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On the overall behavior, microstructure evolution, and macroscopic stability in reinforced rubbers at large deformations: I—Theory

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Abstract

This work presents an analytical framework for determining the overall constitutive response of elastomers that are reinforced by *rigid* or *compliant* fibers, and are subjected to finite deformations. The framework accounts for the evolution of the underlying microstructure, including particle rotation, which results from the finite changes in geometry that are induced by the applied loading. In turn, the evolution of the microstructure can have a significant *geometric* softening (or hardening) effect on the overall response, leading to the possible development of macroscopic instabilities through loss of strong ellipticity of the homogenized incremental moduli. The theory is based on a recently developed "second-order" homogenization method, which makes use of information on both the first and second moments of the fields in a suitably chosen "linear comparison composite," and generates fairly explicit estimates—linearizing properly—for the large-deformation effective response of the reinforced elastomers. More specific applications of the results developed in this paper will be presented in Part II.

Keywords: Microstructures; Finite strain; Rubber material; Particulate reinforced material; Variational calculus

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1. Introduction

Elastomeric materials are used pervasively in industry. Applications include rubber tires, shoes, flexible tubes and catheters, cable coatings, conveyor and transmission belts, balloons, shock absorbers, etc. More often than not, these materials are reinforced with particles, or fibers to improve their mechanical properties and, in particular, their overall stiffness. The standard example is a rubber tire, which derives its black color from the presence of carbon-black particles that are distributed randomly in a matrix of a synthetic rubber. At a larger length scale, rubber tires are also reinforced with steel, or other types of fibers. Other commonly used micron- and nano-sized fillers include silica, mica, talc, clay, calcium carbonate particles, as well as carbon nanotubes. In addition, there is a large class of thermoplastic polymers, which exhibit rubber-like behavior, namely, thermoplastic elastomers (TPEs). These materials are block copolymers where the "hard" glassy blocks self-aggregate into an "inclusion" phase that is embedded in a "matrix" of the "soft" rubbery blocks, thus leading to a "particulate" microstructure with an overall rubbery response. The hard blocks, which can appear in the form of layers, fibers or particles, are distributed in a periodic arrangement, and play the role of the reinforcing phase. They are increasingly being used in industry—where they are replacing standard cross-linked rubbers in many technological applications—due to their superior mechanical and recycling properties.

Because these materials are often used in situations involving large deformations, it is of practical, as well as theoretical interest to develop sound constitutive models that somehow incorporate the effect of the fillers on their overall behavior. But the models must be simple enough to implement in standard finite element codes to be able to carry out simulations at the structural level. This presents a challenging problem in *homogenization* for at least two reasons. First, there is the strong material nonlinearity that is present in constitutive models for pure, or "neat" elastomers, and second, there is the additional complication of the evolution of the size, shape, position and orientation of the fillers, or microstructure, due to the finite changes in geometry induced during loading. Presumably because of the technical difficulties associated with modeling this complex behavior, most of the work in the literature to date has been based on empirical or ad hoc models, such as those making use of the notion of a strain-amplification factor (Mullins and Tobin, 1965; Treolar, 1975; Meinecke and Taftaf, 1988; Govindjee and Simo, 1991). There are also recent numerical simulations based on unit-cell computations, either for periodic media (Lahellec et al., 2004; Triantafyllidis et al., 2005), or for systems with more complex microstructures (Govindjee, 1997; Bergström and Boyce, 1999). In terms of rigorous work, there is the Voigt-type upper bound (Ogden, 1978), as well as some non-trivial lower bounds (Ponte Castañeda, 1989). Unfortunately, these bounds are microstructure-independent, and therefore not very useful for particle-reinforced rubbers. An exact result has been generated recently (deBotton, 2005) for hyperelastic composites with a very special type of microstructure known as sequentially laminated microstructures. Again this result is rather special, and it is not clear whether, or not, it corresponds to filled elastomers with more realistic types of microstructures.

In this work, use will be made of some recently developed nonlinear homogenization techniques, which are based on suitably constructed variational principles utilizing the notion of a "linear comparison composite." The first attempt along these lines for hyperelastic composites was carried out by Ponte Castañeda and Tiberio (2000) (see also

Willis, 2000; Lahellec et al., 2004), who made use of the so-called "second-order" variational procedure, initially proposed for viscoplastic materials by Ponte Castañeda (1996). While the resulting estimates certainly had some desirable properties, such as the ability to account for the particle stiffness, shape, concentration and distribution, they also had some shortcomings. Thus, for example, they were able to recover only approximately the overall incompressibility constraint associated with rigidly reinforced elastomers with an incompressible matrix phase (typical of rubbers). In retrospect, this was not too surprising in view of the strong nonlinearity associated with the incompressibility constraint on the determinant of the deformation. Here, use will be made of an improved second-order method, also first developed in the context of viscoplastic composites (Ponte Castañeda, 2002), but then extended to hyperelastic composites by Lopez-Pamies and Ponte Castañeda (2004a), which makes use of the local field fluctuations in the determination of the relevant linear comparison composite. A first application of this method in the context of particle-reinforced rubbers with isotropic microstructures was carried out by Lopez-Pamies and Ponte Castañeda (2004a). It was found to provide much more accurate estimates satisfying exactly the overall incompressibility constraint for rigidly reinforced elastomers with an incompressible matrix phase. In the present work, we consider composite elastomers reinforced by ellipsoidal particles, leading to much more complex overall responses, on account of the possible rotation of the particles at large deformations. As will be seen in Part II of this article (Lopez-Pamies and Ponte Castañeda, 2006), the models to be developed in this part (I) can lead to the development of macroscopic instabilities of the "flopping" type, where the effective incremental shear modulus of the composite (transverse to the compressive axis) vanishes when a sufficiently high *compressive* deformation is applied along the long axes of the particles. This example serves to demonstrate that the macroscopic behavior of composite elastomers, and, in particular, particle-reinforced rubbers, depends very sensitively on the evolution of the microstructure, which, in turn, is highly dependent on the specific loading conditions that are applied to the material.

For simplicity, we will ignore here hysteresis, temperature and rate-dependent effects, which can be important for these materials (Bergström and Boyce, 1998), as well as the possible development of damage, through particle debonding at interfaces. However, it should be mentioned that models of the type to be developed here for particle-reinforced elastomers are also being developed for porous elastomers (Lopez-Pamies and Ponte Castañeda, 2004b).

2. Preliminaries on hyperelastic composites

Consider a material made up of N different (homogeneous) phases distributed randomly in a specimen occupying a volume Ω_0 in the reference configuration, where the characteristic length of the inhomogeneities (e.g., particles) is assumed to be much smaller than the size of the specimen and the scale of variation of the applied loading.

The constitutive behavior of the phases is characterized by stored-energy functions $W^{(r)}$ $(r = 1, \ldots, N)$, which are taken to be non-convex functions of the deformation gradient tensor $\mathbf{F}$. Thus, the local stored-energy function of the hyperelastic composite is expressible as:

$$W(\mathbf{X}, \mathbf{F}) = \sum_{r=1}^{N} \chi^{(r)}(\mathbf{X}) W^{(r)}(\mathbf{F}), \tag{1}$$

where the characteristic functions $\chi^{(r)}$ are equal to 1 if the position vector $\mathbf{X}$ is inside phase r (i.e., $\mathbf{X} \in \Omega_0^{(r)}$) and zero otherwise. The local or microscopic constitutive relation for the composite is then 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 $\mathbf{F}$. The stored-energy functions of the phases are, of course, assumed to be *objective* so that $W^{(r)}(\mathbf{KF}) = W^{(r)}(\mathbf{F})$ for all proper orthogonal $\mathbf{K}$ and arbitrary deformation gradients $\mathbf{F}$. In particular, by making use of the polar decomposition $\mathbf{F} = \mathbf{RU}$, where $\mathbf{U}$ is the right stretch tensor and $\mathbf{R}$ is the rotation tensor, it follows that $W^{(r)}(\mathbf{F}) = W^{(r)}(\mathbf{U})$. Furthermore, the stored-energy functions $W^{(r)}$ will be assumed to be such that $W^{(r)}(\mathbf{F}) \to \infty$ as $\det \mathbf{F} \to 0+$, to ensure the *material impenetrability* condition: $\det \mathbf{F}(\mathbf{X}) > 0$ for $\mathbf{X}$ in Ω_0. Note that this condition would be automatically satisfied for incompressible materials, where $\det \mathbf{F}$ is required to be identically 1.

Under the further hypothesis of *statistical uniformity*, the global or macroscopic constitutive relation for the composite is given by (Hill, 1972)

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

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

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

is the *effective stored-energy function* of the composite. In the above expressions, the brackets $\langle . \rangle$ and $\langle . \rangle^{(r)}$ denote volume averages over the composite (Ω_0) and over the phase r ($\Omega_0^{(r)}$), respectively, so that the scalars $c_0^{(r)} = \langle \chi^{(r)} \rangle$ represent the initial volume fractions of the given phases. Furthermore, $\mathscr{K}$ denotes the set of admissible deformation gradients:

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

Note that $\widetilde{W}$ physically represents the average elastic energy stored in the composite when subjected to an affine displacement boundary condition. Moreover, from definition (4) and the objectivity of $W^{(r)}$, it can be shown that $\widetilde{W}$ is objective, namely, $\widetilde{W}(\overline{\mathbf{F}}) = \widetilde{W}(\overline{\mathbf{U}})$. Here, $\overline{\mathbf{U}}$ represents the macroscopic right-stretch tensor associated with the macroscopic polar decomposition $\overline{\mathbf{F}} = \overline{\mathbf{R}}\,\overline{\mathbf{U}}$, with $\overline{\mathbf{R}}$ denoting the macroscopic rotation tensor (of course, $\langle \mathbf{U} \rangle \neq \overline{\mathbf{U}}$ and $\langle \mathbf{R} \rangle \neq \overline{\mathbf{R}}$). In turn, the objectivity of $\widetilde{W}$ implies the macroscopic rotational balance equation $\overline{\mathbf{S}}\,\overline{\mathbf{F}}^{\mathrm{T}} = \overline{\mathbf{F}}\,\overline{\mathbf{S}}^{\mathrm{T}}$ (Hill, 1972).

It is further recalled that since W cannot be convex, suitable hypothesis are needed to ensure the existence of minimizers in (4). Ball (1977) has provided sufficient conditions for the existence of such minimizers, including the hypothesis of *polyconvexity* of W, together with suitable growth conditions for W. More mathematically precise definitions of the effective energy $\widetilde{W}$ for *periodic* microstructures have been given by Braides (1985) and Müller (1987). Such definitions generalize the classical definition of the effective energy for periodic media with convex energies (Marcellini, 1978), by accounting for the fact that, in the non-convex case, it is not sufficient to consider one-cell periodic solutions, as solutions involving interactions between several unit cells may lead to lower overall energies.

