Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
International Journal of Solids and Structures 42 (2005) 6409–6432
INTERNATIONAL JOURNAL OF SOLIDS and STRUCTURES
www.elsevier.com/locate/ijsolstr

A Lagrangian-based continuum homogenization approach applicable to molecular dynamics simulations

P.C. Andia, F. Costanzo *, G.L. Gray

Engineering Science and Mechanics Department, The Pennsylvania State University, 212 Earth and Engineering Sciences Building, University Park, PA 16802, USA

Received 15 July 2004; received in revised form 19 May 2005
Available online 18 July 2005

Abstract

The continuum notions of effective mechanical quantities as well as the conditions that give meaningful deformation processes for homogenization problems with large deformations are reviewed. A continuum homogenization model is presented and recast as a Lagrangian-based approach for heterogeneous media that allows for an extension to discrete systems simulated via molecular dynamics (MD). A novel constitutive relation for the effective stress is derived so that the proposed Lagrangian-based approach can be used for the determination of the "stress–deformation" behavior of particle systems. The paper is concluded with a careful comparison between the proposed method and the Parrinello–Rahman approach to the determination of the "stress–deformation" behavior for MD systems. When compared with the Parrinello–Rahman method, the proposed approach clearly delineates under what conditions the Parrinello–Rahman scheme is valid.

PACS: 02.70.Ns; 46.05.+b; 46.15.−x; 62.20.Dc; 62.25.+g

Keywords: Nonlinear homogenization; Effective stress; Effective strain; Molecular dynamics; Parrinello–Rahman

1. Introduction

The objective of this paper is to formulate a Lagrangian-based approach to the determination of the stress–deformation behavior of continua as well as of particle systems, where by "stress–deformation"

* Corresponding author. Tel.: +1 814 863 2030; fax: +1 814 865 9974.
E-mail addresses: pcandia@psu.edu (P.C. Andia), costanzo@engr.psu.edu (F. Costanzo), gray@engr.psu.edu (G.L. Gray).

0020-7683/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijsolstr.2005.05.027

behavior we mean the stress (or deformation) history that results from a prescribed deformation (or stress) history. Specifically, we intend to present a Lagrangian-based approach that can be implemented using molecular dynamics (MD) and that can deliver the stress response of solid systems in a regime of large deformations. For this purpose, homogenization theory gives one a framework for constructing a scheme that, if possible, will lead to a valid constitutive relation that is in accordance with a boundary value problem defined beforehand. Excellent discussions on homogenization theory, although in a context of infinitesimal deformations, are, for example, the works by Suquet (1985, 1987) and Maugin (1992). Based on these discussions, the first step in constructing a homogenization scheme involves the choice of a representative volume element (RVE) of the heterogeneous material under study, i.e., a section of the material that can be taken as a representative sample for constructing an equivalent homogeneous material that resembles and behaves as the original material in some specified average sense. Consequently, this step introduces two levels of description of the material: one at the macroscopic scale and the other at the microscopic scale. It is the objective of a homogenization scheme to properly link the material theories at these two scales. In doing so, one has to be aware of the relation between the macroscopic and microscopic quantities, the initial/boundary value problem (I/BVP) of the RVE, the conditions that the RVE can be subjected to, and the constitutive law at the microscopic scale. In addition, some useful guidelines that homogenization theory imposes are that at the microscopic scale continuum mechanics concepts are applicable, and that the macroscopic or effective quantities are taken to be the boundary averages of their microscopic counterparts.

In this context, and as stated earlier, the goal of this paper is to use homogenization theory to derive a form of a constitutive relation for an effective mechanical variable that is appropriate for use in MD. For this purpose, the authors have carefully re-examined the definitions of effective deformation gradient and stress tensors (see Costanzo et al., 2004), and defined the properties that give meaningful deformation processes as well as the sufficient conditions for them to hold in an RVE undergoing large deformations (see Costanzo et al., 2005). These concepts are of crucial importance for establishing the homogenization procedure. Moreover, a Lagrangian-based approach will be formulated for presenting the equilibrium equations imposed on the RVE as well as for quantifying its effective stress from the microscopic variables and prescribed mechanical quantities.

The authors' interest lies also in understanding and quantifying average mechanical properties of materials that can be utilized in applications related to areas of nanotechnology. More specifically, in how, for example, MD simulations are formulated for calculating time and space averages of properties of materials represented by a system of particles behaving under a specified I/BVP. In this context, the main objective of this paper is to offer a rigorous derivation of a homogenization formalism applicable to both continua and particle systems alike. Hence, although we do not present any MD calculations, we will derive a new analytical MD framework. This framework consists of a Lagrangian-based scheme that we rigorously derive from "first principles".[1] Furthermore, we will offer a formal comparison between our scheme and the Parrinello–Rahman scheme, one of the widely used Lagrangian-based methods applicable to the study of the stress response of particle systems. For the sake of generality, we choose to develop a homogenization scheme in a context of finite deformations so as to study deformation histories that take a chosen material element from its reference configuration all the way to failure. We believe that such a choice is the appropriate one since at the spatial scale in which MD is applicable, that is, at the nanoscale, and depending on the loading conditions, one can more easily investigate deformations of the material that will more likely be of similar magnitude to the material's dimensions and, therefore, the deformations can no longer be taken to be infinitesimal.

[1] We use the expression "first principles" in the context of classical analytical mechanics, as opposed to quantum mechanics.

Finally, some sections of this paper are a review of the authors' work that has been published and discussed in detail in Costanzo et al. (2004, 2005). However, the primary results presented herein have not been included elsewhere and, wherever there is repetition, it is only in the interest of clarity and to present a self-contained discussion.

2. Notation

The derivations presented in this paper are carried out using direct notation following common conventions (see, e.g., Bowen, 1989; Chadwick, 1999; Gurtin, 1981; Spencer, 2004). However, for completeness, in this section we provide the index notation corresponding to the chosen direct notation.

We will denote by $\mathscr{E}$ the standard three-dimensional Euclidean point space, and by $\mathscr{V}$ the corresponding translation vector space. Vectors, i.e., elements of $\mathscr{V}$, will be denoted by lower-case bold italic Roman or Greek letters, e.g., $\boldsymbol{n}$ or $\boldsymbol{\chi}$. We adopt the standard definition of scalar product of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$, and will denote it by $\boldsymbol{a}\cdot\boldsymbol{b}$. For simplicity, as basis for $\mathscr{V}$ we choose an orthonormal basis $\{\boldsymbol{e}_1,\boldsymbol{e}_2,\boldsymbol{e}_3\}$, i.e., a triplet of vectors such that $\boldsymbol{e}_i\cdot\boldsymbol{e}_j=\delta_{ij}$ $(i,j=1,\ldots,3)$, where $\delta_{ij}=1$ if $i=j$ and $\delta_{ij}=0$ if $i\neq j$. The components of a vector $\boldsymbol{a}$ with respect to this basis will be denoted by a_i $(i=1,\ldots,3)$ and can be computed as follows: $a_i=\boldsymbol{a}\cdot\boldsymbol{e}_i$. Hence, using index notation and adopting the standard summation convention according to which the repetition of an index in an expression implies a summation with respect to that index, we have that the scalar product of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ can be represented as a_ib_i.

We will denote the tensor product of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ by $\boldsymbol{a}\otimes\boldsymbol{b}$. The action of the tensor product of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ onto a vector $\boldsymbol{q}$ will be denoted by $(\boldsymbol{a}\otimes\boldsymbol{b})\boldsymbol{q}$ and will be defined in the standard fashion, i.e., $(\boldsymbol{a}\otimes\boldsymbol{b})\boldsymbol{q}=(\boldsymbol{b}\cdot\boldsymbol{q})\boldsymbol{a}$. As such, the tensor product of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ is a linear operation from $\mathscr{V}$ into $\mathscr{V}$ since it maps any vector $\boldsymbol{q}$ into the vector $(\boldsymbol{b}\cdot\boldsymbol{q})\boldsymbol{a}$. We will denote by $\mathrm{Lin}(\mathscr{V})$ the collection of all linear functions from $\mathscr{V}$ into $\mathscr{V}$ and we will refer to $\mathrm{Lin}(\mathscr{V})$ as the space of second order tensors. Elements of $\mathrm{Lin}(\mathscr{V})$ will be denoted by upper-case sans serif letters such as A. Following Gurtin (1981), the ijth component of A is defined as $A_{ij}=\boldsymbol{e}_i\cdot\mathsf{A}\boldsymbol{e}_j$. We adopt the standard definitions of all the usual tensor algebra operations. For example, for the product of two tensors A and B we write AB and its ij-component is determined by $(\mathsf{AB})_{ij}=A_{ik}B_{kj}$, where the expression $(\cdot)_{ij}$ denotes the ij-component of the term in parentheses. Similarly, we write $\mathsf{A}\cdot\mathsf{B}=A_{ij}B_{ij}$ for the scalar product of two tensors, $\mathrm{tr}(\mathsf{A})=A_{ii}$ for the trace of a tensor, and $(\mathsf{A}\boldsymbol{b})_i=A_{ij}b_j$ for the action of a tensor on a vector.

The material system under consideration in its deformed configuration will be denoted by Ω and in its reference configuration will be denoted by Ω_κ. Both Ω and Ω_κ are assumed to be regular subsets of $\mathscr{E}$. The boundaries of Ω and Ω_κ will be denoted by $\partial\Omega$ and $\partial\Omega_\kappa$, respectively. The volumes of Ω and Ω_κ will be denoted by $\mathrm{Vol}(\Omega)$ and $\mathrm{Vol}(\Omega_\kappa)$, respectively. The boundaries $\partial\Omega$ and $\partial\Omega_\kappa$ are oriented by the outward unit normal vector fields $\boldsymbol{n}$ and $\boldsymbol{n}_\kappa$, respectively. The position of points in the reference configuration will be denoted by $\boldsymbol{\chi}$ and in the deformed configuration by $\boldsymbol{x}$.

The operators 'Div' and 'div' indicate the divergence operators with respect to $\boldsymbol{\chi}$ and $\boldsymbol{x}$, respectively. For example, if $\boldsymbol{b}$ is a vector field[2] we have that $\mathrm{Div}\,\boldsymbol{b}=\partial b_i/\partial\chi_i$, whereas $\mathrm{div}\,\boldsymbol{b}=\partial b_i/\partial x_i$. Similarly, if A is a tensor field, then $(\mathrm{Div}\,\mathsf{A})_i=\partial A_{ik}/\partial\chi_k$ and $(\mathrm{div}\,\mathsf{A})_i=\partial A_{ik}/\partial x_k$.

The operators 'Grad' and 'grad' indicate the gradient operators with respect to $\boldsymbol{\chi}$ and $\boldsymbol{x}$, respectively. For example, if $\boldsymbol{b}$ is a vector field we have that $(\mathrm{Grad}\,\boldsymbol{b})_{ij}=\partial b_i/\partial\chi_j$, whereas $(\mathrm{grad}\,\boldsymbol{b})_{ij}=\partial b_i/\partial x_j$.

Finally, the symbol $\triangleq$ will indicate a definition.

[2] By "field" we mean a "function of position". As such, whenever $\boldsymbol{x}$ is a one-to-one function of $\boldsymbol{\chi}$, fields can be viewed as functions of $\boldsymbol{\chi}$ *or* $\boldsymbol{x}$.

