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A new look at the atomic level virial stress: on continuum-molecular system equivalence

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The virial stress is the most commonly used definition of stress in discrete particle systems. This quantity includes two parts. The first part depends on the mass and velocity (or, in some versions, the fluctuation part of the velocity) of atomic particles, reflecting an assertion that mass transfer causes mechanical stress to be applied on stationary spatial surfaces external to an atomic-particle system. The second part depends on interatomic forces and atomic positions, providing a continuum measure for the internal mechanical interactions between particles. Historic derivations of the virial stress include generalization from the virial theorem of Clausius (1870) for gas pressure and solution of the spatial equation of balance of momentum. The virial stress is a *stress-like* measure for momentum change in space. This paper shows that, contrary to the generally accepted view, the virial stress is not a measure for mechanical force between material points and cannot be regarded as a measure for mechanical stress in any sense. The lack of physical significance is both at the individual atom level in a time-resolved sense and at the system level in a statistical sense. It is demonstrated that the interatomic force term alone is a valid stress measure and can be identified with the Cauchy stress. The proof in this paper consists of two parts. First, for the simple conditions of rigid translation, uniform tension and tension with thermal oscillations, the virial stress yields clearly erroneous interpretations of stress. Second, the conceptual flaw in the generalization from the virial theorem for gas pressure to stress and the confusion over spatial and material equations of balance of momentum in theoretical derivations of the virial stress that led to its erroneous acceptance as the Cauchy stress are pointed out. Interpretation of the virial stress as a measure for mechanical force violates balance of momentum and is inconsistent with the basic definition of stress. The versions of the virial-stress formula that involve total particle velocity and the thermal fluctuation part of the velocity are demonstrated to be measures of spatial momentum flow relative to, respectively, a fixed reference frame and a moving frame with a velocity equal to the part of particle velocity not included in the virial formula. To further illustrate the irrelevance of mass transfer to the evaluation of stress, an equivalent continuum (EC) for dynamically deforming atomistic particle systems is defined. The equivalence of the continuum to discrete atomic systems includes (i) preservation of linear and angular momenta, (ii) conservation of internal, external and inertial work rates, and (iii) conservation of mass. This equivalence allows fields of work- and momentum-preserving Cauchy stress, surface traction, body force and deformation

to be determined. The resulting stress field depends only on interatomic forces, providing an independent proof that as a measure for internal material interaction stress is independent of kinetic energy or mass transfer.

Keywords: virial stress; atomic stress; Cauchy stress; pressure tensor; molecular dynamics; equivalent continuum

1. Introduction

The widely used virial stress for atomic systems is a tensor quantity that measures the time rate of change of momentum for spatial regions. Implied in its definition is the fact that it accounts for the effects on momentum change in a spatial region of both mechanical forces and mass transport across the boundary of the spatial region. On the other hand, the true mechanical stress (Cauchy stress) measures the time rate of change of momentum possessed by a fixed amount of material mass. By definition, the Cauchy stress measures the pure effect on momentum change of mechanical forces alone. This paper demonstrates that, contrary to the belief of some in the physics/mechanics/materials communities, the virial stress is not the Cauchy stress or any other form of mechanical stress. It does not measure internal mechanical force in any sense. One version of the virial stress formula involves the total atomic velocity. Another version involves only the thermal fluctuation of the atomic velocity. It is shown in this paper that the version that involves the total particle velocity defines a measure for spatial momentum flow as it appears to an observer fixed in space. Similarly, the version that involves only the thermal fluctuation velocity defines a measure for momentum flow relative to a reference frame moving with a velocity equal to the part of the particle velocity not included in that version of the virial formula. The discussions in this paper focus primarily on the first version of the virial stress, since the meaning of the second version will become clear through the discussions. However, discussions will be given to the second version to outline the conceptual confusion leading to its acceptance by some as a form of mechanical stress. We begin with a review of the virial concept of stress.

The continuum stress interpretation of atomic force fields is important since it allows the intensity and nature of internal interactions in materials to be measured. One of the commonly used definitions of stress in molecular dynamical (MD) systems is the virial stress. This 'stress' is based on a generalization of the virial theorem of Clausius (1870) for gas pressure and includes two parts (cf. McLellan 1974; Tsai 1979; Rowlinson & Widom 1982; Swenson 1983). It is also called the 'local atomic level stress', 'system level stress', 'total stress' or the 'pressure tensor'. In this definition, the average virial stress over a volume Ω around a particle i at position $\boldsymbol{r}_i$ is

$$\bar{\boldsymbol{\Pi}} = \frac{1}{\Omega}\left(-m_i\dot{\boldsymbol{u}}_i \otimes \dot{\boldsymbol{u}}_i + \frac{1}{2}\sum_{j\,(\neq i)} \boldsymbol{r}_{ij} \otimes \boldsymbol{f}_{ij}\right), \tag{1.1}$$

where m_i is the mass of i, $\boldsymbol{u}_i$ is the displacement of i relative to a reference position, $\dot{\boldsymbol{u}}_i = \mathrm{d}\boldsymbol{u}_i/\mathrm{d}t$ represents material time derivative of $\boldsymbol{u}_i$, $\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i$ and $\otimes$ denotes the tensor product of two vectors. Here, tensile stresses are defined positive. The interparticle force $\boldsymbol{f}_{ij}$ applied on particle i by particle j is

$$\boldsymbol{f}_{ij} = \frac{\partial \Phi(r_{ij})}{\partial r_{ij}}\frac{\boldsymbol{r}_{ij}}{r_{ij}}, \tag{1.2}$$

where $r_{ij} = |\boldsymbol{r}_{ij}|$ is the central distance between particles i and j, $\Phi(r_{ij})$ is the energy of the atomic ensemble and $\partial\Phi(r_{ij})/\partial r_{ij} > 0$ if $\boldsymbol{f}_{ij}$ is attractive. Note that Newton's third law requires that $\boldsymbol{f}_{ij} = -\boldsymbol{f}_{ji}$.