Physically, this corresponds to the possible development of "microscopic" instabilities in the composite at sufficiently high deformation. In this connection, it is important to remark that Geymonat et al. (1993), following earlier work by Triantafyllidis and Maker (1985) for laminated materials, have shown rigorously that loss of strong ellipticity in the homogenized behavior of the composite corresponds to the development of long-wavelength (i.e., "macroscopic") instabilities in the form of localized shear bands. Furthermore, the "failure surfaces" defined by the loss of strong ellipticity condition of this homogenized behavior provide upper bounds for the onset of other types of instabilities.

Because of the difficulties associated with the computation of the microscopic instabilities mentioned in the previous paragraph, especially for composites with random microstructures, a more pragmatic approach will be followed here. Assuming that the materials of interest have a stress-free configuration at $\mathbf{F}=\mathbf{I}$, and that their behavior is characterized by the standard theory of linear elasticity for small enough deformations, it follows that, at least in a neighborhood of $\mathbf{F}=\mathbf{I}$, 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 nonlinear range, the composite material may reach a point at which this "principal" solution bifurcates into lower-energy solutions. This point corresponds to the onset of a *microscopic* 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. This means that, in practice, we will estimate the effective stored-energy function (4) by means of the *stationary* variational statement:

$$\widehat{W}(\overline{\mathbf{F}})=\operatorname*{stat}_{\mathbf{F}\in\mathscr{K}(\overline{\mathbf{F}})}\sum_{r=1}^{N}c_0^{(r)}\langle W^{(r)}(\mathbf{F})\rangle^{(r)}, \tag{6}$$

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 $\widetilde{W}(\overline{\mathbf{F}})=\widehat{W}(\overline{\mathbf{F}})$ up to the onset of the first *microscopic* instability. Beyond this point, and up to the onset of the first *macroscopic* instability, $\widetilde{W}(\overline{\mathbf{F}})\leqslant\widehat{W}(\overline{\mathbf{F}})$. The point is that while the microscopic instabilities are difficult to compute, the macroscopic instabilities are easy to estimate from $\widehat{W}(\overline{\mathbf{F}})$. Furthermore, it is often the case (Geymonat et al., 1993; Triantafyllidis et al., 2005) 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 the homogenized moduli associated with $\widehat{W}(\overline{\mathbf{F}})$. More generally, the first instability is of finite wavelength (i.e., small compared to the size of the specimen), but even in this case, it so happens, as we have already mentioned, that the loss of strong ellipticity of the homogenized energy $\widehat{W}(\overline{\mathbf{F}})$ provides an upper bound for the development of microscopic instabilities. In other words, the composite material will become unstable before reaching the "failure surface" defined by the macroscopic instabilities. Furthermore, recent work (Michel et al., 2005) suggests that the macroscopic instabilities may be the more relevant ones for random systems, since many of the microscopic instabilities in periodic systems tend to disappear as the periodicity of the microstructure is broken down.

The primary objective of this work is to obtain estimates for the effective stored-energy function of the above-defined hyperelastic composites subjected to finite deformations, with particular interest in the special case of particle-reinforced elastomers. A second objective will be to study the evolution of the underlying microstructure, as well as the possible loss of strong ellipticity of the homogenized behavior of these materials. Because of the difficulties mentioned in the previous paragraphs, there are very few *analytical* estimates for $\widetilde{W}$ in the literature. As already mentioned, there is the Voigt-type bound that can be generated by making use of the trivial trial field $\mathbf{F}=\overline{\mathbf{F}}$ in (4) (Ogden, 1978), as well as some non-trivial lower bounds that can be generated by exploiting the *polyconvexity* hypothesis (Ponte Castañeda, 1989). Our proposal here will be to use the "second-order" homogenization theory of Ponte Castañeda (2002). This homogenization technique—still under development—was first applied to hyperelastic composites by Lopez-Pamies and Ponte Castañeda (2004a), and has the distinguishing feature of being exact to second-order in the heterogeneity contrast. Even if the theory still remains to be fully optimized, it has recently been shown to provide accurate estimates not only for the effective behavior, but even for the more sensitive information on the onset of macroscopic instabilities, for composite elastomers with periodic microstructures (Michel et al., 2005). For completeness, a concise derivation is given in the next section of the second-order homogenization procedure, including an up-to-date discussion of the optimality of the method.

3. Second-order homogenization method

The main idea behind the second-order homogenization theory is the construction of a *fictitious* linear comparison composite (LCC) with the same microstructure as the nonlinear composite (i.e., the same $\chi^{(r)}$). Thus, the local stored-energy function of the LCC may be written as:

$$W_T(\mathbf{X},\mathbf{F})=\sum_{r=1}^{N}\chi^{(r)}(\mathbf{X})W_T^{(r)}(\mathbf{F}), \tag{7}$$

where the quadratic functions $W_T^{(r)}$ are given by the second-order Taylor approximations of the nonlinear stored-energy functions $W^{(r)}$ about some reference deformation gradients $\mathbf{F}^{(r)}$:

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

Here, use has been made of the notation $\mathscr{S}^{(r)}(\mathbf{F})=\partial W^{(r)}(\mathbf{F})/\partial\mathbf{F}$, and the $\mathbf{L}^{(r)}$ are fourth-order tensors with major symmetry to be determined later.

Next, "corrector" functions $V^{(r)}$ are introduced such that

$$V^{(r)}(\mathbf{F}^{(r)},\mathbf{L}^{(r)})=\operatorname*{stat}_{\hat{\mathbf{F}}^{(r)}}[W^{(r)}(\hat{\mathbf{F}}^{(r)})-W_T^{(r)}(\hat{\mathbf{F}}^{(r)})]. \tag{9}$$

These functions, which are multiple-valued depending on the parameters $\mathbf{F}^{(r)}$ and $\mathbf{L}^{(r)}$, serve to measure the nonlinearity of the phases of the original material, so that, under appropriate hypotheses, the local stored-energy functions of the phases of the nonlinear composite may be written as

$$W^{(r)}(\mathbf{F})=\operatorname*{stat}_{\mathbf{L}^{(r)}}\{W_T^{(r)}(\mathbf{F})+V^{(r)}(\mathbf{F}^{(r)},\mathbf{L}^{(r)})\} \tag{10}$$

for any choice of the reference deformations $\mathbf{F}^{(r)}$. In connection with this expression, it should be emphasized that the appropriate branches of the functions $V^{(r)}$ must be chosen in order to recover the equality. Note that this relation may still be used in an *approximate* sense, even when the local potentials are such that the equality in relation (10) does not hold strictly.

Now, by making use of (10) and interchanging the stationarity operations with respect to $\mathbf{F}$ and $\mathbf{L}^{(r)}$ in expression (6), it follows that the effective stored-energy function $\widehat{W}$ of the nonlinear composite may be correspondingly expressed as:

$$\widehat{W}(\overline{\mathbf{F}}) = \underset{\mathbf{L}^{(s)}(\mathbf{X})}{\operatorname{stat}} \left\{ \widehat{W}_T(\overline{\mathbf{F}}; \mathbf{F}^{(s)}, \mathbf{L}^{(s)}) + \sum_{r=1}^{N} c_0^{(r)} \langle V^{(r)}(\mathbf{F}^{(r)}, \mathbf{L}^{(r)}) \rangle^{(r)} \right\}, \tag{11}$$

where

$$\widehat{W}_T(\overline{\mathbf{F}}; \mathbf{F}^{(s)}, \mathbf{L}^{(s)}) = \underset{\mathbf{F} \in \mathscr{K}}{\operatorname{stat}} \langle W_T(\mathbf{X}, \mathbf{F}) \rangle = \underset{\mathbf{F} \in \mathscr{K}}{\operatorname{stat}} \sum_{r=1}^{N} c_0^{(r)} \langle W_T^{(r)}(\mathbf{F}) \rangle^{(r)} \tag{12}$$

is the effective stored-energy function associated with the LCC defined by relations (7) and (8).

It is important to emphasize at this point that expression (11) provides a variational principle for the effective stored-energy function $\widehat{W}$ of the elastomeric composite, where the relevant trial fields are the modulus tensors $\mathbf{L}^{(s)}(\mathbf{X})$ of the N phases in the LCC. The main advantage of this variational principle over the original form (6) is that the trial fields $\mathbf{L}^{(s)}(\mathbf{X})$ do not need to satisfy any differential constraints, such as the compatibility requirement. Of course, for the resulting estimates to make sound physical sense, the compatibility requirement must be, and indeed is, enforced through the use of the LCC with effective stored-energy function $\widehat{W}_T$ given by (12). In this context, it is natural to exploit the variational structure of (11) by restricting our attention to *constant-per-phase* trial fields $\mathbf{L}^{(s)}$ in order to generate the following estimate for $\widehat{W}$:

$$\widehat{W}(\overline{\mathbf{F}}) \approx \underset{\mathbf{L}^{(s)}}{\operatorname{stat}} \left\{ \widehat{W}_T(\overline{\mathbf{F}}; \mathbf{F}^{(s)}, \mathbf{L}^{(s)}) + \sum_{r=1}^{N} c_0^{(r)} V^{(r)}(\mathbf{F}^{(r)}, \mathbf{L}^{(r)}) \right\}, \tag{13}$$

where the stat(ionary) condition in this last expression is now over constant-per-phase, fourth-order tensors $\mathbf{L}^{(s)}$.

Next, it is relevant to spell out the stationarity conditions in expressions (9) and (13). They read as follows:

$$\mathscr{S}^{(r)}(\hat{\mathbf{F}}^{(r)}) - \mathscr{S}^{(r)}(\mathbf{F}^{(r)}) = \mathbf{L}^{(r)}(\hat{\mathbf{F}}^{(r)} - \mathbf{F}^{(r)}), \tag{14}$$

and

$$\frac{\partial \widehat{W}_T}{\partial \mathbf{L}^{(r)}} + c_0^{(r)} \frac{\partial V^{(r)}}{\partial \mathbf{L}^{(r)}} = \mathbf{0}, \tag{15}$$

respectively. But using the facts that

$$\left. \frac{\partial \widehat{W}_T}{\partial \mathbf{L}^{(r)}} \right|_{\mathbf{F}^{(r)}} = \frac{c_0^{(r)}}{2} \langle (\mathbf{F} - \mathbf{F}^{(r)}) \otimes (\mathbf{F} - \mathbf{F}^{(r)}) \rangle^{(r)}, \tag{16}$$

and

$$\left.\frac{\partial V^{(r)}}{\partial \mathbf{L}^{(r)}}\right|_{\mathbf{F}^{(r)}} = -\frac{1}{2}(\hat{\mathbf{F}}^{(r)} - \mathbf{F}^{(r)}) \otimes (\hat{\mathbf{F}}^{(r)} - \mathbf{F}^{(r)}), \tag{17}$$

where the notation $.|_{\mathbf{F}^{(r)}}$ has been used to emphasize that the derivatives with respect to $\mathbf{L}^{(r)}$ are taken with $\mathbf{F}^{(r)}$ fixed, the stationary condition (15) can be rewritten in the form

$$\langle (\mathbf{F} - \mathbf{F}^{(r)}) \otimes (\mathbf{F} - \mathbf{F}^{(r)}) \rangle^{(r)} = (\hat{\mathbf{F}}^{(r)} - \mathbf{F}^{(r)}) \otimes (\hat{\mathbf{F}}^{(r)} - \mathbf{F}^{(r)}), \tag{18}$$

