Reviewing the roots of continuum formulations in molecular systems. Part I: Particle dynamics, statistical physics, mass and linear momentum balance equations

Denis Davydov and Paul Steinmann

Friedrich-Alexander-University of Erlangen-Nuremberg, Germany

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Abstract

The link between atomistic quantities and continuum fields has been the subject of research for at least half a century. Nevertheless, there are still many open questions and misleading discussions in the literature. Therefore, based on the fundamental principles of classical mechanics and statistical physics we construct the basic framework for the link between the atomistic and continuum worlds. In doing so, considerable attention is paid to the central force decomposition and multi-body potentials, balance of angular momentum for the system of particles and its relationship to the extended third Newton axiom and the difference between the theorem of change of kinetic energy and the energy balance law. A number of general theorems related to the convolution properties of statistically averaged quantities, as well as their rates are also proven. These theorems make the derivation of balance equations far simpler when compared to the approaches used by others. Such theorems also make the link between space–time averaging and space–probability averaging more transparent.

In this contribution the balance laws of mass and linear momentum are derived. The remaining balance laws of angular momentum and energy as well as the particular forms of fluxes, such as the stress, are discussed in the follow-up contributions of this series.

Keywords

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

1. Introduction

The last decade has seen a growing interest among researchers in the link between the atomistic and continuum worlds. With the increase in computational power more complex phenomena observed at the nano-scale can be modeled using molecular dynamics (MD) simulations. Strictly speaking, continuum theories should be used at relatively large length and time scales. However, they have been shown to be applicable also to describing nano-scale objects (see for example, Mitrushchenkov et al. [1]). Thus, the phenomena which are usually described by atomistic models can also be captured relatively well by (generalized) continuum theories. That raises a question about the relationship between continuum quantities (such as density, stress, heat flux, etc.) and atomistics. Making this relationship transparent helps with the coupling of high-resolution atomistic methods with the efficient continuum formulation to study complex phenomena. One might argue that it is not possible to relate

Corresponding author:

Denis Davydov, Chair of Applied Mechanics, Friedrich-Alexander-University of Erlangen-Nuremberg, Egerlandstrasse 5, 91058 Erlangen, Germany.
Email: denis.davydov@ltn.uni-erlangen.de

MD to continuum mechanics since it is the quantum laws which describe the behavior of matter at the nano-scale. However, we believe that classical mechanics can contribute a lot to the understanding of continuum mechanics and atomistics.

The averaging procedure we follow was initially introduced in the 1950s by Irving and Kirkwood [2]. Discrete quantities are linked to the continuum using the δ -distribution function together with concepts from statistical physics. A few years later, Noll [3] proposed a more mathematically rigorous formulation. Given the importance of this contribution and the increasing interest in the field, ref. [3] was recently translated to English [4]. In 1981, Hardy [5] applied essentially the same ideas to study shock waves and the validity of a continuum description. His derivations do not rely on statistical physics, however he was probably one of the first to introduce a general averaging kernel instead of the δ -function. Yet, only two-body potentials were studied. Pitteri [6] proposed an extension of Noll's approach [3] to non-conservative (dependent on velocity and/or time) inter-particle forces. Such forces can be used, for example, to describe the dynamics of systems of N point-mass particles with electric charges [7]. Using ideas similar to Hardy [5], Murdoch [8–10] has been developing this approach for the identification of (generalized) continuum concepts with variables of discrete (atomistic) system.

Although the link between atomistic quantities and continuum fields has been the subject of research for at least half a century, there are still many open questions in the literature. Probably one of the biggest discussion concerns stresses/fluxes [11–13], including objectiveness of their definition [14], the difference between pressure and stress [15] and a link to quantum mechanics [16, 17], to name but a few. Other questions include the relationship to generalized continua [18–21] as well as an applicability of the method to systems with many-body interaction potentials [22, 23].

We believe that some of the questions debated in the literature could be answered from the basic principles of classical mechanics which are often touched upon only very briefly. It seems that some contributions lack an appropriate appreciation of the fundamentals of classical mechanics in general and continuum mechanics in particular, which is very important since we aim to relate the discrete particle world to its continuum counterpart.

In this paper, based on the fundamental principles of classical mechanics and statistical physics, we aim to construct the basic framework for the link between the atomistic and continuum worlds. By carefully discussing the basics of classical mechanics we draw attention to some important issues related to the above-mentioned questions. We also pave the ground for our further developments in the field including application to systems with interfaces/interphases.

The paper is structured as follows. In Section 2 we discuss the dynamics of particles including Newtonian, Lagrangian and Hamiltonian equations, Euler laws and the law of balance of energy. In Section 3 we recall the basics of statistical physics. Following the ideas pioneered by Irving and Kirkwood [2] and Noll [3], in Section 4 we introduce averaging procedures. Using statistical physics we prove a number of important theorems that we will use in the sequel for developing the link between the discrete particle system and the continuum. Finally, in Section 5 we introduce continuum fields and derive balances of mass and linear momentum, followed by the Discussion and Conclusions in Section 6. In order to make this contribution reasonably short, the balance of angular momentum and energy are discussed in the second part of this series [24].

2. Particle dynamics

In this section we consider the fundamentals of particle dynamics by introducing mass, linear and angular momentum, and we also discuss issues such as internal, potential and total energy. All these quantities will be needed for the development of continuum balances of mass and linear momentum, which are treated at the end of this contribution, as well as angular momentum and energy in the second part of this series [24]. We believe that carefully discussing the basic laws of classical mechanics can clarify a lot of principal questions frequently debated in the literature, such as central interactions between particles, energy decomposition and others. In our exposition of particle dynamics we follow the spirit of Eulerian mechanics as advocated by, for example, Zilin [25].

2.1. Inertial reference systems

To study the motion of mechanical systems, one has to choose a reference system. In general, the laws of motion in different reference systems can be different. If one takes an arbitrarily accelerated reference system, it could happen that even a simple motion will follow very complicated laws. Thus, the question of the choice of a

reference system in which the laws of motion have the simplest form arises. In classical mechanics, one can always find a reference system in which space is isotropic and homogeneous and time is isotropic. Such a reference system is called inertial.

Given an inertial reference system, we can introduce another reference system, which moves with constant (linear) velocity with respect to the first one. It turns out that this reference system is also inertial. Thus, there is an infinite number of inertial reference systems. The Galilean invariance principle states that the mechanical laws hold alike in all inertial reference systems.¹

2.2. Kinematics of particles

In particle dynamics each particle is considered a primary and indivisible object (like the atoms of Democritus). These objects are generally introduced by defining suited mathematical structures. Note that such objects are not necessarily restricted to point-particles with translational degrees of freedom (DOF) only, but may also be endowed with DOF of different natures, such as rotational or thermal DOF. As an example, additional rotational DOF may describe the resultant kinematics due to the particle's fine-scale electronic nature.

In what follows, however, for the sake of simplicity we will consider as primary objects point-particles with translational DOF in terms of the particle position only. The corresponding position vector for particle α in Euclidean space with origin $\mathbf{x} = \mathbf{0}$ is denoted by

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

The motion of particle α is then described by the 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 time variable of the (possibly erratic) particle motion. The position map $\mathbf{y}^\alpha$ is introduced to indicate the map from the time interval into Euclidean space of particle positions. For convenience we abbreviate the velocity of the particle by

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

where $_{;\tau}$ denotes total differentiation in time. Each particle has a characteristic property called mass which we denote by m^α . Note, that considering rotational DOF will add additional characteristic properties.² Next the particle can be equipped with the following quantities:

- 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 (w.r.t.) a fixed point³ in space $\mathbf{y}$

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

Note that a particle's mass is invariant under a change of the reference system. This is the most general setting for the kinematics of point-particles without rotational DOF.²

2.3. Kinetics of particles

The motion of a particle α in an inertial reference system is described by the second Newton law

$$\mathbf{p}_{;\tau}^\alpha = \mathbf{f}^\alpha(\{\mathbf{x}^\beta(\tau)\}, \{\mathbf{v}^\beta(\tau)\}, \tau) \quad (7)$$

where the effect of the surrounding environment (including other particles) is modeled by a force $\mathbf{f}^\alpha$ acting on the particle.⁴ Given initial conditions $\{\mathbf{x}^\beta(0)\}$ and $\{\mathbf{v}^\beta(0)\}$ the motion of particle α is then obtained by solving the system of second-order differential equations (7). As an example of forces which depend on both particle's

position and velocity consider the Lorentz force acting on a single isolated charged particle in an electric field $\mathbb{E}(\mathbf{x}, \tau)$ and a field of magnetic induction $\mathbb{B}(\mathbf{x}, \tau)$

$$\mathbf{f}^\alpha(\mathbf{x}^\alpha, \mathbf{v}^\alpha, \tau) = q \mathbb{E}(\mathbf{x}^\alpha, \tau) + q \mathbf{v}^\alpha \times \mathbb{B}(\mathbf{x}^\alpha, \tau) \quad (8)$$

Such equations, which relate kinetic with kinematic quantities are called constitutive equations. It follows from equation (7), that in the case that $\mathbf{f}^\alpha = \mathbf{0}$, the (linear) momentum $\mathbf{p}^\alpha$ is conserved (the first Newton law).

By differentiating equation (6) in time, the change of angular momentum of particle α is⁵

$$\mathbf{l}_{;\tau}^\alpha = \mathbf{m}^\alpha(\tau) \quad \text{with} \quad \mathbf{m}^\alpha := [\mathbf{x}^\alpha(\tau) - \mathbf{y}] \times \mathbf{f}^\alpha(\tau) \quad (9)$$

where we used that $\mathbf{v}^\alpha(\tau) \times \mathbf{p}^\alpha(\tau) = \mathbf{0}$. It is important to note, that the balance of angular momentum for a single particle is not a separate balance law, but rather follows from the balance of linear momentum (this is in contrast to more complex mechanical systems).