Equation (1.1) can also be used to evaluate the average virial stress in a region containing a number of particles. The first term on the right-hand side of (1.1) is included out of the notion that the motion of atoms across a fixed spatial surface (Gibbs dividing surface) at a point 'exerts' a force (dynamic pressure) on that surface. The second term arises from interatomic forces. The kinetic-energy term is usually small compared with the interatomic force term for solids but is dominant for gases. Following the same considerations, Cheung & Yip (1991) defined a stress that varies from the virial stress only slightly in the treatment of stress components on different surfaces. Lutsko (1988) derived an expression similar to that in (1.1) by applying the continuum equation of balance of momentum involving the stress tensor to MD systems and by conducting a volume averaging of the stress distribution so obtained. Specifically, he assumed that the singular pointwise stress function $\boldsymbol{\Pi}(\boldsymbol{r}, t)$ in an MD system satisfies (Lutsko 1988, eqn (1))

$$\frac{\partial}{\partial \boldsymbol{r}} \cdot \boldsymbol{\Pi}(\boldsymbol{r}, t) = \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{p}(\boldsymbol{r}, t), \tag{1.3}$$

where the divergence term is given by $[\partial/\partial \boldsymbol{r} \cdot \boldsymbol{\Pi}(\boldsymbol{r}, t)]_\beta = \partial \Pi_{\alpha\beta}/\partial r_\alpha$ $(\alpha, \beta = 1, 2, 3)$, summation is implied over the repeated index and r_α are Cartesian components of $\boldsymbol{r}$. Note that the time differentiation embodied in $\mathrm{d}\boldsymbol{p}/\mathrm{d}t = \dot{\boldsymbol{p}}$ is the *material time derivative* that must be carried out by following material particles as they travel in space. In contrast, the *spatial time derivative* $\partial \boldsymbol{p}/\partial t$ is carried out for each fixed spatial location $\boldsymbol{r}$; therefore, $\partial \boldsymbol{p}/\partial t \neq \dot{\boldsymbol{p}}$. This difference will prove critical in the ensuing discussions. In general, the material derivative and the spatial derivative are related via $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \dot{\boldsymbol{r}} \cdot \partial/\partial \boldsymbol{r}$.

Here, it must be pointed out first that Lutsko's use of the material time derivative $\mathrm{d}\boldsymbol{p}/\mathrm{d}t$ is in error (detailed discussions will follow shortly below), and perhaps is unintended. It is quite likely that he intended to use (19.11) in Zubarev (1974), which involves the spatial time derivative $\partial \boldsymbol{p}/\partial t$. For thoroughness, the analyses in this paper will consider both scenarios, with one scenario involving the material derivative and the other scenario involving the spatial derivative. It will be shown that if the material time derivative is used as in (1.3), violation of balance of momentum occurs. Consequently, the quantity $\boldsymbol{\Pi}$ defined by this version of the equation would have no physical significance. On the other hand, if the spatial time derivative is used (as is the case in Cormier *et al.* (2001) and perhaps as Lutsko had intended) and the equation is written as

$$\frac{\partial}{\partial \boldsymbol{r}} \cdot \boldsymbol{\Pi}(\boldsymbol{r}, t) = \frac{\partial}{\partial t}\boldsymbol{p}(\boldsymbol{r}, t), \tag{1.4}$$

the quantity $\boldsymbol{\Pi}(\boldsymbol{r}, t)$ would be a measure for momentum change in space (see (2.5) in § 2 *b*), as Lutsko correctly pointed out. More importantly, we will show that this quantity so defined is not a measure for mechanical stress in any sense. This conclusion contradicts the interpretation by Lutsko and a notion widely held by many. Although we will discuss the scenario that involves the material time derivative and (1.3), the primary premise of this paper will be the assumption that Lutsko

correctly used (1.4) in his analysis. For now, we continue our review of Lutsko's analysis.

As Lutsko (1988) stated, the continuum representation of the momentum density $\boldsymbol{p}(\boldsymbol{r},t)$ (momentum per unit volume) of the discrete system is

$$\boldsymbol{p}(\boldsymbol{r},t)=\sum_i m_i\dot{\boldsymbol{u}}_i(\boldsymbol{r}_i,t)\delta(\boldsymbol{r}-\boldsymbol{r}_i)=\sum_i \boldsymbol{p}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i), \tag{1.5}$$

where $\delta(\boldsymbol{x})$ is the Dirac delta function and the summation is performed over all particles in the system. This expression is singular. Its interpretation should be made appropriately in an integral sense in order to obtain dimensional consistency. Another way to look at this issue is to regard $\delta(\boldsymbol{x})$ as having the dimension of $(\text{length})^{-3}$. The integration of (1.4) and (1.5) via Fourier transform (more details will be given in § 4 *a*) as in Lutsko (1988) yields

$$\begin{aligned}\boldsymbol{\Pi}(\boldsymbol{r})=&-\sum_i m_i\dot{\boldsymbol{u}}_i\otimes\dot{\boldsymbol{u}}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i)\\&+\frac{1}{4}\sum_i\sum_{j\,(\neq i)}\boldsymbol{r}_{ij}\otimes\boldsymbol{f}_{ij}\delta[(\boldsymbol{r}-\boldsymbol{r}_i)\times\boldsymbol{r}_{ij}]\\&\qquad\cdot\{s[(\boldsymbol{r}-\boldsymbol{r}_i)\cdot\boldsymbol{r}_{ij}]-s[(\boldsymbol{r}_i-\boldsymbol{r})\cdot\boldsymbol{r}_{ij}]\\&\qquad\qquad-s[(\boldsymbol{r}-\boldsymbol{r}_j)\cdot\boldsymbol{r}_{ij}]+s[(\boldsymbol{r}_j-\boldsymbol{r})\cdot\boldsymbol{r}_{ij}]\},\end{aligned} \tag{1.6}$$

where $s(x)$ is the Heaviside step function. The first term in this solution is singular at atomic positions $\boldsymbol{r}_i$ and zero elsewhere. The second term is singular at all points along line segments connecting atomic position pairs as well as at the atomic positions.

