Chapter 5: A Micromechanics-Based Notion of Stress for Use in the Determination of Continuum-Level Mechanical Properties via Molecular Dynamics

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5.1 Introduction

By formulating a continuum homogenization problem that includes inertia effects, a link is established between continuum homogenization and the estimation of effective mechanical properties for particle ensembles whose interactions are governed by potentials (e.g., as is seen in molecular dynamics). The focus of this chapter is on showing that there is a fundamental consistency of ideas between continuum mechanics and the study of discrete particle systems, and that it is possible to define a notion of effective stress applicable to discrete systems that can be claimed to have the same meaning as it has in continuum mechanics.

5.2 Motivation, Objectives, and Organization

The last 15 years have seen an astonishing growth in nanomechanics-related research. During this time, experimental and theoretical mechanicians alike have had to adapt to a fast-evolving research landscape. Like many others, the authors of this chapter found themselves delving into specialized fields of study such as molecular dynamics (MD) and struggling to learn new languages and methodologies that were outside what they trained on during their graduate work. With this in mind, this chapter is in part the result of

the authors' learning experience in how to use MD to compute mechanical properties of solids. In going through this learning process, the authors had to confront the fundamental issue of what it means to compute the stress response of a particle system and how this measure of stress is related to the continuum mechanical notion of stress. Clearly, this question is not new, since it dates back to the pioneering work by Cauchy who formalized the very notion of stress. However, we feel that we have added something new to the discussion in that we have approached the problem from the viewpoint of continuum homogenization and, in so doing, not only were we able to extend the continuum homogenization notion of effective stress to MD, but we were also able to construct a practical Lagrangian MD scheme that is rigorously based on classical mechanics.

From a conceptual viewpoint, the outcome of this work is that a good part of the MD that is used in nanomechanics can be comfortably understood with classical mechanics and homogenization ideas. In other words, it is possible to define an acceptable concept of stress for discrete systems without ever relying on ideas from statistical mechanics or a kinetic theory of matter. While this fact may be well understood by some researchers, we feel that it is not sufficiently known among classically trained engineers, and we hope that this chapter may reinforce the idea that there is a fundamental unity between the study of continuum and discrete systems.

The organization of this chapter is based on the idea that classical homogenization of heterogeneous systems is intimately related to MD, since both disciplines deal with the computation of effective properties of matter. Hence, we will start by reviewing some basic concepts of homogenization of linear elastic media. We will then discuss the extension of these concepts to the case of homogenization in the context of large deformation. Once this review is done, we will formulate a continuum homogenization problem that shares the basic properties of MD problems. We will show that the homogenization scheme in question can be turned into an MD scheme in which stress is defined such that it can be said to have the same meaning that it has in continuum homogenization. Finally, we will compare the continuum homogenization-based stress concept with the virial stress, the latter being the stress concept typically used in MD.

Before proceeding further, we wish to mention that some elements of this chapter have been presented in [1, 2, 8, 9]. The main contribution of this chapter lies in a presentation that is intended to give a coherent vision of how continuum homogenization and MD are related. With this said, this chapter does contain some new results consisting of more general proofs, with

respect to what had been previously published, on the equivalence between a continuum-based notion of effective stress and virial stress.

5.3 Notation

The material system under consideration will be denoted by Ω in its deformed configuration and will be denoted by Ω_κ in its reference configuration. Both Ω and Ω_κ are assumed to be regular subsets of a three-dimensional Euclidean point space. 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. Similarly, the operators "Grad" and "grad" indicate the gradient operators with respect to $\boldsymbol{\chi}$ and $\boldsymbol{x}$, respectively.

We will use upper-case sans serif letters, such as A, to denote second-order tensors and lower-case bold italic letters, such as $\boldsymbol{a}$, to denote vectors. The notation $\boldsymbol{a} \otimes \boldsymbol{b}$ denotes the tensor product of the vectors $\boldsymbol{a}$ and $\boldsymbol{b}$. The symbol $\triangleq$ will indicate a definition.

5.4 Homogenization of Linear Elastic Heterogeneous Media: A Brief Review

To better illustrate how MD and continuum homogenization are related, it is useful to review some basic concepts from the theory of homogenization of linear elastic heterogeneous media. We will therefore review the essential objectives of homogenization theory and some basic definitions concerning *effective* mechanical properties. In subsequent sections, we will discuss how these definitions need to be adjusted to be useful in a fully nonlinear context in preparation for their application to discrete particle systems.

5.4.1 Homogenization Objectives

Referring to Fig. 5.1, consider a structural component made of a heterogeneous material with overall dimensions that are much larger than the characteristic length over which the material's constitutive properties vary. Conceptually, under the assumption that the material is linear elastic, in

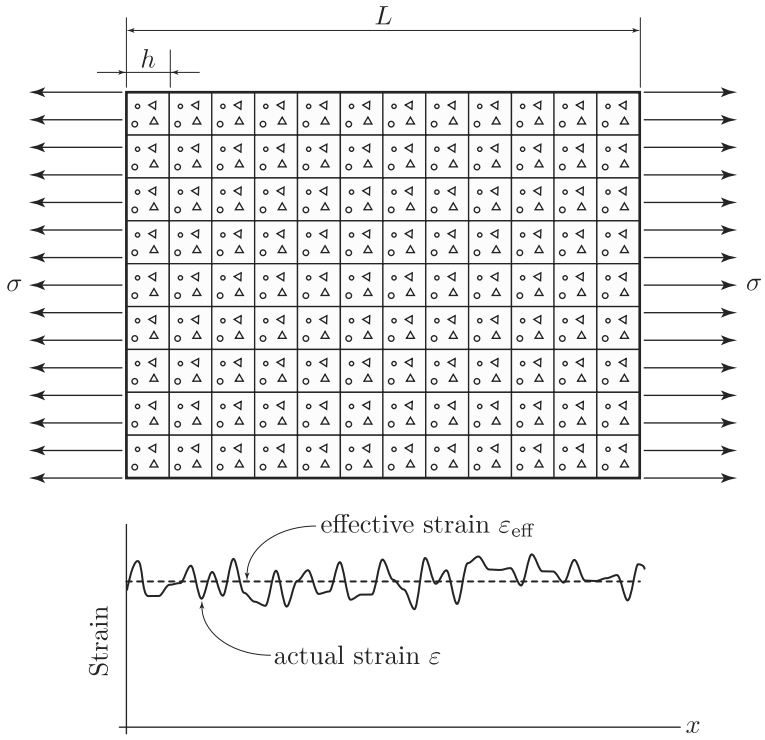

Fig. 5.1. A panel consisting of a heterogeneous material

quasistatic conditions, and in the absence of body forces, the prediction of the component's stress/strain response requires the solution of a boundary value problem (BVP) of the following type

$$\text{BVP}_{\text{exact}}: \quad \text{Div}(\mathsf{C}(\boldsymbol{\chi})[\boldsymbol{\varepsilon}(\boldsymbol{\chi})]) = \mathbf{0} \quad \text{along with BCs}, \tag{5.1}$$

where $\boldsymbol{\chi}$ denotes position, $\mathsf{C}(\boldsymbol{\chi})$ is the (fourth-order) tensor of elastic moduli, $\boldsymbol{\varepsilon}(\boldsymbol{\chi})$ is the small strain tensor field, and the expression "BCs" stands for "boundary conditions." For convenience, we denote by $\boldsymbol{\sigma}(\boldsymbol{\chi})$ the stress field corresponding to $\boldsymbol{\varepsilon}(\boldsymbol{\chi})$, i.e., $\boldsymbol{\sigma}(\boldsymbol{\chi}) = \mathsf{C}(\boldsymbol{\chi})[\boldsymbol{\varepsilon}(\boldsymbol{\chi})]$. Clearly, the structural component's stress/strain response to some applied loading will reflect the spatial variability of the elastic moduli, as schematically represented by the solid line in Fig. 5.1. Unfortunately, from a computational viewpoint, the spatial variability in question may make the solution of the problem in (5.1) difficult, if not impossible, to obtain. With this in mind, a practical way to approach the design of highly heterogeneous components is to construct

a predictive capability that allows one to (1) model the material as homogeneous so as to more easily determine the system's "average" response (see the dashed line in Fig. 5.1) and (2) estimate the deviations from the "average" behavior since this information is essential in assessing failure conditions. The purpose of homogenization is to have both types of predictive capability, though we will only explore the first type here. Before doing so, it is important to recognize that, at this stage, we do not know whether or not what we have called the "average" response will in fact be an average in a strict mathematical sense. Hence, we will refer to the "average" strain and stress response as the *effective* strain and stress response and we will denote these quantities as $\boldsymbol{\varepsilon}_{\text{eff}}$ and $\boldsymbol{\sigma}_{\text{eff}}$, respectively.

