J Elasticity (2007) 88:113–140
DOI 10.1007/s10659-007-9121-5

A Critique of Atomistic Definitions of the Stress Tensor

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Received: 23 January 2007 / Accepted: 31 May 2007 /
Published online: 28 July 2007

Abstract Current interest in nanoscale systems and molecular dynamical simulations has focussed attention on the extent to which continuum concepts and relations may be utilised meaningfully at small length scales. In particular, the notion of the Cauchy stress tensor has been examined from a number of perspectives. These include motivation from a virial-based argument, and from scale-dependent localisation procedures involving the use of weighting functions. Here different definitions and derivations of the stress tensor in terms of atoms/molecules, modelled as interacting point masses, are compared. The aim is to elucidate assumptions inherent in different approaches, and to clarify associated physical interpretations of stress. Following a critical analysis and extension of the virial approach, a method of spatial atomistic averaging (at any prescribed length scale) is presented and a balance of linear momentum is derived. The contribution of corpuscular interactions is represented by a force density field $\mathbf{f}$. The balance relation reduces to standard form when $\mathbf{f}$ is expressed as the divergence of an interaction stress tensor field, $\mathbf{T}^{-}$. The manner in which $\mathbf{T}^{-}$ can be defined is studied, since $\mathbf{T}^{-}$ is unique only to within a divergence-free field. Three distinct possibilities are discussed and critically compared. An approach to nanoscale systems is suggested in which $\mathbf{f}$ is employed directly, so obviating separate modelling of interfacial and edge effects.

Keywords Stress · Molecular averaging · Microscopic interpretation · Weighting function · Nanoscale systems

Mathematics Subject Classification (2000) 74A25

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1 Introduction

The macroscopic behaviour of inanimate matter is usually modelled in terms of deterministic continuum mechanics (cf. e.g., [1–3].) If adopted in isolation this approach can give rise to conceptual difficulties concerning questions of scale, physical interpretation of fields, and reproducibility of phenomena. As pointed out in [4], these difficulties can be resolved by linking continuum concepts, fields, and balance relations to molecular behaviour. Such linkage also helps in reverse, in the interpretation of data from molecular dynamical simulations. Of particular interest are systems and/or phenomena in which at least one spatial dimension is macroscopically small, such as liquid–vapour interfaces, shock waves, and nanoscale bodies. In such cases the number of molecules is usually large enough for a classical, rather than quantal, description to be adopted. Here we discuss and compare molecular-based definitions of the Cauchy stress tensor in which molecules are modelled as interacting point masses. A molecular definition of the average stress, computed over any (bounded) region occupied by a system of molecules in macroscopic equilibrium, and then averaged in time, has been established on the basis of virial considerations [5, 6]. In the context of pulse heating and shock compression in solids, a molecular spacetime average 'internal' stress meaningful *within* the region occupied by the system was introduced by Tsai [7]. Hardy [8] recalled the pioneering work of Irving & Kirkwood [9] in which stress is defined as a pointwise statistical average of molecular variables. Via an ergodic hypothesis this stress is identified with molecular averaging in time but not space. Such an approach was not practical for Hardy's purpose of determining local properties of shock waves from molecular dynamics. By the introduction of a spatial 'localisation' function in place of a probability density distribution, he established balances of linear momentum and energy in which field values, including stress, are defined in terms of local *spatial* averages at *any given scale*. Unaware of Hardy's work, Murdoch & Bedeaux [10] adopted a similar approach, drawing upon simplification of the work of Irving & Kirkwood by Noll [11] to obtain molecular expressions for stress and heat flux together with relevant balance relations. Recognising the importance of identifying field values with experimental data, and noting that local measurement values reflect local averages of molecular behaviour both in space *and* time, in [10] all fields are identified via local space*time* averages. The definitions of stress and heat flux before temporal averaging here differ from Hardy's expressions both in form and choice of localisation/weighting function (cf. [12, 13]). Recently Zimmerman et al. [14] have compared the predictions of Hardy stress with those based upon a so-called 'local' virial stress in molecular simulations of a crystal, and Zhou [15] has argued that no definition of mechanical stress should include contributions from microscopic momentum exchange, in contrast to all aforementioned studies. Such lack of consensus motivates the present study which attempts to trace the physical and mathematical assumptions behind molecular definitions of stress, and to compare critically virial formulations and those proposed by Hardy and Murdoch & Bedeaux.

In Section 2 salient aspects of continuum theory are presented for later reference. A link between the continuum description of a macroscopic body and its molecular content is established in Section 3. By considering the virial of a set of interacting point masses which model molecules, a relation between the average stress in the

body and time-averaged sums of molecular variables is derived. It is shown how the argument can be modified for solids to obtain a local, rather than global, stress average. Shortcomings of the virial approach are listed, after which a much more general approach to the molecular basis of continuum fields is introduced in Section 4. The continuity equation and a form of linear momentum balance are derived via scale-dependent weighting function methodology. The balance relation involves an interaction body force density field $\mathbf{f}_w$. The usual form of balance is obtained by exhibiting a tensor field $\mathbf{T}_w^-$, the interaction stress tensor, for which $\operatorname{div}\mathbf{T}_w^- = \mathbf{f}_w$. The Cauchy stress tensor $\mathbf{T}_w$ is thereupon the sum of $\mathbf{T}_w^-$ with a pressure-like tensor $-\boldsymbol{\mathcal{D}}_w$ of kinematic character whose trace is a measure of heat energy density. The non-uniqueness of $\mathbf{T}_w^-$ is explored in Section 5. Three possibilities are discussed in a systematic way; the first would appear to be new, the second a formulation due to Hardy, and the third a modification of a statistical mechanical expression introduced by Noll. The physical interpretations of the three choices are compared in Section 6 both in terms of pointwise values and their integrals over an infinite plane. A discussion is given in Section 7 of the utility of the weighting function approach, the possible computational advantage of the new definition of $\mathbf{T}_w^-$, and common characteristics of all three candidates for $\mathbf{T}_w^-$. Relevance of the study to nanoscale systems is indicated, and a novel approach is suggested whereby modelling directly in terms of $\mathbf{f}_w$ could be implemented, so obviating separate modelling of bulk, interfacial, and edge effects.

2 The Continuum Viewpoint

The distribution and evolution of matter in a given 'body' are modelled in terms of fields of mass density ρ and velocity $\mathbf{v}$. Mass conservation requires that

$$\partial\rho/\partial t + \operatorname{div}\{\rho\mathbf{v}\} = 0. \tag{2.1}$$

The region 'occupied' by the body at time t is

$$B_t := \{\text{points } \mathbf{x} \,:\, \rho(\mathbf{x}, t) > 0\}. \tag{2.2}$$

The internal and external forces on any part of the body are treated in terms of the Cauchy stress tensor $\mathbf{T}$ and body force density $\mathbf{b}$, respectively. Balance of linear momentum then yields, in an inertial frame,

$$\operatorname{div}\mathbf{T} + \mathbf{b} = \partial/\partial t\{\rho\mathbf{v}\} + \operatorname{div}\{\rho\mathbf{v}\otimes\mathbf{v}\} = \rho\mathbf{a} \tag{2.3}$$

for each point in B_t, where the acceleration field

$$\mathbf{a} := \partial\mathbf{v}/\partial t + (\nabla\mathbf{v})\mathbf{v}. \tag{2.4}$$

If the only external field is gravitational then

$$\mathbf{b} = \rho\mathbf{g}. \tag{2.5}$$

For any surface S (oriented by choice $\mathbf{n}$ of unit normal field) the surface integral of $\mathbf{Tn}$ over S is interpreted to be the force exerted across S *by* that part of the body into which $\mathbf{n}$ is directed *on* that part of the body out of which $\mathbf{n}$ points. If the external

traction field on the boundary ∂B_t of B_t is $\hat{\mathbf{t}}$ and $\mathbf{n}$ denotes the outward unit normal on ∂B_t then, in the absence of surface/interfacial effects,

$$\mathbf{T}\mathbf{n} = \hat{\mathbf{t}} \quad \text{on} \quad \partial B_t. \tag{2.6}$$

3 The Virial Approach to Stress

3.1 The Global Virial Stress

Consider a set of interacting point masses P_i $(i = 1, 2, \ldots, N)$. The motion of P_i in an inertial frame is governed by

$$\sum_{j \neq i} \mathbf{f}_{ij} + \mathbf{b}_i = d/dt\{m_i \mathbf{v}_i\}. \tag{3.1}$$

Here $\mathbf{f}_{ij}$ denotes the force exerted on P_i by P_j (the sum is taken over all particles except P_i), $\mathbf{b}_i$ the resultant force on P_i due to all other agencies (in particular $\mathbf{b}_i$ includes the weight $m_i\mathbf{g}$ of P_i), and m_i and $\mathbf{v}_i$ denote the mass and velocity of P_i, respectively.

If $\mathbf{x}_0$ labels a fixed point in the inertial frame then tensorial premultiplication[1] of (3.1) by the displacement $(\mathbf{x}_i - \mathbf{x}_0)$ of the location $\mathbf{x}_i$ of P_i from $\mathbf{x}_0$, followed by summation over *all* particles, yields

$$\sum_i \sum_{j \neq i} (\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{f}_{ij} + \sum_i (\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{b}_i = \sum_i (\mathbf{x}_i - \mathbf{x}_0) \otimes d/dt\{m_i \mathbf{v}_i\}. \tag{3.2}$$

Now

$$\begin{aligned} \sum_i \sum_{j \neq i} (\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{f}_{ij} &= \frac{1}{2} \sum_{i \neq j} \sum \{(\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{f}_{ij} + (\mathbf{x}_j - \mathbf{x}_0) \otimes \mathbf{f}_{ji}\} \\ &= \frac{1}{2} \sum_{i \neq j} \sum (\mathbf{x}_i - \mathbf{x}_j) \otimes \mathbf{f}_{ij}, \end{aligned} \tag{3.3}$$

upon invoking Newton's third law for interactions:

$$\mathbf{f}_{ji} = -\mathbf{f}_{ij}. \tag{3.4}$$

Further,

$$\sum_i (\mathbf{x}_i - \mathbf{x}_0) \otimes d/dt\{m_i \mathbf{v}_i\} = d/dt \left\{ \sum_i (\mathbf{x}_i - \mathbf{x}_0) \otimes m_i \mathbf{v}_i \right\} - \sum_i \mathbf{v}_i \otimes m_i \mathbf{v}_i. \tag{3.5}$$

It follows from (3.2, 3.3) and (3.5) that

$$\frac{1}{2} \sum_{i \neq j} \sum (\mathbf{x}_i - \mathbf{x}_j) \otimes \mathbf{f}_{ij} + \sum_i (\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{b}_i + \sum_i \mathbf{v}_i \otimes m_i \mathbf{v}_i = d\mathbf{L}/dt, \tag{3.6}$$

[1] In Cartesian tensor notation

$$(\mathbf{a} \otimes \mathbf{b})_{pq} = a_p b_q.$$

where the *generalised* (tensor-valued) *moment of momentum* at time τ about point $\mathbf{x}_0$ is

$$\mathbf{L}(\tau;\mathbf{x}_0) := \sum_i (\mathbf{x}_i(\tau)-\mathbf{x}_0)\otimes m_i\mathbf{v}_i(\tau). \tag{3.7}$$

Now suppose the particles are confined at time t to a bounded region $\mathcal{R}$. In the absence of external electromagnetic fields the external force $\mathbf{b}_i$ on P_i derives only from the effects of gravity and forces which serve to confine the system. To separate these effects we write

$$\mathbf{b}_i = m_i\mathbf{g} + \mathbf{c}_i \tag{3.8}$$

so defining the confining force $\mathbf{c}_i$ on P_i. From (3.6)

$$\sum_i (\mathbf{x}_i-\mathbf{x}_0)\otimes\mathbf{c}_i = d\mathbf{L}/dt + \frac{1}{2}\sum_{i\neq j}\sum (\mathbf{x}_j-\mathbf{x}_i)\otimes\mathbf{f}_{ij} - \sum_i \mathbf{v}_i\otimes m_i\mathbf{v}_i$$
$$-\sum_i (\mathbf{x}_i-\mathbf{x}_0)\otimes m_i\mathbf{g}. \tag{3.9}$$

