied $W(\mathbf{F}) = (\frac{1}{2})(\kappa - \frac{2}{3}\mu)(\mathrm{tr}\,\boldsymbol{\varepsilon})^2 + \mu\,\mathrm{tr}\,\boldsymbol{\varepsilon}^2 + o(\boldsymbol{\varepsilon}^3)$, where $\boldsymbol{\varepsilon}$ is the infinitesimal strain tensor, as $\mathbf{F} \to \mathbf{I}$, so that the stored-energy function (22) linearizes properly. Furthermore, note that to recover incompressible behavior in (22), it suffices to make the parameter κ tend to infinity (in which case $W(\mathbf{F}) = g(I)$ together with theincompressibility constraint $J = 1$).

Experience suggests that "neat" (i.e., pure or unreinforced) elastomers normally do not admit *localized* deformations. Within the context of the material model (22), this property can be easily enforced by simply insisting that $g(I)$ and $h(J) + (\kappa/2)(J-1)^2$ be strictly convex functions of their arguments, which renders the stored-energy function (22) strongly elliptic. Note also that the stored-energy function (22) is an extension of the so-called generalized Neo-Hookean (or I_1-based) materials to account for compressibility. It includes constitutive models widely used in the literature such as the Neo-Hookean, Arruda–Boyce 8-chain (Arruda and Boyce, 1993), Yeoh (Yeoh, 1993), and Gent (Gent,

1996) models. The analysis to follow will be carried out for matrix phases of the general form (22). Results for more specific forms will be presented in Part II.

4.1. Compressible matrix

In this subsection, we specialize the second-order estimate (10) for the effective stored-energy function $\widehat{W}$ to porous elastomers with initial porosity f_0 and *compressible*, isotropic, elastomeric matrix phase characterized by the stored-energy function (22). In addition, we spell out the expressions for the evolution of the associated microstructural variables. The detailed derivation of the results is given in Appendix B, but the final expression for the effective stored-energy function may be written as

$$\begin{aligned}\widehat{W}(\overline{\mathbf{F}}) &= \widehat{\Phi}(\overline{\lambda}_1, \overline{\lambda}_2, \overline{\lambda}_3) \\ &= (1-f_0)[g(\hat{I}^{(1)}) + h(\hat{J}^{(1)}) + \frac{\kappa}{2}(\hat{J}^{(1)}-1)^2 \\ &\quad - (\hat{F}^{(1)}_{11} - \overline{\lambda}^{(1)}_1)(2\overline{g}_I\overline{\lambda}_1 + \overline{h}_J\overline{\lambda}_2\overline{\lambda}_3 + \kappa(\overline{J}-1)\overline{\lambda}_2\overline{\lambda}_3) \\ &\quad - (\hat{F}^{(1)}_{22} - \overline{\lambda}^{(1)}_2)(2\overline{g}_I\overline{\lambda}_2 + \overline{h}_J\overline{\lambda}_1\overline{\lambda}_3 + \kappa(\overline{J}-1)\overline{\lambda}_1\overline{\lambda}_3) \\ &\quad - (\hat{F}^{(1)}_{33} - \overline{\lambda}^{(1)}_3)(2\overline{g}_I\overline{\lambda}_3 + \overline{h}_J\overline{\lambda}_1\overline{\lambda}_2 + \kappa(\overline{J}-1)\overline{\lambda}_1\overline{\lambda}_2)],\end{aligned} \tag{23}$$

where $\overline{g}_I = g_I(\overline{I})$, $\overline{h}_J = h_J(\overline{J})$, $\overline{I} = \overline{\mathbf{F}}\cdot\overline{\mathbf{F}} = \overline{\lambda}_1^2 + \overline{\lambda}_2^2 + \overline{\lambda}_3^2$, and $\overline{J} = \det\overline{\mathbf{F}} = \overline{\lambda}_1\overline{\lambda}_2\overline{\lambda}_3$ have been introduced for convenience.

Further, in estimate (23), the variables $\overline{\lambda}^{(1)}_1$, $\overline{\lambda}^{(1)}_2$, $\overline{\lambda}^{(1)}_3$, which correspond to the principal stretches associated with the phase average deformation gradient $\overline{\mathbf{F}}^{(1)}$ defined by expression (11), are given *explicitly* by expression (41) in Appendix B. They depend ultimately on the applied loading, $\overline{\lambda}_1$, $\overline{\lambda}_2$, $\overline{\lambda}_3$, the initial porosity, f_0, the constitutive functions, g, h, κ, characterizing the elastomeric matrix phase, as well as on the seven variables ℓ^*_α ($\alpha = 1, 2, \ldots, 7$) that are the solution of the nonlinear system of Eqs. (46) in Appendix B. Similarly, the variables $\hat{F}^{(1)}_{11}$, $\hat{F}^{(1)}_{22}$, $\hat{F}^{(1)}_{33}$, given *explicitly* by (43), as well as the variables $\hat{I}^{(1)}$ and $\hat{J}^{(1)}$, given *explicitly* by (48), can be seen to depend ultimately on the applied loading, $\overline{\lambda}_1$, $\overline{\lambda}_2$, $\overline{\lambda}_3$, the initial porosity, f_0, the constitutive functions, g, h, κ, and the seven variables ℓ^*_α ($\alpha = 1, 2, \ldots, 7$).

Thus, in essence, the computation of the second-order estimate (23) amounts to solving a system of seven nonlinear, algebraic equations—provided by relations (46). In general, these equations must be solved numerically, but, depending on the functional character of g and h, and the applied loading conditions, possible simplifications may be carried out.

Next, we spell out the expressions for the evolution of the relevant microstructural variables associated with the second-order estimate (23). To this end, recall from Section 3.2 that the appropriate microstructural variables in the present context are the current porosity, f, the current average aspect ratios, ω_1, ω_2, and the current orientation of the underlying voids in the deformed configuration—as determined from the average deformation gradient in the porous phase $\overline{\mathbf{F}}^{(2)}$, by means of the tensor $\mathbf{Z} = \overline{\mathbf{F}}^{(2)^{-1}}$. (No reference is made here to the evolution of the distribution of pores, since it is assumed to be controlled by the applied macroscopic deformation $\overline{\mathbf{F}}$.) Recall as well that, by employing overall objectivity and isotropy arguments, attention has been restricted (without loss of generality) to diagonal loadings (16). It then follows that within the framework of the second-order estimate (23), the current porosity and current average aspect ratios of the voids in the deformed configuration are given, respectively, by

$$f = \frac{\overline{\lambda}_1^{(2)}\overline{\lambda}_2^{(2)}\overline{\lambda}_3^{(2)}}{\overline{\lambda}_1\overline{\lambda}_2\overline{\lambda}_3} f_0 \tag{24}$$

and

$$\omega_1 = \frac{\overline{\lambda}_1^{(2)}}{\overline{\lambda}_3^{(2)}}, \quad \omega_2 = \frac{\overline{\lambda}_2^{(2)}}{\overline{\lambda}_3^{(2)}}, \tag{25}$$

where $\overline{\lambda}_i^{(2)} = (\overline{\lambda}_i - (1-f_0)\overline{\lambda}_i^{(1)})/f_0$ $(i = 1,2,3)$ denote the principal stretches associated with $\overline{\mathbf{F}}^{(2)}$ and the variables $\overline{\lambda}_i^{(1)}$ are given by expression (41) in Appendix B. In the context of relations (24) and (25), it is important to recognize that $\overline{\lambda}_i^{(2)}$ $(i = 1,2,3)$ depend ultimately on the same variables that the stored-energy function (23).

