Reviewing the roots of continuum formulations in molecular systems. Part II: Energy and angular momentum balance equations

Denis Davydov and Paul Steinmann

Applied Mechanics, University of Erlangen, Erlangen, Germany

Received 27 February 2013; accepted 15 April 2013

Abstract

This paper is the second part of a series dedicated to reviewing the fundamental link between discrete and continuum formulations, which is established by space averaging followed by probability density averaging. On obtaining the continuum balance laws of mass and linear momentum in the part I, here the balance laws of angular momentum and energy are re-derived from a discrete (atomistic/molecular) description. Different approaches (explicit and implicit) for the consideration of the potential energy are reviewed. Thereby for the explicit approach ambiguous possibilities for the localization of the potential energy are briefly discussed. Thereby we conclude that the explicit approach is preferable from the practical application point of view, however it becomes cumbersome when applied to multi-body interactions systems, whereas the implicit approach has no ambiguity in the localization of the potential energy to each particle and is easily applicable to any multi-body potential. Possible solutions for continuum fluxes (couple stresses, heat flux) are postponed until part III of the series.

Keywords

Molecular mechanics, continuum mechanics, statistical mechanics, balance equations, averaging

1. Introduction

Recent progress in the modelling of complex structures at the nano-scale using molecular dynamics (MD) renewed the interest in linking atomistic/molecular descriptions to continuum mechanics. One of the motivations is to enhance and to develop methods that concurrently couple discrete and continuum formulations (see, for example, [1–7]). Thereby, different formulations are used in different parts of a domain, which allows to achieve a very detailed (atomistic/molecular) description of phenomena in regions of interest (e.g. in the vicinity of a crack) and a less detailed but computationally much more efficient continuum description elsewhere.

In order to apply the fundamentally different discrete and continuum descriptions concurrently, a suited methodology to bridge these approaches is required. One of the possibilities to link a discrete particle system and a continuum dates back to the works of Irving and Kirkwood [8] and Noll [9]. Nowadays there is a growing interest in this topic [10–16], yet in the scientific community there are still a lot of debated issues, probably the most important one being the atomistic expression for the Cauchy stress. Thus, the balance laws of mass and linear momentum are most often considered, whereas the balance laws of angular momentum and energy are usually skipped in the procedure of linking the discrete system to the continuum. In those rare publications which discuss the latter balance equations, different researchers yet have different views on the link between

Corresponding author:

Paul Steinmann, Applied Mechanics, University of Erlangen, Egerlandstraße 5, Erlangen 91058, Germany.
Email: paul.steinmann@lrm.uni-erlangen.de

the two approaches. Murdoch and Bedeaux [17] do not explicitly derive the rate of potential energy from the underlying discrete model, whereas Noll [9] explicitly defines the continuum density of potential energy which is used to derive the balance of energy. In the latter case one has to assign/distribute a multi-body potential energy to each particle, which is generally ambiguous as discussed in [18–20]. The two approaches to derive the balance of energy will be denoted in the following as either implicit or explicit, respectively. We aim to point out the main differences between the two approaches and their possible limitations.

This paper is a second part of a series devoted to the link between atomistic and continuum descriptions, which follows the ideas pioneered in [8, 9]. In the first part [21] we carefully discussed the basics of particle mechanics and its balance laws. That allowed us to draw important conclusions on central interactions in systems of rotation-free particles. Continuum fields were introduced as space-probability averaged atomistic quantities. The machinery of statistical physics was used to derive the general balance equations of thus-defined fields. Using this, the balance equations of mass and linear momentum were derived. In this contribution the balances of energy and angular momentum are considered. For the explicit approach the localization of the potential energy is briefly discussed for two- and three-point potentials. Finally, based on the results obtained in part I [21] we derive the balance of energy (explicit and implicit formulations) and angular momentum.

This paper has the following structure. In Section 2, we introduce the notation for particle systems and recall what properties are attributed to each particle. In Section 3, we remind the reader the basic results of [21] which will be used here. Having performed these preparation steps, we develop the balance of energy and angular momentum in Sections 4 and 5, respectively, followed by a discussion and some conclusions.

2. Particle dynamics

In [21] we discussed in detail the dynamics of particle systems including Euler laws, Lagrangian and Hamiltonian representations and the balance of energy. Here, we briefly recall the mathematical structures which are associated with each particle as well as the balance laws they follow.

In what follows, we consider a system with $N = \text{constant}$ particles with translational degrees of freedom (DoFs) only, i.e. each particle α has neither internal structure nor additional DoFs and is endowed with mass m^α and (linear) momentum $\mathbf{p}^\alpha$ only. The corresponding position vector for a particle α in Euclidean space is denoted by

$$\mathbf{x}^\alpha \in \mathbb{E}^3. \quad (1)$$

The motion of the particle α is described by a position map $\mathbf{y}^\alpha$

$$\mathbf{x}^\alpha \Leftarrow \mathbf{y}^\alpha(\tau) \quad \text{with} \quad \mathbf{y}^\alpha : \tau \mapsto \mathbf{x}^\alpha, \mathbb{R}_+ \rightarrow \mathbb{E}^3 \quad (2)$$

where τ denotes the fast time variable of the (possibly erratic) particle motion. For convenience we abbreviate the velocity of the particle by

$$\mathbf{v}^\alpha := \mathbf{x}_{;\tau}^\alpha \quad (3)$$

where $_{;\tau}$ denotes (absolute) differentiation in time. Next, the following quantities are associated with particle α :

- kinetic energy

$$k^\alpha = \frac{1}{2} m^\alpha |\mathbf{v}^\alpha(\tau)|^2; \quad (4)$$

- linear momentum

$$\mathbf{p}^\alpha = \frac{\partial k^\alpha}{\partial \mathbf{v}^\alpha} = m^\alpha \mathbf{v}^\alpha(\tau); \quad (5)$$

- angular momentum with respect to a fixed point in space $\mathbf{y}$

$$\mathbf{l}^\alpha = [\mathbf{x}^\alpha(\tau) - \mathbf{y}] \times \mathbf{p}^\alpha(\tau). \quad (6)$$

Then the balance (conservation) of mass for each particle α reads

$$m_{;\tau}^\alpha = 0. \quad (7)$$

Thus, we do not consider any physical phenomena which might lead to the change of mass (such as radioactive decay). The balance of linear momentum (second Newton law) in an inertial reference system reads

$$\mathbf{p}_{;\tau}^\alpha = \mathbf{f}^\alpha(\tau) \quad (8)$$

where $\mathbf{f}^\alpha(\tau)$ are (possibly) highly oscillatory forces in the fast time variable. Such forces are conventionally decomposed into external and internal contributions with respect to the considered particle system

$$\mathbf{f}^\alpha = \mathbf{f}_{\text{int}}^\alpha(\tau) + \mathbf{f}_{\text{ext}}^\alpha(\tau). \quad (9)$$

Internal forces are due to the interactions between the particles which have to obey Newton's third law, see [21]:

$$\mathbf{f}_{\text{int}}^\alpha = \sum_{\beta} \mathbf{f}^{\alpha\beta}(\tau) \quad \text{with} \quad \mathbf{f}^{\alpha\beta} = -\mathbf{f}^{\beta\alpha} \quad (10)$$

whereas external forces represent the environment of the considered particle system.

Inter-particle distance vectors and velocities are denoted by

$$\mathbf{x}^{\alpha\beta} = \mathbf{x}^\alpha - \mathbf{x}^\beta \quad \text{with} \quad x^{\alpha\beta} = |\mathbf{x}^{\alpha\beta}| \quad (11)$$

and

$$\mathbf{v}^{\alpha\beta} = \mathbf{x}_{,\tau}^{\alpha\beta} = \mathbf{v}^\alpha - \mathbf{v}^\beta, \quad (12)$$

respectively.