As suggested above, a fundamental objective of continuum homogenization is to use the knowledge of the material's microstructure to formulate a BVP whose solution is the system's effective response, i.e., homogenization theory delivers the possibility of predicting the effective system's response by solving the following BVP

$$\text{BVP}_{\text{eff}}: \quad \text{Div}(\mathsf{C}_{\text{eff}}[\boldsymbol{\varepsilon}_{\text{eff}}(\boldsymbol{\chi})]) = \mathbf{0} \quad \text{along with BCs}, \tag{5.2}$$

where it is essential to notice that, in the new BVP, the moduli C_{eff}, which are called the *material's effective moduli*, are not a function of position. Therefore, one way to interpret (5.2) is to say that homogenization theory takes information concerning the original *heterogeneous* material and maps it into the properties of an equivalent *homogenous* material. Finally, we will refer to the field $\mathsf{C}_{\text{eff}}[\boldsymbol{\varepsilon}_{\text{eff}}(\boldsymbol{\chi})]$ as the effective stress field and we will denote it by $\boldsymbol{\sigma}_{\text{eff}}(\boldsymbol{\chi})$, i.e.,

$$\boldsymbol{\sigma}_{\text{eff}} = \mathsf{C}_{\text{eff}}[\boldsymbol{\varepsilon}_{\text{eff}}(\boldsymbol{\chi})]. \tag{5.3}$$

So far, we have only sketched a conceptual map of what homogenization does without considering the important details needed to show that one can indeed go from the BVP in (5.1) to that in (5.2). Most of these "details" are outside the scope of this chapter and they can be easily found in the literature. For example, excellent references on the subject are the presentations in [18, 20, 28, 31]. For discussions that are more technical from a mathematical viewpoint, one can see the presentations in [3, 4, 15]. While we will stay away from the technical details of homogenization theory, a few important remarks are now needed for extending homogenization ideas to MD.

Remark 1 *(Representative Volume Element).* To solve the BVP in (5.2), one must first determine the effective moduli C_{eff} and this can be done via several methods. Often, especially in engineering applications, the determination of

the effective moduli is carried out by solving a special BVP defined over a portion of the material such that both the composition and the geometry of this portion are able to represent the material as a whole. This subset of material is called a *representative volume element* (RVE), which is schematically shown in Fig. 5.2. In general the determination of the RVE may not be

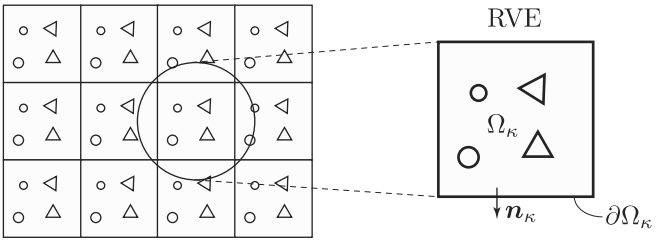

Fig. 5.2. A representative volume element for the special case of a periodic medium

straightforward, however, for periodic media, the RVE is readily identified with the periodic cell of the material. Furthermore, in the case of periodic media, there are rigorous proofs showing that the determination of C_{eff} by asymptotic expansion methods (see, e.g., [3, 4]) delivers the same result as the solution of the RVE BVP so long as the periodicity of the material is properly accounted for.

Remark 2 *(Definition of Effective Quantities).* Roughly speaking, in formal homogenization theory, $\boldsymbol{\varepsilon}_{\text{eff}}(\boldsymbol{\chi})$ and $\boldsymbol{\sigma}_{\text{eff}}(\boldsymbol{\chi})$ are defined as the leading terms of an asymptotic expansion of the fields $\boldsymbol{\varepsilon}(\boldsymbol{\chi})$ and $\boldsymbol{\sigma}(\boldsymbol{\chi})$ with respect to a scaling parameter, say λ, defined as the ratio between the length over which the moduli vary and the overall (large) dimension of the component (for example, referring to Fig. 5.1, one can set $\lambda = h/L$). With this in mind, and referring to Fig. 5.2, one can show that, when using the RVE as a way to determine the effective moduli, these definitions can be given the following form

$$\boldsymbol{\varepsilon}_{\text{eff}} = \frac{1}{2\,\text{Vol}(\Omega_\kappa)} \int_{\partial\Omega_\kappa} (\boldsymbol{u} \otimes \boldsymbol{n}_\kappa + \boldsymbol{n}_\kappa \otimes \boldsymbol{u}) \mathrm{d}A, \tag{5.4}$$

$$\boldsymbol{\sigma}_{\text{eff}} = \frac{1}{\text{Vol}(\Omega_\kappa)} \int_{\partial\Omega_\kappa} (\boldsymbol{\sigma}\boldsymbol{n}_\kappa \otimes \boldsymbol{\chi}) \mathrm{d}A, \tag{5.5}$$

where $\boldsymbol{u}$ denotes the displacement field. The essential feature of these definitions is that $\boldsymbol{\varepsilon}_{\text{eff}}(\boldsymbol{\chi})$ and $\boldsymbol{\sigma}_{\text{eff}}(\boldsymbol{\chi})$ are determined by gathering information on the boundary of the RVE rather than its interior. If the RVE is a simply

connected regular domain, a straightforward application of the divergence theorem tells us that

$$\boldsymbol{\varepsilon}_{\text{eff}} = \frac{1}{\text{Vol}(\Omega_\kappa)} \int_{\Omega_\kappa} \boldsymbol{\varepsilon} \, \mathrm{d}V \quad \text{and} \quad \boldsymbol{\sigma}_{\text{eff}} = \frac{1}{\text{Vol}(\Omega_\kappa)} \int_{\Omega_\kappa} \boldsymbol{\sigma} \, \mathrm{d}V, \tag{5.6}$$

where the second of (5.6) requires that the pointwise[1] balance law is $\text{Div}(\mathsf{C}(\boldsymbol{\chi})[\boldsymbol{\varepsilon}(\boldsymbol{\chi})]) = \mathbf{0}$. Equation (5.6) implies that there are cases in which the word "effective" does mean "volume average," but, in general, effective strain and stress must be understood as given in (5.4) and (5.5) to be useful mathematical constructs. In addition, there is a strong physically based reason for defining effective quantities via boundary integrals, as eloquently remarked by Hill ([13]; see also [18, 27, 28]):

> Experimental determinations of mechanical behaviour rest ultimately on measured loads or mean displacements over pairs of opposite faces of a representative cube. Macro-variables intended for constitutive laws should thus be capable of definition in terms of surface data alone, either directly or indirectly. It is not necessary, by any means, that macro-variables so defined should be unweighed volume averages of their microscopic counterparts.

Remark 3 *(Basic Properties of $\boldsymbol{\varepsilon}_{\text{eff}}$ and $\boldsymbol{\sigma}_{\text{eff}}$).* In a small strain theory, one expects the strain and stress measures to be symmetric tensors. Referring to (5.4), it is easy to see that the effective strain is, by definition, a symmetric tensor. Furthermore, one can easily show that under most conditions $\boldsymbol{\sigma}_{\text{eff}}$ is symmetric. What needs to be observed here is that, at least at first glance, no special steps are needed to make sure that the above-defined effective quantities have the properties that one usually expects of the corresponding pointwise quantities. As we will see, this is certainly not the case when dealing with the definitions of the effective stress and deformation concepts in nonlinear homogenization.

5.4.2 Boundary Conditions for the RVE Problem

When relying on an RVE for the determination of the effective moduli, one must pose and solve a BVP over the RVE in question. This BVP is usually

[1] The "point" in pointwise refers to a *continuum material point*, by which we mean a point in a regular subset of $\mathbb{R}^3$. This is not to be confused with a material particle, by which we mean an abstract physical entity endowed with a given fixed mass.

called a *localization problem* and its governing partial differential equations are those in (5.1). As far as the BCs are concerned, these need to be carefully stated to match the particular nature of the problem. In fact, in a localization problem one is not interested in computing the solution's pointwise behavior. Rather, one needs to control the solution's *effective* behavior in such a way that the effective moduli can be calculated. With this in mind, it turns out that it is indeed possible to control the value of the effective strain or stress by specifying some specific sets of BCs. These BCs are as follows:

1. *Uniform strain*: $\boldsymbol{u} = \hat{\boldsymbol{\varepsilon}}\boldsymbol{\chi}$ on $\partial\Omega_\kappa$, with $\hat{\boldsymbol{\varepsilon}}$ a *given* symmetric second-order tensor.

2. *Uniform stress*: $\boldsymbol{\sigma}\boldsymbol{n}_\kappa = \hat{\boldsymbol{\sigma}}\boldsymbol{n}_\kappa$ on $\partial\Omega_\kappa$, with $\hat{\boldsymbol{\sigma}}$ a *given* symmetric second-order tensor.

3. *Periodic*: If the RVE is a periodic cell, then the displacement field is decomposed such that $\boldsymbol{u} = \hat{\boldsymbol{\varepsilon}}\boldsymbol{\chi} + \boldsymbol{u}^*$ *everywhere* in the RVE, with $\hat{\boldsymbol{\varepsilon}}$ a *given* symmetric second-order tensor and with $\boldsymbol{u}^*$ being an unknown vector field whose boundary values are constrained to be periodic, i.e., $\boldsymbol{u}^*$ is constrained to take on identical values on homologous points of the boundary. Furthermore, in addition to constraining the boundary values of the field $\boldsymbol{u}^*$, one must also constrain the behavior of the field $\boldsymbol{\sigma}\boldsymbol{n}_\kappa$ to be antiperiodic.

If one chooses BCs of type 1 or 3, it is relatively straightforward to prove (see, e.g., [18, 28]) that the controlled parameter $\hat{\boldsymbol{\varepsilon}}$ determines the value of the effective strain, i.e., $\boldsymbol{\varepsilon}_{\text{eff}} = \hat{\boldsymbol{\varepsilon}}$. If one chooses condition 2, then it is not difficult to show that the controlled parameter $\hat{\boldsymbol{\sigma}}$ determines the value of the effective stress, i.e., $\boldsymbol{\sigma}_{\text{eff}} = \hat{\boldsymbol{\sigma}}$.