or, equivalently, as

$$\mathbf{C}_{\mathbf{F}}^{(r)} = (\hat{\mathbf{F}}^{(r)} - \mathbf{F}^{(r)}) \otimes (\hat{\mathbf{F}}^{(r)} - \mathbf{F}^{(r)}) - (\overline{\mathbf{F}}^{(r)} - \mathbf{F}^{(r)}) \otimes (\overline{\mathbf{F}}^{(r)} - \mathbf{F}^{(r)}), \tag{19}$$

where $\overline{\mathbf{F}}^{(r)} \doteq \langle \mathbf{F} \rangle^{(r)}$ and $\mathbf{C}_{\mathbf{F}}^{(r)} \doteq \langle (\mathbf{F} - \overline{\mathbf{F}}^{(r)}) \otimes (\mathbf{F} - \overline{\mathbf{F}}^{(r)}) \rangle^{(r)}$ have been introduced to denote the average and covariance tensor of the fluctuations of the deformation gradient over phase r in the linear comparison composite. Thus, expression (19) can be seen to provide a set of conditions on the fluctuations of the deformation-gradient fields in the phases of the LCC. It is important to realize that these conditions are overly constraining, in general, as they would require that the fourth-order tensors $\langle (\mathbf{F} - \overline{\mathbf{F}}^{(r)}) \otimes (\mathbf{F} - \overline{\mathbf{F}}^{(r)}) \rangle^{(r)}$ be of rank 2. This suggests that it may not be possible to optimize with respect to completely general tensors $\mathbf{L}^{(r)}$ in the variational statement (13). As will be discussed in more detail in the next subsection, one possible way out of this problem is to optimize with respect to suitably chosen *subclasses* of tensors $\mathbf{L}^{(r)}$. In this case, the optimality conditions with respect to the $\mathbf{L}^{(r)}$ would still be of the form (15), where the derivatives would be taken with respect to the appropriate components of the $\mathbf{L}^{(r)}$ in the relevant subclass. But the form (19) of these conditions would need to be replaced by suitable traces of these expressions, depending on the specific form selected for the $\mathbf{L}^{(r)}$.

By making use of conditions (14) and (15), the general second-order estimate (13) may be shown to reduce to

$$\widehat{W}(\overline{\mathbf{F}}) = \sum_{r=1}^{N} c_0^{(r)} [W^{(r)}(\hat{\mathbf{F}}^{(r)}) - \mathscr{S}^{(r)}(\mathbf{F}^{(r)}) \cdot (\hat{\mathbf{F}}^{(r)} - \overline{\mathbf{F}}^{(r)})]. \tag{20}$$

It is interesting to remark that relation (20) depends directly on the average deformation gradients $\overline{\mathbf{F}}^{(r)}$ in the phases of the LCC. In addition, expression (20) also exhibits an explicit dependence on the variables $\hat{\mathbf{F}}^{(r)}$, which are associated with the field fluctuations of the deformation fields in the phases of the LCC through relations of type (19). Moreover, the estimate (20) can be shown to be exact to second order in the heterogeneity contrast, provided that the corresponding estimates for the LCC are also taken to be exact to second order in the contrast, and that the reference variables $\mathbf{F}^{(r)}$ be assumed to tend to the macroscopic average $\overline{\mathbf{F}}$ in the small-contrast limit.

In connection with the general second-order estimate (20), it should be emphasized that this estimate is, in principle, valid for any choice of the reference deformation gradients $\mathbf{F}^{(r)}$, which suggests optimizing with respect to these variables. However, it has been found (Lopez-Pamies and Ponte Castañeda, 2004a) that the result of such an optimization appears to be inconsistent with conditions of the type (19) on the field fluctuations. As a consequence, it becomes necessary to appeal to other physically based considerations to make a choice for the variables $\mathbf{F}^{(r)}$. Among such considerations is the requirement of *objectivity* of the effective stored-energy function $\widehat{W}$. Indeed, this is a non-trivial

requirement in the context of the second-order variational estimate (20), which makes use of a LCC with local stored-energy functions $W_T^{(r)}$, defined by (8), that are a priori not objective (i.e., $W_T^{(r)}(\mathbf{QF}) \neq W_T^{(r)}(\mathbf{F})$, for all proper orthogonal $\mathbf{Q}$). However, remarking that the reference variables $\mathbf{F}^{(r)}$, as well as the modulus tensors $\mathbf{L}^{(r)}$, ultimately depend on the macroscopic deformation gradient $\overline{\mathbf{F}}$, it follows that these tensors must be objective quantities in order to ensure the objectivity of the effective stored-energy function: $\widehat{W}(\overline{\mathbf{Q}}\,\overline{\mathbf{F}}) = \widehat{W}(\overline{\mathbf{F}})$ for all proper orthogonal tensors $\overline{\mathbf{Q}}$. Therefore, it will be required here that the tensors $\mathbf{F}^{(r)}$ and $\mathbf{L}^{(r)}$ satisfy the following invariance relations under the change of observer (frame) defined by the rotation tensor $\overline{\mathbf{Q}}$:

$$F_{ij}^{(r)} \longrightarrow \overline{Q}_{ik} F_{kj}^{(r)} \quad \text{and} \quad L_{ijkl}^{(r)} \longrightarrow \overline{Q}_{ip}\overline{Q}_{kq} L_{pjql}^{(r)}, \tag{21}$$

where indicial notation has been used to indicate precisely the products involved in the second relation for the $\mathbf{L}^{(r)}$. Here and throughout in this paper, Latin indices range from 1 to 3, and the usual summation convention is employed. Parenthetically, it is interesting to remark that, under conditions (21), the effective stored-energy function $\widehat{W}_T$ of the LCC can also be shown to be an objective scalar function of $\overline{\mathbf{F}}$, even though, again, the constituent phases $W_T^{(r)}$ are locally *not* objective.

Similarly, the stored-energy function $\widehat{W}$ of the composite must satisfy the overall symmetry requirements of the system, that is, $\widehat{W}(\overline{\mathbf{F}}\,\overline{\mathbf{K}}) = \widehat{W}(\overline{\mathbf{F}})$ for all orthogonal, second-order tensors $\overline{\mathbf{K}}$ belonging to the symmetry group of the material, $\mathscr{G}$. For instance, for a composite with isotropic constituents and an isotropic distribution of the phases, the symmetry group $\mathscr{G}$ would correspond to the full orthogonal group. In this work, the interest will be on composite elastomers with isotropic phases, but with *non*-isotropic distribution of the phases. For this class of materials, it can be shown that requiring the variables $\mathbf{F}^{(r)}$ and $\mathbf{L}^{(r)}$ to be invariant under each of the transformations (changes of reference configuration defined by) $\overline{\mathbf{K}} \in \mathscr{G}$ leads to estimates (20) for the stored-energy function that satisfy the overall symmetry requirements of the material. Hence, it will be required here that the tensors $\mathbf{F}^{(r)}$ and $\mathbf{L}^{(r)}$ satisfy the following invariance relations:

$$F_{ij}^{(r)} \longrightarrow F_{ik}^{(r)}\overline{K}_{kj} \quad \text{and} \quad L_{ijkl}^{(r)} \longrightarrow L_{ipkq}^{(r)}\overline{K}_{pj}\overline{K}_{ql}, \tag{22}$$

for all symmetry transformations defined by orthogonal, second-order tensors $\overline{\mathbf{K}} \in \mathscr{G}$.

In essence, conditions (21) and (22) provide general invariance requirements that must be satisfied by the reference deformation gradients $\mathbf{F}^{(r)}$ and the modulus tensors $\mathbf{L}^{(r)}$ in the phases of the LCC. In practice, however, enforcing conditions (21) and (22) is not a simple matter because of the implicit manner in which $\mathbf{F}^{(r)}$ and $\mathbf{L}^{(r)}$ enter the stationary conditions (14) and (15). In the next subsection, we provide specific choices (motivated by the local isotropy of the phases) for $\mathbf{F}^{(r)}$ and $\mathbf{L}^{(r)}$ that satisfy the invariance requirements (21) and (22).

3.1. On the specific choice of the variables $\mathbf{F}^{(r)}$ and $\mathbf{L}^{(r)}$ for isotropic phases

It is clear from expressions (8) for the stored-energy functions $W_T^{(r)}$ of the phases in the LCC that requiring the variables $\mathbf{F}^{(r)}$ and $\mathbf{L}^{(r)}$ be isotropic functions of the *local* deformation gradient $\mathbf{F}$ would be sufficient to ensure the isotropy of these linear phases. However, given approximation (13) for $\widehat{W}$, the variables $\mathbf{F}^{(r)}$ and $\mathbf{L}^{(r)}$ are constant per phase, and therefore it is not possible to choose them in this manner. On the other hand,

recalling that the "generalized secant" tensors $\mathbf{L}^{(r)}$ provide a generalization of the tangent moduli tensors $\mathscr{L}^{(r)} \doteq \partial^2 W^{(r)}(\mathbf{F}^{(r)})/\partial \mathbf{F}^2$, it is sensible to require $\mathbf{L}^{(r)}$ to satisfy the same objectivity and material symmetry restrictions, with respect to $\mathbf{F}^{(r)}$, as those satisfied by $\mathscr{L}^{(r)}$. In the particular context of phases that are characterized by *objective* and *isotropic* stored-energy functions $W^{(r)}$, the corresponding tangent moduli tensors $\mathscr{L}^{(r)}$ must satisfy the following conditions:

$$\mathscr{L}^{(r)}_{ijkl}(\mathbf{Q}\mathbf{F}^{(r)}\mathbf{Q}') = Q_{im}Q_{kn}\mathscr{L}^{(r)}_{mpnq}(\mathbf{F}^{(r)})Q'_{pj}Q'_{ql}, \tag{23}$$

for all proper orthogonal, second-order tensors $\mathbf{Q}$ and $\mathbf{Q}'$. In other words, the $\mathscr{L}^{(r)}$ are objective and isotropic tensor functions of the variables $\mathbf{F}^{(r)}$.