The balance of angular momentum for a single particle follows from Newton's second law:

$$\mathbf{l}_{,\tau}^\alpha = \mathbf{m}^\alpha(\tau) \quad \text{with} \quad \mathbf{m}^\alpha = [\mathbf{x}^\alpha(\tau) - \mathbf{y}] \times \mathbf{f}^\alpha(\tau), \quad (13)$$

where the moments of forces with respect to $\mathbf{y}$ are decomposed into the external and the internal contributions as

$$\begin{aligned} \mathbf{m}^\alpha &= \mathbf{m}_{\text{int}}^\alpha(\tau) + \mathbf{m}_{\text{ext}}^\alpha(\tau), \\ \mathbf{m}_{\text{int}}^\alpha &= [\mathbf{x}^\alpha(\tau) - \mathbf{y}] \times \mathbf{f}_{\text{int}}^\alpha(\tau) = [\mathbf{x}^\alpha(\tau) - \mathbf{y}] \times \sum_{\beta} \mathbf{f}^{\alpha\beta}(\tau), \\ \mathbf{m}_{\text{ext}}^\alpha &= [\mathbf{x}^\alpha(\tau) - \mathbf{y}] \times \mathbf{f}_{\text{ext}}^\alpha(\tau). \end{aligned} \quad (14)$$

Similar to the balance of angular momentum, the rate of kinetic energy (which we could denote as a "balance" of kinetic energy) for a single particle follows from Newton's second law:

$$\mathbf{k}_{,\tau}^\alpha = \mathbf{p}^\alpha(\tau) \quad \text{with} \quad \mathbf{p}^\alpha = \mathbf{x}_{,\tau}^\alpha(\tau) \cdot \mathbf{f}^\alpha(\tau) \quad (15)$$

whereby the power of forces can also be decomposed into the external and the internal contributions as

$$\begin{aligned} \mathbf{p}^\alpha &= \mathbf{p}_{\text{ext}}^\alpha(\tau) - \mathbf{p}_{\text{int}}^\alpha(\tau), \\ \mathbf{p}_{\text{int}}^\alpha &= -\mathbf{v}^\alpha(\tau) \cdot \mathbf{f}_{\text{int}}^\alpha(\tau) = -\mathbf{v}^\alpha(\tau) \cdot \sum_{\beta} \mathbf{f}^{\alpha\beta}(\tau), \\ \mathbf{p}_{\text{ext}}^\alpha &= \mathbf{v}^\alpha(\tau) \cdot \mathbf{f}_{\text{ext}}^\alpha(\tau). \end{aligned} \quad (16)$$

Note that we chose the sign of $\mathbf{p}_{\text{int}}^\alpha$ intentionally to later achieve a better comparison with the stress power in a continuum description.

Remark 1 This might give the reader the impression that Newton's second law for a single particle is enough to consider the behavior of a system made of several particles. However, that is not the case. Interactions of the arbitrary system of particles with its environment have to be defined, resulting in the balance of energy and the balance of angular momentum for the total system. For a further discussion, we refer the reader to part I of this series [21].

3. Space-probability averaging

In this section we introduce the notation and the basic results obtained from the first part of this series [21].

3.1. Probability density function

The state of a particle system is fully defined by the phase space coordinates denoted as

$$\mathbf{z} = \{\mathbf{x} = \{\mathbf{x}^\alpha\}, \mathbf{p} = \{\mathbf{p}^\alpha\}\} \in \mathbb{E}^{3N} \times \mathbb{E}^{3N}. \quad (17)$$

The motion of the system is then described by the corresponding position and (linear) momentum map

$$\mathcal{P} \ni \mathbf{z} \leftarrow \{\mathbf{y}(\tau), \mathbf{m}\mathbf{v}(\tau)\} \quad \text{with} \quad \{\mathbf{y}, \mathbf{m}\mathbf{v}\} : \tau \mapsto \mathbf{z}, \mathbb{R}_+ \rightarrow \mathbb{E}^{3N} \times \mathbb{E}^{3N}. \quad (18)$$

where $\mathcal{P}$ denotes phase space.

In statistical physics the behavior of the system is fully described by a probability density function

$$\mathbf{W} = \mathbf{W}(\mathbf{z}, \tau) \quad (19)$$

which for convenience satisfies the normalization condition

$$\int_{\mathcal{P}} \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} = 1 \quad (20)$$

and represents the probability of a state $\mathbf{z}$ per unit volume in phase space $\mathcal{P}$. The expectation value of a (dynamical) quantity $f = f(\mathbf{z})$ is then defined as

$$\langle f(\mathbf{z}) \rangle_{\mathcal{P}} := \int_{\mathcal{P}} f(\mathbf{z}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z}. \quad (21)$$

Here $\langle \bullet \rangle_{\mathcal{P}}$ denotes probability averaging with the averaging kernel defined by the probability density $\mathbf{W}(\mathbf{z}, \tau)$.

The link between the discrete system and the continuum is achieved as follows. Let us define the δ -distribution of an extensive (additive) property g^α as

$$g_\delta(\mathbf{z}, \xi) := \sum_{\alpha} g^\alpha(\mathbf{z}) \delta(\mathbf{x}^\alpha - \xi). \quad (22)$$

The total property density is then introduced as

$$\overset{\pi}{g}(\xi, \tau) := \langle g_\delta(\mathbf{z}, \xi) \rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} g^\alpha(\mathbf{z}) \delta(\mathbf{x}^\alpha - \xi) \right\rangle_{\mathcal{P}}. \quad (23)$$

Note, that this quantity is a function (or rather δ -distribution) of the rough space variable ξ . That is, the usage of the delta function for localization will result in a very “rough” field in ξ since only those particles which are situated at $\mathbf{x}^\alpha \equiv \xi$ (in a statistical sense) will contribute to the continuum field. Therefore, the total property density g is introduced using a general averaging kernel w as

$$g(\mathbf{x}, \tau) := \left\langle \overset{\zeta}{g}(\mathbf{z}, \mathbf{x}) \right\rangle_{\mathcal{P}} := \left\langle \sum_{\alpha} g^\alpha(\mathbf{z}) w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}} \quad (24)$$

where the (space) ζ -distribution of the extensive (additive) property g^α is defined as

$$\overset{\zeta}{g}(\mathbf{z}, \mathbf{x}) := \sum_{\alpha} \overset{\zeta}{g}^\alpha(\mathbf{z}, \mathbf{x}) := \sum_{\alpha} g^\alpha(\mathbf{z}) w(\mathbf{x}^\alpha - \mathbf{x}) = \int_S g_\delta(\mathbf{z}, \xi) w(\xi - \mathbf{x}) d\xi = \langle g_\delta(\mathbf{z}, \xi) \rangle_S. \quad (25)$$

Here $\langle \bullet \rangle_S$ denotes space averaging with averaging kernel $w(\xi - \mathbf{x})$, whereby $\mathbf{x}$ denotes the smooth space variable.

Based on the Liouville theorem we have shown in [21] that the partial time derivative of the total property density can be expressed as

$$g_{,\tau}(\mathbf{x}, \tau) = \left\langle \sum_{\alpha} \overset{\zeta}{g}_{,\tau}^\alpha(\mathbf{z}, \mathbf{x}) \right\rangle_{\mathcal{P}} - \text{div} \left(\left\langle \sum_{\alpha} \overset{\zeta}{g}^\alpha(\mathbf{z}, \mathbf{x}) \otimes \mathbf{v}^\alpha \right\rangle_{\mathcal{P}} \right) \quad (26)$$

whereby the abbreviation

$$\frac{\varsigma}{\mathbf{g};\tau}^\alpha := \mathbf{g}_{;\tau}^\alpha(\mathbf{z})\mathbf{w}(\mathbf{x}^\alpha - \mathbf{x}) \quad (27)$$

denotes the (space) ς -averaged rate of the property associated with the particle α , and $_{,\tau}$ denotes the partial time derivative at fixed $\mathbf{x}$.

3.2. Continuum fields, balance of mass and linear momentum

Following the procedure outlined in the above, in part I of this series [21] the following continuum fields were introduced:

- mass density

$$\varrho(\mathbf{x}, \tau) := \langle \mathbf{m}_\delta(\mathbf{z}, \xi) \rangle_S \big|_{\mathcal{P}} = \int_{\mathcal{P}} \sum_{\alpha} m^{\alpha} \mathbf{w}(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z}; \quad (28)$$

- linear momentum density

$$\mathbf{p}(\mathbf{x}, \tau) := \langle \mathbf{p}_\delta(\mathbf{z}, \xi) \rangle_S \big|_{\mathcal{P}} = \int_{\mathcal{P}} \sum_{\alpha} \mathbf{p}^{\alpha} \mathbf{w}(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z}; \quad (29)$$

- continuum velocity

$$\mathbf{v}(\mathbf{x}, \tau) := \frac{\mathbf{p}(\mathbf{x}, \tau)}{\varrho(\mathbf{x}, \tau)} = \frac{\int_{\mathcal{P}} \sum_{\alpha} \mathbf{p}^{\alpha} \mathbf{w}(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z}}{\int_{\mathcal{P}} \sum_{\alpha} m^{\alpha} \mathbf{w}(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z}}; \quad (30)$$