From a conceptual viewpoint, the determination of the elastic moduli in RVE-based linear homogenization is carried out by the following procedure. Choosing uniform strain BCs for the sake of discussion, one can set $\hat{\varepsilon}_{11} = 1$ and all other components of $\hat{\boldsymbol{\varepsilon}}$ equal to zero. Then, one solves the RVE BVP and thus determines the $\boldsymbol{\sigma}$ component of the solution. Next, one uses the $\boldsymbol{\sigma}$ field in question, along with (5.5), to determine $\boldsymbol{\sigma}_{\text{eff}}$. Finally, due to the linearity of problem and referring to (5.3), the $\boldsymbol{\sigma}_{\text{eff}}$ just computed coincides with the "$ij11$" components of C_{eff} ($ij = 1, 2, 3$). This process is then repeated by selecting setting all components of $\hat{\boldsymbol{\varepsilon}}$ equal to zero, except say $\hat{\varepsilon}_{pq}$, which is set to unity so that the "$ijpq$" components of the elastic moduli can be found.

5.5 The RVE Problem and Large Deformations

In this section, we discuss the concepts of effective strain and stress in a context of large deformations. This discussion is again meant to properly setup a stage for the extension of continuum homogenization ideas to MD problems. Choosing to work in a large deformation context is motivated by the fact that we want the discussion to be as general as possible.[2] Before proceeding to the presentation of effective measures of deformation and stress, it is important to remark that the field of nonlinear homogenization is not as well developed as the corresponding linear theory. In particular, there are fewer theoretical results linking an asymptotic approach to homogenization to the RVE-based averaging procedures. With this in mind, as has been done by other authors (see, e.g., [12–14, 25]), we will simply assume that the RVE problem is a valid way to compute effective properties. This assumption allows us to focus our attention on the RVE approach to homogenization, as opposed to considering the (more technically difficult) formal asymptotic approach.

5.5.1 Definition of Effective Deformation and Stress

In general, in a context of large deformation, one must take into consideration two measures of stress, namely the Cauchy stress and the first Piola–Kirchhoff stress, depending on whether one chooses the deformed or reference configurations, respectively, to write the system's equation of motion. The two notions of stress are related by the well-known relation (see, e.g., [11])

$$\mathsf{S} = \det(\mathsf{F})\mathsf{T}(\mathsf{F}^{-1})^{\mathrm{T}}, \tag{5.7}$$

where S denotes the first Piola–Kirchhoff stress tensor, F denotes the deformation gradient, T denotes the Cauchy stress tensor, and the superscript T denotes transposition. The relationship in (5.7) reminds us that, when we define effective deformation and stress in a context of large deformation, we need to (1) provide definitions that are based both on the reference and the deformed configurations and (2) discuss how these definitions relate to one another. With this in mind, we introduce two *independent* measures of effective deformation: the *effective deformation gradient tensor*, denoted by

[2] In choosing to work in a regime of large deformations, we assume that the kinematics at both the micro- and macroscales is fully nonlinear. Correspondingly, we do not assume that any aspect of the constitutive theory is linear.

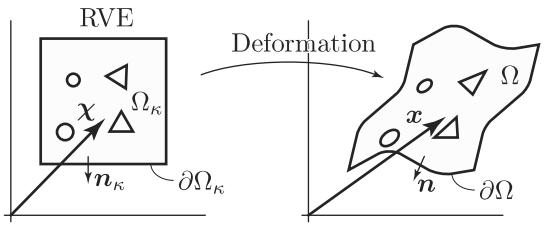

Fig. 5.3. The RVE in its reference (*left*) and deformed (*right*) configurations

$[\![\mathsf{F}]\!]$, and the *effective inverse deformation tensor*, denoted by $[\![\mathsf{F}^{-1}]\!]$. These quantities are defined as follows

$$[\![\mathsf{F}]\!] \triangleq \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \int_{\partial\Omega_\kappa} \boldsymbol{x} \otimes \boldsymbol{n}_\kappa \, \mathrm{d}A, \quad [\![\mathsf{F}^{-1}]\!] \triangleq \frac{1}{\mathrm{Vol}(\Omega)} \int_{\partial\Omega} \boldsymbol{\chi} \otimes \boldsymbol{n} \, \mathrm{d}a, \tag{5.8}$$

where the RVE is subject to a motion $\boldsymbol{x} = \boldsymbol{x}(\boldsymbol{\chi}, t)$, and the symbols are defined in Fig. 5.3. As far as stress is concerned, we will define the *effective first Piola–Kirchhoff stress tensor* and the *effective Cauchy stress tensor*, denoted by $[\![\mathsf{S}]\!]$ and $[\![\mathsf{T}]\!]$, respectively, as follows:

$$[\![\mathsf{S}]\!] \triangleq \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \int_{\partial\Omega_\kappa} (\mathsf{S}\boldsymbol{n}_\kappa) \otimes \boldsymbol{\chi} \, \mathrm{d}A, \quad [\![\mathsf{T}]\!] \triangleq \frac{1}{\mathrm{Vol}(\Omega)} \int_{\partial\Omega} (\mathsf{T}\boldsymbol{n}) \otimes \boldsymbol{x} \, \mathrm{d}a. \tag{5.9}$$

To the best of the authors' knowledge, the definitions of effective deformation and effective stress in a regime of large deformation were first systematically discussed in [13] (see also [14]). Important contributions to this subject also include the works in [12, 26]. More recent discussions have been given in [16, 25]. It should be pointed out that Hill [13, 14] does not include in his discussions the definition of $[\![\mathsf{F}^{-1}]\!]$. However, we feel that the definition of $[\![\mathsf{F}^{-1}]\!]$ is important because it has a bearing on the type of phenomena that we will choose as being *physically meaningful* when extending the above notions of effective deformation and stress to discrete systems.

Going back to (5.8) and (5.9), it is important to notice that we have once more defined effective quantities via boundary integrals rather than via volume averages. However, as was done in Sect. 5.4, under standard regularity and smoothness assumptions, a straightforward application of the divergence theorem yields (cf. [13])

$$[\![\mathsf{F}]\!] = \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \int_{\Omega_\kappa} \mathsf{F} \, \mathrm{d}V \quad \text{and} \quad [\![\mathsf{F}^{-1}]\!] = \frac{1}{\mathrm{Vol}(\Omega)} \int_{\Omega} \mathsf{F}^{-1} \, \mathrm{d}v. \tag{5.10}$$

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., governed by a *quasistatic* form of the local balance of linear momentum without body forces, an application of the divergence theorem allows one to show that

$$[\![\mathsf{S}]\!] = \frac{1}{\operatorname{Vol}(\Omega_\kappa)} \int_{\Omega_\kappa} \mathsf{S} \, \mathrm{d}V \quad \text{and} \quad [\![\mathsf{T}]\!] = \frac{1}{\operatorname{Vol}(\Omega)} \int_{\Omega} \mathsf{T} \, \mathrm{d}v. \tag{5.11}$$

Before proceeding further, we should keep in mind that one of the objectives of this chapter is to extend continuum homogenization notions of effective stress and strain to the discrete systems analyzed via MD. Although often disregarded in continuum homogenization of elastic systems, time evolution and time averaging are central to MD calculations. Hence, we introduce here a time averaging operation that will be employed later in the chapter. This operation will be denoted by the use of angle brackets and defined as follows

$$\langle f \rangle \triangleq \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} f(t) \mathrm{d}t, \tag{5.12}$$

where t denotes time, $f(t)$ is a generic function of time, and t_0 is the initial time. Without loss of generality, we will assume that $t_0 = 0$. Adopting concepts from statistical mechanics, we will view the time average operation defined in (5.12) as a way of translating the effects of fast dynamics into corresponding thermal effects.

5.5.2 Meaningful Deformation Processes

Now that we have introduced the definition of effective deformation and stress in a regime of large deformation, we need to address the problem of clearly identifying those RVE motions for which the definitions in question are useful in some sense. Specifically, it should be observed that each of the definitions we have given is independent of the others. Therefore, one cannot expect that, for example, $[\![\mathsf{F}^{-1}]\!] = [\![\mathsf{F}]\!]^{-1}$ for all possible RVE motions. By the same reasoning, in general, we cannot expect that the effective Cauchy and the first Piola–Kirchhoff stresses are related by a relationship such as (5.7), i.e., the relation satisfied the corresponding pointwise stress measures.

These observations indicate that there is a need for the establishment of conditions that guarantee the ability to attach physical meaning to the definitions given above. In fact, it can be argued that Hill's macrohomogeneity conditions [13, 14], i.e., those conditions under which certain products of effective quantities are equal to the volume average of the product

of the corresponding local quantities, play the role of defining the set of physically meaningful averaging processes. Here, since we are interested in a rigorous extension of the continuum concepts of Cauchy stress and first Piola–Kirchhoff stress to discrete systems, we propose slightly more stringent requirements (with respect to Hill's macrohomogeneity conditions). We therefore introduce the following definition.

Definition 1 (Meaningful Deformation Processes). By a large deformation process with meaningful space averages, we mean a deformation process possessing all of the following properties:

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

This definition is motivated by a desire to have effective quantities that formally behave just like their local counterparts. Now, similarly to Hill's approach (cf. [14]), instead of attempting to derive necessary and sufficient conditions for satisfying Definition 1, we will only provide a list of *sufficient conditions*. These conditions are found by demanding that the RVE motions satisfy specific BCs. As observed in Sect. 5.4, the "right" choice of BCs is crucial for successfully solving the RVE problem that delivers the effective elastic moduli. In this section, we see that the right choice of BCs is crucial for establishing the very meaning of the definitions of effective quantities. In determining the type of BCs in question, one can start with analyzing the three "canonical" BCs we have discussed in Sect. 5.4.2. With this in mind, the first step is to properly redefine these BCs in a regime of large deformations. We do this next.