It is the tensor moment of confinement forces delivered by (3.9) which provides the link with the macroscopic description. Confinement forces are, from the continuum viewpoint, modelled via the traction field $\hat{\mathbf{t}}$ on the boundary $\partial\mathcal{R}$ of $\mathcal{R}$. In particular, the tensor moment of confinement forces about fixed point $\mathbf{x}_0$ at any time is represented by

$$\int_{\partial\mathcal{R}} (\mathbf{x}-\mathbf{x}_0)\otimes\hat{\mathbf{t}}\,dS = \int_{\partial\mathcal{R}} (\mathbf{x}-\mathbf{x}_0)\otimes\mathbf{T}\mathbf{n}\,dS$$
$$= \int_{\mathcal{R}} \{(\mathbf{x}-\mathbf{x}_0)\otimes\operatorname{div}\mathbf{T} + \mathbf{T}^T\}dV, \tag{3.10}$$

on invoking (2.6). Here use has been made of the divergence theorem for rank two tensor fields.[2] Identifying the two expressions (3.9) and (3.10) for the moment of confinement forces about $\mathbf{x}_0$, and also making the identification

$$\sum_i (\mathbf{x}_i-\mathbf{x}_0)\otimes m_i\mathbf{g} = \int_{\mathcal{R}} (\mathbf{x}-\mathbf{x}_0)\otimes\rho\mathbf{g}\,dV \tag{3.11}$$

for the resultant tensor moment of gravitational forces about $\mathbf{x}_0$, we have

$$d\mathbf{L}/dt + \frac{1}{2}\sum_{i\neq j}\sum (\mathbf{x}_j-\mathbf{x}_i)\otimes\mathbf{f}_{ij} - \sum_i \mathbf{v}_i\otimes m_i\mathbf{v}_i$$
$$= \int_{\mathcal{R}} (\mathbf{x}-\mathbf{x}_0)\otimes(\operatorname{div}\mathbf{T}+\rho\mathbf{g}) + \mathbf{T}^T dV. \tag{3.12}$$

In the case of macroscopic equilibrium in a terrestrial frame of reference (2.3) becomes

$$\operatorname{div}\mathbf{T} + \rho\mathbf{g} = \mathbf{0} \tag{3.13}$$

[2] $\operatorname{div}\mathbf{T}$ is that vector field with Cartesian components $(\operatorname{div}\mathbf{T})_p = T_{pq,q}$; $\mathbf{T}^T$ denotes the transpose of $\mathbf{T}$ so $(\mathbf{T}^T)_{pq} = (\mathbf{T})_{qp} = T_{qp}$.

if the effect of the Earth's motion relative to any inertial frame is neglected. Thus taking the transpose of (3.12) yields

$$\mathbf{T}_{av}(\mathcal{R}) = \frac{1}{\text{vol}\,(\mathcal{R})}\left\{\frac{d\mathbf{L}^T}{dt} + \frac{1}{2}\sum_{i\neq j}\sum \mathbf{f}_{ij}\otimes(\mathbf{x}_j-\mathbf{x}_i) - \sum_i \mathbf{v}_i\otimes m_i\mathbf{v}_i\right\}, \tag{3.14}$$

where

$$\mathbf{T}_{av}(\mathcal{R}) := \int_{\mathcal{R}} \mathbf{T}\,dV/\text{vol}\,(\mathcal{R}). \tag{3.15}$$

Integrating (3.14) over the time interval $t-\Delta \le \tau \le t$ and dividing by its duration Δ,

$$\overline{\mathbf{T}}^{\Delta}_{av}(\mathcal{R}) = \frac{1}{\text{vol}\,(\mathcal{R})}\left\{\mathbf{A} + \frac{1}{2}\sum_{i\neq j}\sum \overline{\mathbf{f}_{ij}\otimes(\mathbf{x}_j-\mathbf{x}_i)}^{\Delta} - \sum_i \overline{\mathbf{v}_i\otimes m_i\mathbf{v}_i}^{\Delta}\right\}. \tag{3.16}$$

Here

$$\mathbf{A}(t;\Delta) := \Delta^{-1}\{\mathbf{L}^T(t) - \mathbf{L}^T(t-\Delta)\}, \tag{3.17}$$

and the superposed bar, annotated 'Δ', denotes the Δ-time average of the quantity in question: that is, for any time-dependent function $F(\,.\,)$,

$$\bar{F}^{\Delta}(t) := \frac{1}{\Delta}\int_{t-\Delta}^{t} F(\tau)d\tau. \tag{3.18}$$

We note that

$$\textit{if}\quad \mathbf{L}\ \textit{is bounded for all time} \tag{3.19}$$

then, from (3.17),

$$\mathbf{A}(t;\Delta)\to\mathbf{0}\quad\text{as}\quad\Delta\to\infty. \tag{3.20}$$

Accordingly, from (3.16)

$$\lim_{\Delta\to\infty}\left\{\overline{\mathbf{T}_{av}(\mathcal{R})}^{\Delta}\right\} = \frac{1}{\text{vol}\,(\mathcal{R})}\lim_{\Delta\to\infty}\left\{\frac{1}{2}\sum_{i\neq j}\sum \overline{\mathbf{f}_{ij}\otimes(\mathbf{x}_j-\mathbf{x}_i)}^{\Delta} - \sum_i \overline{\mathbf{v}_i\otimes m_i\mathbf{v}_i}^{\Delta}\right\}. \tag{3.21}$$

The first limit on the right-hand side of (3.21) is, upon recalling (3.3), a generalisation of the *virial of Clausius* (see [16], p.84).

Remark 1 Macroscopic equilibrium (that is, $\mathbf{v}=\mathbf{0}$) in a terrestrial frame $\mathcal{F}$ implies from (2.1) that in this frame ρ is time-independent. Approximation (3.13) also implies that if $\mathcal{R}$ is a fixed region in $\mathcal{F}$ over which $\mathbf{g}$ is essentially constant (note that to an inertial observer $\mathbf{g}$ will change direction with time) then div $\mathbf{T}$ is independent of time. Thus (modulo a possible time-dependent divergence-free field) $\mathbf{T}$ is time-independent, and $\overline{\mathbf{T}_{av}(\mathcal{R})}^{\Delta} = \mathbf{T}_{av}(\mathcal{R})$. Accordingly the left-hand side of (3.21) is just $\mathbf{T}_{av}(\mathcal{R})$.

Remark 2 Since, by assumption, $\mathcal{R}$ is a bounded region, distance $\|\mathbf{x}_i(\tau) - \mathbf{x}_0\|$ of P_i from fixed point $\mathbf{x}_0$ remains bounded for all times. In the event that the kinetic energy of P_i is also bounded for all τ then $\mathbf{v}_i$ is likewise bounded, and it follows from (3.7) that hypothesis (3.19) is satisfied. Such boundedness of individual kinetic energies would follow were the system to be thermomechanically isolated (so the total system energy would be constant) and interactions were delivered by pair-potentials that are bounded below (such as Lennard–Jones potentials).

Remark 3 If $\mathbf{A}(t; \Delta)$ is negligible for $\Delta \sim \Delta_0$ then the time average limits in (3.21) can be replaced by simple time averages of duration Δ_0. (For example, $\mathbf{L}$ might be essentially periodic with period Δ_0: cf. [16], p.84.)

Remark 4 The foregoing essentially follows [5] and [6], although these works omitted gravity and did not emphasise that they were only deriving results for macroscopic equilibrium (cf. [5] after Equation (25) and [6], Equation (22)).

Remark 5 Since the objective is to obtain an expression, valid in a general dynamical context, for the Cauchy stress $\mathbf{T}(\mathbf{x}, t)$ at a point $\mathbf{x}$ and time t in terms of microscopic quantities, it is clear that relation (3.21) falls far short of this aim. Specifically, this relation holds only for global macroscopic equilibrium and only delivers an average of $\mathbf{T}$ taken over the whole region.

In the following subsection we indicate how the foregoing can be modified so as to involve only an arbitrary subregion $\mathcal{P}$ of $\mathcal{R}$ and hence deliver *local* averages of $\mathbf{T}$. It turns out that a sensible average exists for *solids* in macroscopic equilibrium, but that the argument is unsatisfactory for fluids.

3.2 A Local Virial Stress for Solids

Following the procedure of Subsection 3.1 one can, at any given time τ, restrict the summations in (3.2) by requiring that the 'i' sum be taken only over those particles P_i which lie in an arbitrary given subregion $\mathcal{P}$ of $\mathcal{R}$. However, since in the first term of (3.2) the double sum is computed over *all* particles P_j except P_i, simplification (3.3) does not hold. Further, and more crucially, simplification (3.5) will no longer hold if the particle population of $\mathcal{P}$ changes with time. Specifically, evaluation of the time derivative of

$$\sum_{\substack{P_i \in \mathcal{P} \\ \text{at time } \tau}} (\mathbf{x}_i(\tau) - \mathbf{x}_0) \otimes m_i \mathbf{v}_i(\tau)$$

requires that account be taken of particle migration between $\mathcal{P}$ and the rest of $\mathcal{R}$. Such migration is inevitable and non-trivial for fluids. The situation is different for solids in equilibrium. In such case individual molecular mass centres undergo rapid erratic localised motions. The time scale of such motions is typically of order 10^{-13} s. It is thus meaningful to regard the macroscopically small (say 10^{-6} s) time-averaged

location of a molecular mass centre to be a fixed point.[3] We denote the averaged location of P_i by $\bar{\mathbf{x}}_i$ (so $\bar{\mathbf{x}}_i$ is time-independent for macroscopic equilibrium). Now consider those particles for which $\bar{\mathbf{x}}_i$ lies within any region $\mathcal{P}$ which lies strictly within $\mathcal{R}$ (so that its boundary $\partial\mathcal{P}$ is not in the proximity of the surface $\partial\mathcal{R}$ which confines the system). Then the analogue of (3.2) for particles P_i with $\bar{\mathbf{x}}_i \in \mathcal{P}$ is

$$\sum_i{}' \sum_{j\neq i} (\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{f}_{ij} + \sum_i{}' (\mathbf{x}_i - \mathbf{x}_0) \otimes m_i \mathbf{g}$$
$$= \sum_i{}' (\mathbf{x}_i - \mathbf{x}_0) \otimes d/dt(m_i \mathbf{v}_i). \tag{3.22}$$

Here the superposed prime attached to sums signifies that only particles for which $\bar{\mathbf{x}}_i \in \mathcal{P}$ are involved. The nature of $\mathcal{P}$ means that such particles will for all time be uninfluenced by the molecules of the confining system and the analogue of (3.8) is $\mathbf{b}_i = m_i \mathbf{g}$. Since a fixed set of particles is involved, relation (3.5) holds for primed sums. Further,

$$\sum_i{}' \sum_j (\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{f}_{ij} = \frac{1}{2} \sum_i{}' \sum_j{}' (\mathbf{x}_i - \mathbf{x}_j) \otimes \mathbf{f}_{ij} + \sum_i{}' \sum_j{}'' (\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{f}_{ij}. \tag{3.23}$$

Here $\sum_j{}' \left(\sum_j{}'' \right)$ denotes a sum over particles P_j for which $\bar{\mathbf{x}}_j \in \mathcal{P} (\bar{\mathbf{x}}_j \notin \mathcal{P})$ and use has been made of (3.4) for particle pairs whose averaged locations *both* lie in $\mathcal{P}$.

From (3.22), the analogue of (3.5), and (3.23) we have

$$\sum_i{}' (\mathbf{x}_i - \mathbf{x}_0) \otimes m_i \mathbf{g} = \frac{1}{2} \sum_i{}' \sum_j{}' (\mathbf{x}_j - \mathbf{x}_i) \otimes \mathbf{f}_{ij} - \sum_i{}' \sum_j{}'' (\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{f}_{ij}$$
$$+ \; d\mathbf{L}'/dt - \sum_i{}' \mathbf{v}_i \otimes m_i \mathbf{v}_i. \tag{3.24}$$

Here [see (3.7)]

$$\mathbf{L}'(\tau; \mathbf{x}_0) := \sum_i{}' (\mathbf{x}_i(\tau) - \mathbf{x}_0) \otimes m_i \mathbf{v}_i(\tau). \tag{3.25}$$

Making identification (3.11) (with $\sum_i$ replaced by $\sum_i{}'$ and $\mathcal{R}$ replaced by $\mathcal{P}$) and invoking (3.13, 3.24) yields

$$\frac{1}{2} \sum_i{}' \sum_j{}' (\mathbf{x}_j - \mathbf{x}_i) \otimes \mathbf{f}_{ij} - \sum_i{}' \sum_j{}'' (\mathbf{x}_i - \mathbf{x}_0) \otimes \mathbf{f}_{ij} - \sum_i{}' \mathbf{v}_i \otimes m_i \mathbf{v}_i + d\mathbf{L}'/dt$$
$$= -\int_{\mathcal{P}} (\mathbf{x} - \mathbf{x}_0) \otimes \operatorname{div} \mathbf{T} \, dV$$
$$= -\int_{\partial\mathcal{P}} (\mathbf{x} - \mathbf{x}_0) \otimes \mathbf{T}\mathbf{n} \, dS + \int_{\mathcal{P}} \mathbf{T}^T dV. \tag{3.26}$$

[3] Notice the discussion is restricted to macroscopic equilibrium; in dynamical contexts such time-averaged locations will change, essentially tracing out the macroscopic motion.