- continuum fluctuation of the particle velocity

$$\tilde{\mathbf{v}}^{\alpha}(\mathbf{x}, \tau) := \mathbf{v}^{\alpha} - \mathbf{v}(\mathbf{x}, \tau), \quad (31)$$

which satisfies [21]

$$\left\langle \sum_{\alpha} m^{\alpha} \tilde{\mathbf{v}}^{\alpha}(\mathbf{x}, \tau) \mathbf{w}(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} = 0; \quad (32)$$

- Particle kinetic energy tensor and the particle diffusive momentum flux

$$\mathbf{k}^{\alpha} = \frac{1}{2} \mathbf{p}^{\alpha} \otimes \mathbf{v}^{\alpha} \quad \text{and} \quad \tilde{\mathbf{s}}^{\alpha} = \frac{1}{2} \mathbf{p}^{\alpha} \otimes \tilde{\mathbf{v}}^{\alpha}(\mathbf{x}, \tau). \quad (33)$$

It was shown that the continuum kinetic energy tensor satisfies

$$\boldsymbol{\kappa} := \frac{1}{2} \mathbf{p}(\mathbf{x}, \tau) \otimes \mathbf{v}(\mathbf{x}, \tau) = \langle \langle \mathbf{k}_\delta(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} - \langle \langle \tilde{\mathbf{s}}_\delta(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_S \rangle_{\mathcal{P}} =: \mathbf{k} - \tilde{\mathbf{s}}. \quad (34)$$

and

$$\tilde{\mathbf{s}} := \langle \langle \tilde{\mathbf{s}}_\delta(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_S \rangle_{\mathcal{P}} = \langle \sum_{\alpha} \frac{1}{2} m^{\alpha} \tilde{\mathbf{v}}^{\alpha} \otimes \tilde{\mathbf{v}}^{\alpha} \mathbf{w}(\mathbf{x}^{\alpha} - \mathbf{x}) \rangle_{\mathcal{P}}. \quad (35)$$

Using the quantities defined in the above the following two balance equations were obtained:

- balance of mass

$$\varrho_{,\tau} + \operatorname{div} \mathbf{p} = 0; \quad (36)$$

- balance of linear momentum

$$\mathbf{p}_{,\tau} + \operatorname{div}(\mathbf{p} \otimes \mathbf{v}) = \operatorname{div} \mathbf{s}(\mathbf{x}, \tau) + \mathbf{b}(\mathbf{x}, \tau). \quad (37)$$

Here the linear momentum flux $\mathbf{s}$ (the Cauchy stress) and the linear momentum source $\mathbf{b}$ are defined via

$$\operatorname{div} \hat{\mathbf{s}} := \operatorname{div}(\mathbf{s} + 2\tilde{\mathbf{s}}) := \langle \langle \mathbf{f}_{\text{int},\delta}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} \mathbf{f}_{\text{int}}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} \quad (38)$$

and

$$\mathbf{b} := \langle \langle \mathbf{f}_{\text{ext},\delta}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} \mathbf{f}_{\text{ext}}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}, \quad (39)$$

respectively.

Remark 2 In order to obtain the expression for the stresses, Equation (38) has to be solved for $\mathbf{s}$. Different solution strategies for such equations and their results are discussed in part III of this series [22].

4. Balance of energy

4.1. Kinetic energy

Following space-probability averaging (Section 3), the kinetic energy density is introduced as

$$k(\mathbf{x}, \tau) = \langle \langle \mathbf{k}_{\delta}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} = \int_{\mathcal{P}} \sum_{\alpha} \mathbf{k}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z}. \quad (40)$$

It follows from Equation (34) that the continuum kinetic energy density equals

$$\kappa = \operatorname{tr}(\boldsymbol{\kappa}) = \frac{1}{2} \varrho(\mathbf{x}, \tau) |\mathbf{v}(\mathbf{x}, t)|^2 = \langle \langle \mathbf{k}_{\delta}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} - \langle \langle \tilde{\mathbf{s}}_{\delta}(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_S \rangle_{\mathcal{P}} = k - \tilde{s}. \quad (41)$$

Note, that the total continuum kinetic energy equals the statistical average of the total particle kinetic energy minus the diffusive kinetic energy

$$\int_S \kappa d\mathbf{x} = \int_{\mathcal{P}} \sum_{\alpha} [\mathbf{k}^{\alpha} - \tilde{\mathbf{s}}^{\alpha}] \int_S w(\mathbf{x}^{\alpha} - \mathbf{x}) d\mathbf{x} \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} = \left\langle \mathbf{K} - \sum_{\alpha} \tilde{\mathbf{s}}^{\alpha} \right\rangle_{\mathcal{P}}. \quad (42)$$

Using Equation (40) in Equation (26) and recalling Equation (15), the rate of kinetic energy follows as

$$k_{,\tau} + \operatorname{div} \left\langle \sum_{\alpha} \mathbf{k}^{\alpha} \mathbf{x}_{,\tau}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} \mathbf{p}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}. \quad (43)$$

Next the term on the right-hand side is developed using the decomposition of the velocity into fluctuation and continuum parts (31), and the forces into external and internal parts (9):

$$\begin{aligned} \left\langle \sum_{\alpha} \mathbf{p}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} &= \left\langle \sum_{\alpha\beta} \mathbf{v}^{\alpha} \cdot \mathbf{f}^{\alpha\beta} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} + \left\langle \sum_{\alpha} \mathbf{v}^{\alpha} \cdot \mathbf{f}_{\text{ext}}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} \\ &= \left\langle \sum_{\alpha\beta} \mathbf{v}^{\alpha} \cdot \mathbf{f}^{\alpha\beta} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} + \mathbf{v} \cdot \mathbf{b} + r \end{aligned} \quad (44)$$

where we have defined a space-probability averaged external fluctuation work (heat source) as

$$r := \langle \langle \tilde{\mathbf{p}}_{\delta}^{\text{ext}}(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_S \rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} \tilde{\mathbf{v}}^{\alpha}(\mathbf{x}, \tau) \cdot \mathbf{f}_{\text{ext}}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}. \quad (45)$$

Now we switch our attention to the term under the divergence, using Equation (32) and Equation (35) one can rewrite it as follows

$$\begin{aligned} \left\langle \sum_{\alpha} k^{\alpha} \tilde{\mathbf{v}}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} &= \left\langle \sum_{\alpha} \frac{1}{2} m^{\alpha} \mathbf{v}^{\alpha} \cdot \mathbf{v}^{\alpha} \tilde{\mathbf{v}}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} = \\ &= \left\langle \sum_{\alpha} \frac{1}{2} m^{\alpha} \tilde{\mathbf{v}}^{\alpha} \cdot \tilde{\mathbf{v}}^{\alpha} \tilde{\mathbf{v}}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} + \left\langle \sum_{\alpha} \frac{1}{2} m^{\alpha} \mathbf{v} \cdot \tilde{\mathbf{v}}^{\alpha} \tilde{\mathbf{v}}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} + \\ &= \left\langle \sum_{\alpha} \frac{1}{2} m^{\alpha} \tilde{\mathbf{v}}^{\alpha} \cdot \mathbf{v} \tilde{\mathbf{v}}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} + \left\langle \sum_{\alpha} \frac{1}{2} m^{\alpha} \mathbf{v} \cdot \mathbf{v} \tilde{\mathbf{v}}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} =: \\ &= -2\tilde{\mathbf{q}} + 2\mathbf{v} \cdot \tilde{\mathbf{s}} \end{aligned} \quad (46)$$

with the diffusive energy flux defined as

$$\tilde{\mathbf{q}} := -\frac{1}{2} \left\langle \sum_{\alpha} \tilde{\mathbf{s}}^{\alpha}(\mathbf{x}, \tau) \tilde{\mathbf{v}}^{\alpha}(\mathbf{x}, \tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}. \quad (47)$$

It then follows that

$$\begin{aligned} \left\langle \sum_{\alpha} k^{\alpha} \mathbf{x}_{;\tau}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} &= \left\langle \sum_{\alpha} k^{\alpha} \tilde{\mathbf{v}}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} + \mathbf{v} \left\langle \sum_{\alpha} k^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} \\ &= -2\tilde{\mathbf{q}} + 2\mathbf{v} \cdot \tilde{\mathbf{s}} + [\kappa + \tilde{\mathbf{s}}]\mathbf{v}. \end{aligned} \quad (48)$$

Using Equation (44), Equation (41) and Equation (48) in Equation (43) leads finally to

$$\mathbf{v} \cdot \mathbf{b} + r + \left\langle \sum_{\alpha\beta} \mathbf{v}^{\alpha} \cdot \mathbf{f}^{\alpha\beta} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} = [\kappa + \tilde{\mathbf{s}}]_{;\tau} + \operatorname{div}(-2\tilde{\mathbf{q}} + 2\mathbf{v} \cdot \tilde{\mathbf{s}} + [\kappa + \tilde{\mathbf{s}}]\mathbf{v}). \quad (49)$$