Finally, it remains to point out that under the applied, diagonal, loading conditions (16), the average orientation of the pores does not evolve with the deformation, but instead it remains fixed. In this connection, it is important to remark that in the present context the average deformation gradient in the pores, $\overline{\mathbf{F}}^{(2)}$, can be shown to be an objective and isotropic tensor function of the applied deformation gradient $\overline{\mathbf{F}}$ (i.e., $\overline{\mathbf{F}}^{(2)}(\overline{\mathbf{K}}\,\overline{\mathbf{F}}\,\overline{\mathbf{K}}') = \overline{\mathbf{K}}\,\overline{\mathbf{F}}^{(2)}(\overline{\mathbf{F}})\overline{\mathbf{K}}'$ for all $\overline{\mathbf{F}}$, and all proper, orthogonal, second-order tensors $\overline{\mathbf{K}}$, $\overline{\mathbf{K}}'$). As a result, from the general loading $\overline{\mathbf{F}} = \overline{\mathbf{R}}\,\overline{\mathbf{Q}}\,\overline{\mathbf{D}}\,\overline{\mathbf{Q}}^{\mathrm{T}}$ used in the context of expression (13), it follows that $\overline{\mathbf{F}}^{(2)}(\overline{\mathbf{F}}) = \overline{\mathbf{R}}\,\overline{\mathbf{Q}}\,\overline{\mathbf{F}}^{(2)}(\overline{\mathbf{D}})\overline{\mathbf{Q}}^{\mathrm{T}}$. In turn, it follows that the tensor $\mathbf{Z}^{\mathrm{T}}\mathbf{Z}$ in (20) can be simply written as $\mathbf{Z}^{\mathrm{T}}\mathbf{Z} = \mathbf{H}\mathbf{A}\mathbf{H}^{\mathrm{T}}$, where $\mathbf{A} = \mathrm{diag}(\overline{\lambda}_1^{(2)^{-2}}, \overline{\lambda}_2^{(2)^{-2}}, \overline{\lambda}_3^{(2)^{-2}})$ in the frame of reference of choice and $\mathbf{H} = \overline{\mathbf{R}}\,\overline{\mathbf{Q}}$. In essence, this result reveals that for a general applied deformation $\overline{\mathbf{F}}$, the current, average orientation of the pores is characterized *explicitly* by $\mathbf{H} = \overline{\mathbf{R}}\,\overline{\mathbf{Q}}$, where it is recalled that $\overline{\mathbf{R}}$ is the macroscopic rotation tensor in the polar decomposition of $\overline{\mathbf{F}}$, and $\overline{\mathbf{Q}}$ is the proper-orthogonal, second-order tensor describing the orientation of the macroscopic Lagrangian principal axes. The above expressions for f, ω_1, and ω_2 are not affected, of course, since they depend exclusively on the principal stretches associated with $\overline{\mathbf{F}}^{(2)}$.

4.2. Incompressible matrix

Elastomers are known to be essentially incompressible, since they usually exhibit a ratio between the bulk and shear moduli of the order of 10^4. Accordingly, it is of practical interest to generate estimates for the effective behavior of porous elastomers with *incompressible* matrix phases. This can be efficiently accomplished by taking the limit $\kappa \to \infty$ in the second-order estimate (23). The corresponding asymptotic analysis has been included in Appendix C, but the final result for the effective stored-energy function $\widehat{W}^I$ for the class of porous elastomers considered in this work, with elastomeric matrix phase characterized by the stored-energy function (22) (with $\kappa = \infty$), reduces to the form:

$$\widehat{W}^I(\overline{\mathbf{F}}) = \widehat{\Phi}^I(\overline{\lambda}_1, \overline{\lambda}_2, \overline{\lambda}_3) = (1-f_0)g(\hat{I}^{(1)}), \tag{26}$$

where $\hat{I}^{(1)}$ is given by expression (62) in Appendix C. Here, it should be emphasized that $\hat{I}^{(1)}$ depends ultimately on the applied loading, $\overline{\lambda}_1$, $\overline{\lambda}_2$, $\overline{\lambda}_3$, the initial porosity, f_0, the constitutive function, g, as well as on the seven variables u_α $(\alpha = 1,2,\ldots,7)$ defined by (60), that are the solution of the system of seven nonlinear equations formed by relations (57) and (58) in Appendix C. Thus, similar to its compressible counterpart (23), the computation of the second-order estimate (26) for the effective stored-energy function of porous elastomers with incompressible matrix phases amounts to solving a system of seven nonlinear, algebraic equations.

In general, it is not possible to solve these equations in closed form. However, for certain applied deformations, estimate (26) may be written down more explicitly. For instance, for the case of hydrostatic loading $\overline{\lambda}_1 = \overline{\lambda}_2 = \overline{\lambda}_3 = \overline{\lambda}$, expression (62) for $\hat{I}^{(1)}$ can be shown to simplify to

$$\hat{I}^{(1)} = \frac{\overline{\lambda}^2[9u^2 f_0 - 6uf_0\overline{\lambda}(\overline{\lambda}^3 - 1) + (2 + f_0)\overline{\lambda}^2(\overline{\lambda}^3 - 1)^2]}{3u^2 f_0}, \tag{27}$$

where the variable u satisfies the following condition:

$$27f_0^{3/2}u^3 - 27f_0^{3/2}\overline{\lambda}^4 u^2 + 9(f_0 - 1)\sqrt{f_0}(\overline{\lambda}^3 - 1)\overline{\lambda}^5 u - (\sqrt{f_0} - 1)^2(2 + \sqrt{f_0})(\overline{\lambda}^3 - 1)^2\overline{\lambda}^6 = 0. \tag{28}$$

Of course, the solution to the cubic equation (28) may be worked out in closed form. However, for all practical purposes, it is simpler to solve (28) numerically. In this regard, it is emphasized that only 1 of the 3 roots[2] of (28) leads to the correct linearized behavior; hence, this is the root that should be selected.

We conclude this subsection by noticing that expressions (24) and (25) continue to apply for determining the current porosity, f, and the current aspect ratios, ω_1, ω_2, of the underlying voids in porous elastomers with *incompressible* matrix phases, provided that the leading-order terms in expression (52) in Appendix C be used for the stretches $\overline{\lambda}_i^{(1)}$ $(i = 1, 2, 3)$. In this light, f, ω_1, ω_2, are seen to depend ultimately on the same variables as the effective stored-energy function (26).

4.3. Small-strain elastic moduli

In the limit of small strains, estimates (23) and (26) linearize properly, and therefore recover the classical HS upper bounds for the effective shear and bulk moduli of the composite. To be precise, the estimate (23) with *compressible* matrix phases linearizes to $\widehat{W}(\overline{\mathbf{F}}) = \frac{1}{2}(\widetilde{\kappa} - \frac{2}{3}\widetilde{\mu})(\mathrm{tr}\,\overline{\boldsymbol{\varepsilon}})^2 + \widetilde{\mu}\,\mathrm{tr}\,\overline{\boldsymbol{\varepsilon}}^2 + o(\overline{\boldsymbol{\varepsilon}}^3)$, as $\overline{\mathbf{F}} \to \mathbf{I}$, where $\overline{\boldsymbol{\varepsilon}} = \frac{1}{2}(\overline{\mathbf{F}} + \overline{\mathbf{F}}^{\mathrm{T}} - 2\mathbf{I})$ is the macroscopic, infinitesimal strain tensor, and

$$\widetilde{\mu} = \frac{(1 - f_0)(9\kappa + 8\mu)\mu}{(9 + 6f_0)\kappa + 4(2 + 3f_0)\mu}, \quad \widetilde{\kappa} = \frac{4(1 - f_0)\kappa\mu}{3f_0\kappa + 4\mu}, \tag{29}$$

are the effective shear and bulk moduli, respectively. Similarly, the estimate (26) with *incompressible* matrix phases linearizes to $\widehat{W}^I(\overline{\mathbf{F}}) = 1/2(\widetilde{\kappa}^I - 2/3\widetilde{\mu}^I)\,(\mathrm{tr}\,\overline{\boldsymbol{\varepsilon}})^2 + \widetilde{\mu}^I\mathrm{tr}\,\overline{\boldsymbol{\varepsilon}}^2 + o(\overline{\boldsymbol{\varepsilon}}^3)$, as $\overline{\mathbf{F}} \to \mathbf{I}$, where

$$\widetilde{\mu}^I = \frac{3(1 - f_0)}{3 + 2f_0}\mu, \quad \widetilde{\kappa}^I = \frac{4(1 - f_0)}{3f_0}\mu. \tag{30}$$

It should be recalled that the HS effective moduli (29) and (30) are actually *exact* results in the limit of dilute concentration of spherical voids (i.e., for $f_0 \to 0$). Moreover, the effective moduli (29) and (30) are known to correlate well with experimental results for the

[2]The correct root linearizes as $u = 1 + (1 + 3f_0)/f_0(\overline{\lambda} - 1) + O(\overline{\lambda} - 1)^2$.

elastic constants of isotropic porous rubbers with small to moderate initial porosities (see, e.g., O'Rourke et al., 1997).

4.4. Exact evolution of porosity

To conclude this section, we recall that for porous elastomers with *incompressible* matrix phase, it is possible to compute—from a simple kinematical argument—the exact evolution of the porosity in terms of the applied macroscopic deformation. The result is

$$f = 1 - \frac{1 - f_0}{\det \overline{\mathbf{F}}}. \tag{31}$$

In general, the specialization of the second-order estimate (24) for f to porous elastomers with incompressible matrix phases does not recover the exact result (31). Nonetheless, expression (24), when specialized to incompressible matrix phases, can be shown to be exact up to second order in the strain (i.e., up to $O(\bar{\varepsilon}^2)$). For larger finite deformations, as shown in Part II, relation (24) provides estimates that are in very good agreement with the exact result (31), except for the limiting case of large hydrostatic tension together with small initial porosities.