Given (3.19), $\mathbf{L}'$ must be bounded for all time. Thus taking the Δ-time average of the transpose of (3.26) yields

$$\lim_{\Delta\to\infty}\left\{\int_{\mathcal{P}}\bar{\mathbf{T}}^{\Delta}dV-\int_{\partial\mathcal{P}}\bar{\mathbf{T}}^{\Delta}\mathbf{n}\otimes(\mathbf{x}-\mathbf{x}_0)dS\right\}$$
$$=\lim_{\Delta\to\infty}\left\{\frac{1}{2}{\sum_{i}}'{\sum_{j}}'\overline{\mathbf{f}_{ij}\otimes(\mathbf{x}_j-\mathbf{x}_i)}^{\Delta}-{\sum_{i}}'\overline{\mathbf{v}_i\otimes m_i\mathbf{v}_i}^{\Delta}-{\sum_{i}}'{\sum_{j}}''\overline{\mathbf{f}_{ij}\otimes(\mathbf{x}_i-\mathbf{x}_0)}^{\Delta}\right\}. \tag{3.27}$$

Noting that the last sum in (3.27) involves interactions between particles P_i and P_j for which $\bar{\mathbf{x}}_i\in\mathcal{P}$ and $\bar{\mathbf{x}}_j\notin\mathcal{P}$ it is natural, in view of the interpretation of $\mathbf{Tn}$ (see Section 2), to make the identification

$$\lim_{\Delta\to\infty}\left\{\int_{\partial\mathcal{P}}\bar{\mathbf{T}}^{\Delta}\mathbf{n}\otimes(\mathbf{x}-\mathbf{x}_0)dS\right\}=\lim_{\Delta\to\infty}\left\{{\sum_{i}}'{\sum_{j}}''\overline{\mathbf{f}_{ij}\otimes(\mathbf{x}_i-\mathbf{x}_0)}^{\Delta}\right\}. \tag{3.28}$$

Accordingly it follows from (3.27) that

$$\lim_{\Delta\to\infty}\{\overline{\mathbf{T}_{av}(\mathcal{P})}^{\Delta}\}=\frac{1}{\mathrm{vol}\,(\mathcal{P})}\lim_{\Delta\to\infty}\left\{\frac{1}{2}{\sum_{i}}'{\sum_{j}}'\overline{\mathbf{f}_{ij}\otimes(\mathbf{x}_j-\mathbf{x}_i)}^{\Delta}-{\sum_{i}}'\overline{\mathbf{v}_i\otimes m_i\mathbf{v}_i}^{\Delta}\right\}, \tag{3.29}$$

where $\mathbf{T}_{av}(\mathcal{P})$ is defined by (3.15) with $\mathcal{R}$ replaced by $\mathcal{P}$.

Remark 6 Relation (3.29) provides a *local* version of (3.21), valid for macroscopic equilibrium of solids, since $\mathcal{P}$ may be arbitrarily small. Exactly as in Remark 1 we can argue that $\overline{\mathbf{T}_{av}(\mathcal{P})}^{\Delta}=\mathbf{T}_{av}(\mathcal{P})$ on neglect of inertial terms.

Remark 7 Writing relation (3.26) for two differing choices $\hat{\mathbf{x}}_0$ and $\tilde{\mathbf{x}}_0$ of fixed point $\mathbf{x}_0$ and then subtracting yields

$$-\mathbf{d}\otimes{\sum_{i}}'{\sum_{j}}''\mathbf{f}_{ij}+\mathbf{d}\otimes d/dt\left\{{\sum_{i}}'m_i\mathbf{v}_i\right\}=-\mathbf{d}\otimes\int_{\partial\mathcal{P}}\mathbf{Tn}\,dS, \tag{3.30}$$

where $\mathbf{d}:=\tilde{\mathbf{x}}_0-\hat{\mathbf{x}}_0$. The arbitrary nature of $\mathbf{d}$ implies that

$$\int_{\mathcal{P}}\mathrm{div}\,\mathbf{T}\,dV={\sum_{i}}'{\sum_{j}}''\mathbf{f}_{ij}-d/dt\left\{{\sum_{i}}'m_i\mathbf{v}_i\right\}. \tag{3.31}$$

Accordingly

$$(\mathrm{div}\,\mathbf{T})_{av}(\mathcal{P})=\frac{1}{\mathrm{vol}(\mathcal{P})}\left\{{\sum_{i}}'{\sum_{j}}''\mathbf{f}_{ij}-d/dt\left\{{\sum_{i}}'m_i\mathbf{v}_i\right\}\right\} \tag{3.32}$$

Thus the local volume average of div $\mathbf{T}$ taken over region $\mathcal{P}$ consists of two terms: the first is the volume average of the resultant force on particles P_i for which $\bar{\mathbf{x}}_i\in\mathcal{P}$

exerted by particles P_j for which $\bar{\mathbf{x}}_j \notin \mathcal{P}$, and the second is the time rate of change of momentum of particles P_i for which $\bar{\mathbf{x}}_i \in \mathcal{P}$. As with (3.29) it is seen that one cannot expect the stress $\mathbf{T}$ to have a microscopic interpretation entirely in terms of forces. Thus the conventional interpretation of Section 2 requires modification.

3.3 Shortcomings of the Virial Approach

The approach used in the foregoing is unsatisfactory. In particular we note that

S.1. Results hold only for macroscopic equilibrium.
S.2. Estimates of the virial need to be made before estimates of the temporal limits involved in (3.21) and (3.29) can be made.
S.3. Only the stress (rather, its spatial average) is computed in microscopic terms. As such it is more restrictive and no simpler than other approaches which deal comprehensively with the relationships between *all* macroscopic field values and molecular quantities.

The alternative approaches intimated in S.3. are those of statistical mechanics and local spatial and temporal deterministic averaging. It is the latter procedure that will be addressed hereafter.

4 Continuum Fields as Local Spatial Averages

4.1 General Relations

Rather than study the stress tensor in isolation, as in Section 3, we now outline a systematic and comprehensive approach to linking continuum field values with microscopic behaviour at any prescribed spatial scale. The material system (or 'body') of interest is modelled as a fixed set of point masses P_i as in Subsection 3.1. *Mass* and *momentum density* fields ρ_w and $\mathbf{p}_w$ are defined as local spatial averages via a *weighting/localisation function* w. Specifically,

$$\rho_w(\mathbf{x}, t) := \sum_i m_i w(\mathbf{x}_i(t) - \mathbf{x}), \quad \text{and} \tag{4.1}$$

$$\mathbf{p}_w(\mathbf{x}, t) := \sum_i m_i \mathbf{v}_i(t) w(\mathbf{x}_i(t) - \mathbf{x}). \tag{4.2}$$

Here the sums are taken over *all* particles and $\mathbf{x}_i(t) - \mathbf{x}$ denotes the displacement of P_i from geometrical point $\mathbf{x}$ at time t. To accord with the continuum notion of mass density, w should assign greater contributions to point masses near to $\mathbf{x}$ than far therefrom, have physical dimension L^{-3}, and be continuously differentiable on the space of displacements $\mathcal{V}$ in Euclidean space $\mathcal{E}$. To ensure that the integral of ρ_w over all space $\mathcal{E}$ should yield the total mass of the body it is necessary and sufficient that (see [13], p.107)

$$\int_{\mathcal{V}} w(\mathbf{u}) d\mathbf{u} = 1. \tag{4.3}$$

In what follows, the relations which express mass conservation and linear momentum balance are independent of the exact form of w beyond the foregoing constraints. Specific choices are discussed in the next subsection.

Holding $\mathbf{x}$ fixed in (4.1)

$$\begin{aligned}\partial\rho_w/\partial t &= \sum_i m_i \nabla w \cdot \mathbf{v}_i = -\sum_i m_i \nabla_{\mathbf{x}} w \cdot \mathbf{v}_i \\ &= -\sum_i m_i \,\mathrm{div}\{\mathbf{v}_i w\} = -\mathrm{div}\,\mathbf{p}_w. \end{aligned} \tag{4.4}$$

(See [17], p.74 for more explicit details.) Whenever and wherever $\rho_w \neq 0$, the corresponding velocity field

$$\mathbf{v}_w := \mathbf{p}_w/\rho_w. \tag{4.5}$$

Hence, from (4.4) and (4.5),

$$\partial\rho_w/\partial t + \mathrm{div}\{\rho_w \mathbf{v}_w\} = 0. \tag{4.6}$$

To derive linear momentum balance we multiply (3.1) by $w(\mathbf{x}_i - \mathbf{x})$ and sum over all particles. This yields

$$\mathbf{f}_w + \mathbf{b}_w = \sum_i d/dt\{m_i \mathbf{v}_i\} w(\mathbf{x}_i - \mathbf{x}), \tag{4.7}$$

where

$$\mathbf{f}_w(\mathbf{x}, t) := \sum_i \sum_{j \neq i} \mathbf{f}_{ij}(t) w(\mathbf{x}_i(t) - \mathbf{x}), \quad \text{and} \tag{4.8}$$

$$\mathbf{b}_w(\mathbf{x}, t) := \sum_i \mathbf{b}_i(t) w(\mathbf{x}_i(t) - \mathbf{x}). \tag{4.9}$$

Remark 8 If the only external forces are gravitational, and $\mathbf{g}$ is the same for all P_i, then $\mathbf{b}_i = m_i \mathbf{g}$ and

$$\mathbf{b}_w = \rho_w \mathbf{g}. \tag{4.10}$$

Since

$$d/dt\{m_i \mathbf{v}_i\} w(\mathbf{x}_i - \mathbf{x}) = \partial/\partial t\{m_i \mathbf{v}_i w(\mathbf{x}_i - \mathbf{x})\} - (m_i \mathbf{v}_i \otimes \mathbf{v}_i)\nabla w$$

and

$$(m_i \mathbf{v}_i \otimes \mathbf{v}_i)\nabla w = -(m_i \mathbf{v}_i \otimes \mathbf{v}_i)\nabla_{\mathbf{x}} w = -\mathrm{div}\{(m_i \mathbf{v}_i \otimes \mathbf{v}_i) w\},$$

the right-hand side of (4.7) becomes

$$\partial/\partial t \left\{ \sum_i m_i \mathbf{v}_i w(\mathbf{x}_i - \mathbf{x}) \right\} + \mathrm{div}\,\mathbf{D}_w, \tag{4.11}$$

where

$$\mathbf{D}_w(\mathbf{x}, t) := \sum_i m_i \mathbf{v}_i(t) \otimes \mathbf{v}_i(t) w(\mathbf{x}_i(t) - \mathbf{x}). \tag{4.12}$$

Substitution of (4.11) in (4.7), noting (4.2) and (4.5), yields

$$\mathbf{f}_w + \mathbf{b}_w = \partial/\partial t\{\rho_w \mathbf{v}_w\} + \operatorname{div} \mathbf{D}_w. \tag{4.13}$$

Writing

$$\hat{\mathbf{v}}_i(t; \mathbf{x}) := \mathbf{v}_i(t) - \mathbf{v}_w(\mathbf{x}, t), \tag{4.14}$$

$$\sum_i m_i \hat{\mathbf{v}}_i(t; \mathbf{x}) w(\mathbf{x}_i(t) - \mathbf{x}) = \mathbf{p}_w(\mathbf{x}, t) - \rho_w(\mathbf{x}, t)\mathbf{v}_w(\mathbf{x}, t) = \mathbf{0}, \tag{4.15}$$

on invoking (4.1), (4.2) and (4.5). It follows that

$$\mathbf{D}_w = \mathcal{D}_w + \rho_w \mathbf{v}_w \otimes \mathbf{v}_w, \tag{4.16}$$

where

$$\mathcal{D}_w(\mathbf{x}, t) := \sum_i m_i \hat{\mathbf{v}}_i(t; \mathbf{x}) \otimes \hat{\mathbf{v}}_i(t; \mathbf{x}) w(\mathbf{x}_i(t) - \mathbf{x}). \tag{4.17}$$

Using (4.17), balance (4.13) becomes

$$-\operatorname{div} \mathcal{D}_w + \mathbf{f}_w + \mathbf{b}_w = \partial/\partial t\{\rho_w \mathbf{v}_w\} + \operatorname{div}\{\rho_w \mathbf{v}_w \otimes \mathbf{v}_w\} \tag{4.18}$$

$$= (\partial \rho_w/\partial t + \operatorname{div}\{\rho_w \mathbf{v}_w\})\mathbf{v}_w + \rho_w \mathbf{a}_w, \tag{4.19}$$

where

$$\mathbf{a}_w := \partial \mathbf{v}_w/\partial t + (\nabla \mathbf{v}_w)\mathbf{v}_w. \tag{4.20}$$

Thus, noting (4.6), linear momentum balance takes the form

$$-\operatorname{div} \mathcal{D}_w + \mathbf{f}_w + \mathbf{b}_w = \rho_w \mathbf{a}_w. \tag{4.21}$$

Relation (4.21) becomes formally equivalent to the standard balance (2.3) upon finding an *interaction stress tensor* $\mathbf{T}_w^-$ for which

$$\operatorname{div} \mathbf{T}_w^- = \mathbf{f}_w. \tag{4.22}$$

In such case

$$\operatorname{div} \mathbf{T}_w + \mathbf{b}_w = \rho_w \mathbf{a}_w, \tag{4.23}$$

where

$$\mathbf{T}_w := \mathbf{T}_w^- - \mathcal{D}_w. \tag{4.24}$$

At this point there are two fundamental issues to be addressed:

F.I.1. *Physical interpretation of the foregoing depends crucially upon the form of* w, and

F.I.2. *Derivation of the standard form* (4.23) *involves computation of* $\mathbf{T}_w^-$ *from* (4.22) *when* $\mathbf{f}_w$ *is given. Such a problem can only yield a solution to within a divergenceless rank two tensor field.*

F.I.1. is addressed in the following subsection, and three distinct candidates for $\mathbf{T}_w^-$ are exhibited and compared in Section 5.