We temporarily set aside the issue concerning the exact physical meaning of the quantity $\boldsymbol{\Pi}(\boldsymbol{r})$ in (1.6) to discuss the evaluation of a continuum average of this mathematical solution. The discussion here solely focuses on the mechanical force term in (1.6). Lutsko used a bond length fraction measure in his calculation of an average of $\boldsymbol{\Pi}(\boldsymbol{r})$ over a certain volume. This bond fraction measure varies from 0 to 1 as one goes from an atom to its neighbour. Details of his calculation can be seen in eqn (12) of his paper. This handling has been accepted by some as correct. In particular, it has been used by Cormier *et al.* (2001). It must be pointed out that, although Lutsko correctly obtained the mathematical solution in (1.6), his interpretation of it as mechanical stress and his evaluation of the average through a line fraction measure are in error.

> His error is in his belief that the part of the solution in (1.6) *between atoms* is physically relevant to and affects balance of momentum. We must point out that *since there is no mass and therefore no momentum at positions between atoms, balance of momentum is not affected by the part of the mathematical solution in (1.6) that concerns positions between atoms.* The part of (1.6) for positions between any two atoms is irrelevant to the physics at hand.

It is an artefact of Lutsko's solution technique (continuum representation for a discrete system) and must be disregarded. Another way to look at this issue is to focus on the physical reality of the discrete system. The atomic force between two atoms is only applied on the two atoms at the atomic positions where material mass exists. The geometric concept of the forces 'going through' the line connecting the atoms

does not mean forces being applied on spatial locations. Atomic forces cannot be and are not applied at pure spatial locations where material mass does not exist. Therefore, stress exists, in a strict sense, only at atomic positions. In physics, quite often we obtain two solutions (roots) of an equation (such as the case of solving for velocity from a quadratic equation). Using physical arguments/considerations, we can determine that one of the solutions (negative, for example) is not physical and not possible. That solution is a pure mathematical artefact and is disregarded. The situation here is similar. *The part of the solution between atoms has no bearing on the physics at hand since the system is fundamentally discrete.* The interpretation of Lutsko of his own mathematical solution is incorrect *physically*. Here, we must realize that the mathematical solution in (1.6) is only *partly* relevant to the physics at hand. Only the part at atomic positions is physically relevant to the discrete atomic system. Physical interpretation of this mathematical solution must use physical considerations.

Having made clear the above points, it is very important to point out that the statement '(singular) atomic stress/force exists only at atomic positions' above should be strictly understood and used in the context of the explicit analysis of discrete atomic systems. It has nothing to do with the evaluation of a continuum equivalent stress measure for the atomic system. Specifically, the average stress obtained using a correct singular atomic solution should be interpreted as a continuous representation that has value even at positions between atoms. This continuum interpretation of the singular fields is useful. Also, the equivalent continuum (EC) fields developed in § 5 is a continuous representation of the discrete system and shares certain attributes of the discrete system in terms of momentum, work rate, energy and mass.

After disregarding the *physically irrelevant* part of (1.6), we obtain the *physically significant* interpretation of the mathematical solution in (1.6) in the context of discrete atomic systems as

$$\boldsymbol{\Pi}(\boldsymbol{r}) = \sum_i \left(-m_i \dot{\boldsymbol{u}}_i \otimes \dot{\boldsymbol{u}}_i + \frac{1}{2} \sum_{j\,(\neq i)} \boldsymbol{r}_{ij} \otimes \boldsymbol{f}_{ij} \right) \delta(\boldsymbol{r} - \boldsymbol{r}_i). \tag{1.7}$$

Both terms in this expression for the local virial stress are singular at atomic positions $\boldsymbol{r}_i$ and are zero between atomic positions. A simple average of the singular stress field in (1.7) over volume Ω around a particle i gives $\bar{\boldsymbol{\Pi}}$ in (1.1). Note that the physically significant interpretation in (1.7) is exactly the same expression obtained by Zubarev (1974, eqn (19.12) on p. 246). *It is commonly believed that Lutsko's version of the virial stress or 'stress' is somewhat different from the version in (1.1). Analyses above have shown that a correct interpretation of Lutsko's mathematical solution yields the same expression for virial stress as used by many other investigators.* This is a secondary finding of this paper. We note that some papers in the literature (see, for example, Cheung & Yip 1991) include an extra factor of $\frac{1}{2}$ for the first term of (1.1). This difference is inconsequential for the discussions here. It will become evident in §§ 2–4 that the version of $\bar{\boldsymbol{\Pi}}$ with this extra factor has neither physical nor geometric significance. One of the primary objectives of this paper is to clarify the meaning of (1.1) and distinguish it from the Cauchy stress, since this expression represents the central point of the 'virial stress' concept.