Note that $[\kappa + \tilde{\mathbf{s}}]_{;\tau} + \operatorname{div}([\kappa + \tilde{\mathbf{s}}]\mathbf{v})$ is related to the total time derivative of $[\kappa + \tilde{\mathbf{s}}]$. In a continuum setting similar relations hold for the rate of other quantities. Indeed, using the balance of mass Equation (36) for a tensorial quantity $\mathbf{a}$ of any order we can prove the following:¹

$$\begin{aligned} [\varrho \mathbf{a}]_{;\tau} + \operatorname{div}(\varrho \mathbf{a} \mathbf{v}) &= \varrho_{;\tau} \mathbf{a} + \varrho \mathbf{a}_{;\tau} + \mathbf{a} \operatorname{div}(\varrho \mathbf{v}) + \operatorname{grad} \mathbf{a} \cdot \varrho \mathbf{v} \\ &= \mathbf{a}[\varrho_{;\tau} + \operatorname{div} \mathbf{p}] + \varrho[\mathbf{a}_{;\tau} + \operatorname{grad} \mathbf{a} \cdot \mathbf{v}] \\ &= \varrho \mathbf{a}_{;\tau}. \end{aligned} \quad (50)$$

Using this intermediate result, it is easy to see that

$$\kappa_{;\tau} + \operatorname{div}(\kappa \mathbf{v}) = \varrho \frac{1}{2} [\mathbf{v} \cdot \mathbf{v}]_{;\tau} = \varrho \mathbf{v} \cdot \mathbf{v}_{;\tau}. \quad (51)$$

Finally, recall the following tensorial relation for an arbitrary vector $\mathbf{a}$ and a second-order tensor $\mathbf{A}$

$$\operatorname{div}(\mathbf{a} \cdot \mathbf{A}) = \mathbf{a} \cdot \operatorname{div} \mathbf{A} + \mathbf{A} : \operatorname{grad} \mathbf{a}. \quad (52)$$

4.2. Implicit formulation

Following Murdoch and Bedeaux [17] one can derive the balance of energy as follows. First, we develop the term related to the interaction forces in Equation (44) using the decomposition of the velocity into the fluctuation and the continuum parts Equation (31) together with Equation (38):

$$\left\langle \sum_{\alpha\beta} \mathbf{v}^{\alpha} \cdot \mathbf{f}^{\alpha\beta} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} = \mathbf{v} \cdot \left\langle \sum_{\alpha\beta} \mathbf{f}^{\alpha\beta} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} + \left\langle \sum_{\alpha\beta} \tilde{\mathbf{v}}^{\alpha} \cdot \mathbf{f}^{\alpha\beta} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} \quad (53)$$

$$=: \mathbf{v} \cdot \operatorname{div}(\mathbf{s} + 2\tilde{\mathbf{s}}) - h, \quad (54)$$

where the space-probability averaged internal fluctuation work is defined as

$$h := \langle \langle \tilde{p}_\delta^{\text{int}}(\mathbf{z}, \boldsymbol{\xi}; \mathbf{x}, \tau) \rangle_S \rangle_{\mathcal{P}} = - \left\langle \sum_{\alpha} \tilde{\mathbf{v}}^{\alpha}(\mathbf{x}, \tau) \cdot \mathbf{f}_{\text{int}}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}. \quad (55)$$

Using Equation (54) in Equation (49) leads to

$$\begin{aligned} \mathbf{v} \cdot \mathbf{b} + \mathbf{v} \cdot \text{div}(\mathbf{s} + 2\tilde{\mathbf{s}}) + r - h &= [\kappa + \tilde{s}]_{,\tau} + \text{div}(-2\tilde{\mathbf{q}} + 2\mathbf{v} \cdot \tilde{\mathbf{s}} + [\kappa + \tilde{s}]\mathbf{v}) \\ &= [\kappa + \tilde{s}]_{,\tau} + \text{div}([\kappa + \tilde{s}]\mathbf{v}) - \text{div}(2\tilde{\mathbf{q}}) + \text{div}(2\tilde{\mathbf{s}}) \cdot \mathbf{v} + 2\tilde{\mathbf{s}} : \text{grad}\mathbf{v}, \end{aligned} \quad (56)$$

that is

$$\mathbf{v} \cdot \mathbf{b} + \mathbf{v} \cdot \text{div}\mathbf{s} + r - h = [\kappa + \tilde{s}]_{,\tau} + \text{div}([\kappa + \tilde{s}]\mathbf{v}) - \text{div}(2\tilde{\mathbf{q}}) + 2\tilde{\mathbf{s}} : \text{grad}\mathbf{v}. \quad (57)$$

We note that we obtain a representation that is coherent with the results of other researchers [12, 17].

Next, we express h using the divergence of the vector quantity $\hat{\mathbf{q}}_i$ and yet another scalar quantity q :

$$h = \langle \langle \tilde{p}_\delta^{\text{int}}(\mathbf{z}, \boldsymbol{\xi}; \mathbf{x}, t) \rangle_{\mathcal{P}} \rangle_S =: \text{div}\hat{\mathbf{q}}_i + q(\mathbf{x}, \tau). \quad (58)$$

Using Equation (58), Equation (57) can be simplified to

$$[\kappa + \nu + \tilde{s}]_{,\tau} + \text{div}([\kappa + \nu + \tilde{s}]\mathbf{v}) = p_{\text{ext}}(\mathbf{x}, \tau) + q_{\text{ext}}(\mathbf{x}, \tau) \quad (59)$$

where the mechanical and the thermal power read

$$p_{\text{ext}} := \mathbf{v}(\mathbf{x}, \tau) \cdot \mathbf{b}(\mathbf{x}, \tau) + \text{div}(\mathbf{v}(\mathbf{x}, \tau) \cdot \mathbf{s}(\mathbf{x}, \tau)) \quad (60)$$

$$q_{\text{ext}} := r(\mathbf{x}, \tau) - \text{div}\mathbf{q}_i(\mathbf{x}, \tau) \quad (61)$$

and the heat flux for the implicit approach is defined as

$$\mathbf{q}_i(\mathbf{x}, \tau) := \hat{\mathbf{q}}_i(\mathbf{x}, \tau) - 2\tilde{\mathbf{q}}(\mathbf{x}, \tau) \quad (62)$$

The rate of the potential energy is implicitly (thus the name for this formulation) introduced as

$$v_{,\tau} + \text{div}(\nu\mathbf{v}) := \text{grad}\mathbf{v}(\mathbf{x}, \tau) : \hat{\mathbf{s}}(\mathbf{x}, \tau) + q(\mathbf{x}, \tau). \quad (63)$$

Remark 3 Note, that the continuum potential energy is defined *implicitly*. In other words, the current value of the continuum potential energy can only be obtained by integrating Equation (63) and is not directly expressible in terms of atomistic quantities. Moreover, this equation depends on the solutions of Equation (58) and Equation (38).

Incorporation of the balances of linear momentum Equation (37) together with Equation (50) and Equation (51) allows eventually rewriting Equation (59) as

$$[\nu + \tilde{s}]_{,\tau} + \text{div}([\nu + \tilde{s}]\mathbf{v}) = r - \text{div}\mathbf{q}_i + \mathbf{s} : \text{grad}\mathbf{v}. \quad (64)$$

Note, that the exact expressions for heat fluxes $\mathbf{q}_i$ depends on the solution of Equation (58), moreover $\nu + \tilde{s}$ may be considered as internal energy.

4.3. Potential energy

In the previous section the density of potential energy was introduced implicitly via an additional differential equation which has to be integrated (Equation (63)). An alternative approach (which was originally used in [8, 9]) is to explicitly introduce the density of potential energy in terms of atomistic quantities. In order to do so one has to distribute the potential energy V of the system between individual particles $\mathbf{v}^{\alpha}$ in such a way that $V = \sum_{\alpha} \mathbf{v}^{\alpha}$ holds. We call this process the “localization” of potential energy. Note, that the potential energy

of particle interaction is inherently attributed to a group of particles (two or more) rather than a single particle (like kinetic energy). The continuum density of potential energy is then introduced based on $\mathbf{v}^\alpha$, as we shall see in a moment.