4.2 A Simple Choice of Weighting Function w and Corresponding Physical Interpretations

The simplest choice of w is given by

$$\left.\begin{array}{ll} w(\mathbf{u}) = V_\epsilon^{-1} & \text{if } \|\mathbf{u}\| < \epsilon \\ w(\mathbf{u}) = 0 & \text{if } \|\mathbf{u}\| \geq \epsilon \end{array}\right\}, \tag{4.25}$$

where $\epsilon > 0$ denotes any given length and $V_\epsilon := 4\pi\epsilon^3/3$. This choice means that $\rho_w(\mathbf{x}, t)$ is the sum of the masses of those particles which lie within that sphere $S_\epsilon(\mathbf{x})$, centred at $\mathbf{x}$ with radius ϵ, at time t, divided by the volume of $S_\epsilon(\mathbf{x})$. Similarly, $\mathbf{p}_w(\mathbf{x}, t)$ is the corresponding momentum/volume quotient, and $\mathbf{v}_w(\mathbf{x}, t)$ is [see (4.5)] the velocity of the mass centre of those particles inside $S_\epsilon(\mathbf{x})$ at time t. Further, from (4.8) and (4.25),

$$\mathbf{f}_w(\mathbf{x}, t) = \sum_{\substack{P_i \text{ in} \\ S_\epsilon(\mathbf{x})}} \left\{ \sum_{\substack{P_j \text{ in} \\ S_\epsilon(\mathbf{x}),\, j \neq i}} \mathbf{f}_{ij}(t) + \sum_{\substack{P_j \text{ not in} \\ S_\epsilon(\mathbf{x})}} \mathbf{f}_{ij}(t) \right\} V_\epsilon^{-1}. \tag{4.26}$$

However, if we assume interactions satisfy (3.4) then

$$\sum_{\substack{P_i, P_j \text{ in } S_\epsilon(\mathbf{x}) \\ j \neq i}} \sum \mathbf{f}_{ij} = \frac{1}{2} \sum_{\substack{P_i, P_j \text{ in } S_\epsilon(\mathbf{x}) \\ j \neq i}} \sum (\mathbf{f}_{ij} + \mathbf{f}_{ji}) = \mathbf{0}.$$

It follows that

$$\mathbf{f}_w(\mathbf{x}, t) = \sum_{\substack{P_i \text{ in} \\ S_\epsilon(\mathbf{x})}} \sum_{\substack{P_j \text{ not in} \\ S_\epsilon(\mathbf{x})}} \mathbf{f}_{ij}(t) V_\epsilon^{-1}. \tag{4.27}$$

That is, $\mathbf{f}_w(\mathbf{x}, t)$ is the resultant force exerted on particles within $S_\epsilon(\mathbf{x})$ by particles outwith $S_\epsilon(\mathbf{x})$, divided by V_ϵ. The definition (4.17) of $\mathcal{D}_w(\mathbf{x}, t)$ involves the velocities $\hat{\mathbf{v}}_i(t; \mathbf{x})$ of individual particles within $S_\epsilon(\mathbf{x})$ at time t relative to the mass centre velocity of all such particles at this time. These velocities correspond to chaotic particle motions and form the basis of the kinetic theory of heat: see Brush [18]. In particular, the *trace* of $\mathcal{D}_w(\mathbf{x}, t)$ yields twice the kinetic energy associated with this chaotic motion of particles within $S_\epsilon(\mathbf{x})$ at time t, divided by V_ϵ. Such kinetic energy is identified with heat, and hence (tr $\mathcal{D}_w$)/2 with heat energy density. For moderately-rarefied gases molecular interactions occur only intermittently, via binary 'collisions', $\mathbf{f}_w$ is negligible, and $\mathcal{D}_w$ is identifiable with the so-called *pressure*

tensor of kinetic theory[4] (cf. [4], Remarks 4.11–16, [19], p. 169). In solid phases $-\boldsymbol{\mathcal{D}}_w$ represents a highly temperature-dependent contribution to the total (Cauchy) stress $\mathbf{T}_w$, vanishing only at absolute zero. Indeed, for bodies constrained to occupy fixed regions it is the contribution of $-\boldsymbol{\mathcal{D}}_w$ which explains the increase in *compressive* mean stress $-tr\,\mathbf{T}_w$ with temperature.

Remark 9 Choice (4.25) for w is discontinuous when $\|\mathbf{u}\| = \epsilon$ and hence fails to satisfy our differentiability requirement. It is, however, a simple matter to 'mollify' w over an interval $\epsilon < \|\mathbf{u}\| < \epsilon + \delta$ in such a way that w has arbitrary smoothness everywhere, with $\delta(> 0)$ arbitrarily small. Specifically we redefine w by

$$w(\mathbf{u}) = \hat{w}(u) \quad \text{with} \quad u := \|\mathbf{u}\|, \tag{4.28}$$

where $\hat{w}(u) = k$, $\phi(u)$, or 0 according as $0 < u < \epsilon$, $\epsilon \le u \le \epsilon + \delta$, or $u > \epsilon + \delta$, respectively, and k is a constant mandated by the normalisation requirement (4.3). (In fact $k = V_\epsilon^{-1}(1 + O(\delta/\epsilon))$: see [4], p.31 or [10], p.160.) Mollifier ϕ is everywhere continuously differentiable, and satisfies

$$\phi(\epsilon) = k,\ \phi'(\epsilon) = 0,\ \phi(\epsilon + \delta) = 0,\ \phi'(\epsilon + \delta) = 0, \tag{4.29}$$

and is monotone decreasing on $\epsilon < u < \epsilon + \delta$. The foregoing ensures that for small enough choice of δ (say $\delta = 10^{-12}m$) the physical interpretations of ρ_w, $\mathbf{p}_w$, $\mathbf{v}_w$, $\mathbf{f}_w$, and $\boldsymbol{\mathcal{D}}_w$ are essentially unchanged.

Remark 10 Since the macroscopic motion is described by $\mathbf{v}_w$, choice (4.25) is natural in that it delivers $\mathbf{v}_w$ as a local mass centre velocity. Alternatively, upon noting that any field F can be averaged via

$$F_w(\mathbf{x}) := \int_{\mathcal{E}} F(\mathbf{y}) w(\mathbf{y} - \mathbf{x}) d\mathbf{y}, \tag{4.30}$$

one might wish to require that repeated averaging at the same scale should deliver nothing new; that is, that

$$(F_w)_w = F_w. \tag{4.31}$$

In such case w is prescribed once the domain of interest is delineated; for example, all $\mathcal{E}$, or the interior of a rectangular box: see [20], Section 3. The relevant choices of w are here not positive everywhere on their domains, although such restriction is often posed: see, for example, [12], p. 3161.

[4]It should be noted that $\boldsymbol{\mathcal{D}}_w$ is not necessarily a multiple of the identity ($-\boldsymbol{\mathcal{D}}_w$ is *pressure-like* in the sense that $-\boldsymbol{\mathcal{D}}_w\,\mathbf{n}\,.\,\mathbf{n} < 0$ for any unit vector $\mathbf{n}$: see (7.6) hereafter) and is to be distinguished from the continuum usage of the term pressure (which corresponds here to $\mathbf{T}_w$ being a negative multiple of the identity).

5 Possible Definitions of the Interaction Stress Tensor

5.1 Simplest Choice ${}_s\mathbf{T}_w^-$

The problem is to obtain a rank two tensor field $\mathbf{T}_w^-$ which satisfies (see (4.22) and (4.8))

$$\operatorname{div}\mathbf{T}_w^- = \sum_i \sum_{j\neq i} \mathbf{f}_{ij}\, w(\mathbf{x}_i - \mathbf{x}). \tag{5.1}$$

Since $\mathbf{f}_{ij}$ does not depend upon $\mathbf{x}$, and hence, for any vector field $\mathbf{a}$,

$$\operatorname{div}\{\mathbf{f}_{ij}\otimes\mathbf{a}\} = (\operatorname{div}\mathbf{a})\mathbf{f}_{ij}, \tag{5.2}$$

it is natural to search for a vector field $\mathbf{a}_i$ such that

$$\operatorname{div}\mathbf{a}_i = w(\mathbf{x}_i - \mathbf{x}). \tag{5.3}$$

The candidate for $\mathbf{T}_w^-$ is then

$${}_s\mathbf{T}_w^- = \sum_i \sum_{j\neq i} \mathbf{f}_{ij}\otimes\mathbf{a}_i. \tag{5.4}$$

Since (see (4.28))

$$w(\mathbf{x}_i - \mathbf{x}) = \hat{w}(\|\mathbf{x}_i - \mathbf{x}\|) = \hat{w}(\|\mathbf{x} - \mathbf{x}_i\|) \tag{5.5}$$

is spherically-symmetric about $\mathbf{x}_i$, it is natural to seek a vector field $\mathbf{a}_i$ of form

$$\mathbf{a}_i = \hat{a}(u)\mathbf{u} \tag{5.6}$$

with

$$\mathbf{u} := \mathbf{x} - \mathbf{x}_i \quad \text{and} \quad u := \|\mathbf{u}\|. \tag{5.7}$$

Accordingly

$$\operatorname{div}\mathbf{a}_i = 3\hat{a} + \hat{a}'u = u^{-2}(d/du)\{u^3\hat{a}\}. \tag{5.8}$$

Hence from (5.3) and (5.5)

$$u^3\hat{a}(u) = \int_0^u s^2\hat{w}(s)ds. \tag{5.9}$$

The definition of $\hat{w}$ in Remark 9 implies that

$$\begin{aligned}
&\hat{a}(u) = k/3 \quad \text{if} \quad 0 \le u \le \epsilon,\\
&\hat{a}(u) = (k/3)(\epsilon/u)^3 + u^{-3}\int_\epsilon^u s^2\phi(s)ds \quad \text{if} \quad \epsilon < u \le \epsilon+\delta,\\
&\hat{a}(u) = (k/3)(\epsilon/u)^3 + u^{-3}\int_\epsilon^{\epsilon+\delta} s^2\phi(s)ds \quad \text{if} \quad u > \epsilon+\delta.
\end{aligned} \tag{5.10}$$

Since $0 \le \phi \le k$ and $\phi(s) = 0$ for $s \ge \epsilon+\delta$, for $u > \epsilon$

$$\left|u^{-3}\int_\epsilon^u s^2\phi(s)ds\right| < \epsilon^{-3}k\int_\epsilon^{\epsilon+\delta} s^2ds = (k\delta/\epsilon)\{1+\delta/\epsilon+(\delta/\epsilon)^2/3\}. \tag{5.11}$$

From (5.4, 5.6) and (5.7),

$$ {}_s\mathbf{T}^-_w(\mathbf{x}) = \sum_i \sum_{j\neq i} \mathbf{f}_{ij} \otimes (\mathbf{x} - \mathbf{x}_i)\hat{a}(\|\mathbf{x} - \mathbf{x}_i\|). \tag{5.12} $$

Noting that the sum may be decomposed into one over particles P_i for which $\|\mathbf{x}_i - \mathbf{x}\| < \epsilon$ and those for which $\|\mathbf{x}_i - \mathbf{x}\| \geq \epsilon$, and neglecting δ/ϵ in comparison with 1 (so $k \sim V_\epsilon^{-1} = 3/4\pi\epsilon^3$: see Remark 9), (5.12) may be written as

$$ \begin{aligned} {}_s\mathbf{T}^-_w(\mathbf{x}) = &\frac{1}{4\pi\epsilon^3} \sum_{P_i \in S_\epsilon(\mathbf{x})} \sum_{j\neq i} \mathbf{f}_{ij} \otimes (\mathbf{x} - \mathbf{x}_i) \\ &+ \frac{1}{4\pi} \sum_{P_i \notin S_\epsilon(\mathbf{x})} \sum_{j\neq i} \mathbf{f}_{ij} \otimes (\mathbf{x} - \mathbf{x}_i)\, (\|\mathbf{x} - \mathbf{x}_i\|)^{-3}. \end{aligned} \tag{5.13} $$

Remark 11 The net contribution from a pair of particles P_i and P_j which both lie in $S_\epsilon(\mathbf{x})$ is, from (5.13), and noting $k/3 = (3V_\epsilon)^{-1} (= (4\pi\epsilon^3)^{-1})$,

$$ \frac{1}{3V_\epsilon}\{\mathbf{f}_{ij} \otimes (\mathbf{x} - \mathbf{x}_i) + \mathbf{f}_{ji} \otimes (\mathbf{x} - \mathbf{x}_j)\} = \frac{1}{3V_\epsilon}\mathbf{f}_{ij} \otimes (\mathbf{x}_j - \mathbf{x}_i), \tag{5.14} $$

upon invoking (3.4). If $\mathbf{f}_{ij}$ is parallel to $\mathbf{x}_j - \mathbf{x}_i$ then this net contribution is symmetric. However, the presence of the remaining terms in (5.13) means that ${}_s\mathbf{T}^-_w$ is not necessarily symmetric. Further, while $\mathrm{div}\{(\|\mathbf{x} - \mathbf{x}_i\|)^{-3}(\mathbf{x} - \mathbf{x}_i)\} = 0$, the divergence of the second double sum does not vanish: this follows from the derivation (and directly from (5.13) on noting the 'i' sum depends upon $\mathbf{x}$ via non-membership of $S_\epsilon(\mathbf{x})$).