In the present context, we define *uniform strain BCs* as follows

$$\boldsymbol{x}(\boldsymbol{\chi}, t) = \hat{\mathsf{F}}(t)\boldsymbol{\chi} \quad \text{for } \boldsymbol{\chi} \in \partial\Omega_\kappa, \tag{5.13}$$

where, for all t of interest, $\hat{\mathsf{F}}(t)$ is a *prescribed* second-order tensor with positive determinant. The definition given here matches the definition given by Hill [13, 14].[3]

Uniform stress BCs are now defined as follows

$$\mathsf{T}(\boldsymbol{x}, t)\boldsymbol{n}(\boldsymbol{x}, t) = \hat{\boldsymbol{\Sigma}}(t)\boldsymbol{n}(\boldsymbol{x}, t) \quad \text{for } \boldsymbol{x} \in \partial\Omega, \tag{5.14}$$

[3] Equation (5.13) is presented under the assumption that the origin of the coordinate system is at the mass center and that the total linear momentum of the system is zero.

where, for all t of interest, $\hat{\mathbf{\Sigma}}(t)$ is a *prescribed* symmetric second-order tensor. In this case it is important to remark that, contrary to the case of the uniform strain BCs, the uniform stress BCs stated here do not match those discussed by Hill [13, 14].

As far as *periodic* BCs are concerned (for a very careful discussion of these BCs, see [9]), we redefine them as follows: We say that the motion $\boldsymbol{x} = \boldsymbol{x}(\boldsymbol{\chi}, t)$ and the boundary traction field $\mathsf{S}(\boldsymbol{\chi}, t)\boldsymbol{n}_\kappa(\boldsymbol{\chi})$ satisfy periodic BCs if:

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

$$\boldsymbol{x}(\boldsymbol{\chi}, t) = \hat{\mathsf{F}}(t)\boldsymbol{\chi} + \tilde{\boldsymbol{u}}(\boldsymbol{\chi}, t), \tag{5.15}$$

   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.

2. $\mathsf{S}(\boldsymbol{\chi}, t)\boldsymbol{n}_\kappa(\boldsymbol{\chi})$ is an Ω_κ-antiperiodic.

When adopting periodic BCs, it is important to keep in mind that the fields $\tilde{\boldsymbol{u}}$ and $\mathsf{S}\boldsymbol{n}_\kappa$ are unknown. In other words, the periodic BCs do not *prescribe* the boundary values of either the motion or the traction field. Rather, they only pose constraints on the class of functions to which both the displacement and the traction fields can belong.

Now that these definitions have been stated we present an important result.

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

$$[\![\mathsf{F}]\!] = \hat{\mathsf{F}}, \tag{5.16}$$

i.e., one can control the effective deformation gradient tensor via the prescribed $\hat{\mathsf{F}}$. *Furthermore, under these BCs, the resulting effective quantities satisfy the conditions stated in Definition 1.*

This proposition combines a number of results whose rigorous proof has been given in [9]. Unfortunately, it is not possible to prove that the adoption of the uniform stress BCs allows one to satisfy Definition 1.

The consequence of the above result is that, on the one hand, there are sets of conditions under which our discussion is indeed meaningful. On the other hand, the uniform stress BCs, while perfectly acceptable in linear homogenization, are no longer usable in the present context. Although we have

not discussed MD up to now, we will see that the loss of the uniform stress BCs as one of the admissible conditions poses possibly severe constraints on how one can define stress-controlled continuum homogenization-based MD schemes.

5.6 Continuum Homogenization and MD

5.6.1 Basic Ideas About MD

To construct a link between continuum homogenization and MD, we first make some cursory observations about MD. We start with observing that, from a conceptual viewpoint, in MD calculations one predicts the motion of a system of N particles using Newton's second law, i.e., $\boldsymbol{f}_i = m_i \ddot{\boldsymbol{r}}_i$, where $\boldsymbol{f}_i$, m_i, and $\boldsymbol{r}_i$ are the force acting on, the mass, and the position of the ith particle in the system, respectively, and where a dot over a quantity denotes the material time derivative, so that $\ddot{\boldsymbol{r}}_i$ is the acceleration of particle i (it is understood that the system's motion is being observed by an inertial observer). The particle ensemble under consideration is viewed as occupying a region of space called a *cell*, which is considered part of an infinite lattice of identical cells. Therefore, in MD computations, the cell under study is considered to be subjected to *periodic* BCs when the particles in the cells are allowed to interact with the particles in the cells that surround the main reference cell (see [9] for additional details). The particles in the cells surrounding the main cell are often called *image particles*. With this in mind, the force $\boldsymbol{f}_i$ acting on particle i is best viewed as follows

$$\boldsymbol{f}_i = \boldsymbol{f}_i^{\text{int}} + \boldsymbol{f}_i^{\text{ext}}, \tag{5.17}$$

where $\boldsymbol{f}_i^{\text{int}}$ is the force on particle i due to its interaction with the other $N-1$ particles in the cell. For this reason, $\boldsymbol{f}_i^{\text{int}}$ can be called an *internal* force, whereas $\boldsymbol{f}_i^{\text{ext}}$ is the force on particle i due to its interaction with the image particles, and therefore *external* to the ensemble. As far as the calculation of $\boldsymbol{f}_i^{\text{int}}$ is concerned, the internal force is derived as the gradient of the total potential energy of the system, this potential energy being the sum of all the potential energies that describe the bonds among the particles in the system. From a mathematical viewpoint, this means that given the N particles in the system and the knowledge of how these particles interact with one another, one can form a function $\Psi = \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$, namely the total potential energy of the system, such that

$$\boldsymbol{f}_i^{\text{int}} = -\frac{\partial \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)}{\partial \boldsymbol{r}_i}. \tag{5.18}$$

As far as the calculation of $\boldsymbol{f}_i^{\text{ext}}$ is concerned, as it turns out, it is carried out in a way very similar to the calculation for the internal forces, i.e., by constructing the potential energy resulting from the interaction between a particle i in the cell and the image particles outside the cell. In view of how the force on a particle is calculated, and borrowing the language of the theory of elasticity, one could say that the particle ensemble is typically taken to be a *hyperelastic* material, i.e., a material whose internal response is completely characterized by a stored energy function (see, e.g., [21, p. 206] or [29, p. 302]).

Another crucial element of MD calculations is the idea, borrowed from statistical mechanics, that the system's total kinetic energy can be mapped via the equipartition theorem (see, e.g., [10]) into a measure of the system's temperature.

Almost without exception, the calculation of stress in particle systems studied via MD is done by computing the system's *virial stress*, which is defined as follows

$$\mathsf{P} \triangleq \frac{1}{\text{Vol}(\Omega)} \sum_{i=1}^{N} \left(\frac{\partial \Psi}{\partial \boldsymbol{r}_i} \otimes \boldsymbol{r}_i - m_i \dot{\boldsymbol{r}}_i \otimes \dot{\boldsymbol{r}}_i \right), \tag{5.19}$$

where $\dot{\boldsymbol{r}}_i$ is the velocity of particle i. In general, the raw measure of stress provided by P is time averaged and treated as a measure of Cauchy stress (for a recent and detailed review of the concept of virial stress, see [32]). Therefore, the measure of effective stress typically done in MD is a time and volume average of a quantity that is related to the amount of potential and kinetic energy in the system.

The question to address is now as follows: Can one formulate a continuum homogenization problem that is formally identical to an MD-based measure of stress? The answer to this question is in the affirmative and to see how to use continuum homogenization to mimic MD, we need to make the following important remark: Traditionally, when applied to the characterization of the elastic response of a material, continuum homogenization is used to map the properties of a *heterogeneous* system *under quasistatic conditions* into those of a companion *homogeneous* system, again *under quasistatic conditions*. By contrast, an MD calculation maps the (discrete) properties of a system subject to the full form of Newton's second law, i.e., including inertial effects, and maps them into the properties of an equivalent thermomechanical system in equilibrium.[4] Therefore, going back to

[4]By contrast, *molecular statics* determines the properties of a material under static equilibrium conditions and therefore it is applicable only in the zero temperature limit.

continuum homogenization, what we need to consider is an RVE, consisting of a hyperelastic medium (heterogeneous or not), whose evolution is governed by a fully dynamic equation of motion, i.e.,

$$\mathrm{Div}(\mathsf{S}) = \rho_\kappa \dot{\boldsymbol{v}}, \tag{5.20}$$

where ρ_κ is the density distribution in the reference configuration and $\boldsymbol{v}$ is the material velocity field. Next, the local properties of this RVE must then be mapped into the properties of an equivalent homogeneous *thermoelastic* solid under quasistatic conditions. Adopting this conceptual framework yields a method for bridging continuum homogenization and MD. This will be shown in detail in the remainder of the chapter.

5.6.2 Effective Cauchy Stress

As we noted earlier, the measure of effective stress in MD is obtained as a time and volume average. Hence, the first result we intend to illustrate concerns what happens to the continuum homogenization notion of effective Cauchy stress under (5.20) when computed as a volume average rather than through boundary integrals and when averaged over time.