By differentiating equation (4) in time, the change of kinetic energy is given by

$$\mathbf{k}_{;\tau}^\alpha = \mathbf{p}^\alpha(\tau) \quad \text{with} \quad \mathbf{p}^\alpha := \mathbf{v}^\alpha(\tau) \cdot \mathbf{f}^\alpha(\tau) \quad (10)$$

The quantity $\mathbf{p}^\alpha$ denotes the power⁶ expended by the force, its integral over time is called work

$$\int_0^t \mathbf{p}^\alpha(\tau) d\tau = \int_{\mathbf{x}^\alpha(0)}^{\mathbf{x}^\alpha(\tau)} \mathbf{f}^\alpha(\mathbf{x}^\alpha, \mathbf{v}^\alpha(\mathbf{x}^\alpha), \tau(\mathbf{x}^\alpha)) \cdot d\mathbf{x}^\alpha \quad (11)$$

If the force is independent of time, the velocity of the particle as well as of the path by which the particle moves from $\mathbf{x}_0^\alpha$ to $\mathbf{x}_\tau^\alpha$, the force is called conservative. In such a case

$$0 = \oint \mathbf{f}^\alpha \cdot d\mathbf{x}^\alpha \Rightarrow \nabla \times \mathbf{f}^\alpha = \mathbf{0} \quad (12)$$

where we used Stokes' theorem. Thus, a conservative force is generated by a potential⁷ $\mathbf{v}^\alpha$ such that

$$\mathbf{f}^\alpha = -\nabla \mathbf{v}^\alpha \quad (13)$$

It follows, that for potential forces the total (mechanical) energy of a single particle

$$\mathbf{e}^\alpha := \mathbf{v}^\alpha + \mathbf{k}^\alpha \quad (14)$$

is conserved in time, i.e.

$$\mathbf{e}_{;\tau}^\alpha = [\nabla \mathbf{v}^\alpha + \mathbf{f}^\alpha] \cdot \mathbf{v}^\alpha = 0 \quad (15)$$

Finally, we mention the third Newton law (actio et reactio), which asserts that the force with which particle α acts on particle β in its surrounding has the same magnitude and the opposite sign as the force from β to α

$$\mathbf{f}^{\alpha\beta} = -\mathbf{f}^{\beta\alpha} \quad (16)$$

This equation obviously involves the basic assumption that contributions to $\mathbf{f}^\alpha$ may be expressed as the sum of uncoupled pairwise interactions.

2.4. Particle systems

Consider a particle system $\mathcal{A}$ which consists of N particles. We will consider closed systems only, that is systems which do not exchange mass with their surroundings. This condition reads

$$\mathbf{m}_{;\tau}^\alpha = \mathbf{0} \quad \text{and} \quad N = \text{constant} \quad (17)$$

In classical mechanics it is necessary to consider the following axiom:⁸

Axiom 1. *The mass, kinetic energy, linear and angular momentum of the system are additive with respect to the particles it consists of.* $\square$

Thus, the total mass of the system is defined as

$$\mathbf{M} := \sum_{\alpha} m^{\alpha} \quad (18)$$

It is convenient to introduce the so-called center of mass of the system (barycentric position)

$$\mathbf{X} := \frac{\sum_{\alpha} m^{\alpha} \mathbf{x}^{\alpha}}{\sum_{\alpha} m^{\alpha}} \quad (19)$$

and the relative positions

$$\mathbf{r}^{\alpha} = \mathbf{x}^{\alpha} - \mathbf{X} \quad (20)$$

It thus follows that for the relative positions

$$\sum_{\alpha} m^{\alpha} \mathbf{r}^{\alpha} = \sum_{\alpha} m^{\alpha} \mathbf{x}^{\alpha} - \sum_{\alpha} m^{\alpha} \mathbf{X} = \mathbf{0} \quad (21)$$

Inter-particle distance vectors are denoted by

$$\mathbf{x}^{\alpha\beta} = \mathbf{x}^{\alpha} - \mathbf{x}^{\beta} \quad (22)$$

By differentiating equation (21) in time with $m^{\alpha}_{;\tau} = 0$, the total linear momentum of the system

$$\mathbf{P} = \sum_{\alpha} \mathbf{p}^{\alpha}(\tau) = \mathbf{M} \mathbf{X}_{;\tau}(\tau) \quad (23)$$

equals the momentum of an imaginary single particle with the mass $\mathbf{M}$ and the velocity $\mathbf{V} = \mathbf{X}_{;\tau}$. The angular momentum w.r.t. $\mathbf{y}$ and the kinetic energy of the system of particles are

$$\mathbf{L}^{\mathbf{y}} = \sum_{\alpha} \mathbf{l}^{\alpha}(\tau) \quad (24)$$

and

$$\mathbf{K} = \sum_{\alpha} k^{\alpha}(\tau) = \frac{1}{2} \sum_{\alpha} m^{\alpha} |\mathbf{x}_{;\tau}^{\alpha}(\tau)|^2 \quad (25)$$

respectively.

2.5. The first Euler law

The first Euler law⁹ for closed systems¹⁰ states axiomatically that the rate of total (linear) momentum change equals the (resultant) force $\mathbf{F}(\mathcal{A}, \mathcal{A}^e)$ which acts on the system $\mathcal{A}$ from its environment $\mathcal{A}^e$

$$\boxed{\mathbf{P}_{;\tau} = \mathbf{F}(\mathcal{A}, \mathcal{A}^e)} \quad (26)$$

Axiom 2. *Force $\mathbf{F}$ is biadditive on mutually disjoint systems, i.e. given $\mathcal{A} = \mathcal{B} \cup \mathcal{C}$ and $0 = \mathcal{B} \cap \mathcal{C}$ the following holds*

$$\mathbf{F}(\mathcal{B} \cup \mathcal{C}, \mathcal{D}) = \mathbf{F}(\mathcal{B}, \mathcal{D}) + \mathbf{F}(\mathcal{C}, \mathcal{D}) \quad (27)$$

$$\mathbf{F}(\mathcal{D}, \mathcal{B} \cup \mathcal{C}) = \mathbf{F}(\mathcal{D}, \mathcal{B}) + \mathbf{F}(\mathcal{D}, \mathcal{C}) \quad (28)$$

$\square$

Thus, the resultant of the external forces can be represented as

$$\mathbf{F}(\mathcal{A}, \mathcal{A}^e) = \mathbf{F}_{\text{ext}} = \sum_{\alpha} \mathbf{f}_{\text{ext}}^{\alpha} \quad (29)$$

Here by $\mathbf{f}_{\text{ext}}^{\alpha}$ we denote forces acting on the particle α from $\mathcal{A}^e$.

By dividing the system $\mathcal{A}$ into the two separate subsystems $\mathcal{B}$ and $\mathcal{C}$ with $\mathcal{A} = \mathcal{B} \cup \mathcal{C}$ and $0 = \mathcal{B} \cap \mathcal{C}$, and writing equation (26) for each subsystem, one can prove that

$$\mathbf{F}(\mathcal{B}, \mathcal{C}) = -\mathbf{F}(\mathcal{C}, \mathcal{B}) \quad (30)$$

Let us denote by $\mathcal{B}^e$ and $\mathcal{C}^e$ the environment of systems $\mathcal{B}$ and $\mathcal{C}$ respectively. Indeed, by adding

$$\mathbf{P}_{;\tau}(\mathcal{B}) = \mathbf{F}(\mathcal{B}, \mathcal{B}^e) = \mathbf{F}(\mathcal{B}, \mathcal{C}) + \mathbf{F}(\mathcal{B}, \mathcal{A}^e), \quad \mathcal{B}^e = \mathcal{C} \cup \mathcal{A}^e \quad (31)$$

to

$$\mathbf{P}_{;\tau}(\mathcal{C}) = \mathbf{F}(\mathcal{C}, \mathcal{C}^e) = \mathbf{F}(\mathcal{C}, \mathcal{B}) + \mathbf{F}(\mathcal{C}, \mathcal{A}^e), \quad \mathcal{C}^e = \mathcal{B} \cup \mathcal{A}^e \quad (32)$$

and using the additivity of linear momentum and the force we immediately obtain

$$\mathbf{0} = \mathbf{F}(\mathcal{B}, \mathcal{C}) + \mathbf{F}(\mathcal{C}, \mathcal{B}) \quad (33)$$

Thus, it is not necessary to assume the third Newton law, instead this property is now a proven theorem and cannot be violated. Moreover it is assumed that

$$\mathbf{F}(\mathcal{B}, \mathcal{B}) = \mathbf{0} \quad (34)$$

Writing equation (26) for a single material point we obtain the second Newton law

$$\mathbf{p}_{;\tau}^{\alpha} = \mathbf{f}^{\alpha} \quad (35)$$

with the decomposition of the force acting on the particle as

$$\mathbf{f}^{\alpha} = \mathbf{f}_{\text{int}}^{\alpha}(\tau) + \mathbf{f}_{\text{ext}}^{\alpha}(\tau) \quad (36)$$

Here

$$\mathbf{f}_{\text{int}}^{\alpha} = \sum_{\beta} \mathbf{f}^{\alpha\beta}(\tau) \quad \text{with} \quad \mathbf{f}^{\alpha\beta} = -\mathbf{f}^{\beta\alpha} \quad (37)$$

are forces between particles which constitute the system $\mathcal{A}$. Note, that the resultant internal force vanishes

$$\mathbf{F}_{\text{int}} = \sum_{\alpha} \mathbf{f}_{\text{int}}^{\alpha} = \sum_{\alpha\beta} \mathbf{f}^{\alpha\beta} = \mathbf{0} \quad (38)$$

Using equation (35), the theorem of balance of kinetic energy follows as

$$\mathbf{K}_{;\tau} = \mathbf{P} \quad (39)$$

where the power of forces

$$\mathbf{P} = \mathbf{P}_{\text{ext}} - \mathbf{P}_{\text{int}} \quad (40)$$

is decomposed into the internal power

$$\mathbf{P}_{\text{int}} := - \sum_{\alpha} \mathbf{x}_{;\tau}^{\alpha} \cdot \mathbf{f}_{\text{int}}^{\alpha} = - \frac{1}{2} \sum_{\alpha\beta} \mathbf{x}_{;\tau}^{\alpha\beta} \cdot \mathbf{f}^{\alpha\beta}$$

and the external power

$$\mathbf{P}_{\text{ext}} := \sum_{\alpha} \mathbf{x}_{;\tau}^{\alpha} \cdot \mathbf{f}_{\text{ext}}^{\alpha}$$

Note, that the structure of the discrete internal power $\mathbf{P}_{\text{int}}$ resembles the continuum one (a multiplication of conjugate stress and strain rate); the sign depends on the definition of the inter-particle distance vector $\mathbf{x}^{\alpha\beta}$, equation (22).