5.2 Hardy's Choice ${}_H\mathbf{T}^-_w$

Notice that (5.1) may be rewritten, modulo (3.4), as

$$ \mathrm{div}\, \mathbf{T}^-_w = \frac{1}{2} \sum_{i\neq j}\sum \mathbf{f}_{ij}(w(\mathbf{x}_i - \mathbf{x}) - w(\mathbf{x}_j - \mathbf{x})). \tag{5.15} $$

Observation (5.2) motivates the search for a vector field $\mathbf{b}_{ij}$ for which

$$ \mathrm{div}\, \mathbf{b}_{ij} = \frac{1}{2}(w(\mathbf{x}_i - \mathbf{x}) - w(\mathbf{x}_j - \mathbf{x})). \tag{5.16} $$

The analogue of (5.4) is here

$$ {}_H\mathbf{T}^-_w = \sum_{i\neq j}\sum \mathbf{f}_{ij} \otimes \mathbf{b}_{ij}. \tag{5.17} $$

A simple solution, bearing in mind the virial-based interaction sums in (3.21) and (3.29), would be of the form

$$ \mathbf{b}_{ij}(\mathbf{x}) = \frac{1}{2}\, \hat{b}_{ij}(\mathbf{x})(\mathbf{x}_j - \mathbf{x}_i), \tag{5.18} $$

where, $\hat{b}_{ij}$ is a scalar field which (see (5.15)), satisfies

$$ (\mathbf{x}_j - \mathbf{x}_i) \,.\nabla \hat{b}_{ij} = w(\mathbf{x}_i - \mathbf{x}) - w(\mathbf{x}_j - \mathbf{x}). \tag{5.19} $$

A solution to (5.19) is (see [8], (2.9)) Hardy's *bond function*

$$\hat{b}_{ij}(\mathbf{x}) := \int_0^1 w(\lambda(\mathbf{x}_j - \mathbf{x}_i) + (\mathbf{x}_i - \mathbf{x}))d\lambda. \tag{5.20}$$

With such choice (5.17) and (5.18) yield

$${}_H\mathbf{T}_w^-(\mathbf{x}) = \frac{1}{2} \sum_{i \neq j} \sum \mathbf{f}_{ij} \otimes (\mathbf{x}_j - \mathbf{x}_i)\hat{b}_{ij}(\mathbf{x}). \tag{5.21}$$

Remark 12 If

$$\mathbf{u} := \lambda(\mathbf{x}_j - \mathbf{x}_i) + (\mathbf{x}_i - \mathbf{x}) \qquad (0 \leq \lambda \leq 1) \tag{5.22}$$

then $\mathbf{x} + \mathbf{u}$ is a point on the line segment joining $\mathbf{x}_i$ to $\mathbf{x}_j$. Choice (4.25) of weighting function implies that the integral in (5.20) is computed only along that portion of this line segment which lies within $S_\epsilon(\mathbf{x})$ (of length $\ell_{ij}(\mathbf{x})$, say) and yields the value

$$\hat{b}_{ij}(\mathbf{x}) = \alpha_{ij}(\mathbf{x})\, V_\epsilon^{-1}, \tag{5.23}$$

where

$$\alpha_{ij}(\mathbf{x}) := \ell_{ij}(\mathbf{x})/\|\mathbf{x}_i - \mathbf{x}_j\|. \tag{5.24}$$

Accordingly, from (5.21),

$${}_H\mathbf{T}_w^-(\mathbf{x}) = (2V_\epsilon)^{-1} \sum_{i \neq j} \sum \mathbf{f}_{ij} \otimes \alpha_{ij}(\mathbf{x})(\mathbf{x}_j - \mathbf{x}_i). \tag{5.25}$$

Of course, $\alpha_{ij}(\mathbf{x})(\mathbf{x}_j - \mathbf{x}_i)$ denotes that portion of the displacement from $\mathbf{x}_i$ to $\mathbf{x}_j$ which lies within $S_\epsilon(\mathbf{x})$.

Remark 13 It should be noted that in [8] and [12] Hardy did not specifically mention choice (4.25) of w. Indeed (5.21), defined via (5.20), holds for *any* choice of weighting function. It is the essential simplicity of physical interpretation which motivates emphasis on choice (4.25). Alternative choices of w are given in [8] and [20].

Remark 14 If interactions are given by separation-dependent pair potentials then $\mathbf{f}_{ij}$ is parallel to $(\mathbf{x}_i - \mathbf{x}_j)$, so ${}_H\mathbf{T}_w^-$ takes symmetric values (for *any* choice of weighting function), and hence, via (4.24), Cauchy stress $\mathbf{T}_w$ is symmetric-valued. Since point masses here model molecules, and neighbouring molecules influence each other, force $\mathbf{f}_{ij}$ must be expected to depend upon instantaneous neighbours of both P_i and P_j, and symmetry cannot be proved since $\mathbf{f}_{ij}$ may not be parallel to $(\mathbf{x}_j - \mathbf{x}_i)$.

5.3 Noll's Choice ${}_N\mathbf{T}_w^-$

Equation (5.16) also has the solution

$$\mathbf{b}_{ij}(\mathbf{x}) := -\frac{1}{2}\int_{\mathcal{V}}\int_0^1 \mathbf{u}w(\mathbf{x}_i - \mathbf{x} - \alpha\mathbf{u})w(\mathbf{x}_j - \mathbf{x} + (1-\alpha)\mathbf{u})d\alpha d\mathbf{u}. \tag{5.26}$$

To verify this we note that

$$\operatorname{div}\mathbf{b}_{ij} = -\frac{1}{2}\int_{\mathcal{V}}\int_0^1 \mathbf{u}\,.\,\mathbf{F}_{ij}(\alpha, \mathbf{u}; \mathbf{x})d\alpha d\mathbf{u}, \tag{5.27}$$

where

$$\begin{aligned}\mathbf{F}_{ij}(\alpha, \mathbf{u}; \mathbf{x}) := {} & (\nabla_{\mathbf{x}} w(\mathbf{x}_i - \mathbf{x} - \alpha\mathbf{u}))w(\mathbf{x}_j - \mathbf{x} + (1-\alpha)\mathbf{u}) \\ & + w(\mathbf{x}_i - \mathbf{x} - \alpha\mathbf{u})\nabla_{\mathbf{x}} w(\mathbf{x}_j - \mathbf{x} + (1-\alpha)\mathbf{u}).\end{aligned} \tag{5.28}$$

Now

$$\begin{aligned}&\frac{\partial}{\partial\alpha}\{w(\mathbf{x}_i - \mathbf{x} - \alpha\mathbf{u})w(\mathbf{x}_j - \mathbf{x} + (1-\alpha)\mathbf{u})\} \\ &\quad = -(\nabla w(\mathbf{x}_i - \mathbf{x} - \alpha\mathbf{u}).\,\mathbf{u})w(\mathbf{x}_j - \mathbf{x} + (1-\alpha)\mathbf{u}) \\ &\qquad -w(\mathbf{x}_i - \mathbf{x} - \alpha\mathbf{u})(\nabla w(\mathbf{x}_j - \mathbf{x} + (1-\alpha)\mathbf{u}).\,\mathbf{u}) \\ &\quad = \mathbf{F}_{ij}(\alpha, \mathbf{u}; \mathbf{x}).\,\mathbf{u}.\end{aligned} \tag{5.29}$$

Accordingly, from (5.27) and (5.29)

$$\begin{aligned}\operatorname{div}\mathbf{b}_{ij} &= -\frac{1}{2}\int_{\mathcal{V}}\int_0^1 \frac{\partial}{\partial\alpha}\{w(\mathbf{x}_i - \mathbf{x} - \alpha\mathbf{u})w(\mathbf{x}_j - \mathbf{x} + (1-\alpha)\mathbf{u})\}d\alpha\, d\mathbf{u} \\ &= -\frac{1}{2}\int_{\mathcal{V}} w(\mathbf{x}_i - \mathbf{x} - \mathbf{u})w(\mathbf{x}_j - \mathbf{x}) - w(\mathbf{x}_i - \mathbf{x})w(\mathbf{x}_j - \mathbf{x} + \mathbf{u})d\mathbf{u} \\ &= -\frac{1}{2}(w(\mathbf{x}_j - \mathbf{x})\cdot 1 - w(\mathbf{x}_i - \mathbf{x}).\,1).\end{aligned} \tag{5.30}$$

The final step follows from normalisation condition (4.3). It follows that with choice (5.26) we have

$${}_N\mathbf{T}_w^-(\mathbf{x}) := \sum_{i\neq j}\sum \mathbf{f}_{ij}\otimes\mathbf{b}_{ij}(\mathbf{x}) \tag{5.31}$$

as the corresponding interaction stress tensor.

6 Comparison of Interaction Stress Tensors

6.1 Preamble

Before making general remarks about the three tensors ${}_S\mathbf{T}_w^-$, ${}_H\mathbf{T}_w^-$ and ${}_N\mathbf{T}_w^-$ we cite contributions thereto for two simple particle-pair locations (calculation details are given in [21]). If $\mathbf{e}$ is a unit vector, $\mathbf{x}_i - \mathbf{x} = -\epsilon\mathbf{e}$ and $\mathbf{x}_j - \mathbf{x} = \epsilon\mathbf{e}$, then the P_i, P_j *net* contributions are, respectively, $(2\pi\epsilon^2)^{-1}\mathbf{f}_{ij}\otimes\mathbf{e}$, $(2\pi\epsilon^2/3)^{-1}\mathbf{f}_{ij}\otimes\mathbf{e}$, and

$(2\pi\epsilon^2/7)^{-1}\mathbf{f}_{ij}\otimes\mathbf{e}$. If $\mathbf{x}_i-\mathbf{x}=\epsilon\mathbf{e}_1$ and $\mathbf{x}_j-\mathbf{x}=\epsilon\mathbf{e}_2$, where $\mathbf{e}_1$ and $\mathbf{e}_2$ are orthonormal, then the *net* contributions are, respectively, $(4\pi\epsilon^2)^{-1}\mathbf{f}_{ij}\otimes(\mathbf{e}_2-\mathbf{e}_1)$, $(4\pi\epsilon^2/3)^{-1}\mathbf{f}_{ij}\otimes(\mathbf{e}_2-\mathbf{e}_1)$, and $(2\pi\epsilon^2)^{-1}\mathbf{f}_{ij}\otimes(\mathbf{e}_2-\mathbf{e}_1)$. In the event that interactions are *central* (that is, $\mathbf{f}_{ij}$ is parallel to $\mathbf{x}_j-\mathbf{x}_i$, as is the case for interactions governed by separation-dependent pair potentials) all foregoing net contributions are symmetric. This is not a general property, but rather a consequence of the special chosen geometries.