For simplicity, we will assume that the RVE is a regular and simply connected domain. In addition, we will assume that there exist positive constants α and β such that, for all times $t \in [0, \infty)$, we have

$$\|\rho \boldsymbol{v} \otimes \boldsymbol{x}\| < \alpha \quad \text{and} \quad \beta < \mathrm{Vol}(\Omega), \tag{5.21}$$

where ρ is the RVE mass density distribution in the deformed configuration. Furthermore, we assume that the volume time rate of change is controllable in the following sense, namely that there exist a positive constant γ and a constant $\delta \in (0, 1)$ such that, for all $\tau \in [0, \infty)$, we have

$$\int_0^\infty \left| \frac{\mathrm{d}}{\mathrm{d}t} \mathrm{Vol}(\Omega) \right| \mathrm{d}t < \gamma \tau^\delta. \tag{5.22}$$

From a practical viewpoint, the above assumptions require that the RVE motion be controllable in such a way that the RVE volume neither shrinks to zero nor grows "too fast" and in such a way that the momentum of the system remains bounded. These assumptions are always achievable under uniform strain and periodic BCs since, from a purely kinematical viewpoint, these BCs imply the satisfaction of the relations in Definition 1, which, in turn, imply the full controllability of the system's volume by an appropriate

choice of $\hat{\mathsf{F}}(t)$. In addition, the assumption concerning the system's momentum is easily achievable in that the BCs in question do not let the RVE to accelerate as a whole or to "spin out of control." With this in mind, we prove the following result.[5]

Proposition 2 (**Effective Stress as a Volume Average).** *Under the assumptions in* (5.21) *and* (5.22)*, and for a regular simply connected RVE governed by* (5.20)*, we have*

$$\langle [\![\mathsf{T}]\!] \rangle = \left\langle \frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega (\mathsf{T} - \rho \boldsymbol{v} \otimes \boldsymbol{v}) \mathrm{d}v \right\rangle . \tag{5.23}$$

Before presenting the proof of this result, it is important to discuss its meaning. Equation (5.23) says that the time average of the effective stress has a structure that is very similar to that of the time average of the virial stress. In fact, for a hyperelastic material, T is completely derived from a potential, as is the first term on the right-hand side of (5.19). Furthermore, (5.23) displays the term $(\rho \, \mathrm{d}v)\boldsymbol{v} \otimes \boldsymbol{v}$, which is formally identical to the term $m_i \dot{\boldsymbol{r}}_i \otimes \dot{\boldsymbol{r}}_i$ appearing in (5.19). Clearly, we still have some work to do to show that indeed $\langle [\![\mathsf{T}]\!] \rangle$ is the same as $\langle \mathsf{P} \rangle$, since we do not have a discrete equivalent of $[\![\mathsf{T}]\!]$ yet. We will deal with this issue later in this chapter.

Proof of Proposition 2. Starting from the second of (5.9) and using the divergence theorem, we obtain

$$\mathrm{Vol}(\Omega) [\![\mathsf{T}]\!] = \int_\Omega (\mathsf{T} \, \mathrm{grad} \, \boldsymbol{x} + (\mathrm{div} \, \mathsf{T}) \otimes \boldsymbol{x}) \mathrm{d}v = \int_\Omega (\mathsf{T} + \rho \dot{\boldsymbol{v}} \otimes \boldsymbol{x}) \mathrm{d}v, \tag{5.24}$$

where we have used the fact that $\mathrm{grad} \, \boldsymbol{x} = \mathsf{I}$ along with (5.20).

Next, using the transport theorem (see, e.g., [11]), we can rewrite the last term in (5.24) as follows:

$$\int_\Omega \rho \dot{\boldsymbol{v}} \otimes \boldsymbol{x} \, \mathrm{d}v = \frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega \rho \boldsymbol{v} \otimes \boldsymbol{x} \, \mathrm{d}v - \int_\Omega \rho \boldsymbol{v} \otimes \boldsymbol{v} \, \mathrm{d}v. \tag{5.25}$$

Substituting the above result into (5.24) and dividing by $\mathrm{Vol}(\Omega)$, we obtain

$$[\![\mathsf{T}]\!] = \frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega (\mathsf{T} - \rho \boldsymbol{v} \otimes \boldsymbol{v}) \mathrm{d}v + \frac{1}{\mathrm{Vol}(\Omega)} \frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v. \tag{5.26}$$

Next we consider the time integral of the last term in the above expression over the interval $(0, \tau)$

[5] A less general version of this result was presented in [9].

$$\int_0^\tau \left\{ \frac{1}{\mathrm{Vol}(\Omega)} \frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right\} \mathrm{d}t = \left[\frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right]_0^\tau + \int_0^\tau \left\{ \frac{1}{(\mathrm{Vol}(\Omega))^2} \left(\frac{\mathrm{d}}{} \mathrm{Vol}(\Omega) \right) \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right\} \mathrm{d}t, \quad (5.27)$$

where use has been made of integration by parts (with respect to t). From the above relation, we conclude that the norm of the term on the left-hand side is such that

$$\left\| \int_0^\tau \left\{ \frac{1}{\mathrm{Vol}(\Omega)} \frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right\} \mathrm{d}t \right\| \leq \left\| \left[\frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right]_0^\tau \right\| + \left\| \int_0^\tau \left\{ \frac{1}{(\mathrm{Vol}(\Omega))^2} \left(\frac{\mathrm{d}}{\mathrm{d}t} \mathrm{Vol}(\Omega) \right) \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right\} \mathrm{d}t \right\|. \quad (5.28)$$

In turn, taking advantage of the first of the assumptions in (5.21), for the first term on the right-hand side of the above expression, we can write

$$\begin{aligned} \left\| \left[\frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right]_0^\tau \right\| &= \left\| \left[\frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right]_{t=\tau} - \left[\frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right]_{t=0} \right\| \\ &\leq \left\| \left[\frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right]_{t=\tau} \right\| + \left\| \left[\frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right]_{t=0} \right\| \\ &\leq \left[\frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega \| \rho \boldsymbol{v} \otimes \boldsymbol{x} \| \mathrm{d}v \right]_{t=\tau} + \left[\frac{1}{\mathrm{Vol}(\Omega)} \int_\Omega \| \rho \boldsymbol{v} \otimes \boldsymbol{x} \| \mathrm{d}v \right]_{t=0} \\ &< \left[\frac{\alpha \, \mathrm{Vol}(\Omega)}{\mathrm{Vol}(\Omega)} \right]_{t=\tau} + \left[\frac{\alpha \, \mathrm{Vol}(\Omega)}{\mathrm{Vol}(\Omega)} \right]_{t=0} \\ &< 2\alpha. \end{aligned} \quad (5.29)$$

As far as the second term on the right-hand side of the inequality in (5.28) is concerned, using the assumptions in (5.21) and (5.22), we have that

$$\begin{aligned}
&\left\| \int_0^\tau \left\{ \frac{1}{(\mathrm{Vol}(\Omega))^2} \left(\frac{\mathrm{d}}{\mathrm{d}t} \mathrm{Vol}(\Omega) \right) \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right\} \mathrm{d}t \right\| \\
&\quad \leq \int_0^\tau \left\{ \frac{1}{(\mathrm{Vol}(\Omega))^2} \left| \frac{\mathrm{d}}{\mathrm{d}t} \mathrm{Vol}(\Omega) \right| \int_\Omega \| \rho \boldsymbol{v} \otimes \boldsymbol{x} \| \, \mathrm{d}v \right\} \mathrm{d}t \\
&\quad < \int_0^\tau \frac{\alpha \, \mathrm{Vol}(\Omega)}{(\mathrm{Vol}(\Omega))^2} \left| \frac{\mathrm{d}}{\mathrm{d}t} \mathrm{Vol}(\Omega) \right| \mathrm{d}t \\
&\quad < \frac{\alpha}{\beta} \int_0^\tau \left| \frac{\mathrm{d}}{\mathrm{d}t} \mathrm{Vol}(\Omega) \right| \mathrm{d}t < \frac{\alpha \gamma}{\beta} \tau^\delta .
\end{aligned} \tag{5.30}$$

Next, substituting the results in (5.29) and (5.30) into (5.28), we have that

$$\left\| \int_0^\tau \left\{ \frac{1}{\mathrm{Vol}(\Omega)} \frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right\} \mathrm{d}t \right\| < 2\alpha + \frac{\alpha \gamma}{\beta} \tau^\delta . \tag{5.31}$$

Finally, observing that

$$\lim_{\tau \to \infty} \frac{1}{\tau} \left(2\alpha + \frac{\alpha \gamma}{\beta} \tau^\delta \right) = 0, \tag{5.32}$$

and recalling the definition of the time average operation in (5.12), we conclude that we must have

$$\left\langle \frac{1}{\mathrm{Vol}(\Omega)} \frac{\mathrm{d}}{\mathrm{d}t} \int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{x}) \mathrm{d}v \right\rangle = \mathsf{0}. \tag{5.33}$$

Finally, taking the time average of (5.26) and taking advantage of the result in (5.33), we obtain (5.23). □

5.6.3 Application of BCs in the "Dynamic" RVE Problem

As discussed earlier in the section, to build a continuum homogenization problem that can mimic an MD calculation, one needs to adopt a fully dynamic form of the pointwise balance of linear momentum law, such as that in (5.20), which we repeat here for convenience

$$\mathrm{Div}(\mathsf{S}) = \rho_\kappa \dot{\boldsymbol{v}}. \tag{5.34}$$

In addition to this balance law, the RVE problem needs to be accompanied by the material's constitutive equations and by a set of BCs. As far as constitutive equations are concerned, for a hyperelastic material, these are given

by assigning a strain energy function $\psi_\kappa(\mathsf{F}, \boldsymbol{\chi})$ so that

$$\mathsf{S}(\mathsf{F}, \boldsymbol{\chi}) = \rho_\kappa \frac{\partial \psi_\kappa(\mathsf{F}, \boldsymbol{\chi})}{\partial \mathsf{F}}. \tag{5.35}$$

As far as the BCs are concerned, as illustrated in Sect. 5.4.2, these are essential to the determination of the effective elastic properties of the material. In fact, the BCs allow one to control, say, the effective deformation and, at the same time, solve the governing equations for the resulting stress field, which can then be used to compute the effective stress response as a function of the specified value of the effective deformation. With this in mind, it is important to be aware of how the parameter controlled by the BCs actually appears in the problem.