The potential energy of the system $\mathbf{V}$ depends on the positions of all particles and does not depend explicitly on time. Since the motion has to be independent of the observer (system of coordinates with a reference time), it is easily concluded that the potential energy can depend only on the scalar relative positions of the particles, that is

$$\mathbf{V} = \mathbf{V}(\mathbf{x}^{\alpha\beta}), \quad \alpha, \beta = \overline{1, N}. \quad (65)$$

Here we exclusively consider the internal part of the potential energy for simplicity. Note that, in practice, the potential energy of the system is given in terms of two-, three- and four-point potentials. For a discussion of potential energy and possible non-uniqueness of its representation in case of five and more particles we refer reader to [13].

Recall, that the internal forces are obtained as

$$\mathbf{f}_{\text{int}}^\alpha(\tau) = -\nabla_{\mathbf{x}_\alpha} \mathbf{V}. \quad (66)$$

Using Equation (65) the force acting on each particle can be written as

$$\begin{aligned} \mathbf{f}_{\text{int}}^\alpha(\tau) &= -\nabla_{\mathbf{x}_\alpha} \mathbf{V} \\ &= -\sum_{\beta} \frac{\partial \mathbf{V}}{\partial \mathbf{x}^{\alpha\beta}} \frac{\partial \mathbf{x}^{\alpha\beta}}{\partial \mathbf{x}^\alpha} \cdot \frac{\partial \mathbf{x}^{\alpha\beta}}{\partial \mathbf{x}^\alpha} \\ &= \sum_{\beta} \mathbf{f}^{\alpha\beta}. \end{aligned}$$

with

$$\mathbf{f}^{\alpha\beta} := -\frac{\partial \mathbf{V}}{\partial \mathbf{x}^{\alpha\beta}} \frac{\partial \mathbf{x}^{\alpha\beta}}{\partial \mathbf{x}^\alpha} = -\frac{\partial \mathbf{V}}{\partial \mathbf{x}^{\alpha\beta}} \frac{\mathbf{x}^{\alpha\beta}}{\mathbf{x}^{\alpha\beta}}. \quad (67)$$

Thus, it follows from Equation (65) that the interaction forces are central, i.e. $\mathbf{f}^{\alpha\beta} \sim \mathbf{x}^{\alpha\beta}$.

As we discussed in [21] for a system of point particles with constant mass, the internal interaction force (no matter whether it is conservative or not) for any two particles is required to be aligned along the difference of the position vectors of these particles in order for the angular momentum of a closed isolated system to be conserved (that is one of the main axioms of mechanics which also follows from the invariance of the Lagrangian to the change of observer). In other words, internal forces are central for all interaction potentials of a system of particles with translational DoFs only.

For conservative forces the same conclusion is drawn from the invariance of the potential energy to the observer which results in Equation (67). In the appendix we show as an example how to obtain the central force decomposition for a three-point angle potential.

Following [8, 9] we next consider two-point interaction for the localization of potential energy. For such a case, the potential energy attributed to each particle $\mathbf{v}^\alpha$ can be introduced as

$$\mathbf{v}^\alpha = \frac{1}{2!} \sum_{\beta} \mathbf{v}^{\alpha\beta}(\mathbf{x}^{\alpha\beta}) \quad (68)$$

where $\mathbf{v}^{\alpha\beta}$ is a potential energy of interaction between particles α and β . In other words, the potential energy is equally distributed among interacting particles.

Using Equation (67), the total time derivative of Equation (68) follows as

$$\mathbf{v}_{;\tau}^\alpha = -\frac{1}{2!} \sum_{\beta} \mathbf{f}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta}. \quad (69)$$

Indeed,

$$\mathbf{V} = \sum_{\alpha} \mathbf{v}^\alpha = \frac{1}{2!} \sum_{\alpha\beta} \mathbf{v}^{\alpha\beta}(\mathbf{x}^{\alpha\beta}) \quad (70)$$

and, therefore,

$$\mathbf{f}^{\gamma\delta} = -\frac{1}{2} \sum_{\alpha\beta} \frac{\partial \mathbf{v}^{\alpha\beta}}{\partial \mathbf{x}^{\gamma\delta}} \frac{\partial \mathbf{x}^{\gamma\delta}}{\partial \mathbf{x}^{\gamma\delta}} = -\frac{\partial \mathbf{v}^{\gamma\delta}}{\partial \mathbf{x}^{\gamma\delta}} \frac{\partial \mathbf{x}^{\gamma\delta}}{\partial \mathbf{x}^{\gamma\delta}}. \quad (71)$$

On the other hand

$$\mathbf{v}_{;\tau}^{\alpha} = \frac{1}{2!} \sum_{\beta} \frac{\partial \mathbf{v}^{\alpha\beta}}{\partial \mathbf{x}^{\alpha\beta}} \frac{\partial \mathbf{x}^{\alpha\beta}}{\partial \mathbf{x}^{\alpha\beta}} \cdot \frac{\partial \mathbf{x}^{\alpha\beta}}{\partial \tau}, \quad (72)$$

which together with Equation (71) renders Equation (69).

4.4. Explicit formulation

Next, the continuum potential energy density is introduced as

$$v(\mathbf{x}, \tau) = \int_{\mathcal{P}} \sum_{\alpha} v^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z}. \quad (73)$$

Using Equation (73) in Equation (26), the rate of the potential energy of the system reads

$$v_{;\tau} + \operatorname{div} \left(\left\langle \sum_{\alpha} \mathbf{v}^{\alpha} \mathbf{v}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} \right) = \left\langle \sum_{\alpha} \mathbf{v}_{;\tau}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} = - \left\langle \frac{1}{2} \sum_{\alpha\beta} \mathbf{f}^{\alpha\beta}(\tau) \cdot \mathbf{v}^{\alpha\beta} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}. \quad (74)$$

Remark 4 It is important to note that all of the derivations which are to follow for the explicitly introduced continuum potential energy density heavily depend on the second equality sign in Equation (74), which only holds for two-point potential interactions. A consideration of three-and-more-point interaction potentials results in a much more complicated expression.² There are several works which introduce the continuum potential density for multi-body interactions explicitly via the equal energy localization [19, 20]. This inevitably leads to cumbersome expressions in the balance of energy equation and limits the applicability of Noll's lemmas. In order to compare the explicit and implicit approaches while keeping the mathematical derivations relatively easy to follow, we will in the following consider the localization of potential energy only for two-point interactions.

Denoting the transport energy flux by

$$\mathbf{q}_T := \left\langle \sum_{\alpha} \mathbf{v}^{\alpha}(\mathbf{x}, \tau) \tilde{\mathbf{v}}^{\alpha}(\mathbf{x}, \tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}, \quad (75)$$

equation Equation (74) can be rewritten as

$$v_{;\tau} + \operatorname{div}(v\mathbf{v}) = -\operatorname{div}\mathbf{q}_T - \left\langle \frac{1}{2} \sum_{\alpha\beta} \mathbf{f}^{\alpha\beta}(\tau) \cdot \mathbf{v}^{\alpha\beta} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}. \quad (76)$$

Summing Equation (76) and Equation (49) one obtains

$$[\kappa + v + \tilde{s}]_{;\tau} + \operatorname{div}([\kappa + v + \tilde{s}]\mathbf{v}) = r - \operatorname{div}\mathbf{q}_T + q_0 + \operatorname{div}(2\tilde{\mathbf{q}} - 2\mathbf{v} \cdot \tilde{\mathbf{s}}) + \mathbf{v} \cdot \mathbf{b} \quad (77)$$

where we have defined

$$q_0 := \left\langle \sum_{\alpha\beta} \mathbf{f}^{\alpha\beta}(\tau) \cdot \frac{\mathbf{v}^{\alpha} + \mathbf{v}^{\beta}}{2} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}. \quad (78)$$

Note, that by using the theorem (26) derived in part one [21] we obtain the same results as in [9, 23], however, with somewhat easier mathematical derivations.

Introducing the flux $\mathbf{q}_0$ as

$$\mathbf{q}_0 =: \operatorname{div}(-\mathbf{q}_0 + 2\mathbf{v} \cdot \tilde{\mathbf{s}} + \mathbf{v} \cdot \mathbf{s}) \quad (79)$$

one obtains

$$[\nu + \kappa + \tilde{s}]_{,\tau} + \text{div}([\nu + \kappa + \tilde{s}]\mathbf{v}) = \text{div}(-\mathbf{q}_T - \mathbf{q}_0 + 2\tilde{\mathbf{q}} + \mathbf{v} \cdot \mathbf{s}) + \mathbf{v} \cdot \mathbf{b} + r. \quad (80)$$

Using Equation (52), Equation (51) together with the balance of linear momentum Equation (37), Equation (80) simplifies to

$$[\nu + \tilde{s}]_{,\tau} + \text{div}([\nu + \tilde{s}]\mathbf{v}) = r - \text{div}\mathbf{q}_e + \mathbf{s} : \text{grad}\mathbf{v} \quad (81)$$

where the total flux for the explicit approach is given by

$$\mathbf{q}_e = [\mathbf{q}_T + \mathbf{q}_0] - 2\tilde{\mathbf{q}} =: \hat{\mathbf{q}}_e - 2\tilde{\mathbf{q}}. \quad (82)$$

Comparing the total heat flux of the explicit formulation Equation (82) to the implicit Equation (62), one observes that they differ in terms $\hat{\mathbf{q}}_e$ and $\hat{\mathbf{q}}_i$.