5. Concluding remarks

In this paper, homogenization-based constitutive models have been derived for the effective mechanical behavior of isotropic porous elastomers subjected to large deformations, by means of the second-order homogenization theory (Lopez-Pamies and Ponte Castañeda, 2006a). The model applies to materials consisting of a random and isotropic distribution of initially spherical pores in compressible and incompressible isotropic matrix phases. A very important feature of the proposed constitutive model is that it accounts for the evolution of the size, shape, orientation, and distribution of the underlying pores in the material, which result from the finite changes in geometry that are induced by the imposed large deformations. This point is essential, since the evolution of the microstructure is known to induce significant geometric softening and stiffening effects on the overall behavior and stability of porous elastomers. A further strength of the model is that—in spite of incorporating fine microstructural details—it is relatively simple, as it amounts to solving a system of seven nonlinear, algebraic equations. For convenience, a Fortran program has been written and is available from the authors upon request.

In Part II of this work, the model developed in this paper will be used to generate estimates for the effective behavior of porous elastomers with specific (compressible and incompressible) strongly elliptic matrix phases under a wide range of loading conditions and levels of initial porosity. The estimates will be shown to be in good agreement with exact and numerical results available from the literature for special loading conditions. For more general conditions, the proposed estimates will be shown to be drastically different from existing models. In particular, the new models proposed in this work predict the development of macroscopic instabilities for loading conditions where such instabilities are expected to occur from physical experience. This is in contrast with existing models that fail to predict the development of such instabilities. The reasons for this result will be linked to the ability of the models proposed in this paper to capture more accurately the subtle influence of the evolution of the microstructure on the mechanical response of porous elastomers.

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Appendix A. Necessary and sufficient conditions for strong ellipticity of isotropic stored-energy functions in 3D

In this appendix, we recall *necessary* and *sufficient* conditions for the strong ellipticity of isotropic stored-energy functions $\widehat{W}(\overline{\mathbf{F}}) = \widehat{\Phi}(\overline{\lambda}_1, \overline{\lambda}_2, \overline{\lambda}_3)$, exclusively in terms of the incremental modulus tensor $\widehat{\mathscr{L}} = \partial^2 \widehat{W}/\partial\overline{\mathbf{F}}^2$. Following Dacorogna (2001) (with some minor changes), the conditions read as follows[3]:

$$\widehat{\mathscr{L}}_{iiii} > 0, \quad i = 1, 2, 3, \tag{32}$$

$$\widehat{\mathscr{L}}_{ijij} > 0, \quad 1 \leqslant i < j \leqslant 3, \tag{33}$$

$$\widehat{\mathscr{L}}_{iiii}\widehat{\mathscr{L}}_{jjjj} + \widehat{\mathscr{L}}^2_{ijij} - (\widehat{\mathscr{L}}_{iijj} + \widehat{\mathscr{L}}_{ijji})^2 + 2\widehat{\mathscr{L}}_{ijij}\sqrt{\widehat{\mathscr{L}}_{iiii}\widehat{\mathscr{L}}_{jjjj}} > 0, \quad 1 \leqslant i < j \leqslant 3, \tag{34}$$

and either

$$m^\delta_{12}\sqrt{\widehat{\mathscr{L}}_{3333}} + m^\delta_{13}\sqrt{\widehat{\mathscr{L}}_{2222}} + m^\delta_{23}\sqrt{\widehat{\mathscr{L}}_{1111}} + \sqrt{\widehat{\mathscr{L}}_{1111}\widehat{\mathscr{L}}_{2222}\widehat{\mathscr{L}}_{3333}} \geqslant 0 \tag{35}$$

or

$$\det M^\delta > 0, \tag{36}$$

where $M^\delta = (m^\delta_{ij})$ is symmetric and

$$m^\delta_{ij} = \begin{cases} \widehat{\mathscr{L}}_{iiii} & \text{if } i = j, \\ \widehat{\mathscr{L}}_{ijij} + \delta_i\delta_j(\widehat{\mathscr{L}}_{iijj} + \widehat{\mathscr{L}}_{ijji}) & \text{if } i \neq j \end{cases} \tag{37}$$

for any choice of $\delta_i \in \{\pm 1\}$.

Here,

$$\widehat{\mathscr{L}}_{iijj} = \frac{\partial^2 \widehat{\Phi}}{\partial\overline{\lambda}_i \partial\overline{\lambda}_j},$$

$$\widehat{\mathscr{L}}_{ijij} = \frac{1}{\overline{\lambda}_i^2 - \overline{\lambda}_j^2}\left(\overline{\lambda}_i \frac{\partial\widehat{\Phi}}{\partial\overline{\lambda}_i} - \overline{\lambda}_j \frac{\partial\widehat{\Phi}}{\partial\overline{\lambda}_j}\right), \quad i \neq j,$$

$$\widehat{\mathscr{L}}_{ijji} = \frac{1}{\overline{\lambda}_i^2 - \overline{\lambda}_j^2}\left(\overline{\lambda}_j \frac{\partial\widehat{\Phi}}{\partial\overline{\lambda}_i} - \overline{\lambda}_i \frac{\partial\widehat{\Phi}}{\partial\overline{\lambda}_j}\right), \quad i \neq j \tag{38}$$

[3] In this appendix, repeated Latin indices do not imply summation.

$(i,j=1,2,3)$ are the components of the effective incremental elastic modulus $\widehat{\mathscr{L}}$ written with respect to the macroscopic Lagrangian principal axis (i.e., the principal axis of $\overline{\mathbf{F}}^{\mathrm{T}}\overline{\mathbf{F}}$). Note that for loadings with $\overline{\lambda}_i=\overline{\lambda}_j$ $(i\neq j)$, suitable limits must be taken for the shear components in (38), namely, Eqs. $(38)_2$–$(38)_3$ reduce to

$$\widehat{\mathscr{L}}_{ijij}=\frac{1}{2}\left(\widehat{\mathscr{L}}_{iiii}-\widehat{\mathscr{L}}_{iijj}+\frac{1}{\overline{\lambda}_i}\frac{\partial\widehat{\Phi}}{\partial\overline{\lambda}_i}\right),\quad i\neq j,$$

$$\widehat{\mathscr{L}}_{ijji}=\frac{1}{2}\left(\widehat{\mathscr{L}}_{iiii}-\widehat{\mathscr{L}}_{iijj}-\frac{1}{\overline{\lambda}_i}\frac{\partial\widehat{\Phi}}{\partial\overline{\lambda}_i}\right),\quad i\neq j, \tag{39}$$

respectively. Furthermore, note that there are three conditions in (32), three in (33), three in (34), and, due to all possible signs, four in (35) or in (36). Thus, there is a total of 13 conditions.

Appendix B. Second-order estimates for isotropic porous elastomers with compressible matrix phases

In this appendix, we spell out the analysis corresponding to the computation of the second-order estimate (23) for the effective stored-energy function $\widehat{W}$ of porous elastomers consisting of initially spherical, polydisperse, vacuous inclusions distributed randomly and isotropically (in the undeformed configuration) in a *compressible*, isotropic matrix phase characterized by the stored-energy function (22).

As a result of the restriction to pure stretch loadings (16), the modulus $\mathbf{L}$ defined by expression (13) of the matrix phase in the linear comparison composite (LCC) reduces to $\mathbf{L}=\mathbf{L}^*$, where it is recalled that $\mathbf{L}^*$ is orthotropic with respect to the frame of reference of choice and possesses, at most, nine independent components. In this work, for simplicity, we introduce further constraints among the components of $\mathbf{L}^*$ in order to reduce them to seven independent components, denoted by the parameters ℓ^*_α $(\alpha=1,2,\ldots,7)$. Thus, the independent principal components of $\mathbf{L}^*$ are chosen to be $L^*_{1111}=\ell^*_1$, $L^*_{2222}=\ell^*_2$, $L^*_{3333}=\ell^*_3$, $L^*_{1122}=\ell^*_4$, $L^*_{1133}=\ell^*_5$, $L^*_{2233}=\ell^*_6$, $L^*_{1212}=\ell^*_7$, while the other non-zero components

$$L^*_{2121}=L^*_{1313}=L^*_{3131}=L^*_{2323}=L^*_{3232}=\ell^*_7,$$

$$L^*_{1221}=\sqrt{(\ell^*_1-\ell^*_7)(\ell^*_2-\ell^*_7)}-\ell^*_4,$$

$$L^*_{1331}=\sqrt{(\ell^*_1-\ell^*_7)(\ell^*_3-\ell^*_7)}-\ell^*_5,$$

$$L^*_{2332}=\sqrt{(\ell^*_2-\ell^*_7)(\ell^*_3-\ell^*_7)}-\ell^*_6, \tag{40}$$

are dependent. The motivation for the constraints (40) is twofold: (i) relations (40) are consistent with the tangent modulus of Neo-Hookean materials; and (ii) conditions (40) simplify considerably the computations involved. It should be emphasized, however, that other choices are possible in principle.