6.2 Pointwise Properties and Interpretations

6.2.1 If $\mathbf{n}$ denotes a unit vector then from (5.13)

$$
\begin{aligned}
{}_{s}\mathbf{T}_{w}^{-}(\mathbf{x})\mathbf{n} = {} & \frac{1}{4\pi\epsilon^3}\sum_{P_i\in S_\epsilon(\mathbf{x})}\alpha_i(\mathbf{x};\mathbf{n})\left(\sum_{j\neq i}\mathbf{f}_{ij}\right)\\
& +\frac{1}{4\pi}\sum_{P_i\notin S_\epsilon(\mathbf{x})}\beta_i(\mathbf{x};\mathbf{n})\left(\sum_{j\neq i}\mathbf{f}_{ij}\right),
\end{aligned}
\tag{6.1}
$$

where

$$
\alpha_i(\mathbf{x};\mathbf{n}) := (\mathbf{x}-\mathbf{x}_i).\mathbf{n} \tag{6.2}
$$

and

$$
\beta_i(\mathbf{x};\mathbf{n}) := (\mathbf{x}-\mathbf{x}_i).\mathbf{n}/\|\mathbf{x}-\mathbf{x}_i\|^3. \tag{6.3}
$$

The sums in (6.1) constitute weighted averages of the resultant force $\sum_{j\neq i}\mathbf{f}_{ij}$ on P_i associated with corpuscular interactions; just which weighting is relevant depends on whether or not $P_i\in S_\epsilon(\mathbf{x})$. In particular, if P_i and P_j *both* lie in $S_\epsilon(\mathbf{x})$ then their *net* contribution to ${}_{s}\mathbf{T}_{w}^{-}(\mathbf{x})\mathbf{n}$ is, via (3.4), $((\mathbf{x}_j-\mathbf{x}_i).\mathbf{n})\mathbf{f}_{ij}/4\pi\epsilon^3$. Since in this case $|(\mathbf{x}_j-\mathbf{x}_i).\mathbf{n}|<2\epsilon$ this contribution is $k\mathbf{f}_{ij}$ where $|k|<1/2\pi\epsilon^2$.

6.2.2 From (5.25) point masses P_i and P_j contribute to ${}_{H}\mathbf{T}_{w}^{-}(\mathbf{x})$ if and only if the line through their locations intersects $S_\epsilon(\mathbf{x})$. For any unit vector $\mathbf{n}$, from (5.25) and (3.4)

$$
{}_{H}\mathbf{T}_{w}^{-}(\mathbf{x})\mathbf{n} = V_\epsilon^{-1}\sum_{i\neq j}\sum\alpha_{ij}(\mathbf{x})((\mathbf{x}_j-\mathbf{x}_i).\mathbf{n})\mathbf{f}_{ij}, \tag{6.4}
$$

where the double sum is, without loss of generality, over particle pairs for which $(\mathbf{x}_j-\mathbf{x}_i).\mathbf{n}>0$. The weighting of $\mathbf{f}_{ij}$ for the *net* contribution of P_i, P_j is the component in the $\mathbf{n}$ direction of that portion of the displacement of P_j from P_i within $S_\epsilon(\mathbf{x})$ divided by V_ϵ.

If interactions are central then (5.25) implies ${}_{H}\mathbf{T}_{w}^{-}$ is symmetric, as will be the corresponding Cauchy stress ${}_{H}\mathbf{T}_{w}:={}_{H}\mathbf{T}_{w}^{-}-\mathcal{D}_w$, via symmetry of $\mathcal{D}_w$.

6.2.3 Changing notation, (5.31) and (5.26) yield

$$
{}_{N}\mathbf{T}_{w}^{-}(\mathbf{x}) = -\frac{1}{2}\sum_{i\neq j}\sum\mathbf{f}_{ij}\otimes\mathcal{F}(\mathbf{x}_i-\mathbf{x},\ \mathbf{x}_j-\mathbf{x}), \tag{6.5}
$$

where, for any $\mathbf{a}, \mathbf{b} \in \mathcal{V}$,

$$\mathcal{F}(\mathbf{a}, \mathbf{b}) := \int_{\mathcal{V}} \int_0^1 \mathbf{u} w(\mathbf{a} - \alpha \mathbf{u}) w(\mathbf{b} + (1-\alpha)\mathbf{u}) d\alpha d\mathbf{u}. \tag{6.6}$$

It is a simple matter, via changes of variable, to show that $\mathcal{F} : \mathcal{V} \times \mathcal{V} \to \mathcal{V}$ satisfies, for every $\mathbf{a}, \mathbf{b} \in \mathcal{V}$,

$$1. \qquad \mathcal{F}(\mathbf{b}, \mathbf{a}) = -\mathcal{F}(\mathbf{a}, \mathbf{b}), \tag{6.7}$$

$$2. \qquad \mathcal{F}(-\mathbf{a}, -\mathbf{b}) = -\mathcal{F}(\mathbf{a}, \mathbf{b}), \tag{6.8}$$

and, for every orthogonal tensor $\mathbf{Q}$,

$$3. \qquad \mathcal{F}(\mathbf{Q}\mathbf{a}, \mathbf{Q}\mathbf{b}) = \mathbf{Q}\mathcal{F}(\mathbf{a}, \mathbf{b}). \tag{6.9}$$

As a consequence of 1.–3. we have the following

Proposition *If* $\boldsymbol{a}$ *and* $\boldsymbol{b}$ *are linearly independent* (*l.i.*) *then*

$$\mathcal{F}(\mathbf{a}, \mathbf{b}) = \tilde{\alpha}(\|\mathbf{a}\|, \mathbf{a} \cdot \mathbf{b}, \|\mathbf{b}\|)\mathbf{a} - \tilde{\alpha}(\|\mathbf{b}\|, \mathbf{a} \cdot \mathbf{b}, \|a\|)\mathbf{b}, \tag{6.10}$$

for some function $\tilde{\alpha} : \mathbb{R}^+ \times \mathbb{R} \times \mathbb{R}^+ \to \mathbb{R}$.

Proof If $\mathbf{a}$ and $\mathbf{b}$ are l.i. then $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{a} \times \mathbf{b}$ are l.i. Hence

$$\mathcal{F}(\mathbf{a}, \mathbf{b}) = \hat{\alpha}(\mathbf{a}, \mathbf{b})\mathbf{a} + \hat{\beta}(\mathbf{a}, \mathbf{b})\mathbf{b} + \hat{\gamma}(\mathbf{a}, \mathbf{b})\mathbf{a} \times \mathbf{b} \tag{6.11}$$

for some scalar-valued functions $\hat{\alpha}$, $\hat{\beta}$ and $\hat{\boldsymbol{\gamma}}$. Invoking (6.9) with $\mathbf{Q} : \mathbf{a} \to -\mathbf{a}, \mathbf{b} \to -\mathbf{b}, \mathbf{a} \times \mathbf{b} \to \mathbf{a} \times \mathbf{b}$ together with (6.8) we have

$$\begin{aligned} &-\hat{\alpha}(\mathbf{a}, \mathbf{b})\mathbf{a} - \hat{\beta}(\mathbf{a}, \mathbf{b})\mathbf{b} + \hat{\gamma}(\mathbf{a}, \mathbf{b})\mathbf{a} \times \mathbf{b} \\ &\quad = \mathbf{Q}\mathcal{F}(\mathbf{a}, \mathbf{b}) = \mathcal{F}(\mathbf{Q}\mathbf{a}, \mathbf{Q}\mathbf{b}) = \mathcal{F}(-\mathbf{a}, -\mathbf{b}) = -\mathcal{F}(\mathbf{a}, \mathbf{b}) \\ &\quad = -\hat{\alpha}(\mathbf{a}, \mathbf{b})\mathbf{a} - \hat{\beta}(\mathbf{a}, \mathbf{b})\mathbf{b} - \hat{\gamma}(\mathbf{a}, \mathbf{b})\mathbf{a} \times \mathbf{b}. \end{aligned}$$

Hence $\hat{\gamma}(\mathbf{a}, \mathbf{b})\mathbf{a} \times \mathbf{b}$ vanishes and

$$\mathcal{F}(\mathbf{a}, \mathbf{b}) = \hat{\alpha}(\mathbf{a}, \mathbf{b})\mathbf{a} + \hat{\beta}(\mathbf{a}, \mathbf{b})\mathbf{b}. \tag{6.12}$$

Using (6.8) we obtain

$$-\hat{\alpha}(-\mathbf{a}, -\mathbf{b})\mathbf{a} - \hat{\beta}(-\mathbf{a}, -\mathbf{b})\mathbf{b} = -\hat{\alpha}(\mathbf{a}, \mathbf{b})\mathbf{a} - \hat{\beta}(\mathbf{a}, \mathbf{b})\mathbf{b}$$

whence $\mathbf{a}$, $\mathbf{b}$ l.i. implies

$$\hat{\alpha}(\mathbf{a}, \mathbf{b}) = \hat{\alpha}(-\mathbf{a}, -\mathbf{b}) \quad \text{and} \quad \hat{\beta}(-\mathbf{a}, -\mathbf{b}) = \hat{\beta}(\mathbf{a}, \mathbf{b}). \tag{6.13}$$

Further (6.7) yields from (6.12)

$$\hat{\alpha}(\mathbf{b}, \mathbf{a})\mathbf{b} + \hat{\beta}(\mathbf{b}, \mathbf{a})\mathbf{a} = -\hat{\alpha}(\mathbf{a}, , \mathbf{b})\mathbf{a} - \hat{\beta}(\mathbf{a}, \mathbf{b})\mathbf{b},$$

whence $\mathbf{a}$, $\mathbf{b}$ l.i. gives

$$\hat{\alpha}(\mathbf{a}, \mathbf{b}) = -\hat{\beta}(\mathbf{b}, \mathbf{a}), \tag{6.14}$$

and (6.12) becomes

$$\mathcal{F}(\mathbf{a}, \mathbf{b}) = \hat{\alpha}(\mathbf{a}, \mathbf{b})\mathbf{a} - \hat{\alpha}(\mathbf{b}, \mathbf{a})\mathbf{b}. \tag{6.15}$$

From (6.9), for every orthogonal tensor $\mathbf{Q}$, (6.15) implies

$$\hat{\alpha}(\mathbf{Qa}, \mathbf{Qb})\mathbf{Qa} - \hat{\alpha}(\mathbf{Qb}, \mathbf{Qa})\mathbf{Qb} = \hat{\alpha}(\mathbf{a}, \mathbf{b})\mathbf{Qa} - \hat{\alpha}(\mathbf{b}, \mathbf{a})\mathbf{Qb}.$$

Since $\mathbf{Qa}$, $\mathbf{Qa}$ are l.i., for all $\mathbf{Q}$

$$\hat{\alpha}(\mathbf{Qa}, \mathbf{Qb}) = \hat{\alpha}(\mathbf{a}, \mathbf{b}). \tag{6.16}$$

It follows (see Truesdell and Noll [7], §11) that $\hat{\alpha}$ may be represented in the form

$$\hat{\alpha}(\mathbf{a}, \mathbf{b}) = \tilde{\alpha}(\|\mathbf{a}\|, \mathbf{a} \,.\, \mathbf{b}, \|\mathbf{b}\|), \tag{6.17}$$

so (6.10) follows from (6.15) and (6.17). □

Corollary *If* $\|\mathbf{x}_i - \mathbf{x}\| = \|\mathbf{x}_j - \mathbf{x}\|$ $(= d,$ *say*$)$ *then*

$$\boldsymbol{\mathcal{F}}(\mathbf{x}_i - \mathbf{x}, \mathbf{x}_j - \mathbf{x}) = \tilde{\alpha}(d, (\mathbf{x}_i - \mathbf{x}) \,.\, (\mathbf{x}_j - \mathbf{x}), d)(\mathbf{x}_i - \mathbf{x}_j) \tag{6.18}$$

if $\mathbf{x}_i - \mathbf{x}$ *and* $\mathbf{x}_j - \mathbf{x}$ *are l.i.*

From (6.5, 6.7) and (3.4), the *net* contribution of P_i and P_j to ${}_N\mathbf{T}^-_w(\mathbf{x})$ is $-\mathbf{f}_{ij} \otimes \boldsymbol{\mathcal{F}}(\mathbf{x}_i - \mathbf{x}, \mathbf{x}_j - \mathbf{x})$. If these point masses are equidistant from $\mathbf{x}$ *and* interactions are central then the corollary shows such contribution is symmetric. In general pairwise contributions will not be symmetric, and hence ${}_N\mathbf{T}^-_w$ and ${}_N\mathbf{T}_w := {}_N\mathbf{T}^-_w - \boldsymbol{\mathcal{D}}_w$ will not necessarily be symmetric-valued.