Next, note that the "reference" deformation gradient tensors $\mathbf{F}^{(r)}$ may be expressed in the form:

$$\mathbf{F}^{(r)} = \mathbf{R}^{(r)}\mathbf{U}^{(r)} = \mathbf{R}^{(r)}\mathbf{Q}^{(r)}\mathbf{D}^{(r)}(\mathbf{Q}^{(r)})^{\mathrm{T}}, \tag{24}$$

where $\mathbf{R}^{(r)}$ and $\mathbf{U}^{(r)}$ correspond, respectively, to the "rotation" and the "right-stretch" tensors associated with the polar decomposition of $\mathbf{F}^{(r)}$, $\mathbf{D}^{(r)}$ is a symmetric, second-order tensor with matrix representation (relative to the principal axes of $\mathbf{U}^{(r)}$) $D^{(r)} = \mathrm{diag}(\lambda_1^{(r)}, \lambda_2^{(r)}, \lambda_3^{(r)})$, with $\lambda_1^{(r)}$, $\lambda_2^{(r)}$, and $\lambda_3^{(r)}$ denoting the principal stretches of $\mathbf{U}^{(r)}$, and $(\mathbf{Q}^{(r)})^{\mathrm{T}}$ is the proper orthogonal, second-order tensor describing the orientation of the principal axes of $\mathbf{U}^{(r)}$ relative to the laboratory frame of reference. It then follows from conditions (23) that

$$\mathscr{L}^{(r)}_{ijkl}(\mathbf{F}^{(r)}) = Q^{(r)}_{rm}Q^{(r)}_{jn}Q^{(r)}_{sp}Q^{(r)}_{lq}R^{(r)}_{ir}R^{(r)}_{ks}\mathscr{L}^{(r)}_{mnpq}(\mathbf{D}^{(r)}), \tag{25}$$

where it is noted that $\mathscr{L}^{(r)}_{mnpq}(\mathbf{D}^{(r)})$ will exhibit orthotropic symmetry with respect to the principal axes of $\mathbf{U}^{(r)}$. Since, as already stated, the generalized moduli tensors $\mathbf{L}^{(r)}$ are expected to also be objective and isotropic tensor functions of $\mathbf{F}^{(r)}$, it is reasonable to prescribe the following requirement for the functional dependence of the moduli tensors $\mathbf{L}^{(r)}$ on the variables $\mathbf{F}^{(r)}$:

$$L^{(r)}_{ijkl}(\mathbf{F}^{(r)}) = Q^{(r)}_{rm}Q^{(r)}_{jn}Q^{(r)}_{sp}Q^{(r)}_{lq}R^{(r)}_{ir}R^{(r)}_{ks}L^{(r)}_{mnpq}(\mathbf{D}^{(r)}), \tag{26}$$

where the $\mathbf{L}^{*(r)} \doteq \mathbf{L}^{(r)}(\mathbf{D}^{(r)})$ will be assumed to be orthotropic, fourth-order tensors with respect to the principal axes of $\mathbf{U}^{(r)}$. Thus, since $\mathbf{R}^{(r)}$ and $\mathbf{Q}^{(r)}$ can be readily determined from $\mathbf{F}^{(r)}$, it is seen that prescription (26) reduces the number of independent components of $\mathbf{L}^{(r)}$ from 45 to only 12, namely, the 12 independent components of the orthotropic tensor $L^{*(r)}_{mnpq}$. At this stage it is useful to note that relation (18) (or (19)) can be thought of as a set of equations for the nine components of the second-order tensor $\hat{\mathbf{F}}^{(r)}$ (for each $r = 1, \ldots, N$). Therefore, the simplest way to generate a *consistent* system of equations out of relation (18) is to further reduce the number of independent components of $L^{*(r)}_{mnpq}$ to 9. (Recall that our objective in the present work is not to obtain the best possible results.) In this case, only 9 equations will be generated by differentiating with respect to these nine independent components, which will involve only certain traces of the fluctuations tensors $\mathbf{C}^{(r)}_{\mathbf{F}}$, as will be seen below. Prescriptions of the type (26), as it will be seen in more detail in Part II of this work, turn out to be consistent with the physical requirements of objectivity $(21)_2$ and overall material symmetry $(22)_2$.

Having established result (26) for the modulus tensors $\mathbf{L}^{(r)}$ for composite elastomers with isotropic phases, it remains to establish a consistent prescription for the variables $\mathbf{F}^{(r)}$. The

simplest prescription satisfying the objectivity and overall material symmetry requirements, $(21)_1$ and $(22)_1$, as well as the requirement that the reference variables $\mathbf{F}^{(r)}$ tend to the macroscopic average $\overline{\mathbf{F}}$ in the small-contrast limit, is, of course,

$$\mathbf{F}^{(r)} = \overline{\mathbf{F}}, \tag{27}$$

which has been used recently by Lopez-Pamies and Ponte Castañeda (2004b) to estimate the effective behavior of porous elastomers. An alternative prescription, also satisfying these requirements, would be to set $\mathbf{F}^{(r)} = \overline{\mathbf{F}}^{(r)}$, as was done by Lopez-Pamies and Ponte Castañeda (2004a) for isotropically reinforced elastomers. In this work, dealing with more general, anisotropically reinforced elastomers, use will be made of prescription (27), which was found to lead to more physically consistent results. However, it should be re-emphasized that it is not yet known what the best prescription for the reference variables $\mathbf{F}^{(r)}$ is.

In the next section, we will make use of conditions (27) for the $\mathbf{F}^{(r)}$ and of conditions (26) for the $\mathbf{L}^{(r)}$ to specialize the general second-order estimate (20) to the case of particle-reinforced elastomers, where both the matrix and the inclusion phase will be taken to be isotropic.

4. Effective behavior of fiber-reinforced elastomers

In this section, we specialize the general second-order estimate (20) for the effective stored-energy function to the specific case of two-phase composites consisting of ellipsoidal particles, with given initial volume fraction $c_0^{(2)} = c_0$ and characterized by the isotropic stored-energy function $W^{(2)}$, which are distributed with "ellipsoidal symmetry" (Willis, 1977) in a compressible elastomeric matrix with isotropic stored-energy function $W^{(1)}$. Recall that by virtue of the objectivity of $\widehat{W}$, only macroscopic pure stretch loading histories (i.e., $\overline{\mathbf{F}} = \overline{\mathbf{U}}$; $\overline{\mathbf{R}} = \mathbf{I}$) need to be considered.

Before proceeding with the computation of the second-order estimates, it is important to make some clarifications with regard to the classical Voigt upper bound and the Reuss-type polyconvex lower bound, which depend only on the initial volume fractions of the phases. (The specializations of these bounds to the case of reinforced elastomers with hyperelastic matrix phase $W^{(1)}$ and reinforcement $W^{(2)}$ are straightforward and therefore will not be detailed here.) First, note that in the limit when the reinforcement phase is made rigid, the Voigt upper bound becomes infinite. Although rigorously an upper bound, the Voigt estimate is physically unrealistic in this limiting case, as it would suggest that the addition of any fraction (even infinitesimal) of rigid reinforcement into an elastomeric matrix would result in a rigid material, which is in contradiction with experimental evidence. On the other hand, the polyconvex lower bound remains finite in this limit, and therefore it can be of use. However, it should be recalled that this bound does not linearize properly (Ponte Castañeda, 1989), i.e., it does not reduce to the classical Reuss lower bound for infinitesimal deformations. The corresponding failures of the Voigt upper bound and the polyconvex lower bound can be used as motivation for generating the new type of estimates that we propose to develop in this work. Although, they are less rigorous in the sense that they are not bounds, they will be much more accurate, providing more realistic predictions, especially, for cases where the reinforcement is much stiffer than the matrix.

4.1. The LCC and estimates for particulate microstructures

The computation of the second-order estimates for particle-reinforced rubbers requires the determination of the effective stored-energy function associated with a *fictitious* linear comparison composite (LCC) with the same microstructure as the original elastomer, as well as the corresponding phase averages $\overline{\mathbf{F}}^{(r)}$ and fluctuations $\mathbf{C}_{\mathbf{F}}^{(r)}$ $(r=1,2)$. It is remarked that the LCC problem at hand involves non-symmetric measures of "stress" and "strain" and hence a suitable generalization of the classical problem is required. This generalization is straightforward and it was carried out by Ponte Castañeda and Tiberio (2000) in the broader context of N-phase "thermoelastic" composites. The general expressions will not be repeated here, instead, only the relevant results specialized to two-phase systems will be considered. In this regard, it is recalled that great simplification of the general relations for thermoelastic composites is available for the special class of two-phase composites. Thus, making use of an appropriate generalization of the Levin relations (Levin, 1967), the effective stored-energy function $\widehat{W}_T$ for the two-phase LCC may be written simply as:

$$\widehat{W}_T(\overline{\mathbf{F}}) = \widetilde{f} + \widetilde{\mathbf{T}}\cdot\overline{\mathbf{F}} + \tfrac{1}{2}\overline{\mathbf{F}}\cdot\widetilde{\mathbf{L}}\overline{\mathbf{F}}, \tag{28}$$

where $\widetilde{f} = \overline{f} + \frac{1}{2}(\Delta\mathbf{L})^{-1}\Delta\mathbf{T}\cdot(\widetilde{\mathbf{L}}-\overline{\mathbf{L}})(\Delta\mathbf{L})^{-1}\Delta\mathbf{T}$, $\widetilde{\mathbf{T}} = \overline{\mathbf{T}} + (\widetilde{\mathbf{L}}-\overline{\mathbf{L}})(\Delta\mathbf{L})^{-1}\Delta\mathbf{T}$ are effective specific-heat and thermal stress quantities, depending on the effective modulus tensor $\widetilde{\mathbf{L}}$, which is characterized in more detail further below. Also, in these expressions, $f^{(r)} = W^{(r)}(\mathbf{F}^{(r)}) - \mathbf{T}^{(r)}\cdot\mathbf{F}^{(r)} - \frac{1}{2}\mathbf{F}^{(r)}\cdot\mathbf{L}^{(r)}\mathbf{F}^{(r)}$, $\mathbf{T}^{(r)} = \mathscr{S}^{(r)}(\mathbf{F}^{(r)}) - \mathbf{L}^{(r)}\mathbf{F}^{(r)}$ $(r=1,2)$, and $\Delta\mathbf{L} = \mathbf{L}^{(1)} - \mathbf{L}^{(2)}$, $\Delta\mathbf{T} = \mathbf{T}^{(1)} - \mathbf{T}^{(2)}$. Furthermore, $\bar{f}$ and $\bar{\mathbf{L}}$ are the volume averages of f and $\mathbf{L}$. Note that the effective stored-energy function $\widehat{W}_T$ is completely determined in terms of $\widetilde{\mathbf{L}}$.