Now, using the facts that $\overline{\mathbf{F}}=\mathrm{diag}(\overline{\lambda}_1,\overline{\lambda}_2,\overline{\lambda}_3)$ and $\mathbf{L}=\mathbf{L}^*$, together with Eq. (17) for the HS estimate for $\widetilde{\mathbf{L}}$, it follows from (11) that the average deformation gradient in the matrix phase of the LCC, needed in the computation of $\widehat{W}$, is of the form $\overline{\mathbf{F}}^{(1)} = \mathrm{diag}(\overline{\lambda}_1^{(1)}, \overline{\lambda}_2^{(1)}, \overline{\lambda}_3^{(1)})$, where the average principal stretches $\overline{\lambda}_i^{(1)}$ $(i = 1, 2, 3)$ in the matrix phase are given by

$$\begin{aligned}
\overline{\lambda}_1^{(1)} = \overline{\lambda}_1 & - f_0 E_{1111}[2\overline{g}_I\overline{\lambda}_1 + (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_2\overline{\lambda}_3] \\
& - f_0 E_{1122}[2\overline{g}_I\overline{\lambda}_2 + (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_1\overline{\lambda}_3] \\
& - f_0 E_{1133}[2\overline{g}_I\overline{\lambda}_3 + (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_1\overline{\lambda}_2], \\
\overline{\lambda}_2^{(1)} = \overline{\lambda}_2 & - f_0 E_{1122}[2\overline{g}_I\overline{\lambda}_1 + (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_2\overline{\lambda}_3] \\
& - f_0 E_{2222}[2\overline{g}_I\overline{\lambda}_2 + (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_1\overline{\lambda}_3] \\
& - f_0 E_{2233}[2\overline{g}_I\overline{\lambda}_3 + (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_1\overline{\lambda}_2], \\
\overline{\lambda}_3^{(1)} = \overline{\lambda}_3 & - f_0 E_{1133}[2\overline{g}_I\overline{\lambda}_1 + (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_2\overline{\lambda}_3] \\
& - f_0 E_{2233}[2\overline{g}_I\overline{\lambda}_2 + (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_1\overline{\lambda}_3] \\
& - f_0 E_{3333}[2\overline{g}_I\overline{\lambda}_3 + (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_1\overline{\lambda}_2].
\end{aligned} \tag{41}$$

In these expressions, $\mathbf{E} = (\mathbf{P}^{-1} - (1-f_0)\mathbf{L})^{-1}$ has been introduced for convenience, and it is recalled that $\overline{g}_I = g_I(\overline{I})$, $\overline{h}_J = h_J(\overline{J})$, with $\overline{I} = \overline{\lambda}_1^2 + \overline{\lambda}_2^2 + \overline{\lambda}_3^2$, $\overline{J} = \overline{\lambda}_1\overline{\lambda}_2\overline{\lambda}_3$. Note that relations (41) provide *explicit* expressions for the non-zero components of $\overline{\mathbf{F}}^{(1)}$ in terms of the applied loading, $\overline{\mathbf{F}}$, the initial porosity, f_0, the constitutive functions, g, h, κ, of the elastomeric matrix phase, as well as of the independent components of $\mathbf{L}$, i.e., ℓ_α^* $(\alpha = 1, 2, \ldots, 7)$.

Having determined $\overline{\mathbf{F}}^{(1)}$, we proceed next to compute the variable $\hat{\mathbf{F}}^{(1)}$, also needed in the computation of $\widehat{W}$. By again making use of the identity $\mathbf{L} = \mathbf{L}^*$, together with conditions (40) and Eq. (17) for the HS estimate for $\widetilde{\mathbf{L}}$, Eq. (14) can be seen to reduce to seven nonlinear, algebraic equations for seven combinations of the components of $\hat{\mathbf{F}}^{(1)}$, namely:

$$(\hat{F}_{11}^{(1)} - \overline{\lambda}_1)^2 + 2f_1\hat{F}_{12}^{(1)}\hat{F}_{21}^{(1)} + 2f_2\hat{F}_{13}^{(1)}\hat{F}_{31}^{(1)} = \frac{2}{1-f_0}\frac{\partial \widehat{W}_T}{\partial \ell_1^*} \doteq k_1,$$

$$(\hat{F}_{22}^{(1)} - \overline{\lambda}_2)^2 + \frac{1}{2f_1}\hat{F}_{12}^{(1)}\hat{F}_{21}^{(1)} + 2f_3\hat{F}_{23}^{(1)}\hat{F}_{32}^{(1)} = \frac{2}{1-f_0}\frac{\partial \widehat{W}_T}{\partial \ell_2^*} \doteq k_2,$$

$$(\hat{F}_{33}^{(1)} - \overline{\lambda}_3)^2 + \frac{1}{2f_2}\hat{F}_{13}^{(1)}\hat{F}_{31}^{(1)} + \frac{1}{2f_3}\hat{F}_{23}^{(1)}\hat{F}_{32}^{(1)} = \frac{2}{1-f_0}\frac{\partial \widehat{W}_T}{\partial \ell_3^*} \doteq k_3,$$

$$(\hat{F}_{11}^{(1)} - \overline{\lambda}_1)(\hat{F}_{22}^{(1)} - \overline{\lambda}_2) - \hat{F}_{12}^{(1)}\hat{F}_{21}^{(1)} = \frac{1}{1-f_0}\frac{\partial \widehat{W}_T}{\partial \ell_4^*} \doteq \frac{k_4}{2},$$

$$(\hat{F}_{11}^{(1)} - \overline{\lambda}_1)(\hat{F}_{33}^{(1)} - \overline{\lambda}_3) - \hat{F}_{13}^{(1)}\hat{F}_{31}^{(1)} = \frac{1}{1-f_0}\frac{\partial \widehat{W}_T}{\partial \ell_5^*} \doteq \frac{k_5}{2},$$

$$(\hat{F}_{22}^{(1)} - \overline{\lambda}_2)(\hat{F}_{33}^{(1)} - \overline{\lambda}_3) - \hat{F}_{23}^{(1)}\hat{F}_{32}^{(1)} = \frac{1}{1-f_0}\frac{\partial \widehat{W}_T}{\partial \ell_6^*} \doteq \frac{k_6}{2},$$

$$(\hat{F}^{(1)}_{12})^2+(\hat{F}^{(1)}_{21})^2+(\hat{F}^{(1)}_{13})^2+(\hat{F}^{(1)}_{31})^2+(\hat{F}^{(1)}_{23})^2+(\hat{F}^{(1)}_{32})^2+2f_4\hat{F}^{(1)}_{12}\hat{F}^{(1)}_{21}$$
$$+2f_5\hat{F}^{(1)}_{13}\hat{F}^{(1)}_{31}+2f_6\hat{F}^{(1)}_{23}\hat{F}^{(1)}_{32}=\frac{2}{1-f_0}\frac{\partial\widehat{W}_T}{\partial\ell^*_7}\doteq k_7. \tag{42}$$

