Journal of the Mechanics and Physics of Solids 93 (2016) 224–239

Contents lists available at ScienceDirect

Journal of the Mechanics and Physics of Solids

journal homepage: www.elsevier.com/locate/jmps

# Geometric derivation of the microscopic stress: A covariant central force decomposition

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ARTICLE INFO

*Article history:*
Received 28 September 2015
Received in revised form
1 March 2016
Accepted 9 March 2016
Available online 10 March 2016

*Keywords:*
Microscopic stress tensor
Statistical mechanics
Continuum mechanics
Doyle–Ericksen formula

ABSTRACT

We revisit the derivation of the microscopic stress, linking the statistical mechanics of particle systems and continuum mechanics. The starting point in our geometric derivation is the Doyle–Ericksen formula, which states that the Cauchy stress tensor is the derivative of the free-energy with respect to the ambient metric tensor and which follows from a covariance argument. Thus, our approach to define the microscopic stress tensor does not rely on the statement of balance of linear momentum as in the classical Irving–Kirkwood–Noll approach. Nevertheless, the resulting stress tensor satisfies balance of linear and angular momentum. Furthermore, our approach removes the ambiguity in the definition of the microscopic stress in the presence of multibody interactions by naturally suggesting a canonical and physically motivated force decomposition into pairwise terms, a key ingredient in this theory. As a result, our approach provides objective expressions to compute a microscopic stress for a system in equilibrium and for force-fields expanded into multibody interactions of arbitrarily high order. We illustrate the proposed methodology with molecular dynamics simulations of a fibrous protein using a force-field involving up to 5-body interactions.



## 1. Introduction

The increasing power of computers enables the atomistic simulation of material systems of growing size and complexity. However, it is difficult to interpret the physics of these systems from bare atomistic trajectories. In particular, there is a pressing need for coarse-grain measures of the effective mechanical behavior underlying molecular ensembles. Continuum mechanics has been successfully applied to understand the mechanics of a variety of systems at the nanoscale, such as carbon nanotubes (Arias and Arroyo, 2008; Yakobson et al., 1996) or biomembranes (Hu et al., 2013; Staykova et al., 2013), and therefore provides a natural framework to interpret molecular simulations of materials. In particular, local stress fields are routinely computed from molecular simulations to understand the mechanics of different materials including defective crystals (Li et al., 2002; Pao et al., 2009; Song et al., 2013; Wei et al., 2012), lipid bilayers (Lindahl and Edholm, 2000; Vanegas et al., 2014), membrane proteins (Ollila et al., 2009; Vanegas and Arroyo, 2014), or isolated molecules (Edwards et al., 2012; Hatch and Debenedetti, 2012).

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http://dx.doi.org/10.1016/j.jmps.2016.03.006
0022-5096/

The mapping from the classical mechanics of a system of point-particles to a continuous stress field is usually understood in terms of the statistical mechanics framework pioneered by Irving and Kirkwood and further substantiated by Noll, referred to here as the IKN procedure (Admal and Tadmor, 2010; Irving and Kirkwood, 1950; Noll, 1955; Schofield and Henderson, 1982). However, it is well-recognized that this mapping is not unique, particularly in the presence of complex force-fields (Admal and Tadmor, 2010; Schofield and Henderson, 1982). The major ambiguity in the theory comes from the non-unique decomposition of the interatomic forces from multibody potentials into pairwise terms. Different force decompositions have been proposed in the literature (Admal and Tadmor, 2010; Costescu and Gräter, 2013; Goetz and Lipowsky, 1998), which lead to stresses satisfying balance of linear momentum by construction. However, we have recently demonstrated that different decompositions lead to significantly different stress fields when complex interatomic potentials are used (Vanegas et al., 2014), and that some widely used decompositions lead to stress fields that violate conservation of angular momentum as a result of molecular chirality (Torres-Sánchez et al., 2015). Only recently has a force decomposition, the so-called central force decomposition (CFD) (Admal and Tadmor, 2010; Tadmor and Miller, 2011), been proposed that provides symmetric stresses by construction, which therefore satisfy balance of angular momentum. The issue is not fully settled, however, because the CFD is not unique for potentials beyond 4-body interactions (Admal and Tadmor, 2010; Murdoch, 2012; Tadmor and Miller, 2011), which are nevertheless popular to model metals or proteins (Daw and Baskes, 1984; MacKerell et al., 2004).