2.6. The second Euler law

The second Euler law¹¹ for closed systems states axiomatically that the rate of total angular momentum change of the system $\mathcal{A}$ is equal to the moment $\mathbf{M}^y(\mathcal{A}, \mathcal{A}^e)$ which acts on the system $\mathcal{A}$ from its environment $\mathcal{A}^e$

$$\boxed{\mathbf{L}_{;\tau}^y(\mathcal{A}) = \mathbf{M}^y(\mathcal{A}, \mathcal{A}^e)} \quad (41)$$

Axiom 3. Moment $\mathbf{M}^y$ is biadditive on mutually disjoint systems, i.e. given $\mathcal{A} = \mathcal{B} \cup \mathcal{C}$ and $0 = \mathcal{B} \cap \mathcal{C}$ the following holds

$$\mathbf{M}^y(\mathcal{B} \cup \mathcal{C}, \mathcal{D}) = \mathbf{M}^y(\mathcal{B}, \mathcal{D}) + \mathbf{M}^y(\mathcal{C}, \mathcal{D}) \quad (42)$$

$$\mathbf{M}^y(\mathcal{D}, \mathcal{B} \cup \mathcal{C}) = \mathbf{M}^y(\mathcal{D}, \mathcal{B}) + \mathbf{M}^y(\mathcal{D}, \mathcal{C}) \quad (43)$$

□

For the case of particles considered here, the resultant moment of external forces reads

$$\begin{aligned} \mathbf{M}^y(\mathcal{A}, \mathcal{A}^e) &= \mathbf{M}_{\text{ext}}(\tau) = \sum_{\alpha} [\mathbf{x}^{\alpha} - \mathbf{y}] \times \mathbf{f}_{\text{ext}}^{\alpha}(\tau) \\ &= \sum_{\alpha} [\mathbf{X} - \mathbf{y}] \times \mathbf{f}_{\text{ext}}^{\alpha}(\tau) + \sum_{\alpha} \mathbf{r}^{\alpha} \times \mathbf{f}_{\text{ext}}^{\alpha}(\tau) \\ &=: [\mathbf{X} - \mathbf{y}] \times \mathbf{F} + \mathbf{M} \end{aligned} \quad (44)$$

Similar to the first Euler law it follows that

$$\mathbf{M}^y(\mathcal{B}, \mathcal{C}) = -\mathbf{M}^y(\mathcal{C}, \mathcal{B}) \quad (45)$$

Indeed, by adding

$$\mathbf{L}_{;\tau}^y(\mathcal{B}) = \mathbf{M}^y(\mathcal{B}, \mathcal{B}^e) = \mathbf{M}^y(\mathcal{B}, \mathcal{C}) + \mathbf{M}^y(\mathcal{B}, \mathcal{A}^e), \quad \mathcal{B}^e = \mathcal{C} \cup \mathcal{A}^e \quad (46)$$

to

$$\mathbf{L}_{;\tau}^y(\mathcal{C}) = \mathbf{M}^y(\mathcal{C}, \mathcal{C}^e) = \mathbf{M}^y(\mathcal{C}, \mathcal{B}) + \mathbf{M}^y(\mathcal{C}, \mathcal{A}^e), \quad \mathcal{C}^e = \mathcal{B} \cup \mathcal{A}^e \quad (47)$$

and using the additivity of angular momentum and the moments one immediately obtains

$$\mathbf{0} = \mathbf{M}^y(\mathcal{B}, \mathcal{C}) + \mathbf{M}^y(\mathcal{C}, \mathcal{B}) \quad (48)$$

It is assumed, that the self moment equals zero

$$\mathbf{M}^y(\mathcal{B}, \mathcal{B}) = \mathbf{0} \quad (49)$$

Let us develop the rate of angular momentum calculated (without loss of generality) w.r.t $\mathbf{y} = \mathbf{0}$

$$\begin{aligned} \mathbf{L}_{;\tau}^0 &= \sum_{\alpha} \mathbf{x}^{\alpha} \times \mathbf{p}_{;\tau}^{\alpha} = \sum_{\alpha} \mathbf{x}^{\alpha} \times \mathbf{f}^{\alpha} \\ &= \sum_{\alpha\beta} \mathbf{x}^{\alpha} \times \mathbf{f}^{\alpha\beta} + \sum_{\alpha} \mathbf{x}^{\alpha} \times \mathbf{f}_{\text{ext}}^{\alpha} \\ &= \frac{1}{2} \sum_{\alpha\beta} [\mathbf{x}^{\alpha} - \mathbf{x}^{\beta}] \times \mathbf{f}^{\alpha\beta} + \sum_{\alpha} \mathbf{x}^{\alpha} \times \mathbf{f}_{\text{ext}}^{\alpha} \end{aligned} \quad (50)$$

However, from the second Euler law the change of angular momentum equals the moment of external forces. Since any pair of particles can be considered as a system, the following theorem holds for a closed system of material points with no rotational DOF

$$\mathbf{f}^{\alpha\beta} \times \mathbf{x}^{\alpha\beta} = \mathbf{0} \quad (51)$$

Thus, for a system of particles with only translational DOF, internal forces are always central in order for the second Euler law to hold. Sometimes, this equation is referred to as the extended third Newton law. However in

classical mechanics it shall not be considered an axiom, but a theorem which cannot be violated. We agree with Zilin [25], that any physical experimental knowledge on non-central interaction forces between particles should not be considered as a proof of invalidity of classical mechanics in general, but as a necessity to introduce additional DOF to the considered primary objects.

This is similar to the discussion in generalized continuum theories. As soon as we accept moment interactions between continuum points, we have to introduce additional kinematic quantities such as the microdeformation gradient in micromorphic theory. Whereas if we consider the Cauchy stress symmetric, no extension is necessary, and vice versa.

Using the third Newton law and equation (51), it is easy to show that the total moment of internal forces vanishes

$$\mathbf{M}_{\text{int}} = \sum_{\alpha} [\mathbf{x}^{\alpha} - \mathbf{y}] \times \mathbf{f}_{\text{int}}^{\alpha}(\tau) = \sum_{\alpha\beta} [\mathbf{x}^{\alpha} - \mathbf{y}] \times \mathbf{f}^{\alpha\beta}(\tau) = \frac{1}{2} \sum_{\alpha\beta} \mathbf{x}^{\alpha\beta} \times \mathbf{f}^{\alpha\beta}(\tau) = \mathbf{0} \quad (52)$$

The angular momentum w.r.t. $\mathbf{y}$ can be expressed as

$$\begin{aligned} \mathbf{L}^y &= \sum_{\alpha} \mathbf{I}^{\alpha}(\tau) = \sum_{\alpha} m^{\alpha} [\mathbf{x}^{\alpha} - \mathbf{y}] \times \dot{\mathbf{x}}_{;\tau}^{\alpha} \\ &= \sum_{\alpha} m^{\alpha} [\mathbf{X} - \mathbf{y}] \times \dot{\mathbf{x}}_{;\tau}^{\alpha} + \sum_{\alpha} m^{\alpha} \mathbf{r}^{\alpha} \times \dot{\mathbf{x}}_{;\tau}^{\alpha} \\ &= [\mathbf{X} - \mathbf{y}] \times \mathbf{P} + \sum_{\alpha} m^{\alpha} \mathbf{r}^{\alpha} \times \dot{\mathbf{r}}_{;\tau}^{\alpha} + \underbrace{\sum_{\alpha} m^{\alpha} \mathbf{r}^{\alpha} \times \mathbf{X}_{;\tau}}_{\mathbf{0}} \\ &= [\mathbf{X} - \mathbf{y}] \times \mathbf{P} + \sum_{\alpha} \mathbf{r}^{\alpha}(\tau) \times \mathbf{p}_{\text{rel}}^{\alpha}(\tau) \\ &=: [\mathbf{X} - \mathbf{y}] \times \mathbf{P} + \mathbf{L} \end{aligned} \quad (53)$$

Here the linear momentum relative to the barycenter is denoted by $\mathbf{p}_{\text{rel}}^{\alpha} := m^{\alpha} \dot{\mathbf{r}}_{;\tau}^{\alpha}$, the total angular momentum w.r.t. the barycenter is denoted by $\mathbf{L}$.

Thus, the balance of angular momentum (41) can be rewritten in terms of the moment of forces and the angular momentum w.r.t. the center of mass of the system as

$$\mathbf{L}_{;\tau} = \mathbf{L}_{;\tau}^y - [\mathbf{X} - \mathbf{y}] \times \dot{\mathbf{P}}_{;\tau} = \mathbf{M}^y(\tau) - [\mathbf{X} - \mathbf{y}] \times \mathbf{F} = \mathbf{M}(\tau) \quad (54)$$

Obviously $[\mathbf{X} - \mathbf{y}] \times \dot{\mathbf{P}}_{;\tau} = [\mathbf{X} - \mathbf{y}] \times \mathbf{F}$ holds trivially due to the validity of the first Euler law.

2.7. The energy balance law

In the above we obtained a theorem for the balance of kinetic energy (39). However, as we will show now using an intriguing example presented by Zilin [25], the two Euler laws are not enough to describe the behavior of a general particle system.

First of all, we assume that both external and internal forces have a conservative part (which originates from a potential) and a dissipative part, that is

$$\begin{aligned} \mathbf{f}_{\text{int}}^{\alpha} &= \sum_{\beta} \mathbf{f}^{\alpha\beta} = -\frac{\partial V_{\text{int}}}{\partial \mathbf{x}^{\alpha}} + \mathbf{f}_{\text{int,d}}^{\alpha} = -\frac{\partial V_{\text{int}}}{\partial \mathbf{x}^{\alpha}} + \sum_{\beta} \mathbf{f}_{\text{d}}^{\alpha\beta} \\ \mathbf{f}_{\text{ext}}^{\alpha} &= -\frac{\partial V_{\text{ext}}}{\partial \mathbf{x}^{\alpha}} + \mathbf{f}_{\text{ext,d}}^{\alpha} \end{aligned} \quad (55)$$

where $\mathbf{f}_{\text{ext,d}}^{\alpha}$ and $\mathbf{f}_{\text{int,d}}^{\alpha} = \sum_{\beta} \mathbf{f}_{\text{d}}^{\alpha\beta}$ are dissipative external and internal (interaction) forces, V_{int} and V_{ext} are internal and external potentials respectively. Using this decomposition, equation (39) can be rewritten as

$$[\mathbf{E}_{\text{M}}]_{;\tau} = \mathbf{P}_{\text{ext,d}} - \mathbf{P}_{\text{int,d}} \quad (56)$$

Here the total mechanical energy and the total potential energy are introduced as $E_M := K + V$ and $V := V_{\text{int}} + V_{\text{ext}}$, respectively. The power of dissipative internal and external forces are denoted as

$$P_{\text{int,d}} = - \sum_{\alpha} \mathbf{v}^{\alpha} \cdot \mathbf{f}_{\text{int,d}}^{\alpha} = - \frac{1}{2} \sum_{\alpha\beta} \mathbf{v}^{\alpha\beta} \cdot \mathbf{f}_d^{\alpha\beta}$$

$$P_{\text{ext,d}} = \sum_{\alpha} \mathbf{v}^{\alpha} \cdot \mathbf{f}_{\text{ext,d}}^{\alpha}$$

with the velocity of the inter-particle distance vector

$$\mathbf{v}^{\alpha\beta} = \mathbf{v}^{\alpha} - \mathbf{v}^{\beta}$$

Note, that E_M is a combination of already defined quantities, moreover it is not a characteristic quantity of the system $\mathcal{A}$ only, since it also includes the external potential field.