Here, $f_1=\partial L^*_{1221}/\partial\ell^*_1$, $f_{2=\partial L^*_{1331}/\partial\ell^*_1,\, f_3=\partial L^*_{2332}/\partial\ell^*_2,\, f_4=\partial L^*_{1221}/\partial\ell^*_7,\, f_5=\partial L^*_{1331}/\partial\ell^*_7,}$ $f_6=\ \partial L^*_{2332}/\partial\ell^*_7$, while k_1, k_2, k_3, k_4, k_5, k_6, k_7 are functions of the independent components of $\mathbf{L}$, i.e., ℓ^*_α $(\alpha=1,2,\ldots,7)$, as well as of the macroscopic deformation $\overline{\mathbf{F}}$, the initial porosity f_0, and the constitutive functions g, h, and κ that characterize the elastomeric matrix phase. It is not difficult to check that the nonlinear system of Eqs. (42) may be solved *explicitly* to yield two distinct solutions for $Y_1\doteq(\hat{F}^{(1)}_{11}-\overline{\lambda}_1)$, $Y_2\doteq(\hat{F}^{(1)}_{22}-\overline{\lambda}_2)$, $Y_3\doteq(\hat{F}^{(1)}_{33}-\overline{\lambda}_3)$ in terms of which the combinations $p_1\doteq\hat{F}^{(1)}_{12}\hat{F}^{(1)}_{21}$, $p_2\doteq\hat{F}^{(1)}_{13}\hat{F}^{(1)}_{31}$, $p_3\doteq\hat{F}^{(1)}_{23}\hat{F}^{(1)}_{32}$, and $s\doteq(\hat{F}^{(1)}_{12})^2+(\hat{F}^{(1)}_{21})^2+(\hat{F}^{(1)}_{13})^2+(\hat{F}^{(1)}_{31})^2+(\hat{F}^{(1)}_{23})^2+(\hat{F}^{(1)}_{32})^2$ may be uniquely determined. The two solutions for Y_1, Y_2, and Y_3 are as follows:

$$Y_1=(\hat{F}^{(1)}_{11}-\overline{\lambda}_1)=\pm\frac{(k_1+f_1k_4+f_2k_5)\sqrt{C_1C_2}}{C_2\sqrt{C_3}},$$

$$Y_2=(\hat{F}^{(1)}_{22}-\overline{\lambda}_2)=\pm\frac{(k_4+4f_1(k_2+f_3k_6))C_2}{2\sqrt{C_1C_2}\sqrt{C_3}},$$

$$Y_3=(\hat{F}^{(1)}_{33}-\overline{\lambda}_3)=\pm\frac{(f_3k_5+f_2(4f_3k_3+k_6))\sqrt{C_3}}{\sqrt{C_1C_2}}, \tag{43}$$

with $C_1=f_2(4f_1k_2+k_4)+4f_1f_3^2(4f_2k_3+k_5)+2f_3(k_1+f_1k_4+f_2k_5+4f_1f_2k_6)$, $C_2=f_2(4f_1k_2+k_4+2f_2k_6)+2f_3(k_1+f_1k_4+2f_2(2f_2k_3+k_5+f_1k_6))$, $C_3=k_1+f_2k_5+2f_1(4f_2f_3k_3+k_4+f_3k_5+f_2k_6)+4f_1^2(k_2+f_3k_6)$, where it must be emphasized that the positive (and negative) signs must be chosen to go together in the roots for Y_1, Y_2, and Y_3. The corresponding final expressions for the remaining combinations read as

$$p_1=Y_1Y_2-k_4/2,\quad p_2=Y_1Y_3-k_5/2,\quad p_3=Y_2Y_3-k_6/2\quad\text{and}$$
$$s=k_7-2(f_4p_1+f_5p_2+f_6p_3). \tag{44}$$

At this point, it is expedient to make a few remarks regarding expressions (43) and (44). From a computational point of view, the variables k_α $(\alpha=1,2,\ldots,7)$ are determined by performing the indicated derivatives of $\widehat{W}_T$, given by (9) in the main body of the text, with respect to the moduli ℓ^*_α. The resulting expressions, which involve suitable traces of the field fluctuations $\mathbf{C}^{(1)}_{\mathbf{F}}$, are rather complicated, but can be simplified in the manner detailed in (Lopez-Pamies and Ponte Castañeda, 2006a) to render:

$$k_\alpha=\frac{1}{f_0}(\overline{\mathbf{F}}-\overline{\mathbf{F}}^{(1)})\cdot\frac{\partial\mathbf{E}^{-1}}{\partial\ell^*_\alpha}(\overline{\mathbf{F}}-\overline{\mathbf{F}}^{(1)})\quad(\alpha=1,2,\ldots,7), \tag{45}$$

where $\mathbf{E}=(\mathbf{P}^{-1}-(1-f_0)\mathbf{L})^{-1}$ has already been introduced in the context of expressions (41). Moreover, it is important to emphasize that relations (43) and (44) provide *explicit* expressions for seven combinations of the components of $\hat{\mathbf{F}}^{(1)}$ in terms of the applied loading $\overline{\mathbf{F}}$, the initial porosity f_0, the constitutive functions g, h, κ of the elastomeric matrix phase, and the moduli ℓ^*_α $(\alpha=1,2,\ldots,7)$. Note, however, that the variable $\hat{\mathbf{F}}^{(1)}$ has nine components, so that two more relations would be needed to entirely characterize $\hat{\mathbf{F}}^{(1)}$, as it will be seen further below.

Each of the two distinct roots (43) for the combinations Y_1, Y_2, Y_3, p_1, p_2, p_3, s may be substituted in the generalized secant condition (12) to yield a system of nine scalar equations for the nine variables constituted by the two combinations of $\hat{\mathbf{F}}^{(1)}$: $p_4 = \hat{F}^{(1)}_{23}\hat{F}^{(1)}_{31}\hat{F}^{(1)}_{12}$, $p_5 = \hat{F}^{(1)}_{32}\hat{F}^{(1)}_{13}\hat{F}^{(1)}_{21}$, and the seven moduli ℓ^*_α. Algebraic manipulation of the resulting system reveals that one equation is satisfied trivially, and the remaining eight equations may be cast in the following form:

$$\begin{aligned}
\ell_1^* Y_1 + \ell_4^* Y_2 + \ell_5^* Y_3 &= 2\hat{g}_I(Y_1+\overline{\lambda}_1) + [\hat{h}_J + \kappa(\hat{J}^{(1)}-1)]((Y_2+\overline{\lambda}_2) \\
&\quad \times (Y_3+\overline{\lambda}_3) - p_3) - 2\overline{g}_I\overline{\lambda}_1 - (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_2\overline{\lambda}_3, \\
\ell_4^* Y_1 + \ell_2^* Y_2 + \ell_6^* Y_3 &= 2\hat{g}_I(Y_2+\overline{\lambda}_2) + [\hat{h}_J + \kappa(\hat{J}^{(1)}-1)]((Y_1+\overline{\lambda}_1) \\
&\quad \times (Y_3+\overline{\lambda}_3) - p_2) - 2\overline{g}_I\overline{\lambda}_2 - (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_1\overline{\lambda}_3, \\
\ell_5^* Y_1 + \ell_6^* Y_2 + \ell_3^* Y_3 &= 2\hat{g}_I(Y_3+\overline{\lambda}_3) + [\hat{h}_J + \kappa(\hat{J}^{(1)}-1)]((Y_1+\overline{\lambda}_1) \\
&\quad \times (Y_2+\overline{\lambda}_2) - p_1) - 2\overline{g}_I\overline{\lambda}_3 - (\overline{h}_J + \kappa(\overline{J}-1))\overline{\lambda}_1\overline{\lambda}_2, \\
L^*_{1221}p_1 &= [\hat{h}_J + \kappa(\hat{J}^{(1)}-1)](p_4 - p_1(Y_3+\overline{\lambda}_3)), \\
L^*_{1331}p_2 &= [\hat{h}_J + \kappa(\hat{J}^{(1)}-1)](p_4 - p_2(Y_2+\overline{\lambda}_2)), \\
L^*_{2332}p_3 &= [\hat{h}_J + \kappa(\hat{J}^{(1)}-1)](p_4 - p_3(Y_1+\overline{\lambda}_1)), \\
\ell_7^* &= 2\hat{g}_I,
\end{aligned} \tag{46}$$

and

$$p_4 = p_5. \tag{47}$$

In these relations, $\hat{g}_I = g_I(\hat{I}^{(1)})$, $\hat{h}_J = h_J(\hat{J}^{(1)})$, with

$$\begin{aligned}
\hat{I}^{(1)} &= \hat{\mathbf{F}}^{(1)}\cdot\hat{\mathbf{F}}^{(1)} = (Y_1+\overline{\lambda}_1)^2 + (Y_2+\overline{\lambda}_2)^2 + (Y_3+\overline{\lambda}_3)^2 + s, \\
\hat{J}^{(1)} &= \det\hat{\mathbf{F}}^{(1)} \\
&= (Y_1+\overline{\lambda}_1)(Y_2+\overline{\lambda}_2)(Y_3+\overline{\lambda}_3) - p_1(Y_3+\overline{\lambda}_3) - p_2(Y_2+\overline{\lambda}_2) \\
&\quad - p_3(Y_1+\overline{\lambda}_1) + 2p_4,
\end{aligned} \tag{48}$$

and it is recalled that L^*_{1221}, L^*_{1331}, L^*_{2332} are given, respectively, by expressions $(40)_2$, $(40)_3$, $(40)_4$. The fact that one of the generalized secant equation (12) is satisfied trivially has the direct implication that $\hat{\mathbf{F}}^{(1)}$ enters the above equations only through eight (instead of nine) independent combinations, namely, Y_1, Y_2, Y_3, p_1, p_2, p_3, s, p_4. As described below, these are the only combinations needed in the computation of the second-order estimate (10) for $\widehat{W}$. Now, by recalling the definitions $p_1 = \hat{F}^{(1)}_{12}\hat{F}^{(1)}_{21}$, $p_2 = \hat{F}^{(1)}_{13}\hat{F}^{(1)}_{31}$, $p_3 = \hat{F}^{(1)}_{23}\hat{F}^{(1)}_{32}$, and $p_4 = \hat{F}^{(1)}_{23}\hat{F}^{(1)}_{31}\hat{F}^{(1)}_{12}$, $p_5 = \hat{F}^{(1)}_{32}\hat{F}^{(1)}_{13}\hat{F}^{(1)}_{21}$, it is seen that Eq. (47) can be solved in closed form to render

$$p_4 = \pm\sqrt{p_1 p_2 p_3}. \tag{49}$$

Each of the two distinct roots (49) for p_4 may be substituted back in Eqs. (46) to finally generate a closed system of seven nonlinear, algebraic equations for the seven independent moduli ℓ^*_α. These equations must be solved numerically.