6.3 Integration of $\mathbf{T}^-_w$ Over Plane $\Sigma(\mathbf{x}_0; \mathbf{n})$ Through Point $\mathbf{x}_0$ with Unit Normal $\mathbf{n}$

6.3.1 Although pointwise values of $\mathbf{T}^-_w$ are of interest (here we have constitutive considerations in mind), it is surface integrals of form

$$\int_S \mathbf{T}_w \mathbf{n} \, dS$$

which have the clearest physical interpretation in the literature: see Section 2. In this connection we study *net* contributions ${}_s\mathbf{c}_{ij}$, ${}_N\mathbf{c}_{ij}$, and ${}_H\mathbf{c}_{ij}$ from particle pairs P_i, P_j to integrals over choice $S = \Sigma(\mathbf{x}_0; \mathbf{n})$ for each of the candidate interaction stress tensors ${}_s\mathbf{T}^-_w$, ${}_N\mathbf{T}^-_w$, and ${}_H\mathbf{T}^-_w$, respectively.

6.3.2 For any point $\mathbf{x}$ on plane $\Sigma(\mathbf{x}_0; \mathbf{n})$

$$(\mathbf{x} - \mathbf{x}_i) \,.\, \mathbf{n} = (\mathbf{x}_0 - \mathbf{x}_i) \,.\, \mathbf{n} =: -z_i. \tag{6.19}$$

It follows that if $|z_i| < \epsilon$ (so P_i lies within a distance ϵ from this plane) then the contribution of P_i to the integral of ${}_s\mathbf{T}_w^-$ over $\Sigma(\mathbf{x}_0; \mathbf{n})$ is, from (6.1, 6.2) and (6.3), $k_i \sum_{j \neq i} \mathbf{f}_{ij}$, where

$$k_i = -\frac{z_i}{4\pi\epsilon^3} \cdot \pi(\epsilon^2 - z_i^2) - \frac{z_i}{4\pi} \int_{\sqrt{\epsilon^2 - z_i^2}}^{\infty} \frac{2\pi r}{(r^2 + z_i^2)^{3/2}}\, dr$$

$$= -\frac{z_i}{4\epsilon} \left\{ 3 - \left(\frac{z_i}{\epsilon} \right)^2 \right\}. \tag{6.20}$$

If $|z_i| \geq \epsilon$, so P_i is distant further than ϵ from the plane, then from (6.1) and (6.3) its contribution is $\ell_i \sum_{j \neq i} \mathbf{f}_{ij}$, where

$$\ell_i = -\frac{z_i}{4\pi} \int_0^{\infty} \frac{2\pi r}{(r^2 + z_i^2)^{3/2}}\, dr = -z_i/2|z_i|. \tag{6.21}$$

It follows that the *net* contribution ${}_s\mathbf{c}_{ij}$ to the integral over $\Sigma(\mathbf{x}_0; \mathbf{n})$ from particles P_i and P_j is, via (3.4), $(k_i - k_j)\mathbf{f}_{ij}$, $(k_i - \ell_j)\mathbf{f}_{ij}$, $(\ell_i - k_j)\mathbf{f}_{ij}$, or $(\ell_i - \ell_j)\mathbf{f}_{ij}$, according to whether P_i and P_j are both within a distance ϵ of $\Sigma(\mathbf{x}_0; \mathbf{n})$, this is true of just P_i, or of just P_j, or of neither. Simple calculation yields, from (6.20) and (6.21),

$$(k_i - k_j)\mathbf{f}_{ij} = \frac{(z_j - z_i)}{4\epsilon} \left\{ 3 - \frac{(z_i^2 + z_i z_j + z_j^2)}{\epsilon^2} \right\} \mathbf{f}_{ij}, \tag{6.22}$$

and

$$(\ell_i - \ell_j)\mathbf{f}_{ij} = -\frac{1}{2}(z_i/|z_i| - z_j/|z_j|)\mathbf{f}_{ij}. \tag{6.23}$$

In particular, if P_i and P_j are further than ϵ from $\Sigma(\mathbf{x}_0; \mathbf{n})$ then from (6.23) their net contribution is zero if they lie on the same side of this plane and $\mathbf{f}_{ij}$ otherwise if, without loss of generality, we take $z_j > 0$. It is also clear from (6.22) and (6.23) that particles on the same side of the plane and at the same distance therefrom yield a zero net contribution.

Factor k_i has a simple geometric interpretation, since from (6.20)

$$k_i = -(\mathrm{sgn}(z_i)/V_\varepsilon) \left\{ \pi\epsilon^2 |z_i| - \frac{\pi}{3} |z_i|^3 \right\}, \tag{6.24}$$

where $\mathrm{sgn}(z_i) := z_i/|z_i|$. Here V_ε, $\pi\epsilon^2|z_i|$ and $|z_i|^3$ are, respectively, the volumes of a sphere of radius ε, a circular cylinder of height $|z_i|$ and radius ε, and cube of side $|z_i|$. Accordingly all four possible expressions for ${}_s\mathbf{c}_{ij}$ can be interpreted geometrically in terms of such volumes.

6.3.3 In [13] the contribution in respect of ${}_N\mathbf{T}_w^-$ was shown to be (see (3.36) therein)

$${}_N\mathbf{c}_{ij} = V_\epsilon^{-1}(V_i^- - V_j^-)\mathbf{f}_{ij} = V_\epsilon^{-1}(V_j^+ - V_i^+)\mathbf{f}_{ij}. \tag{6.25}$$

Here ($k = i$ or j) $V_k^-(V_k^+)$ denotes the volume of that part of $S_\epsilon(\mathbf{x}_k)$ which lies below (above) $\Sigma(\mathbf{x}_0; \mathbf{n})$. In particular, if P_i and P_j lie below and above $\Sigma(\mathbf{x}_0; \mathbf{n})$,

respectively, and are distant greater than ϵ therefrom, then ${}_N\mathbf{c}_{ij} = \mathbf{f}_{ij}$. Interestingly, and in contradiction to the standard interpretation, there may be a net contribution even if both point masses lie on the same side of $\Sigma(\mathbf{x}_0; \mathbf{n})$. For example, if P_i lies $\epsilon/2$ above, and P_j above and distant greater than ϵ from, $\Sigma(\mathbf{x}_0; \mathbf{n})$, then $V_i^- = 5\pi\epsilon^3/24$, $V_j^- = 0$, and ${}_N\mathbf{c}_{ij} = (5/32)\mathbf{f}_{ij}$.

6.3.4 Direct computation of ${}_H\mathbf{c}_{ij}$ for simple choices of P_i and P_j locations is non-trivial. Somewhat surprisingly, given the different pointwise values of ${}_H\mathbf{T}_w^-$ and ${}_N\mathbf{T}_w^-$, the values of ${}_H\mathbf{c}_{ij}$ and ${}_N\mathbf{c}_{ij}$ turn out to be the same if $\overrightarrow{P_iP_j}$ is parallel to $\mathbf{n}$, or P_i is on $\Sigma(\mathbf{x}_0; \mathbf{n})$ and P_j distant greater than ϵ therefrom, or P_i and P_j are both more than ϵ away from this plane. Such results led to a reappraisal of the general form of ${}_H\mathbf{c}_{ij}$ and (to the author) surprising discovery of the following

Proposition

$$\int_\Sigma {}_H\mathbf{T}_w^- \, dS = \int_\Sigma {}_N\mathbf{T}_w^- \, dS, \tag{6.26}$$

where $\Sigma := \Sigma(\mathbf{x}_0; \mathbf{n})$.

Proof From (5.21, 3.4) and (5.20), the *net* contribution of a particle pair P_i, P_j to the left-hand side of (6.26) is (noting also that $\hat{b}_{ji} = \hat{b}_{ij}$ from (5.23) and (5.24))

$${}_H\mathbf{c}_{ij} = a_{ij}((\mathbf{x}_j - \mathbf{x}_i).\mathbf{n})\mathbf{f}_{ij}, \tag{6.27}$$

where

$$a_{ij} := \int_\Sigma \int_0^1 w(\lambda(\mathbf{x}_j - \mathbf{x}_i) + (\mathbf{x}_i - \mathbf{x}))d\lambda dS_\mathbf{x} = a_{ji}. \tag{6.28}$$

Properties (3.4) and $a_{ji} = a_{ij}$ allow us to assume $(\mathbf{x}_j - \mathbf{x}_i).\mathbf{n} \geq 0$ in (6.27) without loss of generality. Writing $\mathbf{u} := \lambda(\mathbf{x}_j - \mathbf{x}_i)$ and reversing the order of integration in (6.28),

$$a_{ij}((\mathbf{x}_j - \mathbf{x}_i).\mathbf{n}) = \int_0^{(\mathbf{x}_j - \mathbf{x}_i).\mathbf{n}} \int_\Sigma w(\mathbf{u} + (\mathbf{x}_i - \mathbf{x}))dS_\mathbf{x} \, d(\mathbf{u}.\mathbf{n}). \tag{6.29}$$

For a given point $\mathbf{x}_i + \mathbf{u}$ on P_iP_j the integrand vanishes for point $\mathbf{x}$ on Σ distant greater than ϵ therefrom and takes the value V_ϵ^{-1} otherwise. Thus

$$a_{ij}(\mathbf{x}_j - \mathbf{x}_i).\mathbf{n} = V_\epsilon^{-1} \int_0^{(z_j - z_i)} A(z)dz, \tag{6.30}$$

where $A(z)$ is the area of intersection of Σ with $S_\epsilon(\mathbf{u} + \mathbf{x}_i)$, $z := \mathbf{u}.\mathbf{n}$, and $z_j - z_i := (\mathbf{x}_j - \mathbf{x}_i).\mathbf{n}$. Such intersections are void, consist of a single point, or are circular plane regions. It follows that $a_{ij}V_\epsilon$ is zero or the volume of part of a sphere of radius ϵ bounded between two planes parallel to Σ. Specifically (see (6.25)) we have

$$a_{ij}((\mathbf{x}_j - \mathbf{x}_i).\mathbf{n})V_\epsilon = V_\epsilon - V_j^- - V_i^+, \tag{6.31}$$

whence (noting $V_j^- + V_j^+ = V_\epsilon$) from (6.27) and (6.25),

$$ {}_H\mathbf{c}_{ij} = V_\epsilon^{-1}(V_j^+ - V_i^+)\mathbf{f}_{ij} = {}_N\mathbf{c}_{ij}. \tag{6.32} $$

□

7 Discussion

7.1 The shortcomings of virial-based expressions for the Cauchy stress (see (3.21), (3.29) and Remark 1) were listed in Subsection 3.3. The weighting function approach is much more general since it delivers dynamic balances of mass, linear momentum, moment of momentum, and energy whose forms are scale-independent. For any given scale the fields which appear in these relations are clearly defined in terms of local spatial molecular averages computed at the chosen scale. Choice (4.25) of weighting function (see also Remark 9) is here favoured because of its particularly simple interpretation of velocity field value $\mathbf{v}_w(\mathbf{x}, t)$ as the velocity of the mass centre of molecules which lie within a distance ϵ of $\mathbf{x}$ at time t. Knowledge of $\mathbf{v}_w$ means the macroscopic motion of the system can be visualised at scale ϵ and the notion of material point (at this scale) motivated and defined (see [17]). This reverses the viewpoint of modern continuum mechanics (e.g. [1, 3]) in which such notion is *primitive* and velocity a derived concept.

7.2 Weighting function methodology gives rise to the unique form (4.21) of linear momentum balance, and accordingly draws attention to the non-uniqueness of the interaction stress tensor $\mathbf{T}_w^-$. Heretofore two candidates, ${}_H\mathbf{T}_w^-$ and ${}_N\mathbf{T}_w^-$, had been proposed. Here a third possibility, ${}_s\mathbf{T}_w^-$, has been derived. *A priori* it would seem from comparison of (5.13), (5.25), and (5.31) that this new choice might offer computational advantages over the other possibilities. All three choices share common aspects when considering the *net* contribution $c_{ij}\mathbf{f}_{ij}$ of a pair of point masses P_i, P_j to the integral of $\mathbf{T}_w^-\,\mathbf{n}$ over an infinite plane $\Sigma_\mathbf{n}$ with unit normal $\mathbf{n}$. Noting that without loss of generality we can take $\overrightarrow{P_iP_j}\,.\,\mathbf{n} \geq 0$, these common properties are:

C.P.1. If P_i and P_j lie within a distance ϵ of $\Sigma_\mathbf{n}$ then c_{ij} decreases smoothly as either of these particles moves closer to $\Sigma_\mathbf{n}$.

C.P.2. If $\overrightarrow{P_iP_j}\,.\,\mathbf{n} = 0$ (so that P_i and P_j are on the same side of $\Sigma_\mathbf{n}$ and the same distance therefrom) then $c_{ij} = 0$.

C.P.3. If P_i and P_j are further than ϵ from $\Sigma_\mathbf{n}$ then (a) $c_{ij} = 0$ if they are on the same side of $\Sigma_\mathbf{n}$, and (b) $c_{ij} = 1$ if they are on opposite sides of $\Sigma_\mathbf{n}$.