Please note, that the assignment of the total potential energy to each particle α

$$V = \sum_{\alpha} v^{\alpha} \quad (57)$$

is discussed in the second part of the series [24].

Obviously, if there are no internal nor external dissipative forces, the mechanical energy of the system is conserved $E_M = \text{const}$. Such systems are called conservative.

Now, consider a closed isolated system which does not interact with its environment, thus $P_{\text{ext,d}} = 0$. However, the mechanical energy of the system is not necessarily conserved since $P_{\text{int,d}} \neq 0$. That contradicts our experience that energy cannot vanish nor appear from nowhere, but can only change from one form to another.

This example demonstrates that another basic law of mechanics is necessary – the balance of energy, which states¹² that the rate of change of the total energy E of the system $\mathcal{A}$ equals the power of external forces P_{ext} plus the rate of the energy supply from the environment r

$$\boxed{E_{;\tau} = P_{\text{ext}} + r} \quad (58)$$

The total energy E

$$E = K + U \quad (59)$$

is assumed to be composed of the kinetic energy K (a measure of the observed motion in the reference system) and the internal energy U – a new characteristic of the system which represents the ability of the system to store energy. Note that the heat source r is not mentioned in the Euler laws. Thus it does not appear in the theorem of balance of mechanical energy (39).

Using equations (56) and (58) we obtain the balance of so-called heat energy

$$[E_H]_{;\tau} := [U - V_{\text{int}}]_{;\tau} = P_{\text{int,d}} + r \quad (60)$$

In the case where there is no exchange of energy with the environment ($r = 0$) and the internal dissipation is zero

$$P_{\text{int,d}} = 0 \iff \mathbf{v}^{\alpha\beta} \cdot \mathbf{f}_d^{\alpha\beta} = 0 \quad (61)$$

the heat energy is constant and can be arbitrarily chosen to be 0, thus

$$U = V_{\text{int}} \quad (62)$$

That corresponds to the particle system considered here, where each particle can only store energy either in kinetic or potential form. In general, however, additional mathematical structures such as the heat capacity of the particle can be introduced in order to allow the irreversible transformation of energy contained in the system from one kind to another, whereby such transformations are related to $P_{\text{int,d}}$.

2.8. Lagrangian equations

The second Newton law can also be generalized using either Lagrangian or Hamiltonian approaches. The Lagrangian approach is useful in the case when there are constraints in the system, it is also used in quantum field theory, whereas the Hamiltonian approach is more suited to statistical physics, which we will use later. Both approaches are generalizations of the second Newton law.

We start by introducing configuration space coordinates (generalized coordinates) of the particle system as

$$\mathbf{x} = \{\mathbf{x}^\alpha\} \in \mathbb{E}^{3N} \quad (63)$$

The motion of the system is fully described by a position map

$$\mathcal{C} \ni \mathbf{x} \leftarrow \mathbf{y}(\tau) \quad \text{with} \quad \mathbf{y} : \tau \mapsto \mathbf{x}, \mathbb{R}_+ \rightarrow \mathbb{E}^{3N} \quad (64)$$

The time sequence of particle positions defines a trajectory in the configuration space. The (generalized) velocity is denoted by

$$\mathbf{v} = \mathbf{x}_{;\tau} \quad (65)$$

It is assumed that the system is fully characterized by the Lagrangian

$$\mathbf{L} = \mathbf{L}(\mathbf{x}, \mathbf{x}_{;\tau}) : TC = \mathcal{C} \times T\mathcal{C} \rightarrow \mathbb{R} \quad (66)$$

where TC is the configuration tangent bundle (also called the velocity phase space) and $T\mathcal{C}$ is the tangent space. Consider the system at two arbitrary states: $\mathbf{x}_1$ at τ_1 and $\mathbf{x}_2$ at τ_2 . For an arbitrary path connecting these states the following quantity is called the action

$$S = \int_{\tau_1}^{\tau_2} \mathbf{L} d\tau \quad (67)$$

The variational principle of Hamilton (the principle of minimum action) states that

$$\delta \int_{\tau_1}^{\tau_2} \mathbf{L} d\tau = 0 \quad (68)$$

Consequently, the Lagrangian equations of motion follow from equation (68) as

$$\boxed{[\nabla_{\mathbf{x}_{;\tau}} \mathbf{L}]_{;\tau} = \nabla_{\mathbf{x}} \mathbf{L}} \quad (69)$$

The second Newton law can be recovered if one takes $\mathbf{L} = \mathbf{K} - \mathbf{V}$, where $\mathbf{V}$ is the (total) potential energy of the conservative system.

Remark 1. *The homogeneity of space and time and the isotropy of space [26] leads to the conclusion that the Lagrangian of the closed isolated non-interacting particle system is a function of the absolute value of velocity only, i.e. $\mathbf{L} = \mathbf{L}(\mathbf{v} \cdot \mathbf{v}) = \mathbf{K}$.* $\square$

Remark 2. *The existence of absolute time and the Galilean invariance principle leads to the conclusion that the potential energy is a function of the particle positions evaluated at the same current time τ . In other words, the interaction between particles is infinitely fast [26].* $\square$

Remark 3. *The conservation of energy for a closed isolated (all alone in the world) system can be obtained from the homogeneity of time. The homogeneity of space gives rise to the conservation of total linear momentum. Finally, the isotropy of space leads to the conservation of the total angular momentum for a closed isolated system. That is one of the basic axioms of classical mechanics, which also follows from the second Euler law. Therefore, we have another reason to consider the second Euler law to hold and not to replace it with the extended third Newton axiom.* $\square$

2.9. Hamiltonian equations

In the Hamiltonian approach one starts with the introduction of phase space coordinates (generalized coordinate and momentum) as¹³

$$\mathbf{z} = \{\mathbf{x} = \{\mathbf{x}^\alpha\}, \mathbf{p} = \{\mathbf{p}^\alpha\}\} \in \mathbb{E}^{3N} \times \mathbb{E}^{3N} \quad (70)$$

The motion of the system in phase space is described by a position and (linear) momentum map

$$\mathcal{P} \ni \mathbf{z} \leftarrow \{\mathbf{y}(\tau), \mathbf{mv}(\tau)\} \quad \text{with} \quad \{\mathbf{y}, \mathbf{mv}\} : \tau \mapsto \mathbf{z}, \mathbb{R}_+ \rightarrow \mathbb{E}^{3N} \times \mathbb{E}^{3N} \quad (71)$$

A time sequence of particle positions and (linear) momenta defines a trajectory in the phase space. It is assumed that the behavior of the system is fully described by the Hamiltonian

$$\mathbf{H} = H(\mathbf{z}) : \mathcal{P} \rightarrow \mathbb{R} \quad (72)$$

Hamilton's equations of motion (also called canonical) read in a concise format as

$$\boxed{\mathbf{z}_{;\tau} = \mathbf{J} \cdot \nabla_{\mathbf{z}} H(\mathbf{z})} \quad (73)$$

where the symplectic matrix

$$\mathbf{J} = \begin{bmatrix} \mathbf{0} & \mathbf{I} \\ -\mathbf{I} & \mathbf{0} \end{bmatrix} \quad (74)$$

has the following properties: $\mathbf{J} = -\mathbf{J}'$ and $\mathbf{J} \cdot \mathbf{J} = -\mathbf{I}$.

The Hamiltonian can be related to the Lagrangian using the Legendre transformation

$$\mathbf{H} = \inf_{\mathbf{x}_{;\tau}} \{L(\mathbf{x}, \mathbf{x}_{;\tau}) - \mathbf{p} \cdot \mathbf{x}_{;\tau}\} \quad (75)$$

Remark 4. Using Hamilton's equations, the theorem of conservation of volume in phase space can be proven straightforwardly

$$\text{div}_{\mathbf{z}}(\mathbf{z}_{;\tau}) = \mathbf{z}_{;\tau} \cdot \nabla_{\mathbf{z}} = -\nabla_{\mathbf{z}\mathbf{z}} H(\mathbf{z}) : \mathbf{J} = 0 \quad (76)$$

In statistical physics, the conservation of volume in phase spaces is denoted the Liouville theorem. $\square$

Recall that the Hamiltonian is an integral of motion for a conservative system, i.e.

$$\mathbf{H}_{;\tau} = \nabla_{\mathbf{z}} H(\mathbf{z}) \cdot \mathbf{J} \cdot \nabla_{\mathbf{z}} H(\mathbf{z}) = 0 \quad (77)$$

By choosing the Hamiltonian of a conservative system as $\mathbf{H} = \sum_{\alpha} \mathbf{p}^\alpha \cdot \mathbf{p}^\alpha / 2m^\alpha + V$, one obviously recovers the second Newton law.

3. Some notions from statistical physics

3.1. Probability density function

Statistical physics deals with systems which consist of a gigantic number of (rotation-free) point-mass particles. As an example, recall the Avogadro number $6.022 \cdot 10^{23}$ which gives a number of atoms in 12 g of the isotope carbon-12 or the number of items in only one mole of stuff. From the deterministic point of view, the solution of the corresponding Newton equations depends on the huge number of initial conditions for all particle positions and velocities, thus making the study of such systems practically inadmissible in a deterministic approach. When the number of particles in a system is extremely large, the system follows statistical laws.

Following Gibbs [27] let us consider an infinite number N_s of independent but equivalent¹⁴ systems $\mathcal{Z}_1, \mathcal{Z}_2, \dots$ with coordinates $\mathbf{z}_1, \mathbf{z}_2, \dots$ in phase space. The collection of such systems is usually called a statistical ensemble. The environment $\mathcal{A}^e(\tau)$ of each system is considered to be the same at any given time. Let us denote by $\Delta \mathbf{z}$ a particular part of phase space and by D_s the number of systems which occupies it. There exists a limit

$\lim_{N_s \rightarrow \infty} (D_s/N_s)$ which gives the probability of finding each system in $\Delta \mathbf{z}$. In transition from $\Delta \mathbf{z}$ to $d\mathbf{z}$, the probability density function is eventually introduced as

$$\mathbf{W} = \mathbf{W}(\mathbf{z}, \tau) \quad (78)$$

It gives the probability of the state $\mathbf{z}$ per unit volume in phase space $\mathcal{P}$. Note, that the probability density function does not depend on the initial state of the system, that is its initial particle positions and velocities. In statistical physics $\mathbf{W}$ is shown to depend only on the additive integrals of motion, that is energy, linear and angular momentum.