3. Effective kinematic and kinetic quantities

A proper homogenization scheme must clearly identify the set of primary variables that will be used at each level of description of the material as well as define their relationships. At the local level, the primary measure of deformation is the point-wise deformation gradient tensor F, whose determinant must be positive for it to represent an admissible deformation process (see, e.g., Gurtin, 1981). The stress at the local level is represented, in the reference configuration, by the point-wise first Piola–Kirchhoff stress tensor S, and, in the deformed configuration, by the point-wise Cauchy stress tensor T; these two tensors are related by $\mathsf{S} = \det(\mathsf{F})\mathsf{T}\mathsf{F}^{-\mathrm{T}}$. The use of these mechanical quantities corresponds to the fact that this work is in a context of finite deformations. At the macroscopic scale, to the best of the authors' knowledge, the definitions of effective deformation and stress in a regime of large deformations were first systematically discussed by Hill (1972) (see also Hill, 1984). Hill (1972) points out that the macrovariables must be defined in terms of the information given on the boundary of the RVE. However, the definitions he presents for effective deformation and stress are given as volume averages, which he then relates to boundary averages. The authors have adopted Hill's principle (not Hill's definitions), which is embraced by a good portion of the micromechanics community (see, e.g., Maugin, 1992; Stolz, 1986; Suquet, 1985, 1987), according to which a fundamental requirement to be met by acceptable notions of effective kinematic and kinetic quantities is that they be defined as boundary averages instead of volume averages. Consequently, given a bounded RVE in its reference configuration Ω_κ subject to a motion $\boldsymbol{x} = \boldsymbol{x}(\boldsymbol{\chi}, t)$, we denote the *effective deformation gradient tensor* by $[\![\mathsf{F}]\!]$ and define it to be

$$[\![\mathsf{F}]\!] \triangleq \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \int_{\partial\Omega_\kappa} \boldsymbol{x} \otimes \boldsymbol{n}_\kappa \, \mathrm{d}A. \tag{1}$$

Along with $[\![\mathsf{F}]\!]$, our primary measure of effective deformation, we introduce two measures of effective stress, the *effective Cauchy stress tensor* and the *effective first Piola–Kirchhoff stress tensor*. These quantities are denoted by $[\![\mathsf{T}]\!]$ and $[\![\mathsf{S}]\!]$, respectively, and are defined as follows:

$$[\![\mathsf{T}]\!] \triangleq \frac{1}{\mathrm{Vol}(\Omega)} \int_{\partial\Omega} (\mathsf{T}\boldsymbol{n}) \otimes \boldsymbol{x} \, \mathrm{d}a, \tag{2}$$

and

$$[\![\mathsf{S}]\!] \triangleq \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \int_{\partial\Omega_\kappa} (\mathsf{S}\boldsymbol{n}_\kappa) \otimes \boldsymbol{\chi} \, \mathrm{d}A. \tag{3}$$

In addition, as it plays a crucial role in the determination of the relationship between $[\![\mathsf{T}]\!]$ and $[\![\mathsf{S}]\!]$, we offer the following definition of *effective inverse deformation gradient tensor*, which we denote by $[\![\mathsf{F}^{-1}]\!]$:

$$[\![\mathsf{F}^{-1}]\!] \triangleq \frac{1}{\mathrm{Vol}(\Omega)} \int_{\partial\Omega} \boldsymbol{\chi} \otimes \boldsymbol{n} \, \mathrm{d}a. \tag{4}$$

Before continuing, it is important to mention that the authors are not aware of any work presenting a definition of $[\![\mathsf{F}^{-1}]\!]$.

The definitions presented in Eqs. (1)–(4) can be related to corresponding volume averages (Costanzo et al., 2004, 2005; Hill, 1972). To illustrate this, assume the RVE to be regular and the deformation process to be smooth. Then a straightforward application of the divergence theorem to Eqs. (1) and (4) yields

$$[\![\mathsf{F}]\!] = \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \int_{\Omega_\kappa} \mathsf{F} \, \mathrm{d}V \quad \text{and} \quad [\![\mathsf{F}^{-1}]\!] = \frac{1}{\mathrm{Vol}(\Omega)} \int_{\Omega} \mathsf{F}^{-1} \, \mathrm{d}v, \tag{5}$$

respectively. Furthermore, if to these assumptions one adds that the underlying deformation process is governed by $\operatorname{div}\mathsf{T} = \mathbf{0}$ (or $\operatorname{Div}\mathsf{S} = \mathbf{0}$), i.e., by a *quasi-static* form of the local balance of linear momentum without body forces, then an application of the divergence theorem to Eqs. (2) and (3) allows one to show that

$$[\![\mathsf{T}]\!] = \frac{1}{\operatorname{Vol}(\Omega)} \int_{\Omega} \mathsf{T}\, \mathrm{d}v \quad \text{and} \quad [\![\mathsf{S}]\!] = \frac{1}{\operatorname{Vol}(\Omega_\kappa)} \int_{\Omega_\kappa} \mathsf{S}\, \mathrm{d}V, \tag{6}$$

respectively. However, if the deformation process is fully dynamic, as it is in an MD simulation, then the relations given in Eq. (6) are no longer valid and a time average operation is required for all effective quantities. For a discussion of the forms taken on by the effective stress tensors in fully dynamical processes, see Costanzo et al. (2004, 2005).

The definitions of effective kinematic and kinetic quantities presented above, i.e., Eqs. (1)–(4), do not guarantee that at the macroscopic scale the deformation process of the equivalent homogeneous material will be physically meaningful. The authors have carefully discussed this issue in Costanzo et al. (2004, 2005), and in order to attach physical meaning to the above effective quantities the following definition has been proposed:

Definition 1. By a *large deformation process with meaningful space averages* we mean a deformation process enjoying the following properties:

(1) $[\![\mathsf{F}]\!]^{-1} = [\![\mathsf{F}^{-1}]\!]$, with $\det([\![\mathsf{F}]\!]) > 0$;
(2) $\operatorname{Vol}(\Omega) = \det([\![\mathsf{F}]\!])\ \operatorname{Vol}(\Omega_\kappa)$; and
(3) $[\![\mathsf{S}]\!] = \det([\![\mathsf{F}]\!])[\![\mathsf{T}]\!][\![\mathsf{F}]\!]^{-\mathrm{T}}$.

This definition is motivated by a desire to have effective quantities that formally behave just like their local counterparts. Consequently, it sets the essential properties that the effective quantities must obey in order for them to represent a physically meaningful large deformation process. This leads one to the following question: what physical conditions on the RVE allow one to work with meaningful effective kinematic and kinetic quantities? The answer to this question will be presented in the next section, and has been carefully discussed in Costanzo et al. (2005). It concerns a detailed discussion of the boundary conditions that one can assign to the RVE. In particular, we have focused on the three "canonical" sets of boundary conditions that are widely accepted by the homogenization community (see, e.g., Suquet, 1987), i.e., uniform strain, uniform stress, and periodic.

4. Boundary conditions and meaningful effective quantities

The three "canonical" sets of boundary conditions presented herein are a generalization of those used in a context where the deformations are taken to be infinitesimal. It is important to mention that they do not necessarily yield a well posed boundary value problem due to the nonlinear nature of the problem at hand. However, since this paper does not deal with any specific homogenization problem, all the derivations to be presented are developed under the assumption that the underlying problem is well posed.

4.1. Uniform strain boundary condition

The first boundary condition typically invoked in homogenization is usually called the *uniform strain boundary condition*. In the present context, a bounded RVE that behaves under the uniform strain boundary condition is one such that

$$\boldsymbol{x}(\boldsymbol{\chi}, t) = \hat{\mathsf{F}}(t)\boldsymbol{\chi} \quad \text{for } \boldsymbol{\chi} \in \partial\Omega_\kappa, \tag{7}$$

where, for all t of interest, $\hat{\mathsf{F}}(t)$ is a *prescribed* second order tensor with positive determinant. Note that quantities with hats will always be considered to be prescribed.

4.2. Uniform stress boundary condition

The second boundary condition typically invoked in homogenization is usually called the *uniform stress boundary condition*. In the present context, a bounded RVE that behaves under the uniform stress boundary condition is one such that

$$\mathsf{T}(\boldsymbol{x},t)\boldsymbol{n}(\boldsymbol{x},t) = \hat{\Sigma}(t)\boldsymbol{n}(\boldsymbol{x},t) \quad \text{for } \boldsymbol{x} \in \partial\Omega, \tag{8}$$

where, for all t of interest, $\hat{\Sigma}(t)$ is a *prescribed* symmetric second order tensor.

4.3. Periodic boundary condition

The third boundary condition typically invoked in homogenization is usually called the *periodic boundary condition* and its definition is somewhat more technical than the previous two given above. In fact, this condition is not a boundary condition in a strict sense in that it does *not* prescribe the boundary values of the position or traction fields. To view a more detailed presentation of the technical issues concerning this condition please refer to Costanzo et al. (2005). Nonetheless, it is important to mention that this condition is only meaningful when the domain Ω_κ is a *periodic cell*, that is, a domain that can be "stacked" along three (nonparallel) directions so as to fill $\mathscr{E}$ completely. Furthermore, it will be understood that a field is Ω_κ-periodic or Ω_κ-anti-periodic, when, on opposite faces of the boundary of the domain Ω_κ, the field has equal values or values that are of opposite sign, respectively. In the present context, a bounded RVE that behaves under the periodic boundary condition is one that obeys the following two conditions:

(1) the deformation function $\boldsymbol{x}(\boldsymbol{\chi},t)$ can be given the form

$$\boldsymbol{x}(\boldsymbol{\chi},t) = \hat{\mathsf{F}}(t)\boldsymbol{\chi} + \tilde{\boldsymbol{u}}(\boldsymbol{\chi},t), \tag{9}$$

where, for all t of interest, $\hat{\mathsf{F}}(t)$ is a *prescribed* second order tensor with positive determinant and $\tilde{\boldsymbol{u}}(\boldsymbol{\chi},t)$ is an Ω_κ-periodic displacement vector field; and

(2) the boundary traction field $\mathsf{S}\boldsymbol{n}_\kappa$ is Ω_κ-anti-periodic.

4.4. Propositions concerning effective quantities

The three propositions to be presented in this subsection have been proved in Costanzo et al. (2005), and are of crucial importance for establishing the homogenization procedure. The first two propositions concern the idea that by enforcing certain boundary conditions it is possible to *control* the effective value of a target quantity. The third proposition answers the question posed at the end of Section 3, and its main consequence is that it restricts one to use only two of the three "canonical" sets of boundary conditions if one is to work with meaningful effective quantities in a context of finite deformations.

Proposition 1. *For any regular, bounded, and simply connected RVE, a smooth deformation process complying with either uniform strain or periodic boundary conditions is one such that*

$$[\![\mathsf{F}]\!] = \hat{\mathsf{F}}, \tag{10}$$

that is, one can control the effective deformation gradient tensor via the prescribed $\hat{\mathsf{F}}$.

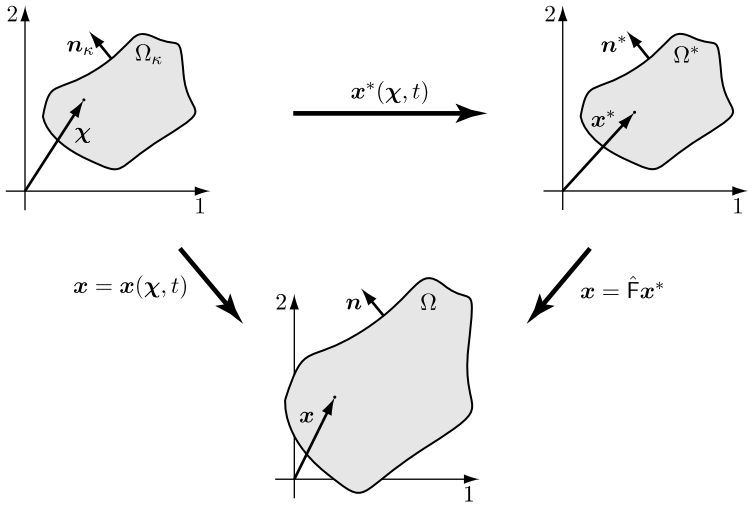

Fig. 1. Two-dimensional schematic of the decomposition formula given in Eq. (12).

Proposition 2. *For any regular, bounded, and simply connected RVE, a smooth deformation process under uniform stress boundary conditions is one such that*

$$[\![\mathsf{T}]\!] = \hat{\Sigma}, \tag{11}$$

that is, using the uniform stress boundary condition one can control the effective Cauchy stress tensor via the prescribed $\hat{\Sigma}$.

Proposition 3. *For any regular, bounded, and simply connected RVE, any smooth deformation process under uniform strain or periodic boundary conditions enjoys all three properties stated in Definition* 1.

Remark 1 (Ω^* configuration). As it will be crucial for performing the proof of the central claim of this paper, we need to mention that in proving Proposition 3 an ad hoc intermediate configuration of the RVE, denoted by Ω^*, was utilized. In particular, we used the following decomposition formula to relate the position fields in the Ω and Ω^* configurations:

$$\boldsymbol{x}(\boldsymbol{\chi}, t) = \hat{\mathsf{F}}(t)\boldsymbol{x}^*(\boldsymbol{\chi}, t). \tag{12}$$

Recalling that the tensor $\hat{\mathsf{F}}$ can always be chosen to belong to $\mathrm{Lin}^+(\mathscr{V})$[3] and recalling that $\mathsf{F} \in \mathrm{Lin}^+(\mathscr{V})$, we have that the deformation gradient F^* of the motion $\boldsymbol{x}^*$, given by

$$\mathsf{F}^*(\boldsymbol{\chi}, t) = \hat{\mathsf{F}}^{-1}(t)\mathsf{F}(\boldsymbol{\chi}, t), \tag{13}$$

is also a member of $\mathrm{Lin}^+(\mathscr{V})$. Since $\mathsf{F}^* \in \mathrm{Lin}^+(\mathscr{V})$, the motion $\boldsymbol{x}^*$, depicted in Fig. 1, is admissible under the uniform strain and periodic boundary conditions. The decomposition in Eq. (12) enjoys another important property, namely that the motion $\boldsymbol{x}^*$ satisfies the same *type* of boundary conditions satisfied by the motion $\boldsymbol{x}$. Specifically, for uniform strain boundary conditions we have that

$$\boldsymbol{x}^* = \boldsymbol{\chi} \quad \forall \boldsymbol{\chi} \in \partial\Omega_\kappa. \tag{14}$$

[3] Here, $\mathrm{Lin}^+(\mathscr{V})$ denotes the subset of $\mathrm{Lin}(\mathscr{V})$ characterized by tensors with positive determinant.