Having computed from (46) the values of all seven independent components of $\mathbf{L}$ (i.e., ℓ^*_α) for a given initial porosity (f_0), given material behavior (g, h, κ), and given loading ($\overline{\lambda}_1$, $\overline{\lambda}_2$, $\overline{\lambda}_3$), the values of the non-zero components of $\overline{\mathbf{F}}^{(1)}$ (i.e., $\overline{\lambda}_1^{(1)}$, $\overline{\lambda}_2^{(1)}$, $\overline{\lambda}_3^{(1)}$) and the relevant combinations of $\hat{\mathbf{F}}^{(1)}$ (i.e., Y_1, Y_2, Y_3, p_1, p_2, p_3, s, p_4) may be readily determined using relations (41), (43), (44), and(49). In turn, these results can be used to compute the second-order estimate (10) for the effective stored-energy function $\widehat{W}$ of isotropic porous elastomers. The final expression for $\widehat{W}$ is given by (23) in the text.

In connection with these results, it is important to remark that there are four possible combinations of the roots introduced in (43) and (49), which lead to four different estimates for $\widehat{W}$. In the case when the bulk modulus of the material (at zero strain) κ is of the order of the shear modulus (at zero strain) μ, all four root combinations lead to very similar results for the effective stored-energy function $\widehat{W}$. However, when the bulk modulus is significantly larger *than* the shear modulus, i.e., $\kappa \gg \mu$, the estimates produced by the four distinct combinations are very different. In fact, for $\kappa \gg \mu$, it will be shown in the next appendix that only one root combination generates physically meaningful estimates that are superior to the other three possibilities.

Appendix C. Second-order estimates for isotropic porous elastomers with incompressible matrix phases

In this appendix, we outline the derivation of the second-order estimate (26) for the effective stored-energy function $\widehat{W}^I$ of porous elastomers consisting of initially spherical, polydisperse, vacuous inclusions distributed randomly and isotropically (in the undeformed configuration) in an *incompressible* matrix phase (22) with $\kappa = \infty$.

In the approach that follows, we start out with the results presented in Appendix B for the second-order estimate (23) for porous elastomers with *compressible* matrix phases and carry out the asymptotic analysis corresponding to the incompressible limit $\kappa \to \infty$. In this context, it is important to realize that two root combinations among the four possible ones described in Appendix B lead to estimates for $\widehat{W}$ that become unbounded in the limit as $\kappa \to \infty$. More precisely, for $\overline{J} > 1$ ($\overline{J} < 1$) the "positive" (+) ("negative" (−)) root in (43) results in estimates for $\widehat{W}$ that blow up as $\kappa \to \infty$, regardless of the choice of roots for p_4 in expression (49). (For $\overline{J} = 1$ the asymptotic behavior of the roots is different and it will be addressed below.) These estimates suggest that a porous elastomer with an incompressible matrix phase would be itself incompressible, which is in contradiction with experimental evidence. Moreover, the two estimates associated with each of the roots in (49) for $\widehat{W}$ that remain finite in the limit of incompressibility of the matrix phase are considerably different, in general. In order to discern which one of them is the better estimate, we make contact with the evolution of the microstructure. First, we recall that the evolution of porosity in porous elastomers with incompressible matrix phases can be computed *exactly* and the result is given by (31) in the text. In this regard, we note that the evolution of porosity associated with the two above finite estimates can be shown to be *exact* up to second order in the strain (i.e., up to $(\overline{\lambda}_i - 1)^2$). However, for larger deformations, the porosities associated with these two roots differ significantly from each other with the choice $p_4 = \text{sign}((\overline{\lambda}_1^{(1)} - \overline{\lambda}_1)(\overline{\lambda}_2^{(1)} - \overline{\lambda}_2)(\overline{\lambda}_3^{(1)} - \overline{\lambda}_3))\sqrt{p_1 p_2 p_3}$ in (49) leading to a better approximation to the exact result (31) than the alternative root. Thus, based on the above-presented physical arguments, there is only one root combination among the four possible choices that lead to physically meaningful, superior estimates in the limit as $\kappa \to \infty$, namely, for $\overline{J}<1$ (for $\overline{J}>1$), the "positive" (+) ("negative" (−)) root in (43) with the choice $p_4 = \text{sign}((\overline{\lambda}_1^{(1)} - \overline{\lambda}_1)(\overline{\lambda}_2^{(1)} - \overline{\lambda}_2)(\overline{\lambda}_3^{(1)} - \overline{\lambda}_3))\sqrt{p_1 p_2 p_3}$ in (49). Regarding these combinations, it is important to make the following two remarks. First, both these combinations can be shown to generate estimates for deformations with $\overline{J}=1$ that are superior to the other two alternatives. Moreover, the full numerical solution suggests that these two superior choices, (+) and (−) in (43) with the $p_4 = \text{sign}((\overline{\lambda}_1^{(1)} - \overline{\lambda}_1)(\overline{\lambda}_2^{(1)} - \overline{\lambda}_2)(\overline{\lambda}_3^{(1)} - \overline{\lambda}_3))\sqrt{p_1 p_2 p_3}$ in (49), lead in fact to the same estimate for $\widehat{W}$ when $\overline{J}=1$. This is difficult to verify analytically, however, since the equations associated with the (+) root develop a singularity as $\kappa \to \infty$ when approaching $\overline{J}=1$. Second, the asymptotic analysis associated with the superior root for deformations with $\overline{J}<1$ leads exactly to the same expression for the effective stored-energy function $\widehat{W}^I$ as the one obtained from the analysis associated with the superior root for deformations with $\overline{J}>1$. In conclusion, the stored-energy function $\widehat{W}^I$ can be written as a single expression valid for all values of $\overline{J}(>0)$. Next, we sketch out the derivation of such expression.

Based on numerical evidence from the results for finite κ, an expansion for the unknowns in this problem, i.e., ℓ_α^* ($\alpha = 1, 2, \ldots, 7$), is attempted in the limit as $\kappa \to \infty$ of the following form:

$$
\begin{aligned}
\ell_1^* &= a_1 \Delta^{-1} + a_2 + a_3 \Delta + O(\Delta^2),\\
\ell_2^* &= b_1 \Delta^{-1} + b_2 + b_3 \Delta + O(\Delta^2),\\
\ell_3^* &= c_1 \Delta^{-1} + c_2 + c_3 \Delta + O(\Delta^2),\\
\ell_4^* &= d_1 \Delta^{-1} + d_2 + d_3 \Delta + O(\Delta^2),\\
\ell_5^* &= e_1 \Delta^{-1} + e_2 + e_3 \Delta + O(\Delta^2),\\
\ell_6^* &= m_1 \Delta^{-1} + m_2 + m_3 \Delta + O(\Delta^2),\\
\ell_7^* &= n_2 + n_3 \Delta + O(\Delta^2),
\end{aligned}
\tag{50}
$$

where $\Delta \doteq 1/\kappa$ is a small parameter and a_1, a_2, a_3, b_1, b_2, b_3, c_1, c_2, c_3, d_1, d_2, d_3, e_1, e_2, e_3, m_1, m_2, m_3, n_2, and n_3 are unknown coefficients to be determined from the asymptotic analysis that follows. It proves useful to spell out the corresponding expansions of the constrained moduli L_{1221}^*, L_{1331}^*, L_{2332}^*, as well as those for (the non-zero components of $\overline{\mathbf{F}}^{(1)}$) $\overline{\lambda}_1^{(1)}$, $\overline{\lambda}_2^{(1)}$, $\overline{\lambda}_3^{(1)}$ and the combinations (of the components of $\hat{\mathbf{F}}^{(1)}$) Y_1, Y_2, Y_3, p_1, p_2, p_3, p_4, and s, in the limit as $\kappa \to \infty$. Thus, substituting expressions (50) in relations (40) for the components L_{1221}^*, L_{1331}^*, L_{2332}^* can be shown to lead to the following expansions:

$$
L_{1221}^* = (\sqrt{a_1 b_1} - d_1)\Delta^{-1} + \frac{a_2 b_1 + a_1 b_2 - (a_1 + b_1) n_2}{2\sqrt{a_1 b_1}} - d_2 + O(\Delta),
$$

$$L^*_{1331} = (\sqrt{a_1c_1} - e_1)\Delta^{-1} + \frac{a_2c_1 + a_1c_2 - (a_1 + c_1)n_2}{2\sqrt{a_1c_1}} - e_2 + O(\Delta),$$

$$L^*_{2332} = (\sqrt{b_1c_1} - m_1)\Delta^{-1} + \frac{b_2c_1 + b_1c_2 - (b_1 + c_1)n_2}{2\sqrt{b_1c_1}} - m_2 + O(\Delta). \tag{51}$$