The virial stress formula in (1.1) has been widely used as a measure for mechanical stress. In particular, it has been often regarded and used as a form of the Cauchy

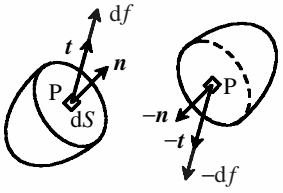

Figure 1. Definition of Cauchy stress.

stress. The most important conclusion of this paper is that the virial stress $\bar{\boldsymbol{\Pi}}$ in (1.1) and its singular form $\boldsymbol{\Pi}$ in (1.7) have a geometric interpretation without any physical significance. Specifically, this paper will show that the virial stress measures the rate of momentum change in space. Contrary to the belief and use of a great majority of investigators, it does not measure mechanical force or mechanical stress in any sense. It will be shown that the interatomic force term in (1.1) alone fully and correctly constitutes the Cauchy stress. In § 3, it will first be illustrated that the virial stress formula yields clearly erroneous interpretation of stress in one simple example. Additional examples illustrating that the virial stress is not mechanical stress will be given in §§ 6 and 7, along with discussions of work conjugacy in the context of general continuum-molecular system equivalence. The development in this paper focuses on the correct interpretation of the virial stress and three types of misconceptions or historic errors in the formulation of the virial stress that led to its use as a measure for mechanical stress. It will be shown that the inclusion of the kinetic-energy term resulted from three historic errors in the formulation of the virial stress. The first common error is the failure to distinguish between internal and external forces in intrinsically dynamic systems and the unjustifiable generalization of the concept of the external, macroscopic and statistical virial pressure (Clausius 1870; Jeans 1967) to the consideration of the dynamic and local concept of stress (McLellan 1974; Tsai 1979; Rowlinson & Widom 1982; Swenson 1983; Ziesche *et al*. 1988). This conceptual failure overlooks the difference and imbalance between internal and external forces for an intrinsically dynamic system and leads to the acceptance of the virial stress as a measure for stress which represents internal-force interaction between material points. The second mistake (see, for example, Cheung & Yip 1991) is in the assumption that momentum transfer through a non-physical spatial plane causes a mechanical force to be applied on that spatial plane. This is a conceptual error that fails to recognize that mechanical force is the interaction between material mass. The third common error is due to an improper treatment of or confusion over material and spatial descriptions of balance of momentum. This error occurred in the theoretical proof first given by Lutsko and later repeated by Cormier *et al*. (2001). A similar error is also made by Yasui *et al*. (1999) and Nakane *et al*. (2000) due to their confusion over material and spatial equations of balance of momentum (more details are given in § 4). All three errors lead to the inclusion of the kinetic-energy term in the physically insignificant virial stress formula. It will be shown that *if the virial stress is treated as a measure of mechanical force*, the balance of momentum would be violated.

We note that some authors argue that only the fluctuation part of the atomic velocity (rather than the total, absolute velocity) should be used in the virial formula. This version of the virial stress has been put forth by Irving & Kirkwood (1950), Hardy (1982), Yasui *et al*. (1999) and Nakane *et al*. (2000), among others. It will

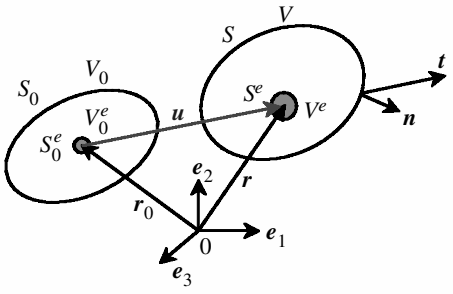

Figure 2. Reference and current configurations of a deforming system.

be shown in § 4 *c* that this version does not represent a measure for stress either. Discussions using specific examples illustrating the invalidity of this version of the virial stress as mechanical stress are also given in §§ 6 and 7 of this paper.

2. Continuum definition of stress and balance of momentum

(*a*) *Definition of Cauchy stress*

Since stress is a continuum concept, the evaluation of stress must follow proper continuum definition of stress and continuum balance laws. To facilitate discussions on the issue of stress in this paper and to properly understand the meaning of the virial stress, it is illustrative to first note that stress is a measure for the *internal* mechanical force interaction *between material mass points in a body.* An illustration of the definition of the Cauchy stress is given in figure 1. This definition is basic and can be found in many mechanics texts. In particular, it can be found in Malvern (1969, p. 69). First, a cut is made through a point P in a body. This is a *material* cut which moves with material point P under consideration. The Cauchy stress $\boldsymbol{\sigma}$ measures the force per unit area between the two sides of the material cut through P. Specifically, it is defined through $\boldsymbol{t} = \boldsymbol{n} \cdot \boldsymbol{\sigma}$, where $\boldsymbol{n}$ is the unit normal to the cut surface and $\boldsymbol{t} = \mathrm{d}\boldsymbol{f}/\mathrm{d}S$ is the traction vector on the cut surface at P. Note that the definition holds for all conditions, fully dynamic as well as static. It is *not* necessary to know what the velocity at the point of interest is. This is because, by definition, the cut always follows mass point P. It is obvious in this definition that stress has nothing to do with velocity. Another way to look at this issue is through the *material* description of balance of momentum. By definition, the Cauchy stress is the components of the force per unit area between the two sides of the *deforming surface* of a fixed amount of mass. Therefore, by definition, there is no mass convection through the surface on which stress is evaluated. This issue is more clearly understood through an analysis of balance of momentum.