In other words, the motion $\boldsymbol{x}^*$ is the identity map for points on the boundary of Ω_κ. For periodic boundary conditions, we have that

$$\boldsymbol{x}^* = \boldsymbol{\chi} + \boldsymbol{u}^* \quad \forall \boldsymbol{\chi} \in \Omega_\kappa, \tag{15}$$

where $\boldsymbol{u}^* = \hat{\mathsf{F}}^{-1}\tilde{\boldsymbol{u}}$ is Ω_κ-periodic. Therefore, on $\partial\Omega_\kappa$, $\boldsymbol{x}^*$ behaves like the identity map modulo a periodic displacement field. Under both uniform strain and periodic boundary conditions one can readily show that the effective deformation gradient tensor for the motion $\boldsymbol{x}^*$ is the identity tensor, i.e., $[\![\mathsf{F}^*]\!] = \mathsf{I}$.

5. A Lagrangian-based approach

As described in the works of Suquet (1985, 1987) and Maugin (1992), a homogenization procedure requires the knowledge of the relations between global and local quantities, the equilibrium equations of the RVE, the boundary conditions enforced on the RVE, and the microscopic constitutive law characterizing the behavior of the RVE. In this section, we will discuss the equilibrium equations and the microscopic constitutive law. The definitions of effective kinematic and kinetic quantities presented in Section 3 correlate the macroscopic and microscopic quantities. The three "canonical" sets of boundary conditions introduced in Section 4 allow one to properly pose the boundary value problem underlying the homogenization process. As far as the microscopic constitutive law is concerned, we will assume that at the local level the RVE behaves as an isothermal elastic material. The constitutive theory of an isothermal elastic material is very well established (see, e.g., Gurtin, 1981; Bowen, 1989), and for the purposes of the present work it can be summarized as follows: when a regular, bounded, and simply connected body is subjected to an isothermal elastic deformation process, its constitutive relations state that the first Piola–Kirchhoff stress tensor is given by

$$\mathsf{S}(\mathsf{F}, \boldsymbol{\chi}) = \rho_\kappa(\boldsymbol{\chi}) \frac{\partial \psi(\mathsf{F}, \boldsymbol{\chi})}{\partial \mathsf{F}}, \tag{16}$$

where ρ_κ is the mass density distribution in the reference configuration and ψ represents the Helmholtz free energy per unit mass, which, generally, is a function of position and strain measure. Now, the last item needed for carrying out the homogenization procedure is the statement of the equilibrium equations of the RVE, which were briefly mentioned and used in Section 3, although not formally introduced. The equilibrium equations of the RVE in the present context are given by the local statement of the balance of linear momentum without considering body forces, which in the reference configuration is written as

$$\mathrm{Div}\,\mathsf{S} = \rho_\kappa \dot{\boldsymbol{v}}, \tag{17}$$

where $\boldsymbol{v}$ denotes the material velocity field and the dot over a quantity denotes the material time derivative of that quantity.

The equations introduced so far are sufficient to carry out the homogenization procedure in a continuum context. However, our interest is to formulate a homogenization scheme that can be applied to both continuum as well as discrete systems, for example, using MD. For this reason, we now proceed to reformulate the homogenization scheme in question using a Lagrangian-based approach. One of the main contributions of this paper is to show that a classical Lagrangian function can be used to formulate a workable MD scheme for the determination of the stress–deformation behavior, as opposed to formulating *ad hoc* Lagrangians, as one can find in commonly used MD schemes such as those of Parrinello and Rahman (1980, 1981, 1982). This point will be better illustrated later in the paper when we present a formal comparison between the cited schemes and the one derived herein.

The Lagrangian of the RVE will be denoted by $\mathscr{L}$ and will be given the following classical expression:

$$\mathscr{L}(\boldsymbol{x}, \boldsymbol{v}) = T - U, \tag{18}$$

where T and U denote the RVE's total kinetic and potential energies, respectively. The total kinetic energy of the RVE is given by (Bedford, 1985; Marsden and Hughes, 1994)

$$T = \int_{\Omega_\kappa} \frac{1}{2}\rho_\kappa \boldsymbol{v}\cdot\boldsymbol{v}\,\mathrm{d}V. \tag{19}$$

For the total potential energy, we will follow the *standard* definition given in continuum mechanics (Germain, 1982; Gurtin, 1981; Marsden and Hughes, 1994). Hence, without considering body forces (although these can be easily included), we have that

$$U = \Psi - \int_{\partial\Omega_{\kappa 2}} \hat{\boldsymbol{s}}_\kappa \cdot (\boldsymbol{x} - \boldsymbol{\chi})\,\mathrm{d}A, \tag{20}$$

where $\partial\Omega_{\kappa 2}$ denotes the portion of the boundary of Ω_κ over which the traction field $\hat{\boldsymbol{s}}_\kappa$ is *prescribed*, with $\hat{\boldsymbol{s}}_\kappa = \mathbf{S}\boldsymbol{n}_\kappa$ by Cauchy law, and Ψ is the total Helmholtz free energy, i.e.,

$$\Psi = \int_{\Omega_\kappa} \rho_\kappa \psi\,\mathrm{d}V. \tag{21}$$

In the case of uniform stress boundary conditions, $\partial\Omega_{\kappa 2} = \partial\Omega_\kappa$. In the case of uniform strain boundary conditions, it is the position field that is prescribed over the entire $\partial\Omega_\kappa$ and, therefore, $\partial\Omega_{\kappa 2}$ is empty. For periodic boundary conditions case, in a continuum context, one can argue that $\partial\Omega_{\kappa 2}$ is empty since the boundary traction field is not prescribed in the strict sense of the word. Therefore, the total potential energy for both uniform strain and periodic boundary conditions reduces to

$$U = \Psi. \tag{22}$$

For periodic boundary conditions, another argument can be offered to justify the conclusion in Eq. (22), namely that the vector fields $\hat{\boldsymbol{s}}_\kappa$ and $\boldsymbol{x} - \boldsymbol{\chi}$ are anti-periodic and periodic, respectively, thus making the scalar field $\hat{\boldsymbol{s}}_\kappa \cdot (\boldsymbol{x} - \boldsymbol{\chi})$ anti-periodic. Consequently, the second term on the right side of Eq. (20) vanishes identically, because the boundary integral of any anti-periodic field is null.

In continuum mechanics, the derivation of the field equations using the Lagrangian formalism is a well established result under "standard" boundary conditions, i.e., under pure displacement, pure traction, or mixed (again see Germain, 1982; Gurtin, 1981; Marsden and Hughes, 1994). However, to the authors' knowledge, a similar result has not been shown in the case of periodic boundary conditions. Therefore, we need to verify that, under periodic boundary conditions, the choice in Eq. (22) does indeed allow one to derive the correct field equations using the standard Lagrangian formalism. This verification is important because of the unusual nature of the periodic boundary conditions. In fact, the expression "periodic boundary conditions" is a bit of a misnomer in the sense that, in enforcing periodic boundary conditions, one is prescribing neither a boundary displacement field nor a boundary traction field. Rather, to impose periodic boundary conditions simply means to simultaneously constrain the *class of functions* to which the admissible boundary displacement *as well as* boundary traction fields belong.

We now verify that by using the Lagrangian of Eq. (18) one recovers the equilibrium equations for the proposed material system via the Euler–Lagrange equations (see, e.g., Marsden and Hughes, 1994), which are

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathscr{L}}{\partial \boldsymbol{v}}\right) - \frac{\partial \mathscr{L}}{\partial \boldsymbol{x}} = \mathbf{0}, \tag{23}$$

where $\partial\mathscr{L}/\partial\boldsymbol{v}$ and $\partial\mathscr{L}/\partial\boldsymbol{x}$ denote the two *vector fields* (i.e., vector-valued functions of position and time) defined via the following relations:

$$\delta_{\boldsymbol{v}}\mathscr{L} = \int_{\Omega_\kappa} \frac{\partial \mathscr{L}}{\partial \boldsymbol{v}} \cdot \delta\boldsymbol{v}\,\mathrm{d}V, \tag{24}$$

and

$$\delta_{\boldsymbol{x}}\mathscr{L} = \int_{\Omega_\kappa} \frac{\partial \mathscr{L}}{\partial \boldsymbol{x}} \cdot \delta \boldsymbol{x}\, \mathrm{d}V, \tag{25}$$

for all variations $\delta\boldsymbol{v}$ and $\delta\boldsymbol{x}$, respectively, and where $\delta_{\boldsymbol{v}}\mathscr{L}$ and $\delta_{\boldsymbol{x}}\mathscr{L}$ denote the variation of the functional $\mathscr{L}$ due to variations in the fields $\boldsymbol{v}$ and $\boldsymbol{x}$, respectively. It is important to note that the terms $\partial\mathscr{L}/\partial\boldsymbol{v}$ and $\partial\mathscr{L}/\partial\boldsymbol{x}$ need to be interpreted as functional derivatives and not as common partial derivatives. In fact, roughly speaking, these derivatives represent the derivatives of the Lagrangian with respect to the entire velocity and position fields, respectively (this notation is also used in Section 9.5.3 of Maugin, 1992 and in Section 5.2 of Suquet, 1987 among others; for a more rigorous treatment of Lagrangian mechanics for continuum systems, consistent with the one presented herein, see Chapter 5 of Marsden and Hughes, 1994).

Proposition 4. *For any regular, bounded, and simply connected RVE behaving as an isothermal elastic material, a smooth deformation process governed by Eq. (17) under uniform strain, uniform stress, or periodic boundary conditions admits the Lagrangian proposed in Eq. (18).*

Proof. Before presenting the proof of Proposition 4, we wish to clarify that the claim of this proposition is novel only with regard to periodic boundary conditions. As far as uniform strain and uniform stress boundary conditions are concerned, the proof can be obtained from classical results concerning Dirichlet and Neumann boundary data, respectively (see, e.g., Section 5.4 in Chapter 5 of Marsden and Hughes, 1994). Here we present the proof for all three cases of interest for convenience. With this in mind, the proof of this proposition will be given by deriving the equilibrium equations of the RVE from the proposed Lagrangian and using the Euler–Lagrange equations. The proof of the entire proposition will be carried out by identifying each term in the Euler–Lagrange equations for each of the boundary conditions and then assembling them for each case. In addition, observe that in order to obtain the terms on the left side of Eq. (23) we will have to resort to variational theory. Hence, we begin by taking the variation of Eq. (18) with respect to the velocity field, which is

$$\delta_{\boldsymbol{v}}\mathscr{L} = \delta_{\boldsymbol{v}} \int_{\Omega_\kappa} \frac{1}{2}\rho_\kappa \boldsymbol{v}\cdot\boldsymbol{v}\, \mathrm{d}V = \int_{\Omega_\kappa} \rho_\kappa \boldsymbol{v}\cdot\delta\boldsymbol{v}\, \mathrm{d}V. \tag{26}$$

Comparing Eq. (26) with Eq. (24), we conclude that

$$\frac{\partial \mathscr{L}}{\partial \boldsymbol{v}} = \rho_\kappa \boldsymbol{v}. \tag{27}$$

Now, taking the time derivative of Eq. (27) we obtain the first term on the left side of Eq. (23), that is,

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathscr{L}}{\partial \boldsymbol{v}}\right) = \rho_\kappa \dot{\boldsymbol{v}}. \tag{28}$$