Finally, $\widetilde{\mathbf{L}}$ is the effective modulus tensor of the two-phase, *linear-elastic* comparison composite with modulus tensors $\mathbf{L}^{(1)}$ and $\mathbf{L}^{(2)}$, and the same microstructure, in its undeformed configuration, as the nonlinear hyperelastic composite. A reasonably good estimate for the type of "particulate" random microstructures considered in this work is the generalized estimate of the Hashin–Shtrikman (HS) type (Willis, 1977):

$$\widetilde{\mathbf{L}} = \mathbf{L}^{(1)} + c_0[(1-c_0)\mathbf{P}^{(1)} - (\Delta\mathbf{L})^{-1}]^{-1}, \tag{29}$$

where the microstructural tensor $\mathbf{P}^{(1)}$ is determined by setting $\mathbf{L}^{(0)}$ equal to $\mathbf{L}^{(1)}$ in the expression:

$$\mathbf{P}^{(0)} = \frac{1}{4\pi\det(\mathbf{Z}_0)}\int_{|\boldsymbol{\xi}|=1}\mathbf{H}^{(0)}(\boldsymbol{\xi})[\boldsymbol{\xi}^{\mathrm{T}}(\mathbf{Z}_0^{\mathrm{T}}\mathbf{Z}_0)^{-1}\boldsymbol{\xi}]^{-3/2}\,\mathrm{d}S. \tag{30}$$

In this relation, $H^{(0)}_{ijkl}(\boldsymbol{\xi}) = N^{(0)}_{ik}\xi_j\xi_l$, with $\mathbf{N}^{(0)} = \mathbf{K}^{(0)^{-1}}$ and $K^{(0)}_{ik} = L^{(0)}_{ijkl}\xi_j\xi_l$, and the symmetric second-order tensor $\mathbf{Z}_0$ serves to characterize the "ellipsoidal symmetry" of the microstructure in the reference configuration. More specifically, the tensor $\mathbf{Z}_0$ serves to define the shape and orientation of the ellipsoidal particles, as well as the "shape" and "orientation" of their two-point correlation function, which are assumed to be initially identical to those of the particles. (This assumption could be relaxed by allowing the shapes and orientations of the particles and of their distribution functions to be different (Ponte Castañeda and Willis, 1995), but this is not done here as it would necessitate the use of two different $\mathbf{P}$ tensors.) Thus, the special case $\mathbf{Z}_0 = \mathbf{I}$ would correspond to an isotropic

distribution of spherical particles. From a computational point of view, it is seen that $\mathbf{P}^{(1)}$ depends on the anisotropy of the modulus $\mathbf{L}^{(1)}$, which in turn depends on the functional form of the potential $W^{(1)}$, as well as the particular type of loading, as determined by $\overline{\mathbf{F}} = \overline{\mathbf{U}}$.

Next, it can be shown (see, for example, Ponte Castañeda and Suquet, 1998) that the average deformations $\overline{\mathbf{F}}^{(1)}$ and $\overline{\mathbf{F}}^{(2)}$ in the matrix and inclusion phase of the LCC can be conveniently determined from the overall average deformation condition, together with the stored-energy function (28), through the relations

$$\overline{\mathbf{F}}^{(1)} = \frac{1}{1-c_0}(\overline{\mathbf{F}} - c_0\overline{\mathbf{F}}^{(2)}) \quad \text{and} \quad \overline{\mathbf{F}}^{(2)} = \frac{1}{c_0}\frac{\partial(\widehat{W}_T - \overline{f})}{\partial \mathbf{T}^{(2)}}\bigg|_{\mathbf{L}^{(2)}}, \tag{31}$$

respectively. Note that the derivative of $\widehat{W}_T - \overline{f}$ with respect to $\mathbf{T}^{(2)}$ in the second of relation (31) must be carried out with $\mathbf{L}^{(2)}$ held fixed.

Furthermore, the fluctuations $\mathbf{C}_{\mathbf{F}}^{(1)}$ and $\mathbf{C}_{\mathbf{F}}^{(2)}$ in the matrix and inclusion phase of the LCC can be readily determined through the relations:

$$\mathbf{C}_{\mathbf{F}}^{(1)} = \frac{2}{1-c_0}\frac{\partial \widehat{W}_T}{\partial \mathbf{L}^{(1)}}\bigg|_{\mathbf{F}^{(1)}=\overline{\mathbf{F}}^{(1)}} \quad \text{and} \quad \mathbf{C}_{\mathbf{F}}^{(2)} = \mathbf{0}, \tag{32}$$

respectively. Note that the derivative of $\widehat{W}_T$ with respect to $\mathbf{L}^{(1)}$ in the RHS of $(32)_1$ must be carried out with $\mathbf{F}^{(1)}$ held fixed. Moreover, the vanishing of the fluctuations in the inclusions, as stated by $(32)_2$, is a direct consequence of the use of the Willis-type estimates (29) in the homogenization process.

4.2. Second-order homogenization estimates: compliant particles

In this subsection, we specialize the general second-order estimate (20) to the case of the two-phase, "particulate" composites introduced above. For later use, it is convenient to present the development for a general reference deformation gradient $\mathbf{F}^{(1)}$. On the other hand, in view of the fact that the fluctuations associated with the Willis-type estimate for the LCC vanish identically in phase 2, it proves computationally simpler to set the reference deformation gradient $\mathbf{F}^{(2)} = \overline{\mathbf{F}}^{(2)}$. It is emphasized that any other prescription (satisfying the conditions of objectivity $(21)_1$ and overall material symmetry $(22)_1$) for $\mathbf{F}^{(2)}$ would lead to exactly the same second-order estimate (as a consequence of the use of the Willis-type estimates (29) for the LCC). Thus, the second-order estimate for particle-reinforced elastomers simplifies to:

$$\widehat{W}(\overline{\mathbf{F}}) = (1-c_0)[W^{(1)}(\hat{\mathbf{F}}^{(1)}) - \mathscr{S}^{(1)}(\mathbf{F}^{(1)}) \cdot (\hat{\mathbf{F}}^{(1)} - \overline{\mathbf{F}}^{(1)})] + c_0 W^{(2)}(\overline{\mathbf{F}}^{(2)}). \tag{33}$$

Here, $\overline{\mathbf{F}}^{(1)}$, $\overline{\mathbf{F}}^{(2)}$, $\hat{\mathbf{F}}^{(1)}$, $\hat{\mathbf{F}}^{(2)}$, together with the modulus tensors $\mathbf{L}^{(1)}$ and $\mathbf{L}^{(2)}$, need to be made explicit. To this end, it is important to realize that by setting $\mathbf{F}^{(2)} = \overline{\mathbf{F}}^{(2)}$ it follows (from the appropriate specialization of Eqs. (14) and (15)) that $\hat{\mathbf{F}}^{(2)} = \overline{\mathbf{F}}^{(2)}$, and that the modulus tensor of the inclusion phase in the LCC reduces to $\mathbf{L}^{(2)} = \partial^2 W^{(2)}(\overline{\mathbf{F}}^{(2)})/\partial \mathbf{F}^2$. Next, it is noted that the average deformation gradient $\overline{\mathbf{F}}^{(1)}$ in the matrix phase of the relevant LCC is determined, in terms of the applied macroscopic loading $\overline{\mathbf{F}}$ and the average deformation gradient $\overline{\mathbf{F}}^{(2)}$ in the inclusion phase of the LCC, from the overall average deformation condition $(31)_1$.

Now, with the above simplifications, Eq. $(31)_2$ leads to

$$\overline{\mathbf{F}}^{(2)} = \overline{\mathbf{F}} - \frac{1}{c_0}(\Delta\mathbf{L})^{-1}(\widetilde{\mathbf{L}} - \bar{\mathbf{L}})(\Delta\mathbf{L})^{-1}[\Delta\mathscr{S} + \mathbf{L}^{(1)}(\overline{\mathbf{F}} - \mathbf{F}^{(1)}) - \mathbf{L}^{(2)}(\overline{\mathbf{F}} - \overline{\mathbf{F}}^{(2)})], \tag{34}$$

where $\Delta\mathscr{S} = \mathscr{S}^{(1)}(\mathbf{F}^{(1)}) - \mathscr{S}^{(2)}(\overline{\mathbf{F}}^{(2)})$. Making use of the Willis estimate (29), this expression can be shown to simplify to

$$\overline{\mathbf{F}} - \overline{\mathbf{F}}^{(2)} = (1 - c_0)\mathbf{P}^{(1)}[\mathbf{L}^{(1)}(\mathbf{F}^{(1)} - \overline{\mathbf{F}}^{(2)}) - \mathscr{S}^{(1)}(\mathbf{F}^{(1)}) + \mathscr{S}^{(2)}(\overline{\mathbf{F}}^{(2)})], \tag{35}$$

which can be seen to constitute a system of nine nonlinear algebraic equations for the nine components of the average deformation gradient $\overline{\mathbf{F}}^{(2)}$. Note that these equations depend directly on the modulus tensor $\mathbf{L}^{(1)}$ of the matrix phase, but, remarkably, *not* on the modulus tensor $\mathbf{L}^{(2)}$ of the inclusion phase.

Next, the generalized secant condition (14) for the matrix phase provides an equation for the variable $\hat{\mathbf{F}}^{(1)}$, which is given by

$$\mathscr{S}^{(1)}(\hat{\mathbf{F}}^{(1)}) - \mathscr{S}^{(1)}(\mathbf{F}^{(1)}) = \mathbf{L}^{(1)}(\hat{\mathbf{F}}^{(1)} - \mathbf{F}^{(1)}). \tag{36}$$

This relation can interpreted as a set of nine nonlinear algebraic equations for the nine components of $\hat{\mathbf{F}}^{(1)}$.

As discussed in the previous section, the modulus tensor $\mathbf{L}^{(1)}$ for the *isotropic* matrix phase will be taken to be of form (26), which is now written as

$$L^{(1)}_{ijkl} = Q^{(1)}_{rm}Q^{(1)}_{jn}Q^{(1)}_{sp}Q^{(1)}_{lq}R^{(1)}_{ir}R^{(1)}_{ks}L^{*}_{mnpq}, \tag{37}$$

where the notation $L^{*}_{ijkl} = L^{(1)}_{ijkl}(\mathbf{D}^{(1)})$ has been introduced for convenience. It is recalled that $\mathbf{L}^{*}$ should be assumed to have orthotropic symmetry relative to the principal axes of $\mathbf{U}^{(1)}$, the right stretch tensor associated with the polar decomposition of $\mathbf{F}^{(1)}$. In order to avoid the potential inconsistencies associated with Eq. (19) for the second moments of the deformation gradient field in the matrix phase of the LCC, the tensors $\mathbf{L}^{*}$ will be chosen here to have only nine independent components, instead of the 12 components that would normally be associated with orthotropic symmetry (for fourth-order tensors with only major symmetry). As will be seen in Part II, the choice of the nine independent components of $\mathbf{L}^{*}$ is somewhat arbitrary, and depends on the specific constitutive behavior of the hyperelastic matrix phase. However, at this stage, it is only important to recognize that the restriction to nine independent components for $\mathbf{L}^{*}$ will translate into internal constraints among the 12 standard components of the orthotropic tensor $\mathbf{L}^{*}$. Then, denoting by ℓ^{*}_{α} ($\alpha = 1, 2, \ldots, 9$) the nine independent components of $\mathbf{L}^{*}$, and repeating the procedure that led from the stationarity condition (15) to expression (18) now gives:

$$(\hat{\mathbf{F}}^{(1)} - \mathbf{F}^{(1)}) \cdot \frac{\partial \mathbf{L}^{(1)}}{\partial \ell^{*}_{\alpha}}(\hat{\mathbf{F}}^{(1)} - \mathbf{F}^{(1)}) = \frac{2}{1 - c_0}\frac{\partial \widehat{W}_T}{\partial \ell^{*}_{\alpha}}\bigg|_{\mathbf{F}^{(1)}}. \tag{38}$$

In this expression $\widehat{W}_T$ is the stored-energy function of the relevant LCC given by (28) with $\mathbf{F}^{(2)} = \overline{\mathbf{F}}^{(2)}$, and $\mathbf{L}^{(2)} = \partial^2 W^{(2)}(\overline{\mathbf{F}}^{(2)})/\partial\mathbf{F}^2$. Thus, the right-hand side of this equation can be computed by performing the indicated derivatives with respect to the moduli ℓ^{*}_{α}. The resulting expressions, which involve suitable traces of the fluctuation tensor $\mathbf{C}^{(1)}_{\mathbf{F}}$, are rather complicated, but can be simplified dramatically by repeated use of the expression (35) for