We draw the readers attention to the fact, that Equation (79) has to be solved. Only then the expression for $\mathbf{q}_0$ in terms of the atomistic quantities can be obtained and thus the total heat flux $\mathbf{q}_e$ for the explicit formulation can be evaluated.

The comparison of the heat fluxes of the two approaches (explicit and implicit) is left for part III of the series [22].

5. Balance of angular momentum

First of all, let us introduce several new definitions (see Figure 1): for an arbitrary chosen point with placement $\mathbf{x}_0$, the macroscopic distance (radius vector) is denoted as

$$\mathbf{r}^\alpha = \mathbf{x}^\alpha - \mathbf{x}_0. \quad (83)$$

The distance between each particle position and the considered continuum point is called microscopic distance

$$\bar{\mathbf{r}}^\alpha = \mathbf{x}^\alpha - \mathbf{x}. \quad (84)$$

Finally, we introduce the continuum distance

$$\mathbf{r} = \mathbf{r}^\alpha - \bar{\mathbf{r}}^\alpha = \mathbf{x} - \mathbf{x}_0. \quad (85)$$

The particle macroscopic and the particle microscopic angular momentum are denoted as

$$\mathbf{l}^\alpha = \mathbf{r}^\alpha \times \mathbf{p}^\alpha \quad \text{and} \quad \bar{\mathbf{l}}^\alpha = \bar{\mathbf{r}}^\alpha \times \mathbf{p}^\alpha. \quad (86)$$

The continuum angular momentum is defined as usual by

$$\boldsymbol{\lambda} := \mathbf{r}(\mathbf{x}) \times \mathbf{p}(\mathbf{x}, \tau). \quad (87)$$

Figure 1. A sketch of the introduced distance vectors.

Next, we introduce the angular momentum density with respect to $\mathbf{x}_0$ as

$$\mathbf{l}(\mathbf{x}, \tau) := \int_{\mathcal{P}} \sum_{\alpha} \mathbf{l}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z} \quad (88)$$

and the angular momentum density with respect to $\mathbf{x}$ as

$$\bar{\mathbf{l}}(\mathbf{x}, \tau) = \int_{\mathcal{P}} \sum_{\alpha} \bar{\mathbf{l}}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z}. \quad (89)$$

It is then easy to show that the continuum angular momentum equals the space-probability average of the particle macroscopic minus the particle microscopic angular momentum:

$$\boldsymbol{\lambda} = \langle \langle \mathbf{l}_{\delta}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} - \langle \langle \bar{\mathbf{l}}_{\delta}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} = \mathbf{l} - \bar{\mathbf{l}}, \quad (90)$$

Proof

$$\begin{aligned} \mathbf{l}^{\alpha} &= \mathbf{r} \times \mathbf{p}^{\alpha} + \bar{\mathbf{l}}^{\alpha}, \\ \mathbf{l}_{\delta}(\mathbf{z}, \xi) &= \mathbf{r} \times \mathbf{p}_{\delta}(\mathbf{z}, \xi) + \bar{\mathbf{l}}_{\delta}(\mathbf{z}, \xi), \\ \langle \langle \mathbf{l}_{\delta}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} &= \mathbf{r} \times \mathbf{p}(\mathbf{x}, \tau) + \langle \langle \bar{\mathbf{l}}_{\delta}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}}. \end{aligned}$$

Note, that the total continuum angular momentum of the system equals the statistically averaged total particle momentum minus the microscopic angular momentum

$$\int_S \boldsymbol{\lambda} d\mathbf{x} = \int_{\mathcal{P}} \sum_{\alpha} [\mathbf{l}^{\alpha} - \bar{\mathbf{l}}^{\alpha}] \int_S w(\mathbf{x}^{\alpha} - \mathbf{x}) d\mathbf{x} \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z} = \langle \mathbf{L} - \sum_{\alpha} \bar{\mathbf{l}}^{\alpha} \rangle_{\mathcal{P}}. \quad (91)$$

5.1. Balance of microscopic angular momentum

Using Equation (89) in Equation (26) leads to

$$\bar{\mathbf{l}}_{,\tau} + \operatorname{div} \left\langle \sum_{\alpha} \bar{\mathbf{l}}^{\alpha} \otimes \underbrace{\mathbf{x}_{,\tau}^{\alpha}}_{2\bar{\mathbf{n}}^{\alpha}} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} \bar{\mathbf{m}}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} \quad (92)$$

where we have used

$$\begin{aligned} \left\langle \sum_{\alpha} \bar{\mathbf{l}}^{\alpha}_{,\tau} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} &= \left\langle \sum_{\alpha} \bar{\mathbf{r}}^{\alpha} \times \mathbf{f}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} + \underbrace{\left\langle \sum_{\alpha} [\mathbf{v}^{\alpha} - \mathbf{v}] \times \mathbf{p}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}}_0 \\ &=: \left\langle \sum_{\alpha} \bar{\mathbf{m}}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}}. \end{aligned} \quad (93)$$

We start with the term under the divergence operator. Let us define the particle microscopic angular momentum flux and particle diffusive microscopic angular momentum flux as

$$\bar{\mathbf{n}}^{\alpha} := \frac{1}{2} \bar{\mathbf{l}}^{\alpha} \otimes \mathbf{v}^{\alpha} \quad \text{and} \quad \tilde{\mathbf{m}}^{\alpha} := \frac{1}{2} \bar{\mathbf{l}}^{\alpha} \otimes \tilde{\mathbf{v}}^{\alpha}(\mathbf{x}, \tau) \quad (94)$$

together with the corresponding continuum microscopic angular momentum fluxes and continuum diffusive microscopic angular momentum fluxes

$$\bar{\mathbf{v}} = \frac{1}{2} \bar{\mathbf{l}}(\mathbf{x}, \tau) \otimes \mathbf{v}(\mathbf{x}, \tau) \quad \text{and} \quad \tilde{\mathbf{m}} = \langle \langle \tilde{\mathbf{m}}_{\delta}(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_S \rangle_{\mathcal{P}}. \quad (95)$$

It is easy to show that

$$\bar{\mathbf{v}} = \langle \langle \bar{\mathbf{n}}_\delta(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} - \langle \langle \tilde{\mathbf{m}}_\delta(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_S \rangle_{\mathcal{P}} = \bar{\mathbf{n}} - \tilde{\mathbf{m}}, \quad (96)$$

which has similarities compared with the particle kinetic tensor and the diffusive momentum flux Equation (34).

Proof

$$\begin{aligned} \bar{\mathbf{n}}^\alpha &= \frac{1}{2} \bar{\mathbf{l}}^\alpha \otimes \mathbf{v}(\mathbf{x}, \tau) + \tilde{\mathbf{m}}^\alpha(\mathbf{x}, \tau), \\ \bar{\mathbf{n}}_\delta(\mathbf{z}, \xi) &= \frac{1}{2} \bar{\mathbf{l}}_\delta(\mathbf{z}, \xi) \otimes \mathbf{v}(\mathbf{x}, \tau) + \tilde{\mathbf{m}}_\delta(\mathbf{z}, \xi; \mathbf{x}, \tau), \\ \langle \langle \bar{\mathbf{n}}_\delta(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} &= \frac{1}{2} \bar{\mathbf{l}}(\mathbf{x}, \tau) \otimes \mathbf{v}(\mathbf{x}, \tau) + \langle \langle \tilde{\mathbf{m}}_\delta(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_S \rangle_{\mathcal{P}}. \end{aligned}$$