Notice that in obtaining the first term on the left side of Eq. (23) there was no need to specify the boundary condition acting upon the RVE. Consequently, Eq. (28) is valid for all three "canonical" sets of boundary conditions. Next, to obtain the second term on the left side of Eq. (23) we take the variation of Eq. (18) with respect to the position field, that is,

$$\begin{aligned}\delta_{\boldsymbol{x}}\mathscr{L} &= -\delta_{\boldsymbol{x}} \int_{\Omega_\kappa} \rho_\kappa \psi\, \mathrm{d}V + \delta_{\boldsymbol{x}} \int_{\partial\Omega_{\kappa 2}} \hat{\boldsymbol{s}}_\kappa \cdot (\boldsymbol{x}-\boldsymbol{\chi})\, \mathrm{d}A = -\int_{\Omega_\kappa} \rho_\kappa \frac{\partial \psi}{\partial \mathsf{F}}\cdot \delta_{\boldsymbol{x}}\mathsf{F}\, \mathrm{d}V + \int_{\partial\Omega_{\kappa 2}} \hat{\boldsymbol{s}}_\kappa \cdot \delta\boldsymbol{x}\, \mathrm{d}A \\ &= -\int_{\Omega_\kappa} \mathsf{S}\cdot(\mathrm{Grad}\,\delta\boldsymbol{x})\, \mathrm{d}V + \int_{\partial\Omega_{\kappa 2}} \hat{\boldsymbol{s}}_\kappa \cdot \delta\boldsymbol{x}\, \mathrm{d}A,\end{aligned} \tag{29}$$

where Eq. (16) and the definition of the deformation gradient tensor have been applied. Recalling that the divergence theorem can be given the form

$$\int_{\partial\mathscr{R}_\kappa} \boldsymbol{a}\cdot \mathsf{A}\boldsymbol{m}_\kappa \,\mathrm{d}A = \int_{\mathscr{R}_\kappa} [\boldsymbol{a}\cdot(\mathrm{Div}\,\mathsf{A}) + \mathsf{A}\cdot(\mathrm{Grad}\,\boldsymbol{a})]\mathrm{d}V, \tag{30}$$

which holds for any vector $\boldsymbol{a}$, smooth tensor A and bounded regular region $\mathscr{R}_\kappa$, and where $\boldsymbol{m}_\kappa$ is the outward unit normal vector field on $\partial\mathscr{R}_\kappa$ (see, e.g., Gurtin, 1981), then we can rewrite Eq. (29) as

$$\delta_{\boldsymbol{x}}\mathscr{L} = -\int_{\partial\Omega_\kappa} \delta\boldsymbol{x}\cdot \mathsf{S}\boldsymbol{n}_\kappa \,\mathrm{d}A + \int_{\Omega_\kappa} \delta\boldsymbol{x}\cdot(\mathrm{Div}\,\mathsf{S})\,\mathrm{d}V + \int_{\partial\Omega_{\kappa 2}} \hat{\boldsymbol{s}}_\kappa\cdot\delta\boldsymbol{x}\,\mathrm{d}A. \tag{31}$$

Now, in order to continue with the development of the variation of the Lagrangian with respect to the position field it will be necessary to invoke the boundary conditions. In the case of the uniform stress boundary condition, Eq. (31) reduces to

$$\delta_{\boldsymbol{x}}\mathscr{L} = \int_{\Omega_\kappa} (\mathrm{Div}\,\mathsf{S})\cdot\delta\boldsymbol{x}\,\mathrm{d}V, \tag{32}$$

since $\partial\Omega_{\kappa 2} = \partial\Omega_\kappa$. Comparing Eq. (32) with Eq. (25), we conclude that the second term on the left side of Eq. (23) under uniform stress boundary conditions is

$$\frac{\partial\mathscr{L}}{\partial\boldsymbol{x}} = \mathrm{Div}\,\mathsf{S}. \tag{33}$$

In the cases of the uniform strain and periodic boundary conditions, Eq. (31) reduces to

$$\delta_{\boldsymbol{x}}\mathscr{L} = -\int_{\partial\Omega_\kappa} \delta\boldsymbol{x}\cdot \mathsf{S}\boldsymbol{n}_\kappa \mathrm{d}A + \int_{\Omega_\kappa} \delta\boldsymbol{x}\cdot(\mathrm{Div}\,\mathsf{S})\,\mathrm{d}V, \tag{34}$$

since $\partial\Omega_{\kappa 2}$ is empty. Now, for the case of the uniform strain boundary condition, Eq. (7) tells us that the motion of the boundary is prescribed at all times. Consequently, the variation of the position field on the boundary of the RVE is zero, i.e., $\delta\boldsymbol{x} = \boldsymbol{0}$ on $\partial\Omega_\kappa$, and Eq. (34) reduces to Eq. (32). Moreover, we conclude that Eq. (33) gives the second term on the left side of Eq. (23) under uniform strain boundary conditions. In the case of periodic boundary conditions, recall the two requirements stated in Section 4.3. The first requirement, given by Eq. (9), implies that the variation of the position field $\delta\boldsymbol{x}$ must have a periodic nature. The second requirement enforces the traction field $\mathsf{S}\boldsymbol{n}_\kappa$ acting upon the boundary of the reference configuration to be anti-periodic. Hence, the scalar field $\delta\boldsymbol{x}\cdot\mathsf{S}\boldsymbol{n}_\kappa$ is anti-periodic and its boundary integral vanishes. Consequently, under periodic boundary conditions the first integral on the right side of Eq. (34) vanishes and, therefore, the development of Eq. (34) for this case is similar to the uniform strain case. More importantly, the second term on the left side of Eq. (23) under periodic boundary conditions is given by Eq. (33).

Finally, by assembling the Euler–Lagrange equations for each of the boundary conditions (i.e., using Eqs. (28) and (33) we obtain the local statement of the balance of linear momentum, i.e., Eq. (17). Therefore, the Lagrangian proposed in Eq. (18) is valid for an isothermal elastic material behaving under this particular boundary value problem for any of the three "canonical" sets of boundary conditions. □

6. An effective constitutive relation

The continuum homogenization model we are presenting is based on the homogenization procedure as outlined by Suquet (1985, 1987) and Maugin (1992), and it aims to obtain an effective constitutive relation

that is consistent with the behavior of the RVE at the microscopic scale as well as with the properties enforced at the macroscopic scale, all in a context of large deformations. In other words, what is missing in the present model is an expression that is able to relate the effective kinematic and kinetic quantities with the local behavior of the RVE. This is no easy task and is sometimes not possible, especially in nonlinear problems such as the one that we are studying. In fact, one of the reasons for introducing a Lagrangian-based approach earlier in this paper is to aid the development of the homogenization procedure for obtaining such an expression. Given this premise, recall that the specification of a type of boundary condition prescribes some effective quantities and, therefore, controls some of the overall behavior of the RVE. Moreover, from Proposition 3 we infer that, in order to *always* guarantee that the underlying averaging process be meaningful (as specified in Definition 1), one can *only* prescribe effective kinematic quantities, i.e., the effective deformation gradient tensor. Therefore, we can conjecture that the constitutive relation that must come out of the model should be capable of expressing the effective first Piola–Kirchhoff stress tensor in terms of the prescribed deformation gradient (i.e., $\hat{\mathsf{F}}$) and the microscopic behavior of the RVE, behavior that is embedded in the RVE's Lagrangian as written in Eq. (18). In summary, we present the following claim:

Proposition 5. *For any regular, bounded, and simply connected RVE behaving as an isothermal elastic material, a smooth deformation process governed by Eq. (17) under uniform strain or periodic boundary conditions obeys the following effective constitutive relation*:

$$[\![\mathsf{S}]\!] = \frac{1}{\mathrm{Vol}(\Omega_\kappa)}\left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathscr{L}}{\partial \dot{\hat{\mathsf{F}}}}\right) - \frac{\partial \mathscr{L}}{\partial \hat{\mathsf{F}}}\right]. \tag{35}$$

Proof. For the sake of conciseness, we present only the proof under periodic boundary conditions since the proof for the uniform strain case can be obtained from the one to be presented by simply letting $\tilde{\boldsymbol{u}} \to \mathbf{0}$ (in boundary integrals only). The strategy we will implement to prove Eq. (35) is to patiently construct the expression on its right side under the specified conditions. Hence, we begin by noting that under the stated assumptions, and due to Proposition 4, the Lagrangian of the RVE is that given in Eq. (18). However, note that the Lagrangian is not directly dependent on the deformation gradient tensor prescribed by either boundary condition. To express the Lagrangian in terms of the prescribed deformation gradient, we will need to use the decomposition scheme of the deformation process of the RVE discussed in Remark 1, illustrated in Fig. 1, and admissible under both boundary conditions. Therefore, recall Eq. (12) and take its material time derivative so as to obtain the velocity field, that is,

$$\boldsymbol{v} = \hat{\mathsf{F}}\boldsymbol{v}^* + \dot{\hat{\mathsf{F}}}\boldsymbol{x}^*. \tag{36}$$

Inserting Eq. (36) into the Lagrangian of the RVE, we can write

$$\mathscr{L} = \int_{\Omega_\kappa} \frac{1}{2}\rho_\kappa(\hat{\mathsf{F}}\boldsymbol{v}^*)\cdot(\hat{\mathsf{F}}\boldsymbol{v}^*)\,\mathrm{d}V + \int_{\Omega_\kappa} \rho_\kappa(\hat{\mathsf{F}}\boldsymbol{v}^*)\cdot(\dot{\hat{\mathsf{F}}}\boldsymbol{x}^*)\,\mathrm{d}V + \int_{\Omega_\kappa} \frac{1}{2}\rho_\kappa(\dot{\hat{\mathsf{F}}}\boldsymbol{x}^*)\cdot(\dot{\hat{\mathsf{F}}}\boldsymbol{x}^*)\,\mathrm{d}V - \int_{\Omega_\kappa} \rho_\kappa\psi\,\mathrm{d}V. \tag{37}$$

Eq. (37) shows in an explicit manner the dependence of the Lagrangian on the prescribed deformation gradient and its material time derivative. It is important to mention that the Helmholtz free energy per unit mass function is also dependent on the prescribed deformation gradient due to Eq. (13). Now, we will begin the development of the right side of Eq. (35) by obtaining the term $\partial\mathscr{L}/\partial\dot{\hat{\mathsf{F}}}$, that is,

$$\frac{\partial \mathscr{L}}{\partial \dot{\hat{\mathsf{F}}}} = \hat{\mathsf{F}}\int_{\Omega_\kappa} \rho_\kappa \boldsymbol{v}^* \otimes \boldsymbol{x}^*\,\mathrm{d}V + \dot{\hat{\mathsf{F}}}\int_{\Omega_\kappa} \rho_\kappa \boldsymbol{x}^* \otimes \boldsymbol{x}^*\,\mathrm{d}V, \tag{38}$$

where the identity $(\mathsf{A}\boldsymbol{a})\otimes\boldsymbol{b}=\mathsf{A}(\boldsymbol{a}\otimes\boldsymbol{b})$ has been used. Next, we take the time derivative of Eq. (38) to obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial\mathscr{L}}{\partial\dot{\hat{\mathsf{F}}}}\right)=\hat{\mathsf{F}}\left(\int_{\Omega_\kappa}\rho_\kappa\dot{\boldsymbol{v}}^*\otimes\boldsymbol{x}^*\,\mathrm{d}V+\int_{\Omega_\kappa}\rho_\kappa\boldsymbol{v}^*\otimes\boldsymbol{v}^*\,\mathrm{d}V\right)+\dot{\hat{\mathsf{F}}}\left(2\int_{\Omega_\kappa}\rho_\kappa\boldsymbol{v}^*\otimes\boldsymbol{x}^*\,\mathrm{d}V+\int_{\Omega_\kappa}\rho_\kappa\boldsymbol{x}^*\otimes\boldsymbol{v}^*\,\mathrm{d}V\right)+\ddot{\hat{\mathsf{F}}}\int_{\Omega_\kappa}\rho_\kappa\boldsymbol{x}^*\otimes\boldsymbol{x}^*\,\mathrm{d}V. \tag{39}$$

Notice that, in obtaining Eq. (39), there was no need to specify the boundary condition acting upon the RVE. Consequently, Eq. (39) is valid for both boundary conditions. Continuing with the development of the right side of Eq. (35), we will now focus on obtaining the term $\partial\mathscr{L}/\partial\hat{\mathsf{F}}$. For this purpose, we take the corresponding partial derivative of Eq. (37) and write

$$\frac{\partial\mathscr{L}}{\partial\hat{\mathsf{F}}}=\hat{\mathsf{F}}\int_{\Omega_\kappa}\rho_\kappa\boldsymbol{v}^*\otimes\boldsymbol{v}^*\,\mathrm{d}V+\dot{\hat{\mathsf{F}}}\int_{\Omega_\kappa}\rho_\kappa\boldsymbol{x}^*\otimes\boldsymbol{v}^*\,\mathrm{d}V-\int_{\Omega_\kappa}\rho_\kappa\frac{\partial\psi}{\partial\hat{\mathsf{F}}}\,\mathrm{d}V, \tag{40}$$

where, again, the identity $(\mathsf{A}\boldsymbol{a})\otimes\boldsymbol{b}=\mathsf{A}(\boldsymbol{a}\otimes\boldsymbol{b})$ has been used. Observe that the last term on the right side of Eq. (40) can be further developed. In particular, using the chain rule along with Eqs. (16) and (13), we can write

$$\int_{\Omega_\kappa}\rho_\kappa\frac{\partial\psi}{\partial\hat{\mathsf{F}}}\,\mathrm{d}V=\int_{\Omega_\kappa}\mathsf{S}(\mathsf{F}^*)^{\mathrm{T}}\,\mathrm{d}V=\int_{\Omega_\kappa}\mathsf{S}\mathsf{F}^{\mathrm{T}}\hat{\mathsf{F}}^{-\mathrm{T}}\,\mathrm{d}V=\left[\int_{\Omega_\kappa}\mathsf{S}(\mathrm{Grad}\,\boldsymbol{x})^{\mathrm{T}}\,\mathrm{d}V\right]\hat{\mathsf{F}}^{-\mathrm{T}}, \tag{41}$$

where the identity $(\mathsf{AB})^{\mathrm{T}}=\mathsf{B}^{\mathrm{T}}\mathsf{A}^{\mathrm{T}}$ and the definition of the deformation gradient tensor have been applied. Noting the following form of the divergence theorem:

$$\int_{\partial\mathscr{R}_\kappa}(\mathsf{A}\boldsymbol{m}_\kappa)\otimes\boldsymbol{a}\,\mathrm{d}A=\int_{\mathscr{R}_\kappa}\left[(\mathrm{Div}\,\mathsf{A})\otimes\boldsymbol{a}+\mathsf{A}(\mathrm{Grad}\,\boldsymbol{a})^{\mathrm{T}}\right]\mathrm{d}V, \tag{42}$$

which holds for any vector $\boldsymbol{a}$, smooth tensor A and bounded regular region $\mathscr{R}_\kappa$, and where $\boldsymbol{m}_\kappa$ is the outward unit normal vector field on $\partial\mathscr{R}_\kappa$ (see, e.g., Gurtin, 1981), we can then rewrite Eq. (41) as

$$\int_{\Omega_\kappa}\rho_\kappa\frac{\partial\psi}{\partial\hat{\mathsf{F}}}\,\mathrm{d}V=\left[\int_{\partial\Omega_\kappa}(\mathsf{S}\boldsymbol{n}_\kappa)\otimes\boldsymbol{x}\,\mathrm{d}A-\int_{\Omega_\kappa}(\mathrm{Div}\,\mathsf{S})\otimes\boldsymbol{x}\,\mathrm{d}V\right]\hat{\mathsf{F}}^{-\mathrm{T}}. \tag{43}$$