Remark 15 Since macroscopic scales far exceed nearest-neighbour separations (of order $2 - 3$ Å in condensed phases) and molecular interactions usually have ranges less than 100 Å, property C.P.3. (b) might seem irrelevant since $\mathbf{f}_{ij}$ in such case would be negligible. However, if the system of interest were to be a collection of ions of the same polarity (for example, a constituent in a reacting mixture) then even Coulombic interactions could be involved. The analysis shows that even in such mixtures there exist interaction partial stress tensors. (Of course, constitutive relations for such stresses would be non-local.)

Remark 16 Consider a body consisting of a cubic array of atoms at rest (so that the body is at zero absolute temperature) and let $\Sigma_{\mathbf{n}}$ be parallel to a lattice plane. The standard interpretation of the integral of the Cauchy stress tensor $\mathbf{T}$ over $\Sigma_{\mathbf{n}}$ is (see Section 2) the resultant force exerted by atoms on that side of $\Sigma_{\mathbf{n}}$ into which $\mathbf{n}$ is directed upon the atoms on the other side of $\Sigma_{\mathbf{n}}$. Moving this plane so as to keep normal $\mathbf{n}$ fixed, consider the situation in which $\Sigma_{\mathbf{n}}$ contains a 'layer' of atoms. The standard interpretation implies that interactions which contribute to the integral in this case involve only atoms at least two lattice spacings apart. However, a slight displacement of $\Sigma_{\mathbf{n}}$ will yield contributions to the integral dominated by nearest-neighbour interactions. Accordingly the standard interpretation implies a jump discontinuity in the value of the integral as the atomic layer is traversed, and is at variance with the macroscopic/continuum viewpoint in which fields change imperceptibly over microscopic distances. In the foregoing atomistic considerations $\mathcal{D}_w = \mathbf{0}$ (since $\mathbf{v}_i = \mathbf{0}$ for all P_i, by assumption) and $\mathbf{T}$ is identified with (see (2.3), (4.23) and (4.24)) $\mathbf{T}_w^-$. The integral of $\mathbf{T}_w^-\mathbf{n}$ over $\Sigma_{\mathbf{n}}$ involves interactions weighted by coefficients which vary imperceptibly as atomic layers are crossed (see C.P.1). Of course, more generally there is a contribution to the integral of $\mathbf{Tn}$ over $\Sigma_{\mathbf{n}}$ due to thermal motions, namely the integral of $-\mathcal{D}_w\mathbf{n}$ over $\Sigma_{\mathbf{n}}$. Further, there is an immediate resolution of the paradox of how, in the case of rarefied gases, one can have stresses which are pressures, despite molecular interactions being negligible: in such case $\mathbf{T}_w^- = \mathbf{0}$ and $\mathbf{T}$ is identified with $-\mathcal{D}_w$. More generally the temperature-dependence of stress is appreciated via the presence of $-\mathcal{D}_w$ in (4.24). Additionally, the scale dependence of field values via choice of w (see (4.25)) is clear and explicit. *The standard, intuitive, interpretation of stress is thus seen to be modified and deepened by microscopic considerations*.

Remark 17 The situation described in Remark 16 (in which the atoms of a body are arranged in a lattice structure at zero absolute temperature) would seem to indicate a shortcoming in the definition of ${}_s\mathbf{T}_w^-$. Suppose the body has been distorted by forces acting on its boundary. In the absence of gravity the resultant force on any atom/molecule P_i remote from the boundary is, from (3.1),

$$\mathbf{F}_i := \sum_{j\neq i} \mathbf{f}_{ij} = \mathbf{0}. \tag{7.1}$$

(Atoms at or near the boundary would also experience a resultant external force $\mathbf{c}_i$: see (3.8)). It follows from (5.4) that, strictly within the interior of the body, the stress ${}_s\mathbf{T}_w^-$ must vanish, no matter how the body has been distorted.[5] More insight is gained by observing that from (4.26) and (4.27), together with Remark 9,

$$\mathbf{f}_w(\mathbf{x}, t) = \sum_i {\sum_j}' \mathbf{f}_{ij}(t) w(\mathbf{x}_i(t) - \mathbf{x}). \tag{7.2}$$

The superposed prime here indicates a sum that is taken only over particles P_j which do not belong to $S_\epsilon(\mathbf{x})$ at time t. Noting that at this time

$$w(\mathbf{x}_i(t) - \mathbf{x}) - w(\mathbf{x}_j(t) - \mathbf{x})$$

[5]The author gratefully acknowledges having this drawn to his attention by a Reviewer.

vanishes if P_i and P_j are both inside or both outside $S_\epsilon(\mathbf{x})$, is $w(\mathbf{x}_i(t)-\mathbf{x})$ if P_i is inside and P_j outside $S_\epsilon(\mathbf{x})$, and is $-w(\mathbf{x}_j(t)-\mathbf{x})$ if P_i is outside and P_j inside $S_\epsilon(\mathbf{x})$, (7.2) may be written as

$$\mathbf{f}_w(\mathbf{x},t)=\frac{1}{2}\sum\sum_{i\neq j}\mathbf{f}_{ij}(t)\{w(\mathbf{x}_i(t)-\mathbf{x})-w(\mathbf{x}_j(t)-\mathbf{x}\}, \tag{7.3}$$

upon invoking (3.4). In this format one is led to consider, via (5.3), another candidate stress tensor (cf. (5.4))

$${}_s\hat{\mathbf{T}}^-_w:=\frac{1}{2}\sum\sum_{i\neq j}\mathbf{f}_{ij}\otimes(\mathbf{a}_i-\mathbf{a}_j). \tag{7.4}$$

However, if (7.1) holds then ${}_s\hat{\mathbf{T}}^-_w$ *also* vanishes. Accordingly one is led, via (4.22) and (7.3), to (5.15). This is the starting point for both the Hardy and Noll versions of $\mathbf{T}^-_\mathbf{w}$, namely solution of (5.16) for vector field $\mathbf{b}_{ij}$.

Remark 18 The arguments advanced in Remarks 16 and 17 involve considerations of equilibrium at absolute zero temperature, and should be regarded as less than conclusive in view of the simplistic modelling adopted. Anomalous behaviour of matter at temperatures near absolute zero indicates the need for a more sophisticated, quantum-mechanical, approach. Here the result of complex interactions between assemblies of nuclei and electrons is modelled in terms of forces between point masses. Each point mass models such an assembly: its mass is that of the assembly and its location the assembly mass centre. Interaction $\mathbf{f}_{ij}(t)$ may be interpreted to be the result of averaging the effect of the assembly modelled by P_j upon that modelled by P_i over an atomic-scale time interval (of duration Δ_1, say). Since neighbouring electron 'clouds' affect each other, $\mathbf{f}_{ij}(t)$ will depend upon not only P_i and P_j, but also neighbouring assemblies. What remain in the simplified model are chaotic aspects of corpuscular motions and fluctuations in (see $(7.1)_1$) $\mathbf{F}_i(t)$ on a time scale in excess of Δ_1 yet which is macroscopically small. For crystalline phases such motions are localised at lattice nodes, and will change their natures with lattice distortion. (For example, uniaxial extension of a lattice may be expected to result in motions in some sense more wide ranging parallel to the axis in question.) It follows that the argument behind the jump discontinuity in Remark 16 is naive: Such discontinuity will not exist since point masses undergo chaotic motions localised about lattice nodes, and hence those corresponding to a lattice plane will cross this plane many times in random fashion over any macroscopic time interval. In respect of Remark 17, notice that in macroscopic equilibrium (so $\mathbf{v}\equiv\mathbf{0}$), from (4.24, 7.1_1, 5.4) and (4.14),

$$\begin{aligned}{}_s\mathbf{T}_w(\mathbf{x},t)&={}_s\mathbf{T}^-_w(\mathbf{x},t)-\boldsymbol{\mathcal{D}}_w(\mathbf{x},t)\\&=\sum_i\{\mathbf{F}_i(t)\otimes\mathbf{a}_i(\mathbf{x}_i(t)-\mathbf{x})-m_i\mathbf{v}_i(t)\otimes\mathbf{v}_i(t)w(\mathbf{x}_i(t)-\mathbf{x})\}.\end{aligned} \tag{7.5}$$

Here each of $\mathbf{F}_i$, $(\mathbf{x}_i-\mathbf{x})$ and $\mathbf{v}_i$ fluctuates: the individual trajectories $\mathbf{x}_i(t)$ have different character for gases, liquids, and solids. In the solid case (see Subsection 3.2) trajectories, governed by $\mathbf{F}_i$, are chaotic but localised: the domain of localisation depends upon the macroscopic deformation of the body. Accordingly, *each of the two contributions to the right-hand side of* (7.5) *depend upon macroscopic deformation*. In view of (7.5) ${}_s\mathbf{T}^-_w$, $\boldsymbol{\mathcal{D}}_w$, and ${}_s\mathbf{T}_w$ fluctuate, but such stochastic behaviour is in general

negligible given the large numbers of particles in the sum and lack of correlation in the chaotic motions. Notice that for any unit vector $\mathbf{n}$

$$-\boldsymbol{\mathcal{D}}_w\,\mathbf{n}\,.\,\mathbf{n} = -\sum_i m_i(\mathbf{v}_i\,.\,\mathbf{n})^2 w(\mathbf{x}_i - \mathbf{x}) < 0. \tag{7.6}$$

Thus if stress ${}_s\mathbf{T}_w$ vanishes within the body then, from (7.3),

$${}_s\mathbf{T}_w^-\mathbf{n}\,.\,\mathbf{n} = \sum_i (\mathbf{F}_i\,.\,\mathbf{n})(\mathbf{a}_i\,.\,\mathbf{n}) > 0. \tag{7.7}$$

7.3 The issue of non-uniqueness of $\mathbf{T}_w^-$ can be avoided by working directly with $\mathbf{f}_w$ (see (4.21)), which is simply a uniquely defined interaction body force density (recall from Subsection 4.2. that $\mathbf{f}_w(\mathbf{x}, t)$ is the resultant force on molecules within a distance ϵ from $\mathbf{x}$ at time t by all other molecules of the system, divided by $4\pi\epsilon^3/3$). This possibility would seem to merit particular attention when considering nanoscale bodies. For such bodies the surface area to volume ratio is much greater than for macroscopic systems, and surface effects can become significant. (For example, it has long been known [22] that cleaving a small crystalline body in vacuo results in surface stresses which give rise to detectable bulk deformation.) Indeed, as the scale of a solid body decreases both surface/interfacial and edge effects must be expected to become more and more evident. Of course, macroscopic modelling of these effects can be adopted, via descriptions of boundary regions in terms of bidimensional continua (see, for example, [23, 24]), and edge effects in terms of one-dimensional continua. However, there are here two drawbacks. The first is that of the complexity of introducing balance equations and constitutive relations for boundaries and edges, and the second is that at very small scales such conventional continuum modelling is no longer valid. By contrast, (4.21) holds formally at *any* scale, and makes physical sense if the scale is such that quantal effects can be neglected together with details of molecular structure. Of course, (4.21) requires to be supplemented by constitutive assumptions in respect of $\mathbf{f}_w$ and $\boldsymbol{\mathcal{D}}_w$.

7.4 Here we have only addressed mass conservation and linear momentum relations from a microscopic perspective. A useful macroscopic description of a specific material system requires a constitutive relation for the Cauchy stress $\mathbf{T}_w$ (or separate relations for either $\mathbf{T}_w^-$ and $\boldsymbol{\mathcal{D}}_w$, or $\mathbf{f}_w$ and $\boldsymbol{\mathcal{D}}_w$) together with relevant boundary and initial conditions. Constitutive aspects are here guided by the explicit atomistic definitions (4.8), (4.17) and choice of (5.13), (5.25) or (5.31). Information concerning atomic locations and interaction models can be used to motivate assumptions which greatly reduce the degrees of freedom of the microscopic description. For example, in Subsection 3.2 neighbouring time-averaged locations $\bar{\mathbf{x}}_i$ could be assumed to be governed by an affine deformation field consistent with the macroscopic motion. It is beyond our purposes here to pursue constitutive considerations or, indeed, to discuss energy balance or the rôle of time-averaging (see [4, 10] and [17]).

7.5 Current interest in small-scale systems has given rise to extensive studies of how specific atomistic knowledge can be incorporated into scale-dependent simplified descriptions. In particular we note the quasi-continuum approach of Miller and Tadmor [25] and continuum (of reduced dimension) view of Friesecke and James [26], both of which are based upon energetic considerations. It is hoped that the

present work will complement such detailed and sophisticated studies by clarifying the scale-dependent microscopic interpretation of continuum concepts and relations.

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