(*b*) *Material and spatial descriptions of balance of momentum*

Since one of the historic mistakes in the theoretical development of the virial stress can be attributed to confusion over the differences between spatial (Eulerian) and material (Lagrangian) representations of balance of momentum, and since the specific issue concerned is the improper handling of the spatial time derivative and the material time derivative, we first briefly review the material and spatial versions

of balance of momentum here. Consider a deforming system which has volume V and surface S at time t, as shown in figure 2. At some reference time t_0, the system has volume V_0 and surface S_0, which are used as a fixed reference configuration. *Note that balance of momentum must be satisfied by a system as a whole and by any portion of it.* The amount of material mass contained in a volume element V_0^e is Δm. Under a general deformation, V_0^e is mapped to a new (the current) configuration V^e. Conservation of mass requires that

$$\Delta m = \int_{V_0^e} \rho_0(\boldsymbol{r}_0)\,\mathrm{d}V = \int_{V^e} \rho(\boldsymbol{r},t)\,\mathrm{d}V,$$

where ρ_0 and ρ are mass densities in the reference configuration and the current configuration, respectively. At time t, Newton's second law (balance of linear momentum) specifies that for mass Δm (with body force neglected),

$$\int_{S^e} \boldsymbol{t}\,\mathrm{d}S = \frac{\mathrm{d}}{\mathrm{d}t}\int_{V^e} [\rho(\boldsymbol{r},t)\dot{\boldsymbol{u}}(\boldsymbol{r},t)]\,\mathrm{d}V, \tag{2.1}$$

where $\boldsymbol{t} = \boldsymbol{n}\cdot\boldsymbol{\sigma}$ is the traction vector on S^e, $\boldsymbol{n}$ is the unit normal to S^e and $\boldsymbol{\sigma}$ is the Cauchy stress tensor. Noting that $\rho(\boldsymbol{r},t)\,\mathrm{d}V = \rho(\boldsymbol{r}_0)\,\mathrm{d}V_0 = \mathrm{d}m$, one can show that

$$\begin{aligned}
\int_{S^e} \boldsymbol{n}\cdot\boldsymbol{\sigma}\,\mathrm{d}S &= \int_{V^e} \frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{\sigma}\,\mathrm{d}V \\
&= \frac{\mathrm{d}}{\mathrm{d}t}\int_{V^e} [\rho(\boldsymbol{r},t)\dot{\boldsymbol{u}}(\boldsymbol{r},t)]\,\mathrm{d}V \\
&= \frac{\mathrm{d}}{\mathrm{d}t}\int_{V_0^e} [\rho(\boldsymbol{r}_0,t_0)\dot{\boldsymbol{u}}[\boldsymbol{r}(\boldsymbol{r}_0),t]]\,\mathrm{d}V_0 \\
&= \int_{V_0^e} \{\rho(\boldsymbol{r}_0,t_0)\ddot{\boldsymbol{u}}[\boldsymbol{r}(\boldsymbol{r}_0),t]\}\,\mathrm{d}V_0 \\
&= \int_{V^e} [\rho(\boldsymbol{r},t)\ddot{\boldsymbol{u}}(\boldsymbol{r},t)]\,\mathrm{d}V,
\end{aligned} \tag{2.2}$$

where $\ddot{\boldsymbol{u}}(\boldsymbol{r},t) = \mathrm{d}^2\boldsymbol{u}(\boldsymbol{r},t)/\mathrm{d}t^2$ and use has been made of the divergence theorem (first equal sign) and Reynolds transport theorem (cf. Truesdell & Toupin 1960). Since V^e is totally arbitrary, equation (2.2) corresponds to

$$\frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{\sigma} = \rho(\boldsymbol{r},t)\ddot{\boldsymbol{u}}(\boldsymbol{r},t) = \dot{\boldsymbol{p}}(\boldsymbol{r},t) - \dot{\rho}(\boldsymbol{r},t)\dot{\boldsymbol{u}}(\boldsymbol{r},t), \tag{2.3}$$

where $\boldsymbol{p} = \rho\dot{\boldsymbol{u}}$ is the momentum density of the continuum in the current configuration. Equations (2.2) and (2.3) are, respectively, the integral and local expressions of the *material* description of balance of momentum. They are *material* in nature, since the analysis follows a mass particle or a fixed amount of mass. They can be found in any continuum mechanics text, in particular, Malvern (1969). The balance of angular momentum is maintained through $\boldsymbol{\sigma} = \boldsymbol{\sigma}^{\mathrm{T}}$. It is important to note that the Cauchy stress tensor $\boldsymbol{\sigma}$ represents the physical force per unit area on S^e. The analysis and the material time differentiation here must be carried out by following Δm, with respect to the deforming surface of Δm, which happens to take the shape and position of S^e at time t. By the same token, the material time differentiation

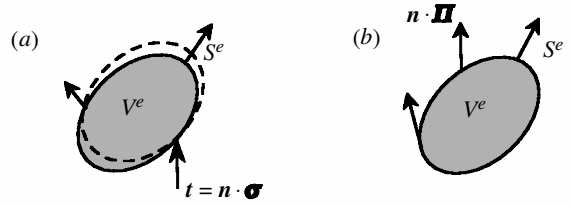

Figure 3. Material and spatial descriptions of balance of momentum; the Cauchy stress $\boldsymbol{\sigma}$ measures the forces on the moving boundary of mass Δm, which happens to coincide with S^e at time t, while the 'virial stress' is a geometric quantity measuring the momentum flow across a stationary spatial surface S^e. (*a*) Balance of momentum for fixed amount of mass occupying V^e at time t, $(\mathrm{d}/\mathrm{d}t)\int_{V^e}\int \rho\dot{\boldsymbol{u}}\,\mathrm{d}V = \int_{S^e}\boldsymbol{n}\cdot\boldsymbol{\sigma}\,\mathrm{d}S$. (*b*) Time rate of change of momentum for region V^e, $(\partial/\partial t)\int_{V^e}\rho\dot{\boldsymbol{u}}\,\mathrm{d}V = \int_{S^e}\boldsymbol{n}\cdot\boldsymbol{\Pi}\,\mathrm{d}S = \int_{S^e}\{-[\boldsymbol{n}\cdot\dot{\boldsymbol{u}}][\rho\dot{\boldsymbol{u}}] + \boldsymbol{n}\cdot\boldsymbol{\sigma}\}\,\mathrm{d}S$.

in (2.3) is carried out with respect to the material point that happens to occupy position at $\boldsymbol{r}$ at time t.