$\overline{\mathbf{F}}^{(2)}$. In the end, Eqs. (38) can be rewritten in the simple form

$$\begin{aligned}
&(\hat{\mathbf{F}}^{(1)}-\mathbf{F}^{(1)})\cdot\frac{\partial\mathbf{L}^{(1)}}{\partial\ell_\alpha^*}(\hat{\mathbf{F}}^{(1)}-\mathbf{F}^{(1)})\\
&\quad=\frac{1}{1-c_0}(\overline{\mathbf{F}}-\mathbf{F}^{(1)})\cdot\frac{\partial\mathbf{L}^{(1)}}{\partial\ell_\alpha^*}(\overline{\mathbf{F}}-\mathbf{F}^{(1)})\\
&\qquad-\frac{c_0}{1-c_0}(\mathbf{F}^{(1)}-\overline{\mathbf{F}}^{(2)})\cdot\frac{\partial\mathbf{L}^{(1)}}{\partial\ell_\alpha^*}(\mathbf{F}^{(1)}-\overline{\mathbf{F}}^{(2)})\\
&\qquad-\frac{c_0}{(1-c_0)^2}(\overline{\mathbf{F}}-\overline{\mathbf{F}}^{(2)})\cdot(\mathbf{P}^{(1)})^{-1}\frac{\partial\mathbf{P}^{(1)}}{\partial\ell_\alpha^*}(\mathbf{P}^{(1)})^{-1}(\overline{\mathbf{F}}-\overline{\mathbf{F}}^{(2)}).
\end{aligned}\tag{39}$$

They constitute a system of 9 scalar equations for the 9 scalar variables ℓ_α^*, which, remarkably, are also independent of the modulus tensor $\mathbf{L}^{(2)}$ of the inclusion phase. (Recall that $\overline{\mathbf{F}}^{(2)}$, as determined by Eq. (35), is independent of $\mathbf{L}^{(2)}$.)

The only variable that remains to be specified is the reference deformation gradient $\mathbf{F}^{(1)}$, which in this work will be set equal to $\overline{\mathbf{F}}$ (i.e., $\mathbf{F}^{(1)}=\overline{\mathbf{F}}$). Therefore, in conclusion, Eqs. (35), (36) and (39) constitute a closed system of 27 nonlinear algebraic equations for the 27 scalar unknowns formed by the nine components of $\overline{\mathbf{F}}^{(2)}$, the nine components of $\hat{\mathbf{F}}^{(1)}$, and the nine independent components of $\mathbf{L}^{(1)}$ (i.e., the nine independent components of $\mathbf{L}^*$, denoted by ℓ_α^*), which, in general, must be solved numerically. Having computed the values of all the components of $\overline{\mathbf{F}}^{(2)}$, $\hat{\mathbf{F}}^{(1)}$, and $\mathbf{L}^{(1)}$ for a given loading $\overline{\mathbf{F}}$, the values of the components of $\overline{\mathbf{F}}^{(1)}$ can be readily determined using relation $(31)_1$. In turn, the second-order estimate for the effective stored-energy function $\widehat{W}$ for particle-reinforced elastomers can now be computed, from relation (33), using these results. It should be emphasized that the resulting estimate is objective, as will be seen in more detail in Part II of this work for some specific examples.

Finally, it is interesting to remark that the just-defined system of equations defining the effective stored-energy function $\widehat{W}$ for a general, two-phase, hyperelastic composite with particulate microstructure does *not* depend explicitly on the modulus tensor $\mathbf{L}^{(2)}$ of the inclusion phase (although, of course, it does depend on the behavior of the hyperelastic inclusion phase through the energy function $W^{(2)}$). This unexpected result is a consequence of the use of the Willis-type estimate (29), which implies vanishing fluctuations in the inclusion phase of the LCC. In any event, the independence of the second-order estimate (33) (together with expressions (35), (36) and (39)) on $\mathbf{L}^{(2)}$ will greatly facilitate the computation of the limiting case of rigid particles, which is considered next.

4.3. Second-order homogenization estimates: rigid particles

In this subsection, we specialize further the general second-order estimate (33) to the limiting case when the particles are taken to be *rigid*. To this end, for simplicity and without loss of generality, the following choice is made for the stored-energy function of the inclusion phase:

$$W^{(2)}(\mathbf{F})=\frac{\mu^{(2)}}{2}(\mathbf{F}\cdot\mathbf{F}-3)-\mu^{(2)}\ln(\det\mathbf{F}),\tag{40}$$

where the shear modulus $\mu^{(2)}$ will be taken to tend to infinity in order to model rigid behavior. Note that this form for $W^{(2)}$ is objective and consistent with the requirement that the deformation gradient $\mathbf{F}$ within the particles should tend to an orthogonal tensor $\mathbf{R}$ (i.e., the particles should undergo a rigid body rotation) in the limit $\mu^{(2)} \to \infty$. Based on this choice for the stored-energy function of the inclusion phase, an expansion for the average deformation gradient $\overline{\mathbf{F}}^{(2)}$ in the particles of the LCC is attempted in the limit as $\mu^{(2)} \to \infty$ of the following form:

$$\overline{\mathbf{F}}^{(2)} = \overline{\mathbf{R}}^{(2)} + \varepsilon \overline{\mathbf{F}}_1^{(2)} + O(\varepsilon^2), \tag{41}$$

where $\varepsilon = 1/\mu^{(2)}$ is a small parameter, and $\overline{\mathbf{R}}^{(2)}$ and $\overline{\mathbf{F}}_1^{(2)}$ are second-order tensors to be determined from the asymptotic analysis that follows. As suggested by (40), $\overline{\mathbf{R}}^{(2)}$ is assumed to be orthogonal. It is now relevant to spell out the asymptotic expansions for the stored-energy function $W^{(2)}$, as well as for the associated stress $\mathscr{S}^{(2)}$, evaluated at the average deformation gradient (41) in the limit as $\varepsilon \to 0$. The results read as follows:

$$W^{(2)}(\overline{\mathbf{F}}^{(2)}) = 0 + O(\varepsilon), \quad \mathscr{S}^{(2)}(\overline{\mathbf{F}}^{(2)}) = \frac{\partial W^{(2)}}{\partial \mathbf{F}}(\overline{\mathbf{F}}^{(2)}) = \mathscr{S}_o^{(2)} + O(\varepsilon), \tag{42}$$

where the second-order tensor $\mathscr{S}_o^{(2)}$ is given by

$$\mathscr{S}_o^{(2)} = \overline{\mathbf{F}}_1^{(2)} + \overline{\mathbf{R}}^{(2)}(\overline{\mathbf{F}}_1^{(2)})^{\mathrm{T}}\overline{\mathbf{R}}^{(2)}. \tag{43}$$

We remark, for later use, that

$$(\overline{\mathbf{R}}^{(2)})^{\mathrm{T}}\mathscr{S}_o^{(2)} = (\mathscr{S}_o^{(2)})^{\mathrm{T}}\overline{\mathbf{R}}^{(2)}. \tag{44}$$

Although this identity can be easily verified algebraically, it is a simple consequence of the objectivity of the stored-energy function (40).

Now, using $\mathbf{F}^{(1)} = \overline{\mathbf{F}}$ for the reference deformation, it follows from the above asymptotic results that the leading-order term in Eq. (35) can be written in the form

$$\mathbf{D}^{(1)}(\overline{\mathbf{F}} - \overline{\mathbf{R}}^{(2)}) + (1 - c_0)[\mathscr{S}^{(1)}(\overline{\mathbf{F}}) - \mathscr{S}_o^{(2)}] = \mathbf{0}, \tag{45}$$

where

$$\mathbf{D}^{(1)} = (\mathbf{P}^{(1)})^{-1} - (1 - c_0)\mathbf{L}^{(1)} \tag{46}$$

is a fourth-order tensor with major symmetry depending only on $\mathbf{L}^{(1)}$ and on the microstructure, and where $\mathscr{S}_o^{(2)}$ is given by expression (43).

Expression (45), which is a *full* second-order tensorial relation (i.e., it contains nine independent scalar equations), can be used to generate an equation for the rotation tensor $\overline{\mathbf{R}}^{(2)}$, which has only three independent components, by first left-multiplying expression (45) by $(\overline{\mathbf{R}}^{(2)})^{\mathrm{T}}$, extracting the skew-symmetric part of this expression, and making use of the identity (44). The resulting equation for the average rigid rotation $\overline{\mathbf{R}}^{(2)}$ of the particles may be written in the form:

$$\begin{aligned}&(\overline{\mathbf{R}}^{(2)})^{\mathrm{T}}[\mathbf{D}^{(1)}(\overline{\mathbf{F}} - \overline{\mathbf{R}}^{(2)})] - [\mathbf{D}^{(1)}(\overline{\mathbf{F}} - \overline{\mathbf{R}}^{(2)})]^{\mathrm{T}}\overline{\mathbf{R}}^{(2)} \\ &\quad + (1 - c_0)[(\overline{\mathbf{R}}^{(2)})^{\mathrm{T}}\mathscr{S}^{(1)}(\overline{\mathbf{F}}) - (\mathscr{S}^{(1)}(\overline{\mathbf{F}}))^{\mathrm{T}}\overline{\mathbf{R}}^{(2)}] = \mathbf{0},\end{aligned} \tag{47}$$

which provides a set of three independent equations for the three components of $\overline{\mathbf{R}}^{(2)}$. It should be clear from the derivation that this equation is independent of the form of the constitutive behavior (40) assumed for the inclusion phase, since the only property that we have really used is the objectivity of $W^{(2)}$.

Having determined $\overline{\mathbf{R}}^{(2)}$ from Eq. (47), it is now a simple matter to obtain $\overline{\mathbf{F}}^{(1)}$ with the help of relation $(31)_1$. The result is

$$\overline{\mathbf{F}}^{(1)} = \frac{1}{1-c_0}(\overline{\mathbf{F}} - c_0\overline{\mathbf{R}}^{(2)}) + O(\varepsilon). \tag{48}$$

The generalized secant modulus expression (36) remains unchanged in the limit as $\varepsilon \to 0$, but expression (39) involving the field fluctuations can be easily shown to reduce to

$$(\hat{\mathbf{F}}^{(1)} - \overline{\mathbf{F}}) \cdot \frac{\partial \mathbf{L}^{(1)}}{\partial \ell_\alpha^*}(\hat{\mathbf{F}}^{(1)} - \overline{\mathbf{F}}) = \frac{c_0}{(1-c_0)^2}(\overline{\mathbf{F}} - \overline{\mathbf{R}}^{(2)}) \cdot \frac{\partial \mathbf{D}^{(1)}}{\partial \ell_\alpha^*}(\overline{\mathbf{F}} - \overline{\mathbf{R}}^{(2)}). \tag{49}$$

Finally, making use of expressions $(42)_1$ and (48) in (33), it is easy to show that the second-order estimate for the effective behavior of elastomers reinforced with *rigid* particles reduces to

$$\widehat{W}(\overline{\mathbf{F}}) = (1-c_0)W^{(1)}(\hat{\mathbf{F}}^{(1)}) + \mathscr{S}^{(1)}(\overline{\mathbf{F}}) \cdot [\overline{\mathbf{F}} - c_0\overline{\mathbf{R}}^{(2)} - (1-c_0)\hat{\mathbf{F}}^{(1)}]. \tag{50}$$

In summary, Eqs. (36), (47) and (49) constitute a closed system of 21 nonlinear algebraic equations for the 21 scalar unknowns formed by the three components of $\overline{\mathbf{R}}^{(2)}$, the nine components of $\hat{\mathbf{F}}^{(1)}$, and the nine components of $\mathbf{L}^{(1)}$ (i.e., the independent components ℓ_α^*), which, in general, must be solved numerically. Having computed all the components of $\overline{\mathbf{R}}^{(2)}$, $\hat{\mathbf{F}}^{(1)}$, and $\mathbf{L}^{(1)}$, for a given loading $\overline{\mathbf{F}}$ and initial microstructure (c_0 and $\mathbf{Z}_0$), the second-order estimate (50) for the effective stored-energy function $\widehat{W}$ of the rigidly reinforced elastomers can be readily obtained.