Here, we propose an alternative geometric derivation of the microscopic Irving–Kirkwood stress, rooted in the Doyle–Ericksen relation of continuum mechanics (Doyle and Ericksen, 1956) rather than on the statement of balance of linear momentum. See Baus and Lovett (1990, 1991) and Mistura (1987) for related work. We further show that this approach allows us to canonically define the microscopic stress for arbitrary multibody potentials. Strikingly, our derivation does not resort to Noll's lemma, required in the IKN procedure, but leads to a specific instance of IKN stress corresponding to a distinguished central force decomposition that we call *covariant central force decomposition* (cCFD). This cCFD coincides with the common definition of the CFD for potentials with 4- or fewer-body interactions, fixes the gauge invariance of CFD for higher-order multibody potentials and provides physically meaningful stress fields (Torres-Sánchez et al., 2015).

The paper is organized as follows. First, we briefly review the definition of the microscopic stress from the Irving–Kirkwood theory, focusing on the lack of uniqueness, and provide the definition of a CFD. We then present an alternative derivation of the microscopic stress based on covariance arguments, which leads to the cCFD. We also show how to practically compute the cCFD for multibody potentials. Finally, we exercise the theory on a coiled–coil structural protein.

## 2. Irving–Kirkwood theory: force decomposition and indefiniteness

Let us briefly review the derivation of the stress tensor in the Irving–Kirkwood theory. In this framework, the continuum density field is defined as

$$\rho(\boldsymbol{x}) = \sum_{\alpha=1}^{N} \langle m^\alpha \delta(\boldsymbol{r}^\alpha - \boldsymbol{x})\rangle, \tag{1}$$

where $\langle\cdot\rangle$ stands for an ensemble average over a non-equilibrium statistical-mechanics distribution, $m^\alpha$ and $\boldsymbol{r}^\alpha$ are the mass and position of particle $\alpha$, $\delta(\boldsymbol{x})$ is the 3D Dirac distribution centered at $\boldsymbol{0}$, and $N$ is the total number of particles in the system. Invoking the equivalence between the macroscopic momentum $\rho(\boldsymbol{x})\boldsymbol{v}(\boldsymbol{x})$ and the microscopic momentum $\sum_\alpha^N \langle m^\alpha \boldsymbol{v}^\alpha \delta(\boldsymbol{r}^\alpha - \boldsymbol{x})\rangle$, the continuum velocity field is defined as

$$\boldsymbol{v}(\boldsymbol{x}) = \frac{1}{\rho(\boldsymbol{x})} \sum_{\alpha=1}^{N} \langle m^\alpha \boldsymbol{v}^\alpha \delta(\boldsymbol{r}^\alpha - \boldsymbol{x})\rangle, \tag{2}$$

where $\boldsymbol{v}^\alpha$ is the velocity of particle $\alpha$. These two fields satisfy the continuity equation $\partial\rho/\partial t + \rho\nabla\cdot\boldsymbol{v} = 0$, expressing balance of mass in continuum mechanics, where $\nabla\cdot$ stands for the divergence operator. In the absence of external forces, the continuum balance of linear momentum requires that

$$\nabla\cdot\boldsymbol{\sigma}(\boldsymbol{x}) = \rho(\boldsymbol{x})\frac{d\boldsymbol{v}(\boldsymbol{x})}{dt}. \tag{3}$$

After invoking Liouville's equation, one finds that for a system in mechanical equilibrium (Admal and Tadmor, 2010; Tadmor and Miller, 2011)

$$\nabla\cdot\boldsymbol{\sigma}(\boldsymbol{x}) = -\nabla\cdot\left(\sum_{\alpha=1}^{N} \langle m^\alpha \boldsymbol{v}^\alpha \otimes \boldsymbol{v}^\alpha \delta(\boldsymbol{r}^\alpha - \boldsymbol{x})\rangle\right) + \sum_{\alpha=1}^{N} \langle \boldsymbol{F}^\alpha \delta(\boldsymbol{r}^\alpha - \boldsymbol{x})\rangle, \tag{4}$$

where $\boldsymbol{F}^\alpha$ is the force on particle $\alpha$ and $\boldsymbol{a}\otimes\boldsymbol{b}$ denotes the dyadic product of vectors $\boldsymbol{a}$ and $\boldsymbol{b}$.

As discussed next, it is possible to obtain a statistical-mechanics expression of the right-hand side of Eq. (4) as the divergence of a tensor. Therefore, this expression provides a connection between the statistical mechanics of the particle system and the continuum stress tensor. However, this equation clearly provides a non-unique definition of $\boldsymbol{\sigma}$ since given