The balance of momentum can also be expressed with respect to fixed *spatial* regions and fixed *spatial* positions, in an Eulerian manner. For the *stationary* spatial region V^e, the expression is (see, for example, Evans & Morriss 1990)

$$\begin{aligned}\int_{V^e}\frac{\partial}{\partial\boldsymbol{r}}\cdot[-\rho(\boldsymbol{r},t)\dot{\boldsymbol{u}}(\boldsymbol{r},t)\otimes\dot{\boldsymbol{u}}(\boldsymbol{r},t)+\boldsymbol{\sigma}]\,\mathrm{d}V&\\ =\int_{S^e}\{-[\boldsymbol{n}\cdot\dot{\boldsymbol{u}}(\boldsymbol{r},t)][\rho(\boldsymbol{r},t)\dot{\boldsymbol{u}}(\boldsymbol{r},t)]+\boldsymbol{n}\cdot\boldsymbol{\sigma}\}\,\mathrm{d}S&\\ =\frac{\partial}{\partial t}\int_{V^e}[\rho(\boldsymbol{r},t)\dot{\boldsymbol{u}}(\boldsymbol{r},t)]\,\mathrm{d}V.&\end{aligned}\tag{2.4}$$

For fixed spatial location $\boldsymbol{r}$, the expression is (Evans & Morriss 1990; Zubarev 1974)

$$\frac{\partial}{\partial\boldsymbol{r}}\cdot[-\rho(\boldsymbol{r},t)\dot{\boldsymbol{u}}(\boldsymbol{r},t)\otimes\dot{\boldsymbol{u}}(\boldsymbol{r},t)+\boldsymbol{\sigma}]=\frac{\partial}{\partial t}[\rho(\boldsymbol{r},t)\dot{\boldsymbol{u}}(\boldsymbol{r},t)].\tag{2.5}$$

Note that Evans & Morriss *unequivocally* and *correctly* stated that $\boldsymbol{\sigma}$ in these equations is the Cauchy stress tensor because it measures the actual mechanical force per unit area (on mass particles that happen to occupy positions on the surface of the spatial region under consideration) (also see eqn (2.9) in Evans & Morriss). Interpretations of (2.2), (2.3) and (2.4), (2.5) are illustrated in parts (*a*) and (*b*) of figure 3, respectively. In the material description, by definition, there is no mass convection across the surface of Δm that happens to coincide with S^e at time t. The momentum change for Δm is purely due to the mechanical forces ($\int_{S^e}\boldsymbol{n}\cdot\boldsymbol{\sigma}\,\mathrm{d}S$) on it and the Cauchy stress $\boldsymbol{\sigma}$ provides a measure for the forces through (2.2) or (2.3). In contrast, the momentum flow across the stationary spatial surface S^e consists of two parts. The first part, $-\int_{S^e}(\boldsymbol{n}\cdot\dot{\boldsymbol{u}})\rho\dot{\boldsymbol{u}}\,\mathrm{d}S$, is due to mass convection through S^e. The second part, $\int_{S^e}\boldsymbol{n}\cdot\boldsymbol{\sigma}\,\mathrm{d}S$, is due to mechanical forces acting upon material points that happen to occupy positions on the spatial surface S^e at time t. Here, $\partial/\partial t = \mathrm{d}/\mathrm{d}t - \dot{\boldsymbol{r}}\cdot\partial/\partial\boldsymbol{r}$ represents the time rate of change at a fixed spatial location or in a fixed spatial region here. Note that if the material time derivative $\mathrm{d}\boldsymbol{p}/\mathrm{d}t = \dot{\boldsymbol{p}}$ in (1.3) is interpreted to be the spatial time rate of change $\partial\boldsymbol{p}/\partial t$, equation (1.3) becomes (1.4), which is exactly (2.5) with $\boldsymbol{\Pi} = -\rho(\boldsymbol{r},t)\dot{\boldsymbol{u}}(\boldsymbol{r},t)\otimes\dot{\boldsymbol{u}}(\boldsymbol{r},t)+\boldsymbol{\sigma}$. This shows that the virial stress $\boldsymbol{\Pi}$ represents the combination of terms in the square

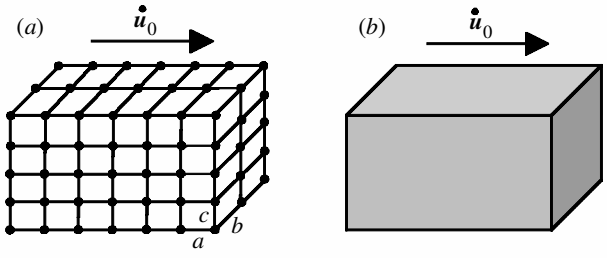

Figure 4. Lattice in equilibrium and stress-free continuum translating in space with uniform velocity.

brackets on the left-hand side of (2.5) and is 'the tensor that measures the momentum change in spatial region V^e or the momentum flow across fixed spatial surface S^e'. It accounts for the contributions of both mass convection and mechanical force. Although it is a *stress-like* quantity (having the dimension of 'force per unit area' and satisfying the spatial version of balance of momentum), it does not in any way represent the physical interaction between material points through mechanical forces. Rather, it is strictly a geometric quantity. If it is interpreted or used as a measure of mechanical stress, as in the literature, violation of balance of momentum occurs. More discussions on this will be given in subsequent sections. Note also that (1.3) cannot not be (2.3) in general.