In passing, it is noted that the above results for rigidly reinforced elastomers provide a generalization of the earlier results of Ponte Castañeda and Tiberio (2000) and Lopez-Pamies and Ponte Castañeda (2004a), where, on account of the considered isotropic symmetry of the microstructure, it was sufficient to set the average rigid rotations for the rigid inclusions equal to the identity (i.e., $\overline{\mathbf{R}}^{(2)} = \mathbf{I}$).

As a final remark, it should be emphasized that the above-developed analysis may lead to remarkably simple estimates for the effective behavior of reinforced elastomers. Indeed, as will be seen in Part II of this paper, the relevant estimates for the effective behavior of fiber-reinforced elastomers with incompressible constituent phases, may be written down in closed form.

4.4. Second-order homogenization estimates: porous elastomers

Although the main concern of this paper is with reinforced elastomers, it is useful to record here for completeness purposes the corresponding results for porous elastomers. Thus, by setting $W^{(2)} = 0$ and $\mathbf{F}^{(1)} = \overline{\mathbf{F}}$, the second-order estimate (33) for the general two-phase elastomers with particulate microstructure reduces to:

$$\widehat{W}(\overline{\mathbf{F}}) = (1-c_0)[W^{(1)}(\hat{\mathbf{F}}^{(1)}) - \mathscr{S}^{(1)}(\overline{\mathbf{F}}) \cdot (\hat{\mathbf{F}}^{(1)} - \overline{\mathbf{F}}^{(1)})], \tag{51}$$

where the variables $\overline{\mathbf{F}}^{(1)}$, $\hat{\mathbf{F}}^{(1)}$, and $\mathbf{L}^{(1)}$ are determined by suitably specializing the relations $(31)_1$, (35), (36) and (39), and eliminating the variable $\overline{\mathbf{F}}^{(2)}$ in these equations in favor of $\overline{\mathbf{F}}^{(1)}$. The resulting equations are (36), which does not change, the following *explicit* equation for the average deformation gradient $\overline{\mathbf{F}}^{(1)}$ in the matrix phase:

$$\overline{\mathbf{F}}^{(1)} = \overline{\mathbf{F}} - c_0(\mathbf{D}^{(1)})^{-1}\mathscr{S}^{(1)}(\overline{\mathbf{F}}), \tag{52}$$

and the field-fluctuations equation:

$$(\hat{\mathbf{F}}^{(1)}-\overline{\mathbf{F}})\cdot\frac{\partial \mathbf{L}^{(1)}}{\partial \ell_\alpha^*}(\hat{\mathbf{F}}^{(1)}-\overline{\mathbf{F}})=\frac{1}{c_0}(\overline{\mathbf{F}}-\overline{\mathbf{F}}^{(1)})\cdot\frac{\partial \mathbf{D}^{(1)}}{\partial \ell_\alpha^*}(\overline{\mathbf{F}}-\overline{\mathbf{F}}^{(1)}). \tag{53}$$

It can be verified that these expressions are equivalent to those given in Section 4.3 of Lopez-Pamies and Ponte Castañeda (2004b) (for version 3 of the second-order estimates) for porous elastomers, but the expressions given here are more explicit (and therefore easier to implement).

5. Microstructure evolution

When a composite material is subjected to finite deformations on its boundary, its microstructure will not remain fixed, but instead will evolve at every step of the deformation. In general, the problem of characterizing the evolution of the microstructure in a detailed manner is a hopelessly difficult task, due to the large number of microstructural variables that would be involved. However, for special classes of microstructures, such as the "particulate" microstructures with "ellipsoidal" symmetry considered in this work, it is possible to develop consistent models for the evolution of suitably chosen microstructural variables. For viscoplastic composites, such types of models have been proposed by Kailasam and Ponte Castañeda (1998), the central idea being that the evolution of the size, shape and orientation of the inclusions should be controlled—on the average—by the average strain-rate and spin fields in the inclusion phase, essentially generalizing notions introduced by Eshelby (1957) for linearly viscous composite systems with dilute concentrations of inclusions. Thus, for the viscoplastic composites with particulate microstructures, the relevant microstructural variables were identified to be the volume fraction of the inclusion phase, and the average aspect ratios and orientation angles of the inclusions, and evolution laws for these variables were generated combining basic kinematics principles with nonlinear homogenization estimates for the average strain-rate and spin fields in the inclusion phase. For non-dilute systems, additional microstructural variables were also identified (Kailasam et al., 1997) serving to characterize the "distribution" of the inclusions in the matrix phase, and evolutions laws for these variables have also been proposed.

For the viscoplastic composites mentioned in the previous paragraph, the development of evolution laws for the relevant microstructural variables was *essential* to be able to describe the constitutive response of these materials under *finite-deformation* histories. Given that the constitutive behavior of these materials is most naturally characterized by means of a Eulerian description of the kinematics, the relevant homogenization procedure is carried out by taking a snapshot of the microstructure at the current instant of time and generating an estimate for the instantaneous constitutive response of the material. This means that this snapshot homogenization process must be supplemented by appropriate laws serving to characterize the evolution of the microstructure from one instant to another instant in time.

In the present work, the interest is on hyperelastic composites, which are characterized, as we have seen, by a Lagrangian description of the kinematics. This means that—unlike the example of viscoplastic composites—the evolution of the microstructure resulting from the finite changes in geometry is already accounted for in the homogenized constitutive

description, given by Eqs. (3) with (4) for these materials. In other words, it is not necessary to obtain *additional* equations to characterize the evolution of the microstructure in these systems. Indeed, the minimizing solution in expression (4) for the effective stored-energy function of the composite elastomer contains implicitly all the necessary information to describe how every point in the specimen moves, and therefore, also how the microstructure evolves. Nevertheless, even if it is not necessary to know how the microstructure evolves in order to determine the effective behavior of a composite elastomer, it is still of interest to have access to this information, as it will be useful to develop a better understanding of the constitutive response of composite elastomers. As will be seen in the context of the applications in Part II of this paper, the evolution of the microstructure plays a critical role in the determination of the overall response of composite elastomers, in general, and of their macroscopic stability, in particular.

For simplicity, the focus here will be on composite elastomers with the "particulate" microstructures described in Section 4.1. These are two-phase composite systems comprised of an elastomeric matrix phase reinforced with ellipsoidal inclusions, which are all taken to be identical in shape and orientation, and are described by a "characteristic ellipsoid" $E_0 = \{\mathbf{X} \,|\, \mathbf{X} \cdot (\mathbf{Z}_0^{\mathrm{T}}\mathbf{Z}_0)\mathbf{X} \leqslant 1\}$ in the *reference* configuration. The symmetric second-order tensor $\mathbf{Z}_0^{\mathrm{T}}\mathbf{Z}_0$ has principal values $1/(z_1^0)^2, 1/(z_2^0)^2$, and $1/(z_3^0)^2$, defining two initial aspect ratios $\omega_1^0 = z_3^0/z_1^0$ and $\omega_2^0 = z_3^0/z_2^0$, and principal directions defining a rectangular Cartesian basis $\{\mathbf{e}_i\}$. In addition, the inclusions are assumed to be distributed with "ellipsoidal symmetry," with the same aspect ratio and orientation as the inclusions in the reference configuration, hence the use of only one microstructural tensor $\mathbf{P}^{(1)}$ (see Ponte Castañeda and Willis, 1995).

Given the significant nonlinearities involved in these hyperelastic composites, the deformation-gradient field $\mathbf{F}$ will *not* be uniform inside the inclusions, even for dilute concentrations ($c_0 \ll 1$). This means that the initially ellipsoidal inclusions will deform into inclusions with shapes that will not, except in the small-deformation domain, continue to be ellipsoidal. However, consistent with the general aims of homogenization, where the interest is not in the details of the deformation fields, but only on average information on these fields, our objective here will be to characterize the evolution of the "average" size, shape and orientation of the inclusions, as determined by the *average deformation gradient* $\overline{\mathbf{F}}^{(2)}$ in the inclusion phase. It is important to mention in this context that this approximation is entirely consistent with the use of the estimates of the Willis-type described in the previous section, since the deformation gradient field $\mathbf{F}$ in this type of approximation is known to be constant inside the inclusions, and therefore, such that $\mathbf{F} = \overline{\mathbf{F}}^{(2)}$ for $\mathbf{X} \in \Omega_0^{(2)}$.

Under these hypotheses, the material inside an inclusion centered at $\mathbf{X}^{\mathrm{c}}$ in the undeformed configuration, which is defined by the ellipsoid:

$$E_0^{\mathrm{c}} = \{\mathbf{X} \,|\, (\mathbf{X} - \mathbf{X}^{\mathrm{c}}) \cdot \mathbf{Z}_0^{\mathrm{T}}\mathbf{Z}_0(\mathbf{X} - \mathbf{X}^{\mathrm{c}}) \leqslant 1\}, \tag{54}$$

will deform according to: $\mathbf{x} - \mathbf{x}^{\mathrm{c}} = \overline{\mathbf{F}}^{(2)}(\mathbf{X} - \mathbf{X}^{\mathrm{c}})$, where $\mathbf{x}^{\mathrm{c}}$ denotes the center of the inclusion in the deformed configuration. It then follows that the inclusion defined by (54) evolves into the ellipsoid:

$$E^{\mathrm{c}} = \{\mathbf{x} \,|\, (\mathbf{x} - \mathbf{x}^{\mathrm{c}}) \cdot \mathbf{Z}^{\mathrm{T}}\mathbf{Z}(\mathbf{x} - \mathbf{x}^{\mathrm{c}}) \leqslant 1\}, \tag{55}$$

in the deformed configuration, where $\mathbf{Z} = \mathbf{Z}_0(\overline{\mathbf{F}}^{(2)})^{-1}$. The symmetric, second-order tensor $\mathbf{Z}^{\mathrm{T}}\mathbf{Z}$ has principal values $1/(z_1)^2, 1/(z_2)^2$, and $1/(z_3)^2$, which serve to define the two *current*

aspect ratios $\omega_1 = z_3/z_1$ and $\omega_2 = z_3/z_2$ for the inclusions (in the deformed configuration). Similarly, the principal directions of $\mathbf{Z}^{\mathrm{T}}\mathbf{Z}$, denoted here by the rectangular Cartesian basis $\{\mathbf{e}_i'\}$, define the principal directions of the inclusion in the *deformed* configuration. Thus, the evolution of the average shape and orientation of the inclusions can thus be characterized (through the tensor $\mathbf{Z}$) from the knowledge of the average deformation gradient $\overline{\mathbf{F}}^{(2)}$ in the inclusion phase, together with the initial shape and orientation of the inclusions in the reference configuration, as determined by $\mathbf{Z}_0$.