Furthermore, notice that one can apply Eq. (9) (from the periodic boundary condition) to the boundary integral on the right side of Eq. (43), while for the volume integral (on the right side of Eq. (43)) one can apply the equilibrium equations and the decomposition formula given by Eqs. (17) and (12), respectively. Therefore, we obtain

$$\int_{\Omega_\kappa}\rho_\kappa\frac{\partial\psi}{\partial\hat{\mathsf{F}}}\,\mathrm{d}V=\left[\int_{\partial\Omega_\kappa}(\mathsf{S}\boldsymbol{n}_\kappa)\otimes(\hat{\mathsf{F}}\boldsymbol{\chi})\,\mathrm{d}A+\int_{\partial\Omega_\kappa}(\mathsf{S}\boldsymbol{n}_\kappa)\otimes\tilde{\boldsymbol{u}}\,\mathrm{d}A-\int_{\Omega_\kappa}\rho_\kappa\dot{\boldsymbol{v}}\otimes(\hat{\mathsf{F}}\boldsymbol{x}^*)\,\mathrm{d}V\right]\hat{\mathsf{F}}^{-\mathrm{T}}. \tag{44}$$

The second integral on the right side of Eq. (44) vanishes. In order to view this, first recall that the traction field $\mathsf{S}\boldsymbol{n}_\kappa$ and the displacement field $\tilde{\boldsymbol{u}}$ are anti-periodic and periodic fields over Ω_κ, respectively, thus making the tensor field $(\mathsf{S}\boldsymbol{n}_\kappa)\otimes\tilde{\boldsymbol{u}}$ anti-periodic. In turn, since the boundary integral of any anti-periodic tensor field vanishes, this implies that Eq. (44) reduces to

$$\int_{\Omega_\kappa}\rho_\kappa\frac{\partial\psi}{\partial\hat{\mathsf{F}}}\,\mathrm{d}V=\int_{\partial\Omega_\kappa}(\mathsf{S}\boldsymbol{n}_\kappa)\otimes\boldsymbol{\chi}\,\mathrm{d}A-\int_{\Omega_\kappa}\rho_\kappa\dot{\boldsymbol{v}}\otimes\boldsymbol{x}^*\,\mathrm{d}V, \tag{45}$$

where the identity $\boldsymbol{a}\otimes(\mathsf{A}\boldsymbol{b})=(\boldsymbol{a}\otimes\boldsymbol{b})\mathsf{A}^{\mathrm{T}}$ has been used. Now, observe that the material time derivative of $\boldsymbol{v}$ can be obtained from Eq. (36), that is,

$$\dot{\boldsymbol{v}} = \hat{\mathsf{F}}\dot{\boldsymbol{v}}^* + 2\dot{\hat{\mathsf{F}}}\boldsymbol{v}^* + \ddot{\hat{\mathsf{F}}}\boldsymbol{x}^*. \tag{46}$$

Hence, inserting Eq. (46) into Eq. (45), we can write

$$\int_{\Omega_\kappa} \rho_\kappa \frac{\partial \psi}{\partial \hat{\mathsf{F}}}\,\mathrm{d}V = \mathrm{Vol}(\Omega_\kappa)[\![\mathsf{S}]\!] - \hat{\mathsf{F}}\int_{\Omega_\kappa} \rho_\kappa \dot{\boldsymbol{v}}^* \otimes \boldsymbol{x}^*\,\mathrm{d}V - 2\dot{\hat{\mathsf{F}}}\int_{\Omega_\kappa} \rho_\kappa \boldsymbol{v}^* \otimes \boldsymbol{x}^*\,\mathrm{d}V - \ddot{\hat{\mathsf{F}}}\int_{\Omega_\kappa} \rho_\kappa \boldsymbol{x}^* \otimes \boldsymbol{x}^*\mathrm{d}V, \tag{47}$$

where we have made use of the definition of the effective first Piola–Kirchhoff stress tensor and the identity $(\mathsf{A}\boldsymbol{a}) \otimes \boldsymbol{b} = \mathsf{A}(\boldsymbol{a} \otimes \boldsymbol{b})$. Referring back to Eq. (40), we can now write

$$\begin{aligned}\frac{\partial \mathscr{L}}{\partial \hat{\mathsf{F}}} = {} & \hat{\mathsf{F}}\left(\int_{\Omega_\kappa} \rho_\kappa \dot{\boldsymbol{v}}^* \otimes \boldsymbol{x}^*\,\mathrm{d}V + \int_{\Omega_\kappa} \rho_\kappa \boldsymbol{v}^* \otimes \boldsymbol{v}^*\,\mathrm{d}V\right) + \dot{\hat{\mathsf{F}}}\left(2\int_{\Omega_\kappa} \rho_\kappa \boldsymbol{v}^* \otimes \boldsymbol{x}^*\,\mathrm{d}V + \int_{\Omega_\kappa} \rho_\kappa \boldsymbol{x}^* \otimes \boldsymbol{v}^*\,\mathrm{d}V\right) \\ & + \ddot{\hat{\mathsf{F}}}\int_{\Omega_\kappa} \rho_\kappa \boldsymbol{x}^* \otimes \boldsymbol{x}^*\,\mathrm{d}V - \mathrm{Vol}(\Omega_\kappa)[\![\mathsf{S}]\!].\end{aligned} \tag{48}$$

Finally, subtracting Eq. (48) from Eq. (39) yields the effective constitutive relation given by Eq. (35). □

7. A Lagrangian-based MD method

In this section we present a Lagrangian-based MD scheme for the determination of the stress–deformation response of particle systems. This MD scheme is viewed as the discrete version of the homogenization scheme outlined in the preceding sections, in which a particle system is subjected to a deformation history by prescribing the history of the effective deformation gradient and for which a corresponding stress history is calculated. In order to better illustrate how the continuum and discrete schemes relate to one another, we first revisit the continuum scheme to make it explicit what variables we view as *prescribed* and what variables we choose as primary *unknowns*.

7.1. Homogenization scheme revisited

To offer a meaningful extension of the homogenization approach outlined thus far to an MD context, we make the following three choices.

(i) Although this choice has already been implicitly made, we now explicitly state that we choose to view the homogenization procedure as being Lagrangian-based. By this we mean that the field equations to be solved in the homogenization problem are the Euler–Lagrange equations obtained from the Lagrangian function given in Eq. (18).
(ii) Since periodic boundary conditions are used in the vast majority of MD schemes, we will limit our discussion to this type of boundary conditions (although the results presented in Section 7.1 also hold under uniform strain boundary conditions).
(iii) We choose to make $\hat{\mathsf{F}}$ appear *explicitly* in the Lagrangian (see, e.g., Eq. (37)) due to the adoption of the decomposition of the system's motion given by Eq. (12).

These choices are not necessary in a continuum homogenization context. However, they turn out to be useful for "porting" the scheme to a discrete context.

As observed in Remark 1, the adoption of the decomposition formula in Eq. (12) is *always* admissible within the stated assumptions and does not add any new constraints on the system's overall motion. In particular, Eq. (12) does *not* limit $\boldsymbol{x}(\boldsymbol{\chi}, t)$ to be a homogeneous deformation. The primary consequence of adopting the decomposition formula in Eq. (12), in which we treat the tensor $\hat{\mathsf{F}}(t)$ as a *given* function of

time, is that the primary unknown of our homogenization scheme is no longer the motion $\boldsymbol{x}(\boldsymbol{\chi},t)$, but is the motion $\boldsymbol{x}^*(\boldsymbol{\chi},t)$. Hence, in view of our stated choices, the time evolution of our primary unknown $\boldsymbol{x}^*(\boldsymbol{\chi},t)$ is determined by solving the I/BVP defined by

(1) the following field equations (defined over Ω_κ):

$$\mathrm{Div}[\mathsf{S}(\mathsf{A})|_{\mathsf{A}=\hat{\mathsf{F}}\mathsf{F}^*}] = \rho_\kappa \hat{\mathsf{F}}\ddot{\boldsymbol{x}}^* + 2\rho_\kappa \dot{\hat{\mathsf{F}}}\dot{\boldsymbol{x}}^* + \rho_\kappa \ddot{\hat{\mathsf{F}}}\boldsymbol{x}^*, \tag{49}$$

$$\mathsf{F}^* = \mathrm{Grad}\,\boldsymbol{x}^*, \tag{50}$$

$$\mathsf{S}(\mathsf{A}) = \rho_\kappa \frac{\partial \psi(\mathsf{A},\boldsymbol{\chi})}{\partial \mathsf{A}} \quad \forall \mathsf{A} \in \mathrm{Lin}^+(\mathscr{V}), \tag{51}$$

where, as discussed in relation to Eq. (16), the function ψ defines the local constitutive equations;

(2) the following initial conditions:

$$\boldsymbol{x}^*(\boldsymbol{\chi},0) = \boldsymbol{p}^*(\boldsymbol{\chi}) \quad \text{and} \quad \dot{\boldsymbol{x}}^*(\boldsymbol{\chi},0) = \boldsymbol{w}^*(\boldsymbol{\chi}) \quad \forall \boldsymbol{\chi} \in \Omega_\kappa, \tag{52}$$

where the functions $\boldsymbol{p}^*$ and $\boldsymbol{w}^*$ are the *prescribed* initial position and velocity fields, respectively, and are related to the true initial position and velocity fields through Eq. (12); and

(3) the following boundary conditions:

$$\boldsymbol{x}^*(\boldsymbol{\chi},t) = \boldsymbol{\chi} + \boldsymbol{u}^*(\boldsymbol{\chi},t) \quad \forall \boldsymbol{\chi} \in \partial\Omega_\kappa \cup \Omega_\kappa, \tag{53}$$

$$\mathsf{S}(\widehat{\mathsf{F}}\mathsf{F}^*,\boldsymbol{\chi})\boldsymbol{n}_\kappa(\boldsymbol{\chi}) = \boldsymbol{s}_\kappa(\boldsymbol{\chi},t) \quad \forall \boldsymbol{\chi} \in \partial\Omega_\kappa, \tag{54}$$

with $\boldsymbol{u}^*(\boldsymbol{\chi},t)$ and $\boldsymbol{s}_\kappa(\boldsymbol{\chi},t)$ being *unknown* functions that are *constrained* to be periodic and anti-periodic over Ω_κ, respectively.

Finally, if a solution $\boldsymbol{x}^*(\boldsymbol{\chi},t)$ corresponding to the prescribed deformation history $\hat{\mathsf{F}}(t)$ can be found, we then substitute this solution into Eq. (35) to determine the corresponding response of the system in terms of the effective first Piola–Kirchhoff stress tensor; and we can then make use of the third relation in Definition 1, which can be *proven* to hold under the stated assumptions (Costanzo et al., 2005) to obtain the corresponding effective Cauchy stress tensor.

Remark 2 (*Swapping viewpoints*). The continuum homogenization scheme presented above has been *derived* starting from the definitions of effective quantities given in Eqs. (1)–(4). However, it is possible to "turn the scheme on its head" and state that, for any given function $\hat{\mathsf{F}}(t) \in \mathrm{Lin}^+(\mathscr{V})$ and $\forall t \in \mathbb{R}$, Eq. (35) *defines* the effective first Piola–Kirchhoff stress tensor corresponding to $\hat{\mathsf{F}}$, as long as the right side of Eq. (35) is evaluated using the solution to the I/BVP stated above. That is, rather than letting the definitions of effective strain and effective stress determine our I/BVP, we let the I/BVP determine the definitions of effective strain and effective stress. This is a rather abstract view of what has been presented herein, but it is a view that can be adapted to other mechanical systems and, in particular, to the particle systems studied in MD.