3. Lack of physical interpretation and irrelevance to material mechanical interaction

We now focus our attention back on the virial stress formula. The mass-transfer term in (1.1) and (1.7) is irrelevant to the concept of stress. In order to illustrate this point, we first consider the simple example of an atomic array at equilibrium and translating in space with uniform velocity $\dot{\boldsymbol{u}}_0$, as shown in figure 4. Assume that all interatomic distances in this array are greater than the cut-off radius (the interatomic distance beyond which direct interaction between two atoms is essentially negligible); therefore, all interatomic forces vanish. Furthermore, assume that no external forces are applied on the atoms. Clearly, the continuum equivalent to this system is a body having the same amount of mass, occupying the same spatial region and moving at the same uniform velocity (figure 4*b*). Just like particles in the discrete atomic array in figure 4*a*, material points in this continuum body are subject to zero forces and are, therefore, stress free. However, an interpretation using the virial stress in (1.1) would yield a 'compressive stress' in the direction of motion (regardless of the sign of $\dot{\boldsymbol{u}}_0$) due to the existence of the kinetic term. Specifically, the tensor quantity in (1.1) for this case is

$$\bar{\boldsymbol{\Pi}} = \frac{1}{abc}\begin{pmatrix} -m_0|\dot{\boldsymbol{u}}_0|^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{3.1}$$

where a, b and c and the lattice constants of the atomic array. Obviously, such an interpretation of stress is inconsistent with reality. If one insists that the kinetic-energy term be included and that a Gibbs dividing (spatial) plane perpendicular to $\dot{\boldsymbol{u}}_0$ 'feels' a force due to the mass transfer across it, as stated in Tsai (1979), then

the lattice or its continuum equivalent in return would 'feel' a reaction force of equal magnitude and opposite direction because of Newton's third law. As a result, the net force on material points in the system would not be zero in general and $\dot{\boldsymbol{u}}_0$ would not be constant, in direct contradiction to the original assumption of the problem. To understand the actual meaning of the quantity in (3.1), we note that the non-zero component in (3.1),

$$\bar{\Pi}_{11} = -\left[\left(\frac{m_0}{abc}\right)|\dot{\boldsymbol{u}}_0|\right]|\dot{\boldsymbol{u}}_0|, \tag{3.2}$$

is the momentum carried by the amount of material mass that, during the course of a unit of time, passes through a unit area of a *fixed spatial plane* that is perpendicular to the x direction or the direction of particle velocity $\dot{\boldsymbol{u}}_0$. In other words, the components of tensor $\bar{\boldsymbol{\Pi}}$ represent the time rate of momentum flow per unit spatial area, not traction or force per unit area of a material body. This interpretation is crucial and will be confirmed to be true in general in § 4 *a* using considerations of balance of momentum.

It will be shown in §§ 6 and 7 that the virial stress also yields clearly incorrect interpretations of the stress states for lattices under uniform tension (with or without thermal fluctuation). The discussions there will involve an account of the stress work as well as internal loading conditions. Also, those discussions will concern versions of the 'virial stress' formula that involve both the total particle velocity and only the fluctuation part of the particle velocity.

The failure of the virial stress to correctly represent the internal material interaction in this example is a direct reflection of its lack of relevance to mechanical loading in a general sense. We shall examine this issue both in a time-resolved explicitly dynamic sense and in a statistical time- and space-averaged sense. The following two sections focus on the conceptual flaw in the formulation of the virial stress by generalization of the virial theorem (Clausius 1870) for gas pressure and on the misconception held by Lutsko (1988) in the theoretical derivation of the virial stress that led to him to regard the virial stress as a measure for mechanical force. It must first be clearly stated that the virial theorem for gas pressure is totally correct in the statistical sense (see the following section for details). However, generalizing it to claim that mechanical stress also depends on mass transfer as well as internal interatomic force is unjustifiable and incorrect (see the following section as well). To further illustrate the irrelevance of mass transfer to the evaluation of stress, an EC is defined for dynamically deforming atomistic particle systems in § 5. In that development, the full fields of momentum- and work-conserving Cauchy stress, surface traction, body force and mass density for the EC are specified. The independence of stress on mass transfer is then demonstrated with full work, momentum, energy and mass equivalence between the EC and the atomic system. Finally, the analytical solution for the stress field of the EC of a lattice under uniform tension is given in § 6 to provide an illustration of the theoretical developments concerning the virial stress and the continuum/molecular system equivalence. This paper ends with an example in § 7 involving thermal vibrations, further illustrating the irrelevance of the 'virial stress' to mechanical stress both for conditions under which fully time-resolved account of total atomic velocity is taken and for conditions under which partitioning of thermal fluctuation velocity and structural deformation velocity is carried out.

4. Historic errors in the formulation of the virial stress as a measure of mechanical stress

Although the original formulation of the virial stress in (1.1) is by a generalization of Clausius' virial theorem for gas pressure and its derivation using spatial balance of momentum considerations occurred later, we first discuss (in § 4 *a*) the geometric meaning of the 'virial stress' from the perspectives of spatial and material balance of momentum. This analysis should also allow us to obtain the correct expression for the Cauchy stress, which is simply the interatomic force term in (1.1). We will then discuss the conceptual flaws involved in the generalization of the virial theorem in § 4 *b*. This choice of order of discussions is a matter of convenience and facilitates the discussions.