From Equation (94) and Equation (86) it is clear that

$$\bar{\mathbf{n}} : \mathbf{i} = 0. \quad (97)$$

Now we concentrate our attention to the right-hand side term of Equation (92). Dividing the moment of forces into the external and the internal parts as in Equation (15) we can introduce the microscopic angular momentum source

$$\bar{\mathbf{c}} := \langle \langle \bar{\mathbf{m}}_\delta^{\text{ext}}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} \bar{\mathbf{m}}_{\text{ext}}^\alpha(\tau) w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}} := \left\langle \sum_{\alpha} \bar{\mathbf{r}}^\alpha \times \mathbf{f}_{\text{ext}}^\alpha(\tau) w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}} \quad (98)$$

and the microscopic angular momentum flux

$$\begin{aligned} \text{div} \hat{\mathbf{m}} &:= \text{div}(\bar{\mathbf{m}} + 2\tilde{\mathbf{m}}) = \langle \langle \bar{\mathbf{m}}_\delta^{\text{int}}(\mathbf{z}, \xi) \rangle_S \rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} \bar{\mathbf{m}}_{\text{int}}^\alpha(\tau) w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}} \\ &= \left\langle \sum_{\alpha} \bar{\mathbf{r}}^\alpha \times \mathbf{f}_{\text{int}}^\alpha(\tau) w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}} \end{aligned} \quad (99)$$

which together with Equation (96) allows eventually to rewrite Equation (92) in the following form

$$\boxed{\bar{\mathbf{l}}_{,\tau} + \text{div}(\bar{\mathbf{l}} \otimes \mathbf{v}) = \text{div} \bar{\mathbf{m}}(\mathbf{x}, \tau) + \bar{\mathbf{c}}(\mathbf{x}, \tau).} \quad (100)$$

5.2. Balance of macroscopic angular momentum

Recall that

$$\text{div}[\mathbf{a} \times \mathbf{M}] = \mathbf{a} \times \text{div} \mathbf{M} + \boldsymbol{\epsilon} : (\mathbf{a} \nabla \cdot \mathbf{M}^T). \quad (101)$$

Here, $\boldsymbol{\epsilon}$ denotes the third-order (Levi-Civita) permutation tensor. From the definition of the continuum angular momentum (87), it follows that

$$\boldsymbol{\lambda}_{,\tau} + \text{div}(\boldsymbol{\lambda} \otimes \mathbf{v}) = \mathbf{r} \times [\mathbf{p}_{,\tau} + \text{div}(\mathbf{p} \otimes \mathbf{v})] + \underbrace{\mathbf{v} \times \mathbf{p} + \boldsymbol{\epsilon} : [\mathbf{p} \otimes \mathbf{v}]}_0. \quad (102)$$

Incorporation of the balance of macroscopic linear momentum (37) leads to

$$\boxed{\boldsymbol{\lambda}_{,\tau} + \text{div}(\boldsymbol{\lambda} \otimes \mathbf{v}) = \text{div} \boldsymbol{\mu}(\mathbf{x}, \tau) + \boldsymbol{\chi}(\mathbf{x}, \tau) - \boldsymbol{\epsilon} : \mathbf{s}^T} \quad (103)$$

with the macroscopic angular momentum flux

$$\boldsymbol{\mu} := \mathbf{r}(\mathbf{x}) \times \mathbf{s}(\mathbf{x}, \tau) \quad (104)$$

and the macroscopic angular momentum source

$$\boldsymbol{\chi} := \mathbf{r}(\mathbf{x}) \times \mathbf{b}(\mathbf{x}, \tau) \quad (105)$$

defined, respectively.

Remark 5 Note, that Equation (103) is actually just a direct consequence of the macroscopic balance of linear momentum and is not a separate balance equation per se. In standard continuum mechanics (as opposed to generalized continuum mechanics) the balance of angular momentum in the form equal to Equation (103) except for the last term $\epsilon : s^T$ follows on assuming that there are no inherent moment (torque) interactions between material points. As a consequence it then follows that $\epsilon : s^T \equiv \mathbf{0}$, i.e. the Cauchy stress is symmetric. It is the balance of microscopic angular momentum (Equation (100)) which indeed represents a separate, new balance equation.

5.3. Balance of total angular momentum

By definition the following holds

$$l_{,\tau} + \operatorname{div}(l \otimes v) = [\bar{l} + \lambda]_{,\tau} + \operatorname{div}([\bar{l} + \lambda] \otimes v). \quad (106)$$

Incorporation of the balance of macroscopic (103) and the microscopic (100) angular momentum leads to

$$l_{,\tau} + \operatorname{div}(l \otimes v) = \operatorname{div} m(x, \tau) + c(x, \tau) - \epsilon : s^T \quad (107)$$

with the total angular momentum flux and the total angular momentum source defined as

$$m := \bar{m}(x, \tau) + \mu(x, \tau) \quad (108)$$

and

$$c := \bar{c}(x, \tau) + \chi(x, \tau) \quad (109)$$

respectively.

Remark 6 Note that in [17] an additional equation, the moment of mass, was obtained. It represents the fact that the center of mass of a “sampled” volume does not necessarily coincide with x . One can look at this as an additional continuum degree of freedom, as in the micromorphic formulation. However, it is reasonable to assume that this term can be made negligible by an appropriate choice of the averaging kernel w . Therefore, we do not consider this additional balance equation here.

6. Discussion and conclusions

First of all, if one considers the temperature T to be due to the erratic microscopic motion, then it can be related to $\tilde{s}$ as follows [24]

$$\tilde{s} =: \frac{3}{2} k_B T N \quad (110)$$

with

$$N = \left\langle \sum_{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} \quad (111)$$

If a system of particles can be macroscopically considered as quasi-static, then all kinetic energy is attributed to temperature.

Even though we obtained the balance of energy and angular momentum, we do not yet have closed-form expressions for the associated fluxes. The situation is similar to the balance of linear momentum. In all cases, the corresponding divergence equations have to be solved. One of the solutions can be obtained using Noll's lemmas [9, 23]. We leave the discussion of the solution for all of the fluxes in the balance equations and their consistency to the continuum formulation for part III of the series.

As we have illustrated, some researchers introduce the continuum potential energy explicitly, whereas others prefer the implicit definition. The disadvantage of the explicit formulation is an ambiguity in the localization of the (internal) potential energy to a spatial point and the dependence of the heat flux on the absolute value of potential energy. The case of multi-body potentials has to be treated separately [19, 20] because of the complexity of the resulting expressions in the balance of potential energy. That also limits the application

of Noll's lemmas. The implicit formulation, on the other hand, does not require the potential energy to be localized to a spatial point. In order to obtain the density of potential energy, a differential equation (63) has to be integrated. The advantage of that approach is its direct applicability to multi-body potentials. An explicit formulation of the balance of potential energy is yet desirable since all of the other balance equations (mass, linear and angular momentum) can be obtained from the balance of energy subjected to the Galilean invariance group. In other words, the balance of energy should not be considered separately from the others.

Applying a space-probability averaging approach in this part we obtained the balance of energy and angular momentum. Both laws were derived using theorems we proved in part I [21], thus facilitating the mathematical derivations and making it easier to follow for the reader.

Both explicit and implicit approaches for the derivation of the balance of energy were reviewed and compared. The energy localization and its limitation were discussed.

A physical interpretation of the quantities arising in both balance equations as well as the necessary solutions for the fluxes are left for part III [22] of the series.

Conflict of Interest

None declared.

Funding

This work was supported by the German Science Foundation (Deutsche Forschungs-Gemeinschaft, DFG; grant number STE 544/46-1).

Notes

1. Here we use the following notation for a gradient of a vector $[\text{grad} \mathbf{a}(\mathbf{x})]_{ij} = \partial a_i / \partial x_j$ to avoid a confusion with another well-used notation where a vector operator is introduced $[\nabla]_j = \partial / \partial x_j$, whereby the gradient of a vector is denoted by $\mathbf{a} \otimes \nabla$.
2. Introducing the localization of three-point potential energy as $\mathbf{v}^\alpha = \frac{1}{3!} \sum_{\beta\gamma} \mathbf{v}^{\alpha\beta\gamma}(\mathbf{x}^{\alpha\beta}, \mathbf{x}^{\alpha\gamma}, \mathbf{x}^{\beta\gamma})$ would result in the following expression in the right-hand side of Equation (74): $-\left\langle \frac{1}{3!} \sum_{\alpha\beta\gamma} [\mathbf{f}^{\alpha\beta(\gamma)} \cdot \mathbf{v}^{\alpha\beta} + \mathbf{f}^{\alpha\gamma(\beta)} \cdot \mathbf{v}^{\alpha\gamma} + \mathbf{f}^{\beta\gamma(\alpha)} \cdot \mathbf{v}^{\beta\gamma}] \mathbf{w}(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}}$, where the inter-particle force $\mathbf{f}^{\delta\eta} = -\sum_{\vartheta(\neq\delta,\eta)} \partial \mathbf{v}^{\delta\eta\vartheta} / \partial \mathbf{x}^{\delta\eta} =: \sum_{\vartheta(\neq\delta,\eta)} \mathbf{f}^{\delta\eta(\vartheta)}$ is a sum of forces due to individual three-point potentials.