Referring to (5.13), if one chooses uniform strain boundary conditions, then the control parameter $\hat{\mathsf{F}}(t)$ directly determines the location of the RVE boundary points in the deformed configuration. Hence, it is easy to see how the RVE "knows" about $\hat{\mathsf{F}}(t)$. However, in the case of periodic BCs, it is less obvious to see how the effective deformation of the RVE is directed to take on the prescribed value $\hat{\mathsf{F}}(t)$. To understand how this happens, one needs to carefully consider (5.15). The first thing to understand about (5.15) is that it is not an assumption: It is a convenient decomposition of the motion of the *entire* RVE. Specifically, it decomposes the entire RVE motion into a homogeneous deformation and an unknown displacement field $\tilde{\boldsymbol{u}}$. This decomposition is always admissible because the controlled parameter $\hat{\mathsf{F}}(t)$ is chosen to be invertible. Next, it must be understood that, under periodic BCs, the RVE "does not know" about $\hat{\mathsf{F}}(t)$ through boundary data, because the only fields whose boundary behavior is controlled are the unknown field $\tilde{\boldsymbol{u}}$ (constrained to be periodic) and the unknown field $\mathsf{S}\boldsymbol{n}_\kappa$ (constrained to be antiperiodic). We must, therefore, conclude that the effective deformation of the RVE is controlled via the governing equations. In fact, using the decomposition in (5.15) to compute the deformation gradient and the velocity of the RVE motion, we have

$$\mathsf{F} = \hat{\mathsf{F}}(\mathsf{I} + \tilde{\mathsf{H}}) \quad \text{and} \quad \dot{\boldsymbol{v}} = \ddot{\hat{\mathsf{F}}}(\boldsymbol{\chi} + \tilde{\boldsymbol{u}}) + 2\dot{\hat{\mathsf{F}}}\dot{\tilde{\boldsymbol{u}}} + \hat{\mathsf{F}}\ddot{\tilde{\boldsymbol{u}}}, \tag{5.36}$$

where $\tilde{\mathsf{H}} = \operatorname{Grad} \tilde{\boldsymbol{u}}$. With this in mind, one can then take F and $\boldsymbol{v}$ as given in (5.36) and combine them with (5.34) and (5.35) to formulate a BVP in the unknown field $\tilde{\boldsymbol{u}}$. By this substitution, we see that the control parameter $\hat{\mathsf{F}}$ will contribute to the governing partial differential equations as a forcing term.

To facilitate the discussion in Sect. 5.6.4, it is useful to notice that one could enforce even the uniform strain BCs as was done in the case of periodic BCs. In fact, no matter what BC set one chooses, given a nonsingular $\hat{\mathsf{F}}(t)$, one can *always* represent the RVE motion as

$$\boldsymbol{x}(\boldsymbol{\chi}, t) = \hat{\mathsf{F}}(t)\boldsymbol{x}^*(\boldsymbol{\chi}, t), \tag{5.37}$$

where $\boldsymbol{x}^*$ is an unknown vector field. Again, (5.37) is not an assumption, it is simply a decomposition that defines an unknown vector field $\boldsymbol{x}^*$. To determine this field, we first compute the RVE deformation gradient and the acceleration, which take on the form

$$\mathsf{F} = \hat{\mathsf{F}}\mathsf{F}^* \quad \text{and} \quad \dot{\boldsymbol{v}} = \ddot{\hat{\mathsf{F}}}\boldsymbol{x}^* + 2\dot{\hat{\mathsf{F}}}\dot{\boldsymbol{x}}^* + \hat{\mathsf{F}}\ddot{\boldsymbol{x}}^*, \tag{5.38}$$

where $\mathsf{F}^* = \operatorname{Grad}\boldsymbol{x}^*$. Next, the relations in (5.38) along with the constitutive relations in (5.35) are substituted into the momentum balance law to obtain a set of partial differential equations in the unknown field $\boldsymbol{x}^*$. Finally, under uniform strain BCs, the boundary value of $\boldsymbol{x}^*$ is such that $\boldsymbol{x}^* = \boldsymbol{\chi}$, whereas in the case of periodic BCs, the boundary value of $\boldsymbol{x}^*$ is such that $\boldsymbol{x}^* = \boldsymbol{\chi} + \boldsymbol{u}^*$, the field $\boldsymbol{u}^*$ being periodic. Clearly, in the case of periodic BCs, one still needs to also make sure that the field $\mathsf{S}\boldsymbol{n}_\kappa$ is antiperiodic.

5.6.4 A Lagrangian Continuum Homogenization Scheme

Now we can deal directly with the question concerning how the continuum homogenization notion of effective stress can be extended to discrete systems. The answer we provide lies in a reformulation of the RVE problem illustrated in Sect. 5.6.3 using the Lagrangian mechanics. Before delving into the details of this reformulation, it is essential to realize that the reformulation in question is *not* useful from the viewpoint of continuum homogenization because the latter requires the solution of a BVP, i.e., a set of partial differential equations and *boundary conditions*. The usefulness of the reformulation lies in the fact that it can be easily applied to discrete systems because, at least formally, the Lagrangian formulation we are about to illustrate does not require the evaluation of boundary information. Therefore, the proposed Lagrangian scheme can be applied to discrete systems without worrying about defining the boundary of such systems.

As observed in Sect. 5.6.3, we mimic what happens in MD by modeling the material as hyperelastic and subject to a fully dynamic version of the momentum balance law. Under these conditions, one can construct the

Lagrangian of the RVE, which, under uniform or periodic BCs, takes on the form (for a careful discussion on the effect of BCs on the Lagrangian of the RVE, see [1])

$$\mathscr{L}(\boldsymbol{x}, \boldsymbol{v}) = T - U, \tag{5.39}$$

where T and U denote the RVE's total kinetic and potential energies, respectively, and, in a continuum mechanics context, are defined in the usual way, i.e.,

$$T = \int_{\Omega_\kappa} \frac{1}{2} \rho_\kappa \boldsymbol{v} \cdot \boldsymbol{v} \, \mathrm{d}V \quad \text{and} \quad U = \int_{\Omega_\kappa} \rho_\kappa \psi_\kappa \, \mathrm{d}V, \tag{5.40}$$

In a continuum context, using the standard Lagrangian formalism, one can start from (5.39) and derive the governing equations of the RVE, namely (5.34) (see [1]). Again, we have no interest in pursuing this because we already have the governing equations of the RVE. Instead, noticing that the terms in (5.40) do not require an explicit knowledge of the boundary of the RVE, the focus of this discussion will be to illustrate how one can compute the effective stresses $[\![\mathsf{S}]\!]$ and $[\![\mathsf{T}]\!]$ *directly* from the Lagrangian function $\mathscr{L}$.

The calculation of $[\![\mathsf{S}]\!]$ and $[\![\mathsf{T}]\!]$ from $\mathscr{L}$ is done by first making sure that the parameter controlling the effective deformation of the RVE is explicitly embedded into the Lagrangian. In turn, this is done by adopting the strategy discussed at the end of Sect. 5.6.3, i.e., we adopt the decomposition in (5.37) and we turn the Lagrangian $\mathscr{L}$ into a function of the control parameter $\hat{\mathsf{F}}$, its time rate of change, the unknown motion $\boldsymbol{x}^*$, and the associated velocity field $\dot{\boldsymbol{x}}^*$

$$\mathscr{L}(\boldsymbol{x}, \boldsymbol{v}) = \mathscr{L}\left(\hat{\mathsf{F}}, \dot{\hat{\mathsf{F}}}, \boldsymbol{x}^*, \dot{\boldsymbol{x}}^*\right), \tag{5.41}$$

where, in view of (5.37), $\boldsymbol{v}$ takes on the form $\boldsymbol{v} = \dot{\hat{\mathsf{F}}}\boldsymbol{x}^* + \hat{\mathsf{F}}\dot{\boldsymbol{x}}^*$. Once the Lagrangian is given the above form, Andia et al. [1] have rigorously proven that

$$[\![\mathsf{S}]\!] = \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \left[\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial \mathscr{L}}{\partial \dot{\hat{\mathsf{F}}}} \right) - \frac{\partial \mathscr{L}}{\partial \hat{\mathsf{F}}} \right]. \tag{5.42}$$

Furthermore, since under uniform or periodic BCs one can rely on the relations in Definition 1, we have that

$$[\![\mathsf{T}]\!] = \frac{1}{\mathrm{Vol}(\Omega)} \left[\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial \mathscr{L}}{\partial \dot{\hat{\mathsf{F}}}} \right) - \frac{\partial \mathscr{L}}{\partial \hat{\mathsf{F}}} \right] \hat{\mathsf{F}}^{\mathrm{T}}. \tag{5.43}$$