7.2. Formulation of the homogenization procedure applicable to MD

Constructing a homogenization procedure for a discrete system starting from the definitions in Eqs. (1)–(4) does not seem a viable option because one would have to come up with some precise notion of boundary of a particle system. Therefore, we will extend the homogenization scheme outlined above to MD following the abstract approach described in Remark 2.

We begin by considering a system of particles in an MD simulation cell. This cell replaces the notion of the RVE in the continuum case. Initial and boundary conditions, as well as an interparticle potential energy

function (or more than one depending on the problem), need to be prescribed in the same way that initial and boundary conditions, as well as the local constitutive law, must be prescribed in the continuum case.

Next we define the Lagrangian of the particle system. Hence, considering an MD cell containing N particles, we denote the Lagrangian of the system of particles by $\mathscr{L}_{\mathrm{MD}}$ and write

$$\mathscr{L}_{\mathrm{MD}}(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,\dot{\boldsymbol{r}}_1,\ldots,\dot{\boldsymbol{r}}_N)=\sum_{i=1}^{N}\frac{1}{2}m_i\dot{\boldsymbol{r}}_i\cdot\dot{\boldsymbol{r}}_i-\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N), \tag{55}$$

where m_i, $\boldsymbol{r}_i$, and $\dot{\boldsymbol{r}}_i$ denote the mass, position, and velocity of the ith particle, respectively, and Ψ denotes the system's energy stored in the *internal* interparticle bonds or interactions. In other words, at a time instant t, the value of the function $\Psi(\boldsymbol{r}_1(t),\ldots,\boldsymbol{r}_N(t))$, corresponding to a given configuration $\{\boldsymbol{r}_1(t),\ldots,\boldsymbol{r}_N(t)\}$, must be computed as if the particle system were *removed from its surroundings*, thus removing the interaction with any agency external to the system. As in the continuum case, the interaction between the system and its surroundings must be accounted for via the enforcement of a chosen set of boundary conditions.

Remark 3 (*Perspectives in Lagrangian mechanics*). As this may be a source of confusion, especially later in the paper, we wish to provide a brief reminder concerning the use of Lagrangian functions. Specifically, it is important to keep in mind that a Lagrangian approach can be set up in essentially two equivalent ways. One way is to define the Lagrangian function as $\mathscr{L}_{\mathrm{a}}=T-U$, where $U=\Psi-Q_iq_i$, q_i being the ith degree of freedom of the system and Q_i being the *external* generalized force conjugate to q_i. With such a definition, the contribution from an external force system is "built-in" into the Lagrangian function and the Euler–Lagrange equations are obtained as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial\mathscr{L}_{\mathrm{a}}}{\partial\dot{q}_i}\right)-\frac{\partial\mathscr{L}_{\mathrm{a}}}{\partial q_i}=0. \tag{56}$$

A second approach (see, e.g., Meirovitch, 1988) is one in which the Lagrangian function is defined as $\mathscr{L}_{\mathrm{b}}=T-\Psi$. In this case, the Lagrangian formalism must be carried out in the following manner:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial\mathscr{L}_{\mathrm{b}}}{\partial\dot{q}_i}\right)-\frac{\partial\mathscr{L}_{\mathrm{b}}}{\partial q_i}=Q_i. \tag{57}$$

For consistency, in Section 7.2 we are following this second approach since in the continuum analysis presented earlier the Lagrangian function we have used for the analysis of periodic (and uniform strain) boundary conditions ended up being of the type '$T-\Psi$', i.e., it accounted for only internal interactions.

Having defined the system's Lagrangian, we continue to lay out our MD scheme by deriving the system's Euler–Lagrange equations. However, before carrying out this derivation, we adopt the discrete version of Eq. (12) to explicitly represent the effective deformation of the system, i.e.,

$$\boldsymbol{r}_i(t)=\hat{\mathsf{F}}(t)\boldsymbol{r}_i^*(t)\quad i=1,\ldots,N, \tag{58}$$

where, by analogy with Eq. (12), $\boldsymbol{r}_i^*$ defines the position of the ith particle in the (discrete) Ω^* configuration and $\hat{\mathsf{F}}(t)\in\mathrm{Lin}^+(\mathscr{V})\ \forall t\in\mathbb{R}$ is viewed as being *prescribed*.[4] Again, this strategy is implemented so as to avoid having to deal with an explicit definition for the system's boundary.

Substituting Eq. (58) into the Lagrangian in Eq. (55), the Euler–Lagrange equations (according to the Lagrangian formalism sketched in Eq. (57)) renders the following equations of motion:[5]

[4] As we will see later in the paper, the proposed scheme is not limited to strain controlled simulations.

[5] It is important to note that Eq. (59), if rewritten in terms of $\boldsymbol{r}_i$, would take on the form $m_i\ddot{\boldsymbol{r}}_i=\boldsymbol{f}_i$, with $\boldsymbol{f}_i$ being the total (i.e., external and internal) force acting on the ith particle. Hence, Eq. (59) is precisely Newton's second law of motion.

$$m_i\hat{\mathsf{F}}\ddot{\boldsymbol{r}}_i^* + 2m_i\dot{\hat{\mathsf{F}}}\dot{\boldsymbol{r}}_i^* + m_i\ddot{\hat{\mathsf{F}}}\boldsymbol{r}_i^* = -\hat{\mathsf{F}}^{-\mathrm{T}}\frac{\partial \Psi}{\partial \boldsymbol{r}_i^*} + \boldsymbol{f}_i^{\mathrm{e}} \quad i = 1,\ldots,N, \tag{59}$$

where the motion $\boldsymbol{r}_i^*$ $(i = 1,\ldots,N)$ represents our primary variables and where $\boldsymbol{f}_i^{\mathrm{e}}$ denotes the total force on particle i due to the interaction of the system with external agencies. Specifically, when imposing periodic boundary conditions, the external agencies interacting with particle i are the particles belonging to a periodic lattice of identical systems. Therefore, the forces $\boldsymbol{f}_i^{\mathrm{e}}$ are determined by accounting for all interactions between the particles in the system of interest and the particles in the surrounding systems. For future reference, we observe here that a straightforward application of the chain rule allows one to rewrite the first term on the right side of Eq. (59) as

$$\hat{\mathsf{F}}^{-\mathrm{T}}\frac{\partial \Psi}{\partial \boldsymbol{r}_i^*} = \frac{\partial \Psi}{\partial \boldsymbol{r}_i}. \tag{60}$$

Remark 4 (*On Eq. (58)*). Following up on the discussion concerning choice (iii) in Section 7.1, it is important to reaffirm that Eq. (58) does not represent a constraint on the possible motion of the system's particles. The reason why it is important to restate this idea here is that, from a formal viewpoint, Eq. (58) resembles the celebrated Cauchy–Born (or, sometimes, Born) rule typically employed in the study of crystal elasticity (see, e.g., the very careful discussions by Ericksen (1984) and Zanzotto (1992)). To see that Eq. (58) is different from the Cauchy–Born rule one needs to observe that Eq. (58) does not map positions in the reference configuration (even when understood as the initial configuration) to positions in the deformed configuration. Indeed, the motion $\boldsymbol{r}_i^*(t)$ $(i = 1,\ldots,N)$ is influenced by the prescribed $\hat{\mathsf{F}}(t)$ only through the equations of motion in Eq. (59) and therefore is *not* subject to the more severe kinematic restrictions that are imposed by the Cauchy–Born rule in crystal elasticity. In fact, in the proposed MD scheme, we are not in a position to restrict a priori the possibility that a particle might change its neighbors with time. This means that, in practice, we are not in a position to prevent our particle ensemble from experiencing diffusion. With this in mind, we wish to make it clear that, for our discrete scheme to be fully consistent with our continuum formalism, its application should be limited to the study of diffusionless deformations of a solid system. The reason for imposing such a restriction is that we have implicitly excluded phenomena such as diffusion in our continuum model. At the same time, Eq. (58) does not impose any intrinsic restriction on the deformation extent, which is therefore not limited to being infinitesimal.

Remark 5 (*Uniform strain boundary conditions*). Since the Lagrangian functions for the periodic and uniform strain boundary conditions are formally identical, one would conclude that the equations of motion in Eq. (59) are also applicable to the uniform strain boundary condition case. However, there are some important differences which are worth discussing to gain a better insight into the distinction between external and internal forces. Hence, suppose that uniform strain boundary conditions are indeed applied. This means that, somehow, one has to define what particles are the "boundary particles" and then prescribe their motion. Specifically, for simplicity, let the particles numbered from 1 to M (with $M < N$) be the boundary particles in question. Then, as required by Eqs. (7) and (58), we have that

$$\boldsymbol{r}_i^*(t) = \boldsymbol{r}_i^*(0) \quad i = 1,\ldots,M \quad \forall t \geqslant 0, \tag{61}$$

where it is understood that $\dot{\boldsymbol{r}}_i^*$ for the boundary particles are equal to zero. As the motion of particles 1 to M is prescribed, the system's only equations of motion are as follows:

$$m_i\hat{\mathsf{F}}\ddot{\boldsymbol{r}}_i^* + 2m_i\dot{\hat{\mathsf{F}}}\dot{\boldsymbol{r}}_i^* + m_i\ddot{\hat{\mathsf{F}}}\boldsymbol{r}_i^* = -\hat{\mathsf{F}}^{-\mathrm{T}}\frac{\partial \Psi}{\partial \boldsymbol{r}_i^*} \quad i = M+1,\ldots,N. \tag{62}$$

Notice that in Eq. (62) we have used the fact that the external forces $\boldsymbol{f}_i^{\mathrm{e}} = \mathbf{0}$ for $i = M+1,\ldots,N$. The reason why there are no external forces acting on the interior particles, is because enforcing uniform strain boundary conditions is physically identical to "glueing" the system's boundary particles to the walls of a container and then prescribing the motion of these walls (i.e., by prescribing $\hat{\mathsf{F}}(t)$). Clearly, this does not mean that the system is isolated. Rather, it means that the interaction between the interior particles and the system's exterior (i.e., the walls) is mediated by the interaction between the interior particles and the boundary particles. This interaction being expressed by the right side of Eq. (62). As far as the boundary particles are concerned, these are being subjected to a system of external (reaction) forces translating the action of the "glue" that keeps the boundary particles from leaving the walls. Following standard Lagrangian mechanics, it turns out that one can rely again on the Euler–Lagrange equations for the boundary particles, this time to *measure* the external forces, i.e.,

$$\boldsymbol{f}_i^{\mathrm{e}} = m_i \ddot{\hat{\mathsf{F}}} \boldsymbol{r}_i^* + \hat{\mathsf{F}}^{-\mathrm{T}} \frac{\partial \Psi}{\partial \boldsymbol{r}_i^*} \quad i = 1,\ldots,M. \tag{63}$$

Remark 6 (*More on periodic boundary conditions in MD*). As discussed earlier, the enforcement of periodic boundary conditions in MD is done by explicitly computing the interaction forces between the system's particles and the external particles that are placed around the system in such a way that the system of interest appears as a unit cell within a lattice of identical cells. This strategy automatically enforces the periodicity of the particle displacements as well as the anti-periodicity of the force system acting through some convenient notion of boundary surface. It should be noted that the description of periodic boundary conditions just given follows a Lagrangian kinematic description of a system's motion. For completeness, we note here that periodic boundary conditions usually employed in MD (see, e.g., Allen and Tildesley, 1987; Frenkel and Smit, 1996) are often enforced according to an Eulerian viewpoint instead of a Lagrangian[6] viewpoint, as used in this paper. In other words, many MD computational schemes place a particle ensemble within a *control volume*. This control volume is a fixed geometrical entity and, similarly to what is typically done in fluid dynamics calculations, the system's particles are allowed to *flow* in and out of the control volume in question. In such a context (i.e., in an Eulerian context), the application of periodic boundary conditions requires that, when a particle exits the control volume, a companion particle with identical mass and velocity be introduced at a location homologous (according to periodicity) to the exit point of the original particle. The message we wish to convey with this remark is that our description of periodic boundary conditions for particle systems does not mention particles flowing in or out of an MD cell because we are adopting a Lagrangian (kinematic) viewpoint.