References

- [1] Mathew, N, Picu, RC and Bloomeld, M. Concurrent coupling of atomistic and continuum models at finite temperature. *Computer Methods in Applied Mechanics and Engineering*, 2011; 200(5–8): 765–773.
- [2] Deng, Q, Xiong, L, and Chen, Y. Coarse-graining atomistic dynamics of brittle fracture by finite element method. *International Journal of Plasticity* 2010; 26(9): 1402–1414.
- [3] Li, S, and Sheng, N. On multiscale non-equilibrium molecular dynamics simulations. *International Journal for Numerical Methods in Engineering* 2010; 83(8–9): 998–1038.
- [4] Klein, PA, and Zimmerman, JA. Coupled atomistic-continuum simulations using arbitrary overlapping domains. *Journal of Computational Physics* 2006; 213(1): 86–116.
- [5] Anciaux, G, Ramisetti, SB, and Molinari, JF. A finite temperature bridging domain method for md-fe coupling and application to a contact problem. *Computer Methods in Applied Mechanics and Engineering* 2012; 205–208(1): 204–212.
- [6] Wang, X, and Lee, JD. Concurrent atomistic/continuum simulation of thermo-mechanical coupling phenomena. *Computer Modeling in Engineering and Sciences* 2010; 62(2): 150–170.
- [7] Liu, WK, Karpov, EG, Zhang, S, and Park, HS. An introduction to computational nanomechanics and materials. *Computer Methods in Applied Mechanics and Engineering*, 2004; 193(17–20): 1529–1578.
- [8] Irving, JH, and Kirkwood, JG. The statistical mechanical theory of transport processes. IV. the equations of hydrodynamics. *The Journal of Chemical Physics* 1950; 18(6): 817–829.
- [9] Noll, W. Die Herleitung der Grundgleichungen der Thermomechanik der Kontinua aus der statistischen Mechanik. *Archive for Rational Mechanics and Analysis* 1955; 4: 627–646.
- [10] Murdoch, AI. A critique of atomistic definitions of the stress tensor. *Journal of Elasticity* 2007; 88: 113–140.
- [11] Murdoch, AI. The motivation of continuum concepts and relations from discrete considerations. *Journal of Mechanics and Applied Mathematics* 1983; 36(2): 163–187.
- [12] Murdoch, AI. On the identification of continuum concepts and fields with molecular variables. *Continuum Mechanics and Thermodynamics* 2011; 23: 1–26.

- [13] Admal, NC, and Tadmor, EB. A unified interpretation of stress in molecular systems. *Journal of Elasticity* 2010; 100: 63–143.
- [14] Chen, Y, and Lee, JD. Atomistic formulation of a multiscale field theory for nano/micro solids. *Philosophical Magazine* 2005; 85(33–35): 4095–4126.
- [15] Davydov, D, Javili, A, Steinmann, P, and McBride, A. A comparison of atomistic and surface enhanced continuum approaches at finite temperature. In Altenbach, H and Morozov, NF (eds), *Surface Effects in Solid Mechanics*, 2013.
- [16] Davydov, D, Javili, A, and Steinmann, P. On molecular statics and surface-enhanced continuum modeling of nano-structures. *Computational Materials Science* 2013; 69: 510–519.
- [17] Murdoch, AI, and Bedeaux, D. Continuum equations of balance via weighted averages of microscopic quantities. *Proceedings of the Royal Society London A* 1994; 445: 157–179.
- [18] Admal, NC, and Tadmor, EB. Stress and heat flux for arbitrary multibody potentials: A unified framework. *The Journal of Chemical Physics* 2011; 134: 184106.
- [19] Delph, TJ. Conservation laws for multibody interatomic potentials. *Modelling and simulation in Materials Science and Engineering* 2005; 13: 585.
- [20] Chen, Y. Local stress and heat flux in atomistic systems involving three-body forces. *The Journal of Chemical Physics* 2006; 124: 054113.
- [21] Davydov, D, and Steinmann, P. Reviewing the roots of continuum formulations in molecular systems. Part I: Particle dynamics, statistical physics, mass and linear momentum balance equations. *Mathematics and Mechanics of Solids* 2013; in press.
- [22] Davydov, D, and Steinmann, P. Reviewing the roots of continuum formulations in molecular systems. Part III: Stresses, couple stresses, heat fluxes. Preprint (2013).
- [23] Lehoucq, RB, and Lilienfeld-Toal, AV. Translation of Walter Noll's 'derivation of the fundamental equations of continuum thermodynamics from statistical mechanics'. *Journal of Elasticity* 2010; 100: 5–24.
- [24] Root, S, Hardy, RJ, and Swanson, DR. Continuum predictions from molecular dynamics simulations: Shock waves. *Journal of Chemical Physics* 2003; 118(7): 3161–3165.

Appendix: Central force decomposition for angle potential

As an illustration of central force decomposition theorem we show how to derive central forces for the angle potential.

Consider a triangle made of points α, β, γ . The angle θ between $\mathbf{x}_{\alpha\beta}$ and $\mathbf{x}_{\gamma\beta}$ is given by

$$\cos \theta := \frac{\mathbf{x}^{\alpha\beta} \cdot \mathbf{x}^{\gamma\beta}}{|\mathbf{x}^{\alpha\beta}| |\mathbf{x}^{\beta\gamma}|}. \quad (112)$$

The triangle is uniquely determined by three distances $\mathbf{x}_{\alpha\beta}$, $\mathbf{x}_{\beta\gamma}$ and $\mathbf{x}_{\alpha\gamma}$, thus the potential energy can be considered to have the following form

$$\mathbf{v}_a^{\alpha\beta\gamma} = \mathbf{v}_a^{\alpha\beta\gamma}(\mathbf{x}^{\alpha\beta}, \mathbf{x}^{\alpha\gamma}, \mathbf{x}^{\beta\gamma}). \quad (113)$$

The cosine theorem states

$$\mathbf{x}_{\alpha\gamma}^2 = \mathbf{x}_{\alpha\beta}^2 + \mathbf{x}_{\beta\gamma}^2 - 2 \mathbf{x}_{\alpha\beta} \mathbf{x}_{\beta\gamma} \cos \theta. \quad (114)$$

Differentiating with respect to $\mathbf{x}_{\alpha\beta}$, $\mathbf{x}_{\beta\gamma}$ and $\mathbf{x}_{\alpha\gamma}$ one easily obtains

$$\begin{aligned} \frac{\partial \cos \theta}{\partial \mathbf{x}_{\alpha\beta}} &= \frac{1}{\mathbf{x}_{\beta\gamma}} - \frac{\cos \theta}{\mathbf{x}_{\alpha\beta}} \\ \frac{\partial \cos \theta}{\partial \mathbf{x}_{\beta\gamma}} &= \frac{1}{\mathbf{x}_{\alpha\beta}} - \frac{\cos \theta}{\mathbf{x}_{\beta\gamma}} \\ \frac{\partial \cos \theta}{\partial \mathbf{x}_{\alpha\gamma}} &= -\frac{\mathbf{x}_{\alpha\gamma}}{\mathbf{x}_{\alpha\beta} \mathbf{x}_{\beta\gamma}}. \end{aligned}$$

Finally, using Equation (67) and considering the potential energy to be a function of angle θ only, i.e. $\mathbf{v}_a^{\alpha\beta\gamma} = \mathbf{v}_a^{\alpha\beta\gamma}(\theta)$ the following expression for the central force between any two particles δ and η is obtained as

$$\begin{aligned} \mathbf{f}_{\delta\eta} &= \mathbf{f}_{\delta\eta} \frac{\mathbf{x}_{\delta\eta}}{\mathbf{x}_{\delta\eta}} \\ \mathbf{f}_{\delta\eta} &= -\frac{\partial \mathbf{v}_a^{\alpha\beta\gamma}}{\partial \mathbf{x}_{\delta\eta}} = -\frac{\partial \mathbf{v}_a^{\alpha\beta\gamma}}{\partial \theta} \frac{\partial \arccos(\cos \theta)}{\partial \cos \theta} \frac{\partial \cos \theta}{\partial \mathbf{x}_{\delta\eta}} = \frac{\partial \mathbf{v}_a^{\alpha\beta\gamma}}{\partial \theta} \frac{1}{|\sin \theta|} \frac{\partial \cos \theta}{\partial \mathbf{x}_{\delta\eta}}. \end{aligned} \quad (115)$$