Similarly, substituting (50) in relations (41) leads to

$$\overline{\lambda}^{(1)}_1 = \mathring{\overline{\lambda}}^{(1)}_1 + \check{\overline{\lambda}}^{(1)}_1\Delta + O(\Delta^2), \quad \overline{\lambda}^{(1)}_2 = \check{\overline{\lambda}}^{(1)}_2 + \mathring{\overline{\lambda}}^{(1)}_2\Delta + O(\Delta^2),$$
$$\overline{\lambda}^{(1)}_3 = \mathring{\overline{\lambda}}^{(1)}_3 + \check{\overline{\lambda}}^{(1)}_3\Delta + O(\Delta^2). \tag{52}$$

The explicit form of the coefficients $\mathring{\overline{\lambda}}^{(1)}_i$, $\check{\overline{\lambda}}^{(1)}_i$ $(i = 1, 2, 3)$ in these last expressions is too cumbersome to be included here. In any case, at this stage, it suffices to remark that they are known in terms of the coefficients $a_1, a_2, a_3, b_1, b_2, b_3, c_1, c_2, c_3, d_1, d_2, d_3, e_1, e_2, e_3, m_1, m_2, m_3, n_2$, and n_3 introduced in (50). Finally, substituting (50) in relations (43), (44), and (in the appropriate root of) (49) leads to:

$$Y_1 = \mathring{Y}_1 + \check{Y}_1\Delta + O(\Delta^2),$$

$$Y_2 = \mathring{Y}_2 + \check{Y}_2\Delta + O(\Delta^2),$$

$$Y_3 = \mathring{Y}_3 + \check{Y}_3\Delta + O(\Delta^2),$$

$$p_1 = \mathring{p}_1 + \check{p}_1\Delta + O(\Delta^2),$$

$$p_2 = \mathring{p}_2 + \check{p}_2\Delta + O(\Delta^2),$$

$$p_3 = \mathring{p}_3 + \check{p}_3\Delta + O(\Delta^2),$$

$$p_4 = \mathring{p}_4 + O(\Delta) = \mathrm{sign}[(\mathring{\overline{\lambda}}^{(1)}_1 - \overline{\lambda}_1)(\mathring{\overline{\lambda}}^{(1)}_2 - \overline{\lambda}_2)(\mathring{\overline{\lambda}}^{(1)}_3 - \overline{\lambda}_3)]\sqrt{\mathring{p}_1\mathring{p}_2\mathring{p}_3} + O(\Delta),$$

$$s = s_1 + O(\Delta), \tag{53}$$

where, similar to (52), the coefficients in these expressions are (known functions of the coefficients defined in (50)) too cumbersome to be included here. For later use, it is convenient to introduce the expansion of $\hat{J}^{(1)} = \det \hat{\mathbf{F}}^{(1)}$:

$$\hat{J}^{(1)} = \hat{J}^{(1)}_1 + \hat{J}^{(1)}_2\Delta + O(\Delta^2), \tag{54}$$

where, making contact with (53), we note that $\hat{J}^{(1)}_1 = (\mathring{Y}_1 + \overline{\lambda}_1)(\mathring{Y}_2 + \overline{\lambda}_2)(\mathring{Y}_3 + \overline{\lambda}_3) - \mathring{p}_1(\mathring{Y}_3 + \overline{\lambda}_3) - \mathring{p}_2(\mathring{Y}_2 + \overline{\lambda}_2) - \mathring{p}_3(\mathring{Y}_1 + \overline{\lambda}_1) + 2\mathring{p}_4$. In addition, it will also prove useful to introduce the following notation for the expansions of the derivatives of the constitutive functions g and h characterizing the elastomeric matrix phase in the limit as $\kappa \to \infty$:

$$\hat{g}_I = \hat{g}'_1 + \hat{g}'_2\Delta + O(\Delta^2),$$

$$\hat{h}_J = \hat{h}'_1 + \hat{h}'_2\Delta + O(\Delta^2), \tag{55}$$

where it is recalled that $\hat{g}_I = g_I(\hat{I}^{(1)})$, $\hat{h}_J = h_J(\hat{J}^{(1)})$, and $\hat{I}^{(1)}$ and $\hat{J}^{(1)}$ are given by (48).

Next, by making use of expressions (50)–(55) in (46), a hierarchical system of equations is obtained for the unknown coefficients introduced in (50). The first set of equations, of order $O(\Delta^{-1})$, can be shown to yield the following non-trivial relations:

$$b_1 = \frac{\overline{\lambda}_1^2}{\overline{\lambda}_2^2} a_1, \quad c_1 = \frac{\overline{\lambda}_1^2}{\overline{\lambda}_3^2} a_1, \quad d_1 = \frac{\overline{\lambda}_1}{\overline{\lambda}_2} a_1, \quad e_1 = \frac{\overline{\lambda}_1}{\overline{\lambda}_3} a_1, \quad m_1 = \frac{\overline{\lambda}_1^2}{\overline{\lambda}_2 \overline{\lambda}_3} a_1, \tag{56}$$

and

$$(\mathring{Y}_1 + \overline{\lambda}_1)(\mathring{Y}_2 + \overline{\lambda}_2)(\mathring{Y}_3 + \overline{\lambda}_3) - \mathring{p}_1(\mathring{Y}_3 + \overline{\lambda}_3) - \mathring{p}_2(\mathring{Y}_2 + \overline{\lambda}_2) \\ - \mathring{p}_3(\mathring{Y}_1 + \overline{\lambda}_1) + 2\mathring{p}_4 = 1. \tag{57}$$

Note that Eqs. (56) correspond actually to *explicit* expressions for the unknowns b_1, c_1, d_1, e_1, and m_1 in terms of the coefficient a_1. Interestingly, relations (56) make the leading order terms in the shear moduli (51) vanish identically, so that, in the limit of incompressibility, these moduli remain finite, as it would normally be expected on physical grounds. On the other hand, Eq. (57)—which can also be written as $\hat{J}_1^{(1)} = 1$—is an *implicit* equation that ultimately involves the coefficients a_1, a_2, b_2, c_2, d_2, e_2, m_2, and n_2. Now, by making use of (56) and (57), the second hierarchy of equations, of order $O(\Delta^0)$, can be shown to ultimately yield the following relations:

$$a_2 \mathring{Y}_1 + d_2 \mathring{Y}_2 + e_2 \mathring{Y}_3 + a_1 \left(\check{Y}_1 + \frac{\overline{\lambda}_1}{\overline{\lambda}_2} \check{Y}_2 + \frac{\overline{\lambda}_1}{\overline{\lambda}_3} \check{Y}_3 \right) \\ = 2\hat{g}_1'(\mathring{Y}_1 + \overline{\lambda}_1) + (\hat{h}_1' + \hat{J}_2^{(1)})[(\mathring{Y}_2 + \overline{\lambda}_2)(\mathring{Y}_3 + \overline{\lambda}_3) - \mathring{p}_3] - 2\overline{g}_I \overline{\lambda}_1 - \overline{h}_J \overline{\lambda}_2 \overline{\lambda}_3,$$

$$d_2 \mathring{Y}_1 + b_2 \mathring{Y}_2 + m_2 \mathring{Y}_3 + a_1 \frac{\overline{\lambda}_1}{\overline{\lambda}_2} \left(\check{Y}_1 + \frac{\overline{\lambda}_1}{\overline{\lambda}_2} \check{Y}_2 + \frac{\overline{\lambda}_1}{\overline{\lambda}_3} \check{Y}_3 \right) \\ = 2\hat{g}_1'(\mathring{Y}_2 + \overline{\lambda}_2) + (\hat{h}_1' + \hat{J}_2^{(1)})[(\mathring{Y}_1 + \overline{\lambda}_1)(\mathring{Y}_3 + \overline{\lambda}_3) - \mathring{p}_2] - 2\overline{g}_I \overline{\lambda}_2 - \overline{h}_J \overline{\lambda}_1 \overline{\lambda}_3,$$