Next, note that the *current* volume fraction of the inclusions in the *deformed* configuration is given by:

$$c \doteq \frac{\int_{\Omega^{(2)}} \mathrm{d}v}{\int_{\Omega} \mathrm{d}v} = \frac{\int_{\Omega_0^{(2)}} \det \mathbf{F}\, \mathrm{d}V}{\int_{\Omega_0} \det \mathbf{F}\, \mathrm{d}V} = \frac{\langle \det \mathbf{F} \rangle^{(2)}}{\langle \det \mathbf{F} \rangle} c_0 = \frac{\langle \det \mathbf{F} \rangle^{(2)}}{\det \overline{\mathbf{F}}} c_0, \tag{56}$$

where Ω and $\Omega^{(2)}$ denote the volume of the specimen and inclusion phase in the *deformed* configuration, respectively, and use has been made of the fact that $\det \mathbf{F}$ is a null-Lagrangian. Now, recalling that within the context of the Willis-type estimates (29), used in the homogenization process for the above-described composites, the fields in the inclusion phase are constant, it follows that $\langle \det \mathbf{F} \rangle^{(2)} = \det \langle \mathbf{F} \rangle^{(2)} = \det \overline{\mathbf{F}}^{(2)}$, so that the current volume fraction of the inclusions in the deformed configuration can be written as

$$c = \frac{\det \overline{\mathbf{F}}^{(2)}}{\det \overline{\mathbf{F}}} c_0, \tag{57}$$

which may be readily computed in terms of the available estimate, $\overline{\mathbf{F}}^{(2)}$, for the average deformation gradient in the inclusion phase, and the known, initial volume fraction, c_0, of the inclusions in the reference configuration.

The above results simplify considerably for the case when the particles are taken to be *rigid*. In this case, the inclusions are constrained to undergo an average rigid rotation $\overline{\mathbf{F}}^{(2)} = \overline{\mathbf{R}}^{(2)}$. This implies that $\det \overline{\mathbf{F}}^{(2)} = 1$, so that the current volume fraction of particles in the deformed configuration simplifies to

$$c = \frac{c_0}{\det \overline{\mathbf{F}}}. \tag{58}$$

When the matrix phase is further assumed to be incompressible, $\det \overline{\mathbf{F}} = 1$, the expression (58) for the current value of the volume fraction of the inclusion phase further reduces to $c = c_0$, as expected on physical grounds. Moreover, in this case, the tensor $\mathbf{Z}^{\mathrm{T}}\mathbf{Z}$ characterizing the shape and orientation of the particles in the deformed configuration reduces to

$$\mathbf{Z}^{\mathrm{T}}\mathbf{Z} = \overline{\mathbf{R}}^{(2)} \mathbf{Z}_0^{\mathrm{T}} \mathbf{Z}_0 (\overline{\mathbf{R}}^{(2)})^{\mathrm{T}}. \tag{59}$$

From this result, it is evident that the principal values of $\mathbf{Z}^{\mathrm{T}}\mathbf{Z}$ are equal to those of $\mathbf{Z}_0^{\mathrm{T}}\mathbf{Z}_0$ for rigid particles. This implies that the shape of the particles will remain fixed upon deformation (i.e., $\omega_1 = \omega_1^0$ and $\omega_2 = \omega_2^0$), which is, of course, consistent with the particles being rigid. On the other hand, the rotation tensor $\overline{\mathbf{R}}^{(2)}$ serves to characterize the reorientation of the principal axes of $\mathbf{Z}^{\mathrm{T}}\mathbf{Z}$ with respect to those of $\mathbf{Z}_0^{\mathrm{T}}\mathbf{Z}_0$.

In summary, it has been shown that the evolution of the volume fraction, the *average* shape, and the *average* orientation of the inclusions in the type of reinforced elastomers considered in this work can be consistently estimated from the knowledge of the average deformation gradient $\overline{\mathbf{F}}^{(2)}$ in the particles, which, in turn, can be readily obtained from the

homogenization estimates of the previous section. Note that we have not said anything so far about the evolution of the *distribution* of the particles (i.e., about the relative motion of the centers of the inclusions). In fact, it is plausible for composites with random microstructures, and can be shown rigorously for periodic composites, that the inclusions will move, on the average, with the macroscopic flow, as determined by the average deformation gradient $\overline{\mathbf{F}}$ (and *not* with the average field $\overline{\mathbf{F}}^{(2)}$ in the inclusions), at least up to the development of the first microscopic instability.

6. The strong ellipticity condition

A complete analysis of the stability of reinforced elastomers with *random* microstructures is an extremely difficult problem and well beyond the scope of this work (see Triantafyllidis et al., 2005 for composites with *periodic* microstructures). However, following Geymonat et al. (1993), it is possible to identify the onset of *macroscopic* instabilities with the loss of strong ellipticity of the homogenized constitutive behavior in the reinforced elastomers, which may be estimated efficiently by means of the second-order variational procedure described in the previous sections. Recall that loss of strong ellipticity for a given constitutive law corresponds to the loss of positive definiteness of the associated acoustic tensor. In the present context, the condition of strong ellipticity for the homogenized reinforced elastomer characterized by the stored-energy function $\widehat{W}$ is expressible as

$$\widehat{K}_{ik}m_i m_k = \widehat{\mathscr{L}}_{ijkl}N_j N_l m_i m_k > 0, \tag{60}$$

for all $\mathbf{m}\otimes\mathbf{N}\neq\mathbf{0}$. Here, $\widehat{K}_{ik}=\widehat{\mathscr{L}}_{ijkl}N_jN_l$ 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 reinforced elastomer. Note that when condition (60) is satisfied, the associated macroscopic equilibrium equations form a system of strongly elliptic partial differential equations.

In connection with condition (60), it should be remarked that, in general, $\widehat{\mathscr{L}}\neq\widetilde{\mathbf{L}}$. That is, the incremental elastic modulus associated with the effective stored-energy function $\widehat{W}$ of the reinforced elastomer does not correspond exactly to the effective modulus of the auxiliary linear comparison composite (LCC). This raises the possibility that the LCC may lose strong ellipticity before the actual nonlinear composite. Given that the LCC is a *fictitious* material whose main role is to allow the estimation of the effective behavior of the actual nonlinear composite, in this work, we will insist on strong ellipticity of the incremental modulus $\widehat{\mathscr{L}}$, and not on strong ellipticity of the effective modulus $\widetilde{\mathbf{L}}$ of the LCC. In passing, it is recalled that the condition of ellipticity requires the acoustic tensor to be merely non-singular and not necessarily positive definite. Hence, strong ellipticity implies ellipticity, but the converse is not true in general. However, the interest here is in the determination of the loss of strong ellipticity of homogenized materials that are strictly convex, and therefore strongly elliptic, for infinitesimal deformations. Then, elliptic regions containing the point $\overline{\mathbf{F}}=\mathbf{I}$, by continuity, will necessarily also be strongly elliptic. Thus, for the cases of interest here, the elliptic and strongly elliptic regions coincide.

In summary, use can be made of the second-order expression (33) (or (50)) to generate estimates for the effective stored-energy function $\widehat{W}$ in order to *estimate* the strongly elliptic domain of reinforced (or rigidly reinforced) elastomers through condition (60).

7. Concluding remarks

In this paper, estimates have been obtained for the macroscopic behavior of fiber-reinforced elastomers subjected to finite deformation, by means of a recently developed "second-order" homogenization method (Ponte Castañeda, 2002). This method makes use of estimates for a "comparison composite" that is defined by a suitable "generalized-secant" linearization of the constitutive behavior of the elastomer phases to generate corresponding estimates for the composite elastomer. As a byproduct of the procedure, estimates are also obtained for the evolution of the relevant microstructural variables, including the fiber rotation. The estimates for the overall behavior, which were enforced to satisfy overall objectivity, can also be used to obtain estimates for the onset of macroscopic instabilities, through loss of ellipticity of the effective incremental moduli of the composite (Geymonat et al., 1993). The specific results given in this paper are valid for non-dilute concentrations of aligned ellipsoidal particles of arbitrary shape and compliance dispersed randomly in an elastomeric matrix with general hyperelastic constitutive behavior. But even more general micro-geometries could be considered, including multiple families of aligned fibers, as well as randomly oriented fibers, by exploiting more general versions of the Willis estimates (Ponte Castañeda and Willis, 1995) for the LCC. It would also be possible to consider elastomeric systems with periodic microstructures, such as the thermoplastic elastomers mentioned in the introduction, by making use of the estimates of the HS type proposed by Suquet (1990) for the LCC. Indeed, work along these lines is already in progress.

In this paper, the limiting case of ideally rigid inclusions, which is a good approximation for many reinforced rubbers, was also considered, and it was found that the resulting estimates simplified considerably. In particular, it was found that the deformation of the fibers in this case reduced to a pure rotation, as expected on physical grounds. This is a remarkable result that bodes well for the power of the method: even though the homogenization is carried out at the level of a *linear* (comparison) composite, the method has the capability of accounting for the *nonlinear* kinematics involved in the actual behavior of the composite elastomer. Another example of the strength of the method developed in this work will be discussed in Part II, where estimates will be obtained for rigidly reinforced elastomers with *incompressible* matrix phases. In such cases, the incompressibility of both phases, which translates into a kinematical constraint on the *determinant* of the local deformation, dictates overall incompressibility for the composite. Thus, it will be seen in Part II that the method is indeed able to recover overall incompressibility for the composite, in spite of the strong nonlinearity associated with the local incompressibility constraint for the phases. In Part II, it will also be seen that the method is able to predict macroscopic instabilities of the shear-band type for fiber-reinforced elastomers, even when the behavior of the constituent phases is itself strongly elliptic, and therefore excludes such types of instabilities at the local level.

Finally, it should be emphasized that the method proposed here for the composite elastomers is still under development. In particular, it is not yet clear what the best choice is for the reference deformation variables $\mathbf{F}^{(r)}$, nor it is yet known what the optimal form is for the modulus tensors $\mathbf{L}^{(r)}$ of the LCC. But we have shown that the method, even at its current stage of development, is already capable of providing physically meaningful estimates for fiber-reinforced elastomers in the finite-deformation regime. To the best of our knowledge, there are no other analytical methods available in the literature with comparable capabilities.

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