The following normalization holds for the probability density

$$\int_{\mathcal{P}} \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} = 1 \quad (79)$$

It is also required that $\mathbf{W}$ decays fast enough as $|\mathbf{z}| \rightarrow \infty$. An expectation value of a (dynamical) quantity $\mathbf{f} = \mathbf{f}(\mathbf{z})$ is calculated as

$$\langle \mathbf{f}(\mathbf{z}) \rangle_{\mathcal{P}} = \int_{\mathcal{P}} \mathbf{f}(\mathbf{z}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} \quad (80)$$

We also call $\langle \mathbf{f}(\mathbf{z}) \rangle_{\mathcal{P}}$ the probability average of $\mathbf{f}(\mathbf{z})$.

3.2. Liouville equation

Let us now follow the motion of each system $\mathcal{Z}_1, \mathcal{Z}_2, \dots$, which at reference time $\tau = \tau_1$ occupy a phase space volume element $\mathcal{R}(\tau_1)$. The systems move along their trajectories and at time $\tau = \tau_2$ they occupy a phase space volume element $\mathcal{R}(\tau_2)$.

If there are no ‘sources’ and or ‘sinks’ for the flux of points in phase space (their trajectories do not intersect, disappear or appear) the principle of conservation of probability in phase space requires the probability density function to follow the continuity equation, i.e.

$$\mathbf{W}_{,\tau} + \text{div}_{\mathbf{z}}(\mathbf{z}_{;\tau} \mathbf{W}) = 0 \quad (81)$$

By expanding the divergence term, the equation above can be rewritten as

$$\mathbf{W}_{,\tau} + \mathbf{W} \text{div}_{\mathbf{z}}(\mathbf{z}_{;\tau}) + \nabla_{\mathbf{z}} \mathbf{W}(\mathbf{z}, \tau) \cdot \mathbf{z}_{;\tau} = 0 \quad (82)$$

Since the motion of a Hamiltonian system conserves volume (equation (76)), it follows that

$$\mathbf{W}_{,\tau}(\mathbf{z}, \tau) = -\nabla_{\mathbf{z}} \mathbf{W}(\mathbf{z}, \tau) \cdot \mathbf{z}_{;\tau} \quad (83)$$

where by $_{,\tau}$ we denote the partial time derivative. Equation (83) is usually called the Liouville equation. It can be rewritten in terms of total time derivative as

$$\mathbf{W}_{;\tau}(\mathbf{z}, \tau) = 0 \quad (84)$$

Thus the probability density function is constant in time.

Note, that the principle of conservation of probability and the conservation of volume in phase space are related. In order to see the connection between the two, consider the motion of points in phase space as a coordinate transformation on the phase space from initial to current time, i.e.

$$\int_{\mathcal{R}(t)} \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} = \int_{\mathcal{R}(0)} \mathbf{W}(\mathbf{z}, 0) J d\mathbf{z} \quad (85)$$

where J is the Jacobian of the transformation. If the volume is preserved during transformation (i.e. $J = 1$) the RHS of equation (85) does not depend on time, by taking the total time derivative one immediately arrives at equation (81). Thus, the Liouville theorem can also be stated as a conservation of the phase space volume of a collection of equivalent systems moving through phase space.

The expectation of the variable in equation (80) is an improper integral containing $\mathbf{W}$. As we will see later, the resulting continuum fields will also include internal forces $\mathbf{f}_{\text{int}}^{\alpha} = -\nabla_{\mathbf{x}^{\alpha}} \mathbf{V}_{\text{int}}$. Thus, certain regularity conditions for $\mathbf{W}$ and $\mathbf{V}_{\text{int}}$ have to be met so that these integrals converge. The following conditions are necessary [3, 4]:

1. There exists a $\delta > 0$ such that the function

$$\mathbf{W}(\mathbf{z}, \tau) \prod_{\alpha=1}^N |\mathbf{x}^\alpha|^{3+\delta} \prod_{\beta=1}^N |\mathbf{x}_{;\tau}^\beta|^{3+\delta} \quad (86)$$

as well as its derivatives are bounded by a constant which depends only on τ .

2. The function V_{int} is defined on the phase space, continuously differentiable and is bounded together with its derivative.

These conditions ensure the convergence of integrals as well as allowing us to swap differentiation and integration.

Let $\mathbf{G}(\mathbf{z})$ be a tensor (of order one or higher) valued C^1 function defined on the phase space. Using integration by parts in phase space one obtains

$$\int_{\mathcal{P}} \text{div}_{\mathbf{z}}(\mathbf{W}(\mathbf{z}, \tau) \mathbf{G}(\mathbf{z})) \, d\mathbf{z} = \int_{\mathcal{P}} \mathbf{W}(\mathbf{z}, \tau) \text{div}_{\mathbf{z}} \mathbf{G}(\mathbf{z}) \, d\mathbf{z} + \int_{\mathcal{P}} \mathbf{G}(\mathbf{z}) \cdot \nabla_{\mathbf{z}} \mathbf{W}(\mathbf{z}, \tau) \, d\mathbf{z} \quad (87)$$

If in addition to the above-mentioned requirements to $\mathbf{W}$, $\mathbf{G}(\mathbf{z})$ satisfies the inequalities

$$\begin{aligned} |\mathbf{G}| &< \mathbf{A}(\tau) \prod_{\beta=1}^N |\mathbf{x}_{;\tau}^\beta|^3 + \mathbf{B}(\tau) \\ |\nabla_{\mathbf{x}^\alpha} \mathbf{G}| &< \mathbf{A}(\tau) \prod_{\beta=1}^N |\mathbf{x}_{;\tau}^\beta|^3 + \mathbf{B}(\tau) \\ |\nabla_{\mathbf{x}_{;\tau}^\alpha} \mathbf{G}| &< \mathbf{A}(\tau) \prod_{\beta=1}^N |\mathbf{x}_{;\tau}^\beta|^3 + \mathbf{B}(\tau) \end{aligned} \quad (88)$$

together with a fast enough decay of $\mathbf{W}$ as $|\mathbf{z}| \rightarrow \infty$, based on the Gauss theorem in phase space the LHS of equation (87) equals zero. Therefore

$$\int_{\mathcal{P}} \mathbf{W}(\mathbf{z}, \tau) \text{div}_{\mathbf{z}} \mathbf{G}(\mathbf{z}) \, d\mathbf{z} = - \int_{\mathcal{P}} \mathbf{G}(\mathbf{z}) \cdot \nabla_{\mathbf{z}} \mathbf{W}(\mathbf{z}, \tau) \, d\mathbf{z} \quad (89)$$

Let us next consider the following special case

$$\mathbf{G} = \mathbf{f}(\mathbf{z}) \mathbf{z}_{;\tau} \quad (90)$$

It then follows that

$$\text{div}_{\mathbf{z}} \mathbf{G} = \mathbf{z}_{;\tau} \cdot \nabla_{\mathbf{z}} \mathbf{f}(\mathbf{z}) + \mathbf{f}(\mathbf{z}) \text{div}_{\mathbf{z}} \mathbf{z}_{;\tau} \quad (91)$$

Thanks to the conservation of volume in phase space, equation (76), the second term equals zero, thus¹⁵

$$\text{div}_{\mathbf{z}} \mathbf{G} = \mathbf{f}_{;\tau}(\mathbf{z}) \quad (92)$$

Using equations (90) and (92) in (89) leads to

$$\int_{\mathcal{P}} \mathbf{f}_{;\tau}(\mathbf{z}) \mathbf{W}(\mathbf{z}, \tau) \, d\mathbf{z} = - \int_{\mathcal{P}} \mathbf{f}(\mathbf{z}) \nabla_{\mathbf{z}} \mathbf{W}(\mathbf{z}, \tau) \cdot \mathbf{z}_{;\tau} \, d\mathbf{z} \quad (93)$$

Based on this result we can prove, that time differentiation and statistical averaging commute

$$\boxed{\partial_{\tau} \langle \mathbf{f}(\mathbf{z}) \rangle_{\mathcal{P}} = \langle \mathbf{f}_{;\tau}(\mathbf{z}) \rangle_{\mathcal{P}}} \quad (94)$$

Proof.

$$\partial_\tau \langle \mathbf{f}(\mathbf{z}) \rangle_{\mathcal{P}} = \int_{\mathcal{P}} \mathbf{f}(\mathbf{z}) \mathbf{W}_{,\tau}(\mathbf{z}, \tau) d\mathbf{z} = - \int_{\mathcal{P}} \mathbf{f}(\mathbf{z}) \nabla_{\mathbf{z}} \mathbf{W}(\mathbf{z}, \tau) \cdot \mathbf{z}_{;\tau} d\mathbf{z} = \int_{\mathcal{P}} \mathbf{f}_{;\tau}(\mathbf{z}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} = \langle \mathbf{f}_{;\tau}(\mathbf{z}) \rangle_{\mathcal{P}}$$

where we used the Liouville equation (83) and equation (93).

Equation (94) is very rarely used in papers which follow the elegant approach of statistical averaging originally proposed by Irving and Kirkwood [2] and Noll [3]. Often it is rather equation (89) which is considered to be the main result of the Liouville theorem equipped with the above-mentioned decay conditions on $\mathbf{W}$. That necessitates a number of additional steps which make the derivation more complicated and harder to follow for the reader. This is especially the case for the angular momentum and the energy balance equations, which we discuss in the second part of this series [24].

4. Averaging

4.1. Probability averaging

In probability theory, the marginal probability density for the position $\xi = \mathbf{x}^\alpha = \mathbf{z}^\alpha$ is defined as

$$\omega^\alpha(\xi) = \int_{\mathcal{P}} \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z}^1 \dots d\mathbf{z}^{\alpha-1} d\mathbf{z}^{\alpha+1} \dots d\mathbf{z}^N d\mathbf{z}^{N+1} \dots d\mathbf{z}^{2N} \quad (95)$$

It gives a probability density function of $\mathbf{x}^\alpha$ with all other variables ‘integrated out’. The expression above can alternatively be considered as a probability per unit volume in phase space $\mathcal{P}$ to find the particle α at the spatial position ξ

$$\omega^\alpha(\xi) = \int_{\mathcal{P}} \delta(\mathbf{x}^\alpha - \xi) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} \quad (96)$$

In a similar manner, the property density (per unit volume in space $\mathcal{S}$) gives the probability of finding the extensive (additive) property $\mathbf{g}^\alpha(\mathbf{z})$ attributed to the particle α at the spatial position ξ

$$\int_{\mathcal{P}} \mathbf{g}^\alpha(\mathbf{z}) \delta(\mathbf{x}^\alpha - \xi) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} \quad (97)$$

Following equation (97), the total property density of property $\mathbf{g}^\alpha(\mathbf{z})$ per unit volume in space $\mathcal{S}$

$$\pi_{\mathbf{g}}(\xi, \tau) := \sum_{\alpha} \int_{\mathcal{P}} \mathbf{g}^\alpha(\mathbf{z}) \delta(\mathbf{x}^\alpha - \xi) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} := \int_{\mathcal{P}} \mathbf{g}_{\delta}(\mathbf{z}, \xi) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} = \langle \mathbf{g}_{\delta}(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \quad (98)$$

is the sum of the probabilities to find the property $\mathbf{g}^\alpha(\mathbf{z})$ attached to the particle α at ξ ; it can also be considered as a probability average of the δ -distribution of a property that we defined as

$$\mathbf{g}_{\delta}(\mathbf{z}, \xi) = \sum_{\alpha} \mathbf{g}_{\delta}^{\alpha}(\mathbf{z}, \xi) := \sum_{\alpha} \mathbf{g}^{\alpha}(\mathbf{z}) \delta(\mathbf{x}^{\alpha} - \xi) \quad (99)$$

Using equation (98) in equation (94) the rate of that quantity at the fixed spatial position ξ is

$$\begin{aligned} \pi_{\mathbf{g},\tau}(\xi, \tau) &= \langle \mathbf{g}_{\delta;\tau}(\mathbf{z}, \xi) \rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} \mathbf{g}_{\delta;\tau}^{\alpha}(\mathbf{z}) \delta(\mathbf{x}^{\alpha} - \xi) \right\rangle_{\mathcal{P}} + \left\langle \sum_{\alpha} \mathbf{g}^{\alpha}(\mathbf{z}) \nabla \delta(\mathbf{x}^{\alpha} - \xi) \cdot \mathbf{x}_{;\tau}^{\alpha} \right\rangle_{\mathcal{P}} \\ &= \left\langle \sum_{\alpha} \mathbf{g}_{\delta;\tau}^{\alpha}(\mathbf{z}) \delta(\mathbf{x}^{\alpha} - \xi) \right\rangle_{\mathcal{P}} - \operatorname{div}_{\xi} \left\langle \sum_{\alpha} \mathbf{g}^{\alpha}(\mathbf{z}) \mathbf{x}_{;\tau}^{\alpha} \delta(\mathbf{x}^{\alpha} - \xi) \right\rangle_{\mathcal{P}} \end{aligned} \quad (100)$$

where the gradient of the Dirac δ has to be understood in a distributional sense

$$\nabla \delta(\mathbf{x}^{\alpha} - \xi) = -\nabla_{\xi} \delta(\mathbf{x}^{\alpha} - \xi) \quad (101)$$

4.2. Space–probability averaging

Up to now, our averaging was defined using the δ -function in space together with the probability density function. As an imaginary experiment, let us consider a one-component crystal in equilibrium at a relatively low temperature. In such a system the atoms will undergo small fluctuations w.r.t. the equilibrium positions in the crystalline lattice. Thus, the total property density defined as equation (98) will be zero almost everywhere except at $\xi = \mathbf{x}^\alpha$. However, from the continuum point of view we aim to consider smooth fields, therefore we convince ourselves that an additional averaging in space is needed. Additional spatial averaging is also required in order to link field values with measurements (which represent macroscopic sampling at a particular length scale). Then the averaging kernel choice is what delivers the physical interpretation of field values.

The space–probability averaging over $\mathcal{S}$ is thus defined as

$$g(\mathbf{x}, \tau) = \langle \bar{g}(\xi, \tau) \rangle_{\mathcal{S}} := \int_{\mathcal{S}} \bar{g}(\xi, \tau) w(\xi - \mathbf{x}) d\xi \quad (102)$$

with the normalization condition for the averaging kernel

$$\int_{\mathcal{S}} w(\xi - \mathbf{x}) d\xi = 1 \quad (103)$$

where $\mathcal{S}$ is a vector space of translations.

Similar to equation (99), let us define the ζ -distribution of property

$$\bar{g}(\mathbf{z}, \mathbf{x}) = \sum_{\alpha} \bar{g}^{\alpha}(\mathbf{z}, \mathbf{x}) := \sum_{\alpha} g^{\alpha}(\mathbf{z}) w(\mathbf{x}^{\alpha} - \mathbf{x}) \quad (104)$$

which turns out to be nothing more but the space-averaged δ -distribution of property $g_{\delta}(\mathbf{z}, \xi)$

$$\begin{aligned} \langle g_{\delta}(\mathbf{z}, \xi) \rangle_{\mathcal{S}} &= \int_{\mathcal{S}} g_{\delta}(\mathbf{z}, \xi) w(\xi - \mathbf{x}) d\xi = \int_{\mathcal{S}} \sum_{\alpha} g^{\alpha}(\mathbf{z}) \delta(\mathbf{x}^{\alpha} - \xi) w(\xi - \mathbf{x}) d\xi \\ &= \sum_{\alpha} g^{\alpha}(\mathbf{z}) w(\mathbf{x}^{\alpha} - \mathbf{x}) = \bar{g}(\mathbf{z}, \mathbf{x}) \end{aligned} \quad (105)$$

4.3. Commutative properties

We can prove that space and probability averaging commute

$$\boxed{g(\mathbf{x}, \tau) = \langle \langle g_{\delta}(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \rangle_{\mathcal{S}} = \langle \langle g_{\delta}(\mathbf{z}, \xi) \rangle_{\mathcal{S}} \rangle_{\mathcal{P}}} \quad (106)$$

Proof.

$$\begin{aligned} \langle \langle g_{\delta}(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \rangle_{\mathcal{S}} &= \int_{\mathcal{S}} \int_{\mathcal{P}} g_{\delta}(\mathbf{z}, \xi) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z} w(\xi - \mathbf{x}) d\xi \\ &= \sum_{\alpha} \int_{\mathcal{P}} g^{\alpha}(\mathbf{z}) \int_{\mathcal{S}} \delta(\mathbf{x}^{\alpha} - \xi) w(\xi - \mathbf{x}) d\xi \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z} \\ &= \sum_{\alpha} \int_{\mathcal{P}} g^{\alpha}(\mathbf{z}) w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z} \\ &= \int_{\mathcal{P}} \bar{g}(\mathbf{z}, \mathbf{x}) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z} \\ &= \langle \bar{g}(\mathbf{z}, \mathbf{x}) \rangle_{\mathcal{P}} \\ &= \langle \langle g_{\delta}(\mathbf{z}, \xi) \rangle_{\mathcal{S}} \rangle_{\mathcal{P}} \end{aligned}$$

where we have used the definitions given in equations (104) and (99), and the property (105).

One can also consider space–probability averaging as a probability averaging with a smeared kernel (from the proof above)

$$g(\mathbf{x}, \tau) = \langle \bar{\mathbf{g}}(\mathbf{z}, \mathbf{x}) \rangle_{\mathcal{P}} \quad (107)$$

We can easily prove, that the divergence of a space-averaged quantity equals space averaging of its divergence

$$\boxed{\operatorname{div}_{\mathbf{x}} \langle \bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) \rangle_S = \langle \operatorname{div}_{\boldsymbol{\xi}} \bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) \rangle_S} \quad (108)$$

Proof.

$$\begin{aligned} \operatorname{div}_{\mathbf{x}} \langle \bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) \rangle_S &= \int_S \bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) \cdot \nabla_{\mathbf{x}} w(\boldsymbol{\xi} - \mathbf{x}) d\boldsymbol{\xi} = - \int_S \bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) \cdot \nabla_{\boldsymbol{\xi}} w(\boldsymbol{\xi} - \mathbf{x}) d\boldsymbol{\xi} \\ &= - \int_S \operatorname{div}_{\boldsymbol{\xi}} (\bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) w(\boldsymbol{\xi} - \mathbf{x})) d\boldsymbol{\xi} + \int_S \operatorname{div}_{\boldsymbol{\xi}} \bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) w(\boldsymbol{\xi} - \mathbf{x}) d\boldsymbol{\xi} = \langle \operatorname{div}_{\boldsymbol{\xi}} \bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) \rangle_S \end{aligned}$$

where $\int_S \operatorname{div}_{\boldsymbol{\xi}} (\bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) w(\boldsymbol{\xi} - \mathbf{x})) d\boldsymbol{\xi} = 0$ thanks to the compact support of the averaging kernel function $w(\boldsymbol{\xi} - \mathbf{x})$.

4.4. Rates of quantities

In order to obtain balance equations for space–probability averaged quantities, one has to develop formulas for their rates. Since time differentiation and integration in space can be exchanged, it immediately follows that the rate of a spatially averaged quantity equals the spatial averaging of its rate

$$\boxed{\partial_{\tau} \langle \bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) \rangle_S = \langle \partial_{\tau} \bar{\mathbf{g}}(\boldsymbol{\xi}, \tau) \rangle_S} \quad (109)$$

With the help of equation (94) we can next show that the rate of the property density associated with the particle α equals

$$\boxed{\partial_{\tau} \langle \bar{\mathbf{g}}^{\alpha}(\mathbf{z}, \mathbf{x}) \rangle_{\mathcal{P}} = \langle \bar{\mathbf{g}}_{;\tau}^{\alpha}(\mathbf{z}, \mathbf{x}) \rangle_{\mathcal{P}} - \operatorname{div} \langle \bar{\mathbf{g}}^{\alpha}(\mathbf{z}, \mathbf{x}) \otimes \mathbf{x}_{;\tau}^{\alpha} \rangle_{\mathcal{P}}} \quad (110)$$

where the ζ -averaged rate of the property associated with the particle α is denoted as

$$\bar{\mathbf{g}}_{;\tau}^{\alpha} = \bar{\mathbf{g}}_{;\tau}^{\alpha}(\mathbf{z}) w(\mathbf{x}^{\alpha} - \mathbf{x}) \quad (111)$$

Proof.

$$\begin{aligned} \partial_{\tau} \langle \bar{\mathbf{g}}^{\alpha}(\mathbf{z}, \mathbf{x}) \rangle_{\mathcal{P}} &= \langle \bar{\mathbf{g}}_{;\tau}^{\alpha}(\mathbf{z}, \mathbf{x}) \rangle_{\mathcal{P}} = \int_{\mathcal{P}} \bar{\mathbf{g}}_{;\tau}^{\alpha}(\mathbf{z}, \mathbf{x}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} \\ &= \int_{\mathcal{P}} \bar{\mathbf{g}}_{;\tau}^{\alpha}(\mathbf{z}) w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} - \operatorname{div} \int_{\mathcal{P}} \bar{\mathbf{g}}^{\alpha}(\mathbf{z}) \otimes \mathbf{x}_{;\tau}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbf{W}(\mathbf{z}, \tau) d\mathbf{z} \end{aligned}$$

Summation over all particles leads to the rate of the total space–probability averaged property density

$$\boxed{g_{,\tau}(\mathbf{x}, \tau) = \left\langle \sum_{\alpha} \bar{\mathbf{g}}_{;\tau}^{\alpha}(\mathbf{z}, \mathbf{x}) \right\rangle_{\mathcal{P}} - \operatorname{div} \left\langle \sum_{\alpha} \bar{\mathbf{g}}^{\alpha}(\mathbf{z}, \mathbf{x}) \otimes \mathbf{x}_{;\tau}^{\alpha} \right\rangle_{\mathcal{P}}} \quad (112)$$

This equation is the basis for the derivation of all balance equations considered in the sequel.

4.5. Integral of quantities

Note finally, that the total property density integrated over space S is not affected by the space-averaging kernel

Proof.

$$\begin{aligned}
 \int_S g(\mathbf{x}, \tau) d\mathbf{x} &= \int_S \sum_{\alpha} \int_{\mathcal{P}} g^{\alpha}(\mathbf{z}) w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} d\mathbf{x} \\
 &= \int_{\mathcal{P}} \sum_{\alpha} g^{\alpha}(\mathbf{z}) \int_S w(\mathbf{x}^{\alpha} - \mathbf{x}) d\mathbf{x} \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} \\
 &= \int_{\mathcal{P}} \sum_{\alpha} g^{\alpha}(\mathbf{z}) \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} \\
 &= \int_{\mathcal{P}} \mathbf{G}(\mathbf{z}) \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} \\
 &= \langle \mathbf{G}(\mathbf{z}) \rangle_{\mathcal{P}}
 \end{aligned} \tag{113}$$

where we introduced the probability average of the total property of the system

$$\mathbf{G}(\mathbf{z}) := \sum_{\alpha} g^{\alpha}(\mathbf{z}) \tag{114}$$

□

For the special case that g^{α} is independent of $\mathbf{z}$ it holds that $\mathbf{G}(\mathbf{z}) = \langle \mathbf{G}(\mathbf{z}) \rangle_{\mathcal{P}}$.

5. Balance equations of mass and linear momentum

5.1. Continuum fields

Having developed the required theoretical background for space–probability averaging we are now ready to define continuum fields based on the properties associated with each particle in the discrete system and then to obtain the balance equations by evaluating the rates of such quantities.

There are essentially four balance equations in continuum mechanics that we shall consider in the sequel: mass, linear and angular momentum, and energy. In this part of the series we discuss only the first two balance equations, that is the balance of mass and the balance of linear momentum. The balances of energy and of angular momentum give rise to other important discussions which we leave for the second part of the series [24].

Let us define the following continuum fields:

- mass density

$$\varrho(\mathbf{x}, \tau) := \langle \langle m_{\delta}(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \rangle_S = \sum_{\alpha} \int_{\mathcal{P}} m^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} \tag{115}$$

- linear momentum density

$$\mathbf{p}(\mathbf{x}, \tau) := \langle \langle \mathbf{p}_{\delta}(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \rangle_S = \sum_{\alpha} \int_{\mathcal{P}} \mathbf{p}^{\alpha} w(\mathbf{x}^{\alpha} - \mathbf{x}) \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} \tag{116}$$

Recall that the total mass of the system as well as the total linear momentum does not depend on the type of space-averaging (113):

$$\int_S \varrho(\mathbf{x}, \tau) d\mathbf{x} = \sum_{\alpha} \int_{\mathcal{P}} m^{\alpha} \left[\int_S w(\mathbf{x}^{\alpha} - \mathbf{x}) d\mathbf{x} \right] \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} = \int_{\mathcal{P}} \sum_{\alpha} m^{\alpha} \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} = \mathbf{M} \tag{117}$$

$$\int_S \mathbf{p}(\mathbf{x}, \tau) d\mathbf{x} = \sum_{\alpha} \int_{\mathcal{P}} \mathbf{p}^{\alpha} \left[\int_S w(\mathbf{x}^{\alpha} - \mathbf{x}) d\mathbf{x} \right] \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} = \int_{\mathcal{P}} \sum_{\alpha} \mathbf{p}^{\alpha} \mathbb{W}(\mathbf{z}, \tau) d\mathbf{z} = \langle \mathbf{P} \rangle_{\mathcal{P}} \tag{118}$$

Given the linear momentum and mass densities, the continuum velocity can be defined as

$$\mathbf{v}(\mathbf{x}, \tau) := \frac{\mathbf{p}(\mathbf{x}, \tau)}{\varrho(\mathbf{x}, \tau)} = \frac{\langle \langle \mathbf{p}_\delta(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \rangle_S}{\langle \langle \mathbf{m}_\delta(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \rangle_S} = \frac{\sum_\alpha \int_{\mathcal{P}} \mathbf{p}^\alpha w(\mathbf{x}^\alpha - \mathbf{x}) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z}}{\sum_\alpha \int_{\mathcal{P}} m^\alpha w(\mathbf{x}^\alpha - \mathbf{x}) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z}} \quad (119)$$

For each particle α , we also define a fluctuation of the particle velocity field as

$$\tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) := \mathbf{v}^\alpha - \mathbf{v}(\mathbf{x}, \tau) \quad (120)$$

For each α it shifts the continuum velocity field $\mathbf{v}$ by a constant (in space) particle velocity $\mathbf{v}^\alpha$. As we will see in the second part of the series [24], this field represents the internal erratic kinetic energy which can be related to the concept of temperature.¹⁶

Similar to equation (120), the fluctuation of linear momentum is defined as

$$\tilde{\mathbf{p}}^\alpha(\mathbf{x}, \tau) := m^\alpha \tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) \quad (121)$$

As a consequence, the following property holds

$$\langle \langle \tilde{\mathbf{p}}_\delta(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_{\mathcal{P}} \rangle_S = \mathbf{0} \quad (122)$$

Proof.

$$\begin{aligned} \sum_\alpha \int_{\mathcal{P}} \tilde{\mathbf{p}}^\alpha(\mathbf{x}, \tau) w(\mathbf{x}^\alpha - \mathbf{x}) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z} &= \sum_\alpha \int_{\mathcal{P}} m^\alpha \mathbf{v}^\alpha w(\mathbf{x}^\alpha - \mathbf{x}) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z} \\ &\quad - \sum_\alpha \int_{\mathcal{P}} m^\alpha w(\mathbf{x}^\alpha - \mathbf{x}) \mathcal{W}(\mathbf{z}, \tau) d\mathbf{z} \mathbf{v}(\mathbf{x}, \tau) \\ &= \mathbf{0} \end{aligned}$$

□

Let us also define the particle kinetic energy tensor and the particle diffusive momentum flux as

$$\mathbf{k}^\alpha := \frac{1}{2} \mathbf{p}^\alpha \otimes \mathbf{v}^\alpha \quad \text{and} \quad \tilde{\mathbf{s}}^\alpha := \frac{1}{2} \mathbf{p}^\alpha \otimes \tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) \quad (123)$$

and the corresponding continuum kinetic energy tensor and the continuum diffusive momentum flux as

$$\boldsymbol{\kappa} = \frac{1}{2} \mathbf{p}(\mathbf{x}, \tau) \otimes \mathbf{v}(\mathbf{x}, \tau) \quad \text{and} \quad \tilde{\mathbf{s}} = \langle \langle \tilde{\mathbf{s}}_\delta(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_{\mathcal{P}} \rangle_S \quad (124)$$

With these definitions at hand we can show that the continuum kinetic energy tensor equals the space–probability average of the particle kinetic tensor energy minus the continuum diffusive momentum flux

$$\boldsymbol{\kappa} = \langle \langle \mathbf{k}_\delta(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \rangle_S - \langle \langle \tilde{\mathbf{s}}_\delta(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_{\mathcal{P}} \rangle_S = \mathbf{k} - \tilde{\mathbf{s}} \quad (125)$$

Proof.

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

□

Note, that our definition in equation (123) of the particle diffusive momentum flux is different from the one often used in the literature

$$\frac{1}{2} \mathbf{m}^\alpha \tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) \otimes \tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) \quad (126)$$

However, it is easy to show that the space-probability average of both quantities coincide

$$\begin{aligned} \left\langle \sum_\alpha \frac{1}{2} \mathbf{m}^\alpha \tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) \otimes \tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}} &= \left\langle \sum_\alpha \frac{1}{2} \mathbf{m}^\alpha [\mathbf{v}^\alpha - \mathbf{v}(\mathbf{x}, \tau)] \otimes \tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}} \\ &= \left\langle \sum_\alpha \frac{1}{2} \mathbf{p}^\alpha \otimes \tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}} \\ &\quad - \mathbf{v}(\mathbf{x}, \tau) \otimes \underbrace{\left\langle \sum_\alpha \frac{1}{2} \mathbf{m}^\alpha \tilde{\mathbf{v}}^\alpha(\mathbf{x}, \tau) w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}}}_0 \\ &= \langle \tilde{\mathbf{s}}_\delta(\mathbf{z}, \xi; \mathbf{x}, \tau) \rangle_{\mathcal{P}_S} \end{aligned}$$

where we have used equation (122). Thus, equation (125) holds for both definitions.

The choice to define the diffusive momentum flux using particle momenta rather than mass and fluctuational velocity is made intentionally so that it allows us to subsequently discover similar terms in the balance of angular momentum [24].

5.2. Deformation map

Given the definition of the velocity field in an Eulerian sense (119), we can integrate it in time to obtain the deformation map

$$\mathbf{x} = \boldsymbol{\varphi}(\mathbf{X}, \tau) \quad (127)$$

To this end, consider the velocity as

$$\boldsymbol{\varphi}_{;\tau}(\mathbf{X}, \tau) = \mathbf{v}(\boldsymbol{\varphi}(\mathbf{X}, \tau), \tau) \quad (128)$$

Integration in time leads to

$$\mathbf{x} = \boldsymbol{\varphi}(\mathbf{X}, \tau) = \mathbf{X} + \int_0^\tau \frac{\langle \sum_\alpha \mathbf{m}^\alpha \mathbf{v}^\alpha w(\mathbf{x}^\alpha - \boldsymbol{\varphi}(\mathbf{X}, \tau)) \rangle_{\mathcal{P}}}{\langle \sum_\alpha \mathbf{m}^\alpha w(\mathbf{x}^\alpha - \boldsymbol{\varphi}(\mathbf{X}, \tau)) \rangle_{\mathcal{P}}} d\tau \quad (129)$$

which is implicit in $\boldsymbol{\varphi}$. Thus, in order to follow the motion in a Lagrangian sense, one has to choose a point $\mathbf{X}$ at the reference time and follow its motion using the continuum velocity $\mathbf{v}(\mathbf{x}, \tau)$.

5.3. Balance of mass

The balance of mass is trivially obtained by using equation (115) in equation (112)

$$\varrho_{,\tau} = -\operatorname{div} \left\langle \sum_\alpha \underbrace{\mathbf{m}^\alpha \mathbf{x}_{;\tau}^\alpha}_{\mathbf{p}^\alpha} w(\mathbf{x}^\alpha - \mathbf{x}) \right\rangle_{\mathcal{P}} \quad (130)$$

that is

$$\boxed{\varrho_{,\tau} + \operatorname{div} \mathbf{p} = 0} \quad (131)$$

Note that this is a special case of a balance equation with vanishing flux and source terms.

5.4. Balance of linear momentum

Using equation (116) in equation (112) and recalling the second Newton law, equation (35) leads to

$$\mathbf{p}_{,\tau} + \operatorname{div} \left\langle \sum_{\alpha} \underbrace{\mathbf{p}^{\alpha} \otimes \mathbf{x}_{;\tau}^{\alpha}}_{2\mathbf{k}^{\alpha}} w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} = \left\langle \sum_{\alpha} \mathbf{f}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \right\rangle_{\mathcal{P}} \quad (132)$$

Dividing the force into its external and internal contributions, equation (36), and using equation (125) allows the rewriting of equation (132) as

$$\boxed{\mathbf{p}_{,\tau} + \operatorname{div}(\mathbf{p} \otimes \mathbf{v}) = \operatorname{div} \mathbf{s}(\mathbf{x}, \tau) + \mathbf{b}(\mathbf{x}, \tau)} \quad (133)$$

where we have defined the linear momentum flux, i.e. the Cauchy stress, implicitly as

$$\operatorname{div} \widehat{\mathbf{s}} := \operatorname{div}(\mathbf{s} + 2\widetilde{\mathbf{s}}) := \langle \langle \mathbf{f}_{\delta}^{\text{int}}(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \rangle_{\mathcal{S}} = \sum_{\alpha} \langle \mathbf{f}_{\text{int}}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \rangle_{\mathcal{P}} \quad (134)$$

and the linear momentum source as

$$\mathbf{b} := \langle \langle \mathbf{f}_{\delta}^{\text{ext}}(\mathbf{z}, \xi) \rangle_{\mathcal{P}} \rangle_{\mathcal{S}} = \sum_{\alpha} \langle \mathbf{f}_{\text{ext}}^{\alpha}(\tau) w(\mathbf{x}^{\alpha} - \mathbf{x}) \rangle_{\mathcal{P}} \quad (135)$$

The balance equations of mass (131) and linear momentum (133) take exactly the same forms as in geometrically non-linear continuum mechanics. Yet, one has to take additional steps in order to have a complete link between atomistic systems and continuum mechanics. In the balance of mass the convective flux (linear momentum) has an explicit definition, equation (116), whereas in the balance of linear momentum one has to solve equation (134) in order to obtain the expression for the corresponding physical flux (stresses). Since the same situation occurs for the balance of angular momentum and energy [24], we discuss possible solutions for all fluxes in the third contribution of this series [28].

6. Discussion and conclusions

The averaging procedure described above is to be applied to MD simulations. However, the probability density function is usually not easily available in MD. The common solution is to replace probability averaging with averaging in time using the ergodic hypothesis. Note, however, that ergodicity is valid only for stationary states. In other words it is assumed that if one observes the system long enough, the phase space is adequately covered by the states of the system.

A general time-kernel, similar to the space-averaging kernel w can be used. Thus, statistical averaging is replaced by an integral in the fast time variable. An alternative approach in developing the link between a discrete system and a continuum is to start with temporal averaging, as was advocated by Murdoch [9]. Temporal averaging has the same commutative properties of time differentiation and divergence in space as the probability density averaging, equations (94) and (108). Therefore, we conclude that the two approaches are interchangeable in practical applications.

Note, that in the development of balance equations an assumption on C^1 continuity has tacitly been made. That means essentially that the results are meaningful only if the averaging in space and time are such that the resulting macroscopic fields are smooth.

Having discussed the fundamental laws of classical mechanics, we believe that any possible application of the space-probability averaging approach to non-central interaction forces should start from the introduction of new DOF for each particle or even qualitatively new types of particles followed by the derivation of the balance equations starting from the Euler laws.

Based on the fundamental principles of classical mechanics and statistical physics, we carefully revised all the steps in linking discrete systems to a continuum. Despite the fact, that the link between atomistic quantities and continuum fields has been the subject of research for at least half a century there are certain important differences which distinguish our contribution from others.

By revising the laws of classical mechanics we argue that internal interactions are always central, independent of the potential they are described by (e.g. two-point, angle, dihedral, etc.). That fact is also in agreement with the invariance of the Lagrangian to the Galilean transformation group. These conclusions are central to the discussion of the symmetry of the resulting Cauchy stress [28] in the follow-up contribution to this series.

On our way to connecting continuum mechanics and particle systems, we start from the definition of the space–probability averaged quantities for which the balance equations are then obtained. Very often [9, 12, 21] it is the balance equations for the probability-averaged quantities which are obtained first, then they are spatially averaged in order to obtain smooth fields. However, as we discuss in the third part of this series [28], this can bring a false impression of the uniqueness of the expression obtained for stresses using the statistical averaging approach compared to temporal averaging.

In the introduction of space–probability averaging we aimed to go through all the important details in a (hopefully) transparent and easy-to-follow way. A number of general theorems related to the convolution properties of statistically-averaged quantities, as well as their rates are also proven (equations (94), (112) and (108)). These theorems make the derivation of the balance equations far more simple when compared to the approach often used in the literature [3, 12]. Such theorems also make the link between space–time averaging [29] and space–probability averaging more transparent, as we discussed earlier.

Finally, we propose a slightly different definition of the particle kinetic energy tensor and particle diffusive momentum flux which will make the link to the angular momentum more transparent [24].

In part two of the series [24] we consider the balance of angular momentum and energy, whereas in the third part [28] different atomistic expressions of fluxes arising in all the balance equations together with the method to obtain them are discussed.

Conflict of interest

None declared.

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Notes

1. In special relativity the Galilean invariance principle is to be replaced by the Lorentz invariance principle.
2. We note that if point-particles with additional rotational DOF are considered (we may denote such particles as spin-particles), their configuration is described by a rotational tensor $\mathbf{R}^\alpha$ in addition to the position vector $\mathbf{x}^\alpha$. The kinetic energy is then postulated as $k^\alpha = \frac{1}{2}m^\alpha \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha + \mathbf{q}^\alpha \mathbf{v}^\alpha \cdot \mathbf{w}^\alpha + \frac{1}{2}j^\alpha \mathbf{w}^\alpha \cdot \mathbf{w}^\alpha$, where $\mathbf{w}^\alpha$ is the angular velocity, i.e. the axial vector of $\mathbf{w}^\alpha = -\frac{1}{2}\dot{\mathbf{R}}^\alpha \cdot [\mathbf{R}^\alpha]^T$, and j^α denotes the isotropic moment of inertia, finally $\mathbf{q}^\alpha$ is an additional parameter that couples linear and angular velocity [25].
3. Note that $\mathbf{l}^\alpha = \mathbf{l}^\alpha(\tau; \mathbf{y})$. However, in order to simplify notation we drop the dependence on $\mathbf{y}$ from now on.
4. In order to shorten the notation we will omit the dependence on the particle positions in the sequel [24].
5. Boldface $\mathbf{m}^\alpha$ denoting the moment should not be confused with the meager m^α denoting the mass. Note, that $\mathbf{m}^\alpha = \mathbf{m}^\alpha(\tau; \mathbf{y})$, however, in order to simplify notation we drop the dependence on $\mathbf{y}$ from now on.
6. Boldface $\mathbf{p}^\alpha$ denoting the linear momentum should not be confused with the meager p^α denoting the power.
7. Boldface $\mathbf{v}^\alpha$ denoting the velocity should not be confused with the meager v^α denoting the potential.
8. In Lagrangian mechanics, the additivity of the kinetic energy follows from an axiom on the additivity of Lagrangians (and thus motion) for non-interacting systems, whereas the additivity of the linear and the angular momentum follows from the homogeneity and the isotropy of space. The existence of the reference system in which the total linear momentum of a closed body in the absence of external forces equals zero, gives the principle of additivity of mass.
9. Originally Euler [30] formulated his laws for a rigid body. However, these laws can also be postulated [25] for a general system of particles. That broadens Newtonian mechanics and allows us to introduce additional DOF such as spinorial motion, which are successfully applied to study complex crystals [31, 32] and electromagnetism [33]. Finally, consider the Noether theorem [34] that homogeneity of space gives rise to the conservation of total linear momentum for a closed isolated system, whereas isotropy of space results in the conservation of total angular momentum. This theorem is reversible. Since homogeneity and isotropy of space are independent concepts, linear and angular balance laws must also be independent.
10. Note, that Euler laws are not limited to closed systems.
11. In Newtonian mechanics this law is sometimes considered as a theorem, which can be proven based on the balance of linear momentum and an additional axiom $\mathbf{f}^{\alpha\beta} \times \mathbf{x}^{\alpha\beta} = \mathbf{0}$ (the extended third Newton law). In such a case, however, invalidity of this axiom would lead to invalidity of classical mechanics in general, which is unacceptable.

12. In case there are rotational DOF, that equation includes the power of moment interactions as well.
13. Generally speaking, velocity belongs to the tangent space to the configuration space. However, in the Euclidean setting these two spaces are indistinguishable.
14. in terms of macroscopic observables such as energy, temperature, linear momentum etc.
15. We would like to draw attention to the fact, that these derivations are valid when $\mathbf{f} = \mathbf{f}(\mathbf{z})$ does not depend explicitly on time. For the case $\mathbf{f} = \mathbf{f}(\mathbf{z}, \tau)$, the divergence reads $\text{div}_{\mathbf{z}} \mathbf{G} = \mathbf{f}_{,\tau} - \mathbf{f}_{,\tau}$. However, this extended case need not be considered here.
16. The choice of velocity which is connected to temperature depends on the researcher's point of view. The part of the velocity which contributes to temperature can alternatively be postulated as $\mathbf{v}^\alpha - \mathbf{v}(\mathbf{x}, \tau) - \mathbf{D} \cdot [\mathbf{x}^\alpha - \mathbf{x}]$ where $\mathbf{D}$ denotes the velocity gradient (see Murdoch [8] for details). In this series, however, we follow the definition as proposed in the literature [2, 3, 5, 35].

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