(*a*) *Measure for momentum flow, not measure for mechanical stress*

It is not clear in Lutsko (1988) if (1.3) and (1.5) are written in a reference configuration or in the current deformed configuration. As it turns out, regardless of the choice of frame of analysis, equation (1.3) violates the balance of linear momentum (Newton's second law of motion), therefore rendering the quantities $\boldsymbol{\Pi}$ and $\bar{\boldsymbol{\Pi}}$ with no clear physical meaning. To facilitate discussions on this issue, we shall examine (1.3) and (1.5) in the contexts of both the reference configuration and the current configuration.

In the current configuration, the material description of balance of linear momentum is (2.3) (cf. Malvern 1969). Note that $\boldsymbol{\sigma}$ is the Cauchy stress, $\rho(\boldsymbol{r}, t)$ is the mass density in the current configuration and $\boldsymbol{p} = \rho\dot{\boldsymbol{u}}$ is the momentum per unit current volume. Since $\rho\ddot{\boldsymbol{u}} = \dot{\boldsymbol{p}} - \dot{\boldsymbol{u}}\dot{\rho} \neq \dot{\boldsymbol{p}}$ in general, equation (1.3) cannot be a true continuum representation consistent with the balance of momentum in the current configuration (equation (2.3)); therefore, $\boldsymbol{\Pi}$ cannot be identified with the Cauchy stress if (1.3) is used. In fact, equation (1.3) is meaningless and does not have any physical significance. We believe that Lutsko's use of the notation $\mathrm{d}/\mathrm{d}t$ in his paper is inadvertent. Indeed, his analysis only has meaning if we regard $\mathrm{d}/\mathrm{d}t$ throughout his paper as being $\partial/\partial t$. Under this premise, we now analyse Lusko's solution with (1.4) as his starting point.

Using (1.4), we can now obtain an interpretation for $\boldsymbol{\Pi}$ or $\bar{\boldsymbol{\Pi}}$ and show that (a) the virial stress is a measure of momentum change in space, and (b) it is used as a measure for mechanical force (stress) violation of balance of momentum occurs. This interpretation can be illustrated in an integral sense involving a finite volume. For this purpose, we integrate (1.4) or (2.5) over a fixed spatial volume element V^e to obtain

$$\begin{aligned}\int_{V^e} \frac{\partial}{\partial \boldsymbol{r}} \cdot \boldsymbol{\Pi}\, \mathrm{d}V &= \int_{S^e} \boldsymbol{n} \cdot \boldsymbol{\Pi}\, \mathrm{d}S = \int_{V^e} \frac{\partial \boldsymbol{p}}{\partial t}\, \mathrm{d}V = \frac{\partial}{\partial t} \int_{V^e} \boldsymbol{p}\, \mathrm{d}V \\ &= \int_{S^e} -(\boldsymbol{n} \cdot \dot{\boldsymbol{u}})(\rho\dot{\boldsymbol{u}})\, \mathrm{d}S + \int_{S^e} \boldsymbol{n} \cdot \boldsymbol{\sigma}\, \mathrm{d}S \\ &= \int_{S^e} -(\boldsymbol{n} \cdot \dot{\boldsymbol{u}})(\rho\dot{\boldsymbol{u}})\, \mathrm{d}S + \frac{\mathrm{d}}{\mathrm{d}t} \int_{V^e} \rho\dot{\boldsymbol{u}}\, \mathrm{d}V. \end{aligned} \tag{4.1}$$

Here, use has been made of the divergence theorem. The third equals sign holds true simply by virtue of the meaning of $(\partial/\partial t) \int_{V^e} \boldsymbol{p}\, \mathrm{d}V$ as the rate of change of

the total momentum contained in spatial region V^e and *the fact that the spatial region V^e is fixed and unchanging*. This identity is given in Malvern (1969, p. 211) as a footnote. To state this identity simply, since the volume of integration is not a function of time, the total rate of momentum change in fixed region V^e must be equal to the sum (integration) of rates of momentum change at all points in the region. $\int_{S^e} -(\boldsymbol{n}\cdot\dot{\boldsymbol{u}})(\rho\dot{\boldsymbol{u}})\,\mathrm{d}S$ is the rate of change of momentum due to mass convection across S^e. $(\mathrm{d}/\mathrm{d}t)\int_{V^e}\rho\dot{\boldsymbol{u}}\,\mathrm{d}V$ is the material time derivative of the momentum of material which happens to occupy the spatial region V^e at the moment of interest. Since the material time derivative $\mathrm{d}/\mathrm{d}t$ follows this constant amount of mass, balance of momentum requires this term to be equal to the total instantaneous force applied on the material in V^e through S^e (body force neglected), i.e.

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V^e}\rho\dot{\boldsymbol{u}}\,\mathrm{d}V=\int_{S^e}\boldsymbol{t}\,\mathrm{d}S,$$

which is (2.1). In contrast, $\boldsymbol{n}\cdot\boldsymbol{\Pi}$ is a 'traction-like' quantity (having the dimension of force/area) and is fixed at the spatial locations of S^e at all times. However, it does not have any physical interpretation as a force. A comparison of $\boldsymbol{\Pi}$ and $\boldsymbol{\sigma}$ is illustrated in figure 3.

To obtain the Cauchy stress tensor, we start with (2.3) and follow the same procedure of Fourier transform and inverse Fourier transform used in Lutsko (1988). Note that when (2.3) is applied to an atomic system,

$$\rho\ddot{\boldsymbol{u}}=\sum_i m_i\ddot{\boldsymbol{u}}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