The importance of (5.42) and (5.43) lies in the fact that one can measure the effective stresses of the RVE without having to carry out the boundary integrations by which $[\![\mathsf{S}]\!]$ and $[\![\mathsf{T}]\!]$ are defined. As important, from a

practical viewpoint, this means that one can use (5.42) and (5.43) to *define* $[\![\mathsf{S}]\!]$ and $[\![\mathsf{T}]\!]$ for a discrete system of particles as long as one can define the Lagrangian of the discrete system in question. With this in mind, constructing the Lagrangian of a system of particles interacting via a bond potential energy is a rather simple operation. In fact, denoting such a Lagrangian function by $\mathscr{L}_{\mathrm{MD}}$, we have that

$$\mathscr{L}_{\mathrm{MD}}(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,\dot{\boldsymbol{r}}_1,\ldots,\dot{\boldsymbol{r}}_N)=\sum_{i=1}^{N}\frac{1}{2}m_i\dot{\boldsymbol{r}}_i\cdot\dot{\boldsymbol{r}}_i-\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N), \quad (5.44)$$

where the various quantities in the above equations have been introduced in Sect. 5.6.1. Next, we explicitly embed the control parameter $\hat{\mathsf{F}}$ into $\mathscr{L}_{\mathrm{MD}}$ similarly to what was done in the case of $\mathscr{L}$, i.e., by adopting the following decomposition of the system's motion:

$$\boldsymbol{r}_i(t)=\hat{\mathsf{F}}(t)\boldsymbol{r}_i^*(t),\quad i=1,\ldots,N. \quad (5.45)$$

The unknown functions $\boldsymbol{r}_i^*(t)$ are determined by solving the system's equations of motion. In turn, these equations are obtained by substituting (5.45) into (5.44) and by using the standard Lagrangian formalism, which, as demonstrated in [1], yields

$$m_i\hat{\mathsf{F}}\ddot{\boldsymbol{r}}_i^*+2m_i\dot{\hat{\mathsf{F}}}\dot{\boldsymbol{r}}_i^*+m_i\ddot{\hat{\mathsf{F}}}\boldsymbol{r}_i^*=-\hat{\mathsf{F}}^{-\mathrm{T}}\frac{\partial\Psi}{\partial\boldsymbol{r}_i^*}+\boldsymbol{f}_i^{\mathrm{e}},\quad i=1,\ldots,N. \quad (5.46)$$

The result in (5.46) is important in that it shows that the somewhat abstract continuum homogenization scheme described earlier has been turned into a practical tool for carrying out MD simulations. In fact, by placing a particle ensemble in an initial reference volume Ω_κ, and by knowing the bond potentials that allow one to compute Ψ, one can assign any given effective deformation $\hat{\mathsf{F}}(t)$ and compute the resulting motion of the particle system by integrating the system of ordinary differential equations in (5.46). Once, this motion has been calculated, the solution can be postprocessed to compute the effective Cauchy and first Piola–Kirchhoff stresses for the discrete system which are now *defined* as follows

$$[\![\mathsf{S}]\!]_{\mathrm{MD}}\triangleq\frac{1}{\mathrm{Vol}(\Omega_\kappa)}\left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial\mathscr{L}_{\mathrm{MD}}}{\partial\dot{\hat{\mathsf{F}}}}\right)-\frac{\partial\mathscr{L}_{\mathrm{MD}}}{\partial\hat{\mathsf{F}}}\right], \quad (5.47)$$

$$[\![\mathsf{T}]\!]_{\mathrm{MD}}\triangleq\frac{1}{\mathrm{Vol}(\Omega)}\left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial\mathscr{L}_{\mathrm{MD}}}{\partial\dot{\hat{\mathsf{F}}}}\right)-\frac{\partial\mathscr{L}_{\mathrm{MD}}}{\partial\hat{\mathsf{F}}}\right]\hat{\mathsf{F}}^{\mathrm{T}}, \quad (5.48)$$

where we have used the subscript "MD" to underscore the fact that (5.47) and (5.48) are the definitions applicable in MD. In addition, it should be noted that the definition in (5.48) is obtained from that in (5.47) and the conditions stated in Definition 1. Therefore, in adopting the definitions in (5.47) and (5.48), it is crucial that the BCs enforced on the discrete system be compatible with Definition 1, e.g., periodic BCs, which are the BCs almost universally used in MD.

Carrying out the calculations implied by (5.47) and (5.48) and using (5.18), (5.45), and (5.46), one can show that $[\![\mathsf{S}]\!]_{\mathrm{MD}}$ and $[\![\mathsf{T}]\!]_{\mathrm{MD}}$ can be given the following simple forms (see [1]):

$$[\![\mathsf{S}]\!]_{\mathrm{MD}} = \frac{1}{\mathrm{Vol}(\Omega_\kappa)} \sum_{i=1}^{N} \boldsymbol{f}_i^{\mathrm{ext}} \otimes \boldsymbol{r}_i^* \quad \text{and} \quad [\![\mathsf{T}]\!]_{\mathrm{MD}} = \frac{1}{\mathrm{Vol}(\Omega)} \sum_{i=1}^{N} \boldsymbol{f}_i^{\mathrm{ext}} \otimes \boldsymbol{r}_i. \tag{5.49}$$

From a conceptual viewpoint, we consider the result in (5.47) and (5.48) to be extremely important in that we can claim that the effective stress measures we have introduced have exactly the same meaning in both a discrete context and a continuum context. For this reason, they demonstrate that one can indeed gain a great deal of understanding of MD methods for computing mechanical properties by relying just on classical mechanics concepts.

5.6.5 Virial Stress/Effective Cauchy Stress Equivalence

Now that we have obtained a continuum homogenization-based notion of effective Cauchy stress applicable to discrete systems, we are in a position to offer a meaningful comparison between such a notion and that of virial stress. This comparison will be expressed via the following.

Proposition 3 (Virial–Cauchy Stress Equivalence). *If there exist positive constants α and β such that, for all times $t \in [0, \infty)$ and all $i = 1, \ldots, N$,*

$$\|m_i \dot{\boldsymbol{r}}_i \otimes \boldsymbol{r}_i\| < \alpha \quad \textit{and} \quad \beta < \mathrm{Vol}(\Omega), \tag{5.50}$$

and assuming that the volume time rate of change is controllable in the sense that there exist a positive constant γ and a constant $\delta \in (0, 1)$ such that, for all $\tau \in [0, \infty)$,

$$\int_0^\infty \left| \frac{\mathrm{d}}{\mathrm{d}t} \mathrm{Vol}(\Omega) \right| \mathrm{d}t < \gamma \tau^\delta, \tag{5.51}$$

then

$$\langle [\![\mathsf{T}]\!]_{\mathrm{MD}} \rangle = \langle \mathsf{P} \rangle. \tag{5.52}$$

Proof of Proposition 3. We consider a reference cell consisting of an ensemble of N particles subject to periodic BCs. Next, using (5.17), we can write

$$\boldsymbol{f}_i^{\text{ext}} = \boldsymbol{f}_i - \boldsymbol{f}_i^{\text{int}}, \tag{5.53}$$

$\boldsymbol{f}_i$ being the total force acting on particle i and $\boldsymbol{f}_i^{\text{int}}$ being the force acting on particle i due to interactions with the other particles internal to the reference cell. Next, we recall that the total force $\boldsymbol{f}_i = m_i \ddot{\boldsymbol{r}}_i$ due to Newton's second law, so that, using (5.18), (5.53) can be rewritten as

$$\boldsymbol{f}_i^{\text{ext}} = m_i \ddot{\boldsymbol{r}}_i + \frac{\partial \Psi}{\partial \boldsymbol{r}_i}. \tag{5.54}$$

Substituting (5.54) into the second of (5.49), we have

$$[\![\mathsf{T}]\!]_{\text{MD}} = \frac{1}{\text{Vol}(\Omega)} \sum_{i=1}^{N} \left(m_i \ddot{\boldsymbol{r}}_i + \frac{\partial \Psi}{\partial \boldsymbol{r}_i} \right) \otimes \boldsymbol{r}_i. \tag{5.55}$$

Now, observe that the term $\ddot{\boldsymbol{r}}_i \otimes \boldsymbol{r}_i$ can be written as

$$\ddot{\boldsymbol{r}}_i \otimes \boldsymbol{r}_i = \frac{\mathrm{d}}{\mathrm{d}t}(\dot{\boldsymbol{r}}_i \otimes \boldsymbol{r}_i) - \dot{\boldsymbol{r}}_i \otimes \dot{\boldsymbol{r}}_i, \tag{5.56}$$

so that (5.55) can be written as

$$\begin{aligned}[\![\mathsf{T}]\!]_{\text{MD}} = \frac{1}{\text{Vol}(\Omega)} \sum_{i=1}^{N} \left(\frac{\partial \Psi}{\partial \boldsymbol{r}_i} \otimes \boldsymbol{r}_i - m_i \dot{\boldsymbol{r}}_i \otimes \dot{\boldsymbol{r}}_i \right) \\ + \frac{1}{\text{Vol}(\Omega)} \sum_{i=1}^{N} m_i \frac{\mathrm{d}}{\mathrm{d}t}(\dot{\boldsymbol{r}}_i \otimes \boldsymbol{r}_i).\end{aligned} \tag{5.57}$$

Next, recalling that the mass of each particle is a constant and substituting (5.19) into (5.57), we can give $[\![\mathsf{T}]\!]_{\text{MD}}$ the following form:

$$[\![\mathsf{T}]\!]_{\text{MD}} = \mathsf{P} + \frac{1}{\text{Vol}(\Omega)} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i=1}^{N} (m_i \dot{\boldsymbol{r}}_i \otimes \boldsymbol{r}_i). \tag{5.58}$$