$$e_2 \mathring{Y}_1 + m_2 \mathring{Y}_2 + c_2 \mathring{Y}_3 + a_1 \frac{\overline{\lambda}_1}{\overline{\lambda}_3} \left(\check{Y}_1 + \frac{\overline{\lambda}_1}{\overline{\lambda}_2} \check{Y}_2 + \frac{\overline{\lambda}_1}{\overline{\lambda}_3} \check{Y}_3 \right) \\ = 2\hat{g}_1'(\mathring{Y}_3 + \overline{\lambda}_3) + (\hat{h}_1' + \hat{J}_2^{(1)})[(\mathring{Y}_1 + \overline{\lambda}_1)(\mathring{Y}_2 + \overline{\lambda}_2) - \mathring{p}_1] - 2\overline{g}_I \overline{\lambda}_3 - \overline{h}_J \overline{\lambda}_1 \overline{\lambda}_2,$$

$$\frac{1}{2}\left(\frac{\overline{\lambda}_1}{\overline{\lambda}_2} a_2 + \frac{\overline{\lambda}_2}{\overline{\lambda}_1} b_2 \right) - \frac{\overline{\lambda}_1^2 + \overline{\lambda}_2^2}{2\overline{\lambda}_1 \overline{\lambda}_2} n_2 - d_2 = (\hat{h}_1' + \hat{J}_2^{(1)}) \left[\frac{\mathring{p}_4}{\mathring{p}_1} - (\mathring{Y}_3 + \overline{\lambda}_3) \right],$$

$$\frac{1}{2}\left(\frac{\overline{\lambda}_1}{\overline{\lambda}_3} a_2 + \frac{\overline{\lambda}_3}{\overline{\lambda}_1} c_2 \right) - \frac{\overline{\lambda}_1^2 + \overline{\lambda}_3^2}{2\overline{\lambda}_1 \overline{\lambda}_3} n_2 - e_2 = (\hat{h}_1' + \hat{J}_2^{(1)}) \left[\frac{\mathring{p}_4}{\mathring{p}_2} - (\mathring{Y}_2 + \overline{\lambda}_2) \right],$$

$$n_2 = 2\hat{g}_1', \tag{58}$$

and

$$\hat{h}_1' + \hat{J}_2^{(1)} = \left[\frac{\mathring{p}_4}{\mathring{p}_3} - (\mathring{Y}_1 + \overline{\lambda}_1) \right]^{-1} \left(\frac{1}{2}\left(\frac{\overline{\lambda}_2}{\overline{\lambda}_3} b_2 + \frac{\overline{\lambda}_3}{\overline{\lambda}_2} c_2 \right) - \frac{\overline{\lambda}_2^2 + \overline{\lambda}_3^2}{2\overline{\lambda}_2 \overline{\lambda}_3} n_2 - m_2 \right). \tag{59}$$

Solving (59) for $\hat{J}_2^{(1)}$, the second term in the expansion (54), and substituting the result in Eqs. (58), can be shown to ultimately lead to a system of seven nonlinear equations—

formed by Eqs. (57) and (58)—for the seven unknowns:

$$u_1 \doteq a_1, \quad u_2 \doteq n_2, \quad u_3 \doteq \overline{\lambda}_1^2 b_2 - \overline{\lambda}_1^2 a_2, \quad u_4 \doteq \overline{\lambda}_3^2 c_2 - \overline{\lambda}_1^2 a_2,$$

$$u_5 \doteq \overline{\lambda}_2 d_2 - \overline{\lambda}_1 a_2, \quad u_6 \doteq \overline{\lambda}_3 e_2 - \overline{\lambda}_1 a_2, \quad u_7 \doteq \overline{\lambda}_2 m_2 - \overline{\lambda}_3 c_2. \tag{60}$$

Here, the primitive coefficients a_1 and n_2 have been relabeled as u_1 and u_2, respectively, for consistency of notation.

At this point, it is important to recognize that knowledge of the seven variables (60), as determined by the system of seven equations (57)–(58), suffices to determine the leading-order terms (of the components of $\overline{\mathbf{F}}^{(1)}$) $\overset{\circ}{\overline{\lambda}}{}_1^{(1)}$, $\overset{\circ}{\overline{\lambda}}{}_2^{(1)}$, $\overset{\circ}{\overline{\lambda}}{}_3^{(1)}$, in (52) and (of the combinations of the components of $\hat{\mathbf{F}}^{(1)}$) $\overset{\circ}{Y}_1$, $\overset{\circ}{Y}_2$, $\overset{\circ}{Y}_3$, $\overset{\circ}{p}_1$, $\overset{\circ}{p}_2$, $\overset{\circ}{p}_3$,$\overset{\circ}{p}_4$, and s_1, in (53), as well as the second-order traces $\breve{\overline{\lambda}}{}_1^{(1)}\overline{\lambda}_2\overline{\lambda}_3 + \breve{\overline{\lambda}}{}_2^{(1)}\overline{\lambda}_1\overline{\lambda}_3 + \breve{\overline{\lambda}}{}_3^{(1)}\overline{\lambda}_1\overline{\lambda}_2$ and $\breve{Y}_1\overline{\lambda}_2\overline{\lambda}_3 + \breve{Y}_2\overline{\lambda}_1\overline{\lambda}_3 + \breve{Y}_3\overline{\lambda}_1\overline{\lambda}_2$. The corresponding final expressions are too cumbersome to be written down here, however, they do satisfy certain interesting, simple relations which worth recording, namely

$$\overset{\circ}{Y}_1 = \overset{\circ}{\overline{\lambda}}{}_1^{(1)} + \overline{\lambda}_1, \quad \overset{\circ}{Y}_2 = \overset{\circ}{\overline{\lambda}}{}_2^{(1)} + \overline{\lambda}_2, \quad \overset{\circ}{Y}_3 = \overset{\circ}{\overline{\lambda}}{}_3^{(1)} + \overline{\lambda}_3,$$

$$\overset{\circ}{p}_1 = \frac{1}{f_0}(\overset{\circ}{\overline{\lambda}}{}_1^{(1)} - \overline{\lambda}_1)(\overset{\circ}{\overline{\lambda}}{}_2^{(1)} - \overline{\lambda}_2), \quad \overset{\circ}{p}_2 = \frac{1}{f_0}(\overset{\circ}{\overline{\lambda}}{}_1^{(1)} - \overline{\lambda}_1)(\overset{\circ}{\overline{\lambda}}{}_3^{(1)} - \overline{\lambda}_3),$$

$$\overset{\circ}{p}_3 = \frac{1}{f_0}(\overset{\circ}{\overline{\lambda}}{}_2^{(1)} - \overline{\lambda}_2)(\overset{\circ}{\overline{\lambda}}{}_3^{(1)} - \overline{\lambda}_3),$$

$$\breve{\overline{\lambda}}{}_1^{(1)}\overline{\lambda}_2\overline{\lambda}_3 + \breve{\overline{\lambda}}{}_2^{(1)}\overline{\lambda}_1\overline{\lambda}_3 + \breve{\overline{\lambda}}{}_3^{(1)}\overline{\lambda}_1\overline{\lambda}_2 = \breve{Y}_1\overline{\lambda}_2\overline{\lambda}_3 + \breve{Y}_2\overline{\lambda}_1\overline{\lambda}_3 + \breve{Y}_3\overline{\lambda}_1\overline{\lambda}_2. \tag{61}$$

Finally, by making use of the above results, it can be shown that the leading-order term of the second-order estimate (23) in the limit of incompressibility is given by (26) in the text, where

$$\hat{I}^{(1)} = (\overset{\circ}{Y}_1 + \overline{\lambda}_1)^2 + (\overset{\circ}{Y}_2 + \overline{\lambda}_2)^2 + (\overset{\circ}{Y}_3 + \overline{\lambda}_3)^2 + s_1. \tag{62}$$

In this relation, it should be emphasized again that the expressions for $\overset{\circ}{Y}_1$, $\overset{\circ}{Y}_2$, $\overset{\circ}{Y}_3$, and s_1 are known—but not shown here for their bulkiness—explicitly in terms of the applied loading, $\overline{\lambda}_1$, $\overline{\lambda}_2$, $\overline{\lambda}_3$, the initial porosity, f_0, the constitutive function, g, and the seven variables u_α, defined by (60), that are the solutions to the system of the seven nonlinear, algebraic equations formed by (57) and (58).

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