Going back to the formulation of the proposed discrete homogenization scheme, we can now conclude our description with the determination of the first Piola–Kirchhoff stress tensor via Eq. (35) by using the expression in Eq. (55) for the system's Lagrangian. This operation yields the following result:

$$[\![\mathsf{S}]\!] = \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \left(\hat{\mathsf{F}} \sum_{i=1}^{N} m_i \ddot{\boldsymbol{r}}_i^* \otimes \boldsymbol{r}_i^* + 2\dot{\hat{\mathsf{F}}} \sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i^* \otimes \boldsymbol{r}_i^* + \ddot{\hat{\mathsf{F}}} \sum_{i=1}^{N} m_i \boldsymbol{r}_i^* \otimes \boldsymbol{r}_i^* + \frac{\partial \Psi}{\partial \hat{\mathsf{F}}} \right). \tag{64}$$

Substituting Eq. (59) into Eq. (64), the expression for the effective first Piola–Kirchhoff stress tensor takes on the following form:

[6] In the present discussion, the adjectives 'Eulerian' and 'Lagrangian' are used as qualifiers of the kinematic description, as opposed to the formalisms used to derive the equations of motion. As is well known, the Eulerian and Lagrangian kinematic descriptions are typically used in fluid and solid mechanics, respectively.

$$[\![\mathsf{S}]\!] = \frac{1}{\mathrm{Vol}(\Omega_\kappa)}\left(\frac{\partial \Psi}{\partial \hat{\mathsf{F}}} - \sum_{i=1}^{N} \hat{\mathsf{F}}^{-\mathrm{T}}\frac{\partial \Psi}{\partial \boldsymbol{r}_i^*}\otimes \boldsymbol{r}_i^* + \sum_{i=1}^{N} \boldsymbol{f}_i^{\mathrm{e}}\otimes \boldsymbol{r}_i^*\right). \tag{65}$$

Next, by applying the chain rule of calculus on the term $\partial\Psi/\partial\hat{\mathsf{F}}$ we see that this term can be rewritten as follows:

$$\frac{\partial \Psi}{\partial \hat{\mathsf{F}}} = \sum_{i=1}^{N}\frac{\partial \Psi}{\partial \boldsymbol{r}_i}\otimes \boldsymbol{r}_i^* = \sum_{i=1}^{N}\hat{\mathsf{F}}^{-\mathrm{T}}\frac{\partial \Psi}{\partial \boldsymbol{r}_i^*}\otimes \boldsymbol{r}_i^*, \tag{66}$$

where we have used Eq. (60) to obtain the last equality. Hence, in view of Eq. (66), we see that the measure of the effective first Piola–Kirchhoff stress takes on the following simple expression:

$$[\![\mathsf{S}]\!] = \frac{1}{\mathrm{Vol}(\Omega_\kappa)}\sum_{i=1}^{N}\boldsymbol{f}_i^{\mathrm{e}}\otimes \boldsymbol{r}_i^*. \tag{67}$$

Finally, using the second and third property in Definition 1, whose validity under the current assumptions has been rigorously proven by Costanzo et al. (2005), one obtains the following form of the effective Cauchy stress:

$$[\![\mathsf{T}]\!] = \frac{1}{\det(\hat{\mathsf{F}})\mathrm{Vol}(\Omega_\kappa)}\left(\sum_{i=1}^{N}\boldsymbol{f}_i^{\mathrm{e}}\otimes \boldsymbol{r}_i^*\right)\hat{\mathsf{F}}^{\mathrm{T}} = \frac{1}{\mathrm{Vol}(\Omega)}\sum_{i=1}^{N}\boldsymbol{f}_i^{\mathrm{e}}\otimes \boldsymbol{r}_i. \tag{68}$$

It is important to notice that this form of the effective Cauchy stress does not coincide with the virial stress (for an extensive review of the concept of the virial stress see Zhou, 2003), i.e., with the stress measure almost universally used in MD calculations, which we will denote by P and that can be given the following form:

$$\mathsf{P} = \frac{1}{\mathrm{Vol}(\Omega)}\sum_{i=1}^{N}\left(\frac{\partial \Psi}{\partial \boldsymbol{r}_i}\otimes \boldsymbol{r}_i - m_i\dot{\boldsymbol{r}}_i\otimes\dot{\boldsymbol{r}}_i\right). \tag{69}$$

For this reason, the proposed scheme is novel both in its derivation and in its measure of the stress. With this in mind, Costanzo et al. (2005) have proven that, for most physically acceptable conditions and at a constant volume, $[\![\mathsf{T}]\!]$ and P coincide *only* in a time average sense, i.e.,

$$\lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau [\![\mathsf{T}]\!]\,\mathrm{d}t = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau \mathsf{P}\,\mathrm{d}t. \tag{70}$$

However, we wish to emphasize that, on an instant by instant basis, i.e., without proper time averaging, the virial stress does *not* have any clear continuum mechanical interpretation.

7.3. Comparison with the Parrinello–Rahman scheme

The current paper is theoretical in nature and therefore a detailed exploration of the numerical predictions in terms of stress–strain curves (along with tangent moduli) that the proposed formulation allows one to predict will be presented in a forthcoming paper. Here we limit ourselves to offer a formal comparison between our formulation and the widely-used Parrinello–Rahman scheme (Parrinello and Rahman, 1980, 1981, 1982). The comparison is relevant because the Parrinello–Rahman scheme, which is a Lagrangian-based MD scheme intended for the study of the effective stress–strain behavior of particle systems, has been, and still is, extensively used either in both its original and modified formulations. For the sake of simplicity, we limit our comparison to the formulation 'A' offered by Parrinello and Rahman (1981), that is, a formulation requiring the effective state of stress to be hydrostatic. However, the comparison in question

can be extended to the more complex formulation 'B' (in the same paper), which is meant to be applicable to more general states of stress. Finally, to facilitate this comparison, we write all relevant equations in the notation adopted herein, as opposed to the notation originally used by Parrinello and Rahman (1981) (see the Appendix A for key relations).

The starting point of the formulation given by Parrinello and Rahman (1981) is the definition of the MD simulation cell. This cell is taken to be a parallelepiped whose sides, as functions of time, are described by three nonparallel vectors $\boldsymbol{\alpha}_i(t)$ $(i = 1, \ldots, 3)$. These vectors are then used to construct a second order tensor H_0, whose ij-component is defined as follows:

$$(\mathsf{H}_0)_{ij} = (\boldsymbol{\alpha}_j(0))_i. \tag{71}$$

Due to its definition, $\mathsf{H}_0 \in \mathrm{Lin}^+(\mathscr{V})$ and is such that

$$\mathrm{Vol}(\Omega_\kappa) = \det(\mathsf{H}_0) \tag{72}$$

if we take our reference configuration to coincide with the initial configuration of the MD cell.

In Parrinello and Rahman (1981), the Lagrangian function is postulated to be

$$\mathscr{L}_{\mathrm{PR}} = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i^* \cdot \hat{\mathsf{F}}^{\mathrm{T}}\hat{\mathsf{F}}\dot{\boldsymbol{r}}_i^* - U(\hat{\mathsf{F}}\boldsymbol{r}_1^*, \ldots, \hat{\mathsf{F}}\boldsymbol{r}_N^*) - p\mathrm{Vol}(\Omega) + \frac{1}{2}W(\dot{\hat{\mathsf{F}}}\mathsf{H}_0 \cdot \dot{\hat{\mathsf{F}}}\mathsf{H}_0), \tag{73}$$

where 'PR' stands for 'Parrinello–Rahman', W has dimensions of mass and is given ad hoc values depending on the system at hand,[7] and

$$[\![\mathsf{T}]\!] = -p\mathsf{I}, \tag{74}$$

I being the identity tensor in $\mathrm{Lin}(\mathscr{V})$. It should be kept in mind that the PR scheme is meant to provide the capability to perform numerical experiments in stress control. Hence, the value of the pressure p is viewed as being prescribed. However, this fact does not cause any problems in our comparison as it is possible, at least in principle, to view both our scheme and the PR scheme as allowing for both stress and strain controlled numerical experiments. Before proceeding further it is important to remark that, concerning the Lagrangian function in Eq. (73), Parrinello and Rahman (1981) freely admit that

"Whether such a Lagrangian is derivable from first principles is a question for further study;"

and they base the validity of their formulation on the resulting equations of motion. In the PR scheme, these equations are given the following form:

$$m_i\hat{\mathsf{F}}\ddot{\boldsymbol{r}}_i^* + m_i\dot{\hat{\mathsf{F}}}\dot{\boldsymbol{r}}_i^* = -\hat{\mathsf{F}}^{-\mathrm{T}}\frac{\partial U}{\partial \boldsymbol{r}_i^*} - m_i\hat{\mathsf{F}}^{-\mathrm{T}}\dot{\hat{\mathsf{F}}}^{\mathrm{T}}\hat{\mathsf{F}}\dot{\boldsymbol{r}}_i^*, \tag{75}$$

and

$$-p\mathsf{I} = \mathsf{P}_{\mathrm{PR}} + \frac{1}{\mathrm{Vol}(\Omega)}\ddot{\hat{\mathsf{F}}}\hat{\mathsf{F}}^{-1}\mathsf{J}_{\mathrm{PR}}, \tag{76}$$

where P_{PR} is a pseudo virial stress, which PR call the "internally generated stress tensor", and that is related to the true virial stress (see Eq. (69)) as follows:

[7] Parrinello and Rahman (1981) indicate that W "determines the relaxation time for recovery from an imbalance between the external pressure and the internal stress". Furthermore, based on a suggestion by Andersen (1980), Parrinello and Rahman (1981) indicate that they choose W so as to make said recovery time to be of the order of L/c, L being the MD cell size and c being the speed of sound (presumably in the bulk material).

$$\mathsf{P}_{\mathrm{PR}} = \mathsf{P} + \frac{1}{\mathrm{Vol}(\Omega)} \sum_{i=1}^{N} m_i \Big[(\dot{\hat{\mathsf{F}}} \boldsymbol{r}_i^*) \otimes (\dot{\hat{\mathsf{F}}} \boldsymbol{r}_i^*) + (\dot{\hat{\mathsf{F}}} \boldsymbol{r}_i^*) \otimes (\hat{\mathsf{F}} \dot{\boldsymbol{r}}_i^*) + (\hat{\mathsf{F}} \dot{\boldsymbol{r}}_i^*) \otimes (\dot{\hat{\mathsf{F}}} \boldsymbol{r}_i^*) \Big], \tag{77}$$

and where J_{PR} has the dimensions of an inertia tensor and is given by

$$\mathsf{J}_{\mathrm{PR}} = W (\hat{\mathsf{F}} \mathsf{H}_0)(\hat{\mathsf{F}} \mathsf{H}_0)^{\mathrm{T}}. \tag{78}$$

Remark 7 (*On boundary conditions and Newton's second law*). Parrinello and Rahman (1981) seem to have followed the Lagrangian formalism sketched in Eq. (56). However, we find it surprising that Eq. (75) does not contain any term suggesting the interactions of the system's particles with the exterior. In fact, Parrinello and Rahman do not explicitly discuss the boundary conditions they apply nor the means with which they apply them. Also, there is no indication that the equations of motion can be related in an exact way to Newton's second law of motion. This should come as no surprise given the previously-quoted statement made by Parrinello and Rahman. In fact, it would be *very* surprising if an ad hoc Lagrangian, such as that used by Parrinello and Rahman, did provide equations of motion satisfying Newton's second law. Finally, notice that, since p is considered a prescribed quantity, Eq. (76) is to be considered an equation of motion for $\hat{\mathsf{F}}$.

Although the PR equations of motion in Eq. (75) are quite different from those in Eq. (59), it turns out that these equations can be made equivalent with one another *under a suitable set of assumptions*. In particular,

(1) assume that the term $m_i \ddot{\hat{\mathsf{F}}} \boldsymbol{r}_i^*$ can be neglected with respect to the other terms in Eq. (59);
(2) recalling that the polar decomposition theorem (see, e.g., Gurtin, 1981) guarantees the existence of a unique rotation $\hat{\mathsf{R}}$ and a unique symmetric $\hat{\mathsf{U}}$ with positive determinant so that $\hat{\mathsf{F}} = \hat{\mathsf{R}}\hat{\mathsf{U}}$, assume that $\hat{\mathsf{R}} = \mathsf{I}$, so that any deviations of $\hat{\mathsf{F}}$ from I are symmetric; and
(3) finally, assume that the overall deformation of the system is small, that is, $\hat{\mathsf{F}} \approx \mathsf{I}$;

then, we have that the term $\hat{\mathsf{F}}^{-\mathrm{T}} \dot{\hat{\mathsf{F}}}^{\mathrm{T}} \hat{\mathsf{F}}$ on the right side of Eq. (75) can be approximated as follows:

$$\hat{\mathsf{F}}^{-\mathrm{T}} \dot{\hat{\mathsf{F}}}^{\mathrm{T}} \hat{\mathsf{F}} \approx \dot{\hat{\mathsf{F}}}^{\mathrm{T}} \approx \dot{\hat{\mathsf{F}}}. \tag{79}$$

Hence, under the approximation in Eq. (79), we see that Eqs. (59) and (75) are equivalent as long as $\boldsymbol{f}_i^{\mathrm{e}} = \boldsymbol{0}$, that is, as long as the system is isolated. Clearly, this conclusion is very troubling in that if a particle system is isolated then the system should be in a stress-free configuration. This is one of the reasons why the present authors speculated that in the PR scheme one may need to enforce some boundary conditions that are not explicitly accounted for in $\mathscr{L}_{\mathrm{PR}}$. However, all things considered, it seems that the PR scheme would require an assumption of small deformation to be comparable to the one presented herein.