Finally, observing that (5.50) and (5.51) are a restatement of (5.21) and (5.22), using the same strategy that we have used to derive (5.33), provided of course that the due adjustments are made to account for the fact that here we are in a discrete context, we have that

$$\left\langle \frac{1}{\text{Vol}(\Omega)} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i=1}^{N} (m_i \dot{\boldsymbol{r}}_i \otimes \boldsymbol{r}_i) \right\rangle = \mathsf{0}, \tag{5.59}$$

which implies that the time average of (5.58) yields (5.52). □

5.6.6 Remarks on the Difference Between $[\![\mathsf{T}]\!]_{\mathrm{MD}}$ and P

In the preceding sections, we have shown that the effective Cauchy stress developed by exclusively relying on continuum homogenization ideas does lead to a useful definition of effective stress for particle systems. In addition, we have shown that, when taken as a time average, the effective Cauchy stress is identical to the stress measure based on the virial stress, provided that the evolution of the RVE is bounded as indicated in Proposition 3. With this in mind, referring to (5.58), we see that, at every instant in time, the difference between the $[\![\mathsf{T}]\!]_{\mathrm{MD}}$ and P is given by the volume average of the time rate of change of the tensor

$$\mathsf{H} = \sum_{i=1}^{N} (m_i \dot{\boldsymbol{r}}_i \otimes \boldsymbol{r}_i). \tag{5.60}$$

The tensor H can be interpreted as the generalized moment of momentum (or angular momentum) of the system. In fact, taking advantage of the one-to-one mapping that exists between second-order skew-symmetric tensors and vectors (see, e.g., [11]), it is not difficult to show that the components of $\mathrm{skw}(\mathsf{H})$, the skew-symmetric part of H, are the components of the system's total angular momentum. Therefore, so long as the overall moment of the external forces acting on the reference cell (computed with respect to some fixed point in an inertial frame of reference) is equal to zero, as is normally the case in MD, then the balance of angular momentum for the reference cell demands that $(\mathrm{d}/\mathrm{d}t)\,\mathrm{skw}(\mathsf{H}) = \mathsf{0}$. In turn, this means that the difference between $[\![\mathsf{T}]\!]_{\mathrm{MD}}$ and P is given by the term

$$\frac{1}{\mathrm{Vol}(\Omega)}\,\mathrm{sym}(\dot{\mathsf{H}}), \tag{5.61}$$

where $\mathrm{sym}(\mathsf{H})$ is the symmetric part of H. As it turns out, the term in (5.61) does not vanish on a instant by instant basis. This can be seen in Fig. 5.4, which was obtained by conducting an MD simulation for an ensemble of 500 particles interacting via the Lennard–Jones potential and at constant volume (details about this simulation are reported in [2]). Keeping in mind that $[\![\mathsf{T}]\!]_{\mathrm{MD}}$ and P are indeed different notions of stress (for additional comments concerning this discussion, see [32]), thanks to Proposition 3, we know that the time average of their difference vanishes when averaging over long time periods. However, Andia et al. [2] have reported some surprising numerical results in which the time average of $([\![\mathsf{T}]\!]_{\mathrm{MD}} - \mathsf{P})$ becomes negligible even over relatively small timescales. However, a question that remains open to

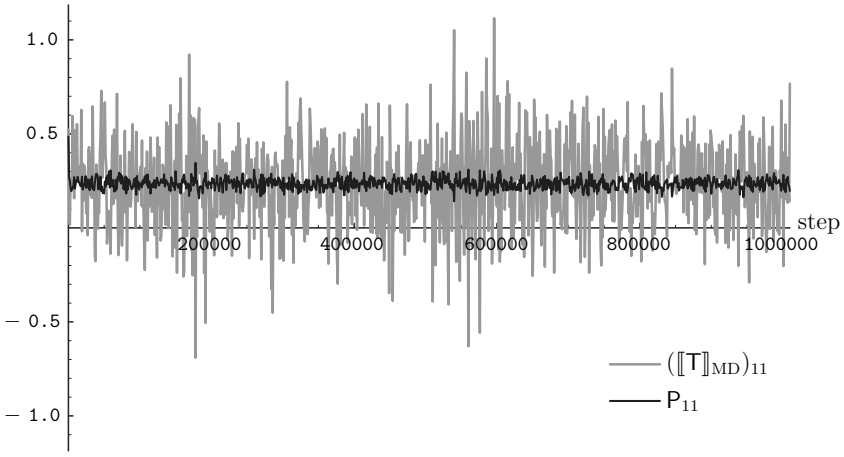

Fig. 5.4. Plot of the 11 components $\llbracket \mathsf{T} \rrbracket_{\mathrm{MD}}$ and P in nondimensional form obtained in a microcanonical ensemble simulation of a three-dimensional Lennard–Jones material. The *horizontal axis* shows the number of (identical) time integration steps during the MD simulation

investigation is whether or not there exists an intrinsic timescale over which the time average of $(\llbracket \mathsf{T} \rrbracket_{\mathrm{MD}} - \mathsf{P})$ can be said to be negligible in some physically based way.

5.6.7 Is There a Continuum-Level Virial Stress?

From a conceptual viewpoint, this chapter is focused on how the concepts from a continuum context can be used to define equivalent concepts in a discrete context. What we have not dealt with are questions such as how to derive a continuum-level concept corresponding to the virial stress or, at a more fundamental level, how do we theoretically establish rigorous continuum limits of the mechanical response of a discrete system. This second question has been studied by many researchers (see, for example, [6, 17, 19]; new rigorous results have been presented in [5]) and is outside the scope of the present chapter. However, the first question can be answered within the framework presented here. In fact, carefully comparing the proofs of Propositions 2 and 3, there is strong indication that indeed one could define the continuum-level virial stress to be the following second-order tensor

$$\mathsf{P}_{\mathrm{CL}} \triangleq \mathsf{T} - \rho \boldsymbol{v} \otimes \boldsymbol{v}, \tag{5.62}$$

where the subscript CL stands for "continuum level." What is interesting about this result is that it is not at all original. In fact, although absent from most (if not all) of the continuum mechanics textbooks published in the last 20 years, in reality the stress tensor P_{CL} is well known in the fluid mechanics literature and has been discussed, although without being explicitly called "the virial stress," by Truesdell and Toupin [30, Article 207] and then recalled in their presentation of the virial theorem (cf. [7, Article 219]). Truesdell and Toupin [30] call the component $\rho \boldsymbol{v} \otimes \boldsymbol{v}$ of the tensor P_{CL} the "apparent stress due to transfer of momentum" and show that it appears naturally in a fully Eulerian restatement of the pointwise linear momentum balance law. Using the tensor P_{CL}, this restatement of the momentum balance law takes on the form

$$\operatorname{div} \mathsf{P}_{\mathrm{CL}} + \rho \boldsymbol{b} = \frac{\partial(\rho \boldsymbol{v})}{\partial t}, \tag{5.63}$$

where $\boldsymbol{b}$ is the (external) body force field per unit mass and $\partial(\rho \boldsymbol{v})/\partial t$ is often referred to as the "apparent" rate of change of linear momentum.

5.6.8 Remarks on the Proposed MD Scheme

As mentioned earlier, our continuum homogenization-based extension of the notion of effective stress to MD relied on a Lagrangian scheme which can be used in practice. This result is remarkable for at least two reasons (1) the derivation is based solely on classical mechanics ideas and (2) it is completely rigorous (again, within the confines of classical mechanics). With this in mind, it should be mentioned that there are various Lagrangian schemes for MD simulations of solid systems, most of which are variants of the scheme first proposed in [22–24]. Many of these Lagrangian schemes account for various effects that are not included in the Lagrangian scheme we have derived. However, these schemes are often based on ad hoc Lagrangian functions that cannot be reduced to the canonical form $T - U$ dictated by classical mechanics. Therefore, the Lagrangian scheme proposed herein offers the opportunity for rigorous comparisons with existing methods as has been done in the case of the original Parrinello–Rahman method in [1].

Another observation that can be made concerning the Lagrangian scheme derived herein is that, in view of (5.46), it is easily implementable as a "strain-control" MD method, i.e., a method in which $\hat{\mathsf{F}}$ dictates the simulation cell deformation.

With this in mind, it is possible to conceive of a stress-control variant of the method in which the governing equations are those in (5.46) *along with* (5.48), where the function $[\![\mathsf{T}]\!]_{\mathrm{MD}}$ is a given of the problem and where

the effective deformation $\hat{\mathsf{F}}$ is found as part of the solution. The difficulty of this approach lies in the fact that one would have to solve a complex algebraic/differential system of nonlinear equations. To the authors' knowledge, the practical implementation of such an MD scheme has yet to be successfully done.

5.7 Conclusions

In this chapter, we have presented a strategy to use continuum homogenization ideas to determine the stress/deformation response of particle systems using MD. From a conceptual viewpoint, the main points of the chapter are that most of the MD techniques used for the determination of mechanical properties of solids can be understood by classical mechanics methods and, in fact, by methods often used by engineers for the study of composite materials. Specifically, we have proposed a rigorous extension of the concept of effective stress from continuum homogenization to the context of discrete particle systems. This extension has been carried out by formulating a practically implementable MD Lagrangian scheme, which, by being grounded in classical mechanics, offers a way of better understanding the sort of approximations that are done in the implementation of MD schemes based on ad hoc Lagrangian functions.

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