We now attempt to reconcile Eq. (68) with Eq. (76). We start by using the simplified form of the equations of motion, that is, that one obtained by neglecting the term $m_i \ddot{\hat{\mathsf{F}}} \boldsymbol{r}_i^*$ in Eq. (59),[8] and we substitute these simplified relations into Eq. (64), which can then be rewritten as

$$[\![\mathsf{S}]\!] = \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \left(\frac{\partial \Psi}{\partial \hat{\mathsf{F}}} - \sum_{i=1}^{N} \hat{\mathsf{F}}^{-\mathrm{T}} \frac{\partial \Psi}{\partial \boldsymbol{r}_i^*} \otimes \boldsymbol{r}_i^* + \sum_{i=1}^{N} \boldsymbol{f}_i^{\mathrm{e}} \otimes \boldsymbol{r}_i^* + \ddot{\hat{\mathsf{F}}} \sum_{i=1}^{N} m_i \boldsymbol{r}_i^* \otimes \boldsymbol{r}_i^* \right), \tag{80}$$

[8] The comparison of our stress relation with PR's only requires the first of the three assumptions needed to compare our equations of motion with PR's.

which, using Eq. (66), can be further simplified to

$$[\![\mathsf{S}]\!] = \frac{1}{\mathrm{Vol}(\Omega_\kappa)}\left(\sum_{i=1}^{N} \boldsymbol{f}_i^{\mathrm{e}} \otimes \boldsymbol{r}_i^* + \ddot{\hat{\mathsf{F}}} \sum_{i=1}^{N} m_i \boldsymbol{r}_i^* \otimes \boldsymbol{r}_i^*\right). \tag{81}$$

Now, implementing the transformation that takes the first Piola–Kirchhoff stress tensor into the corresponding Cauchy stress tensor, we have that the above expression takes on the form

$$\hat{\mathsf{T}} = \frac{1}{\mathrm{Vol}(\Omega)}\left(\sum_{i=1}^{N} \boldsymbol{f}_i^{\mathrm{e}} \otimes \boldsymbol{r}_i + \ddot{\hat{\mathsf{F}}}\hat{\mathsf{F}}^{-1}\mathsf{J}\right), \tag{82}$$

where, adopting a PR viewpoint, $\hat{\mathsf{T}}$ is the desired value of the effective Cauchy stress and J is *the* system's inertia tensor, i.e.,

$$\mathsf{J} = \sum_{i=1}^{N} m_i \boldsymbol{r}_i \otimes \boldsymbol{r}_i. \tag{83}$$

Note that, due to the approximation being used in the current derivation, $\hat{\mathsf{T}}$ cannot be expected to satisfy Eq. (68) point-wise in time. Now, comparing Eqs. (82) and (76), we have that $\hat{\mathsf{T}}$ plays the same role played by $-p\mathsf{I}$ since, in the present context, they must be interpreted as prescribed stress states. Furthermore, we see that the pseudo virial stress P_{PR} plays the role of the first term on the right side of Eq. (82). However, notice that in order for P_{PR} to be equal to P one must have $\hat{\mathsf{F}} = \mathsf{0}$. In addition, even if one could claim that P_{PR} represents P in some sense, there still remains the fact that, as discussed earlier, P is a meaningful measure of mechanical stress only in a time average sense at constant volume. These observations lead to the conclusion that the PR scheme is intrinsically limited to a regime of small deformations. Finally, by comparing the two inertia tensors J_{PR} and J, one has a rigorous way of attributing a meaning to the quantity W. In fact, we have shown that there is no need to make any ad hoc assumptions concerning W since one can rigorously show that the correct inertia tensor to use is *the* inertia tensor!

8. Conclusion

A continuum homogenization model has been presented for heterogeneous media that behave locally as isothermal elastic materials within a context of finite deformations. The homogenization procedure discussed led to an effective constitutive relation, which is, to the best of the authors' knowledge, novel. A Lagrangian-based approach was introduced for performing the homogenization procedure. In addition, such an approach has been used to create a corresponding homogenization scheme applicable to MD. The proposed MD scheme has been compared with the widely-used PR scheme, and it was shown that the PR scheme is recovered only when severe approximations are made concerning the behavior of the particle system at hand. Specifically, it has been shown that the applicability of the PR approach should be limited to a regime of small deformations and (approximately) constant volume calculations. While the approach presented in this work naturally lends itself to strain controlled MD simulations, stress controlled simulations are possible. In fact, to do a stress controlled simulation one would begin by prescribing $[\![\mathsf{T}]\!]$ in the form of Eq. (68) that explicitly contains $\hat{\mathsf{F}}$ and then simultaneously solve the resulting algebraic equation along with the differential equations of motion given by Eq. (59). This results in a differential-algebraic system for $\hat{\mathsf{F}}$ and $\boldsymbol{r}_i^*$. This is the price one pays for deriving the governing equations from first principles rather than using an ad hoc scheme as is done in PR. On the other hand, this also emphasizes the attractiveness of the PR scheme since the numerical solution to their problem under stress control is much more straightforward. Above all, we have shown that the proposed scheme can be derived from first principles in

a rigorous way and does not require any of the ad hoc assumptions that are typically made in the PR scheme.

Acknowledgements

The authors gratefully acknowledge partial support from the Air Force Office of Scientific Research through Grant No. F49620-02-1-0106.

Appendix A. Translation between our notation and that of Parrinello and Rahman

In this Appendix A we provide the key relationships to allow one to rewrite the formulation presented in Parrinello and Rahman (1981) using the notation adopted in this paper.

As mentioned earlier, the starting point of the formulation given by Parrinello and Rahman (1981) is the definition of the MD simulation cell. This cell is taken to be a parallelepiped whose sides, as functions of time, are described by three nonparallel vectors $\boldsymbol{a}(t)$, $\boldsymbol{b}(t)$, and $\boldsymbol{c}(t)$, which we have denoted by $\boldsymbol{\alpha}_i(t)$ $(i = 1, \ldots, 3)$. Specifically, we write

$$\boldsymbol{\alpha}_1(t) = \boldsymbol{a}(t), \quad \boldsymbol{\alpha}_2(t) = \boldsymbol{b}(t), \quad \boldsymbol{\alpha}_3(t) = \boldsymbol{c}(t). \tag{A.1}$$

These vectors are then used to construct a second order tensor, which they call h, whose ij-component is defined as follows:

$$(\mathsf{h}(t))_{ij} = (\boldsymbol{\alpha}_j(t))_i, \tag{A.2}$$

where, for convenience, we have defined the components of h using our notation. Therefore, with reference to Eq. (71), we see that our tensor H_0 is obtained as

$$\mathsf{H}_0 = \mathsf{h}(t)|_{t=0}. \tag{A.3}$$

Furthermore, we believe that the relation connecting H_0 to $\mathsf{h}(t)$ defines the effective deformation gradient, i.e.,

$$\mathsf{h}(t) = \hat{\mathsf{F}}(t)\mathsf{H}_0. \tag{A.4}$$

In Parrinello and Rahman (1981), the position $\boldsymbol{r}_i(t)$ of the ith particle is identified via a nondimensional vector $\boldsymbol{s}_i(t)$, so that

$$\boldsymbol{r}_i(t) = \boldsymbol{a}(t)(\boldsymbol{s}_i(t))_1 + \boldsymbol{b}(t)(\boldsymbol{s}_i(t))_2 + \boldsymbol{c}(t)(\boldsymbol{s}_i(t))_3. \tag{A.5}$$

This implies that

$$\boldsymbol{r}_i(t) = \mathsf{h}(t)\boldsymbol{s}_i(t). \tag{A.6}$$

Finally, by comparing Eqs. (A.6) and (58) we have that

$$\boldsymbol{r}_i(t) = \mathsf{h}(t)\boldsymbol{s}_i(t) = \hat{\mathsf{F}}(t)\boldsymbol{r}_i^*(t). \tag{A.7}$$

References

Allen, M.P., Tildesley, D.J., 1987. Computer Simulation of Liquids. Clarendon Press, Oxford.

Andersen, H.C., 1980. Molecular dynamics simulations at constant pressure and/or temperature. Journal of Chemical Physics 72 (4), 2384–2393.

Bedford, A., 1985. Hamilton's Principle in Continuum Mechanics, Research Notes in Mathematics, vol. 139. Pitman Advanced Publishing Program, Boston.

Bowen, R.M., 1989. Introduction to Continuum Mechanics for Engineers, Mathematical Concepts and Methods in Science and Engineering, vol. 39. Plenum Press, New York.

Chadwick, P., 1999. Continuum Mechanics: Concise Theory and Problems, second ed. Dover Publications, Inc., Mineola, NY.

Costanzo, F., Gray, G.L., Andia, P.C., 2004. On the notion of average mechanical properties in MD simulation via homogenization. Modelling and Simulation in Materials Science and Engineering 12, S333–S345.

Costanzo, F., Gray, G.L., Andia, P.C., 2005. On the definitions of effective stress and deformation gradient for use in MD: Hill's macro-homogeneity and the virial theorem. International Journal of Engineering Science 43 (7), 533–555.

Ericksen, J.L., 1984. The Cauchy and Born hypotheses for crystals. In: Gurtin, M.E. (Ed.), Phase Transformations and Material Instabilities in Solids. Academic Press, New York, pp. 61–78.

Frenkel, D., Smit, B., 1996. Understanding Molecular Simulation: From Algorithms to Applications. Academic Press, San Diego.

Germain, P., 1982. Sur certaines définitions liées à l'énergie en mécanique des solides. International Journal of Engineering Science 20 (2), 245–259.

Gurtin, M.E., 1981. An Introduction to Continuum Mechanics. Mathematics in Science and Engineering, vol. 158. Academic Press, San Diego.

Hill, R., 1972. On constitutive macro-variables for heterogeneous solids at finite strain. Proceedings of the Royal Society of London A: Mathematical and Physical Sciences 326, 131–147.

Hill, R., 1984. On macroscopic effects of heterogeneity in elastoplastic media at finite strain. Mathematical Proceedings of the Cambridge Philosophical Society 95, 481–494.

Marsden, J.E., Hughes, T.J.R., 1994. Mathematical Foundations of Elasticity. Dover Publications, Inc., New York, the Dover ed., first published in 1994, is an unabridged, corrected republication of the work first published by Prentice-Hall, Inc., Englewood Cliffs, NJ, 1983.

Maugin, G.A., 1992. The Thermomechanics of Plasticity and Fracture. Cambridge Texts in Applied Mathematics. Cambridge University Press, Cambridge.

Meirovitch, L., 1988. Methods of Analytical Dynamics. Advanced Engineering Series. McGraw-Hill.

Parrinello, M., Rahman, A., 1980. Crystal structure and pair potentials: A molecular-dynamics study. Physical Review Letters 45 (14), 1196–1199.

Parrinello, M., Rahman, A., 1981. Polymorphic transitions in single crystals: A new molecular dynamics method. Journal of Applied Physics 52 (12), 7182–7190.

Parrinello, M., Rahman, A., 1982. A new molecular dynamics method for the study of crystal structure transformations. In: Kalia, R.K., Vashishta, P. (Eds.), Melting, Localization, and Chaos. Elsevier Science Publishing Co. Inc., pp. 97–109.

Spencer, A.J.M., 2004. Continuum Mechanics. Dover Publications Inc., Mineola, NY.

Stolz, C., 1986. General relationships between micro and macro scales for the non-linear behaviour of heterogeneous media. In: Gittus, J., Zarka, J. (Eds.), Modelling Small Deformations of Polycrystals. Elsevier Science Publishing Co. Inc., New York, pp. 89–115.

Suquet, P.M., 1985. Local and global aspects in the mathematical theory of plasticity. In: Sawczuk, A., Bianchi, G. (Eds.), Plasticity Today: Modelling, Methods and Applications. Elsevier Science Publishing Co. Inc., New York, pp. 279–310.

Suquet, P.M., 1987. Elements of homogenization for inelastic solid mechanics. In: Sanchez-Palencia, E., Zaoui, A. (Eds.), Homogenization Techniques for Composite Media, CISM Lecture Notes. Springer-Verlag, Berlin, pp. 193–278.

Zanzotto, G., 1992. On the material symmetry group of elastic crystals and the Born rule. Archive for Rational Mechanics and Analysis 121, 1–36.

Zhou, M., 2003. A new look at the atomic level virial stress: on continuum-molecular system equivalence. Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences 459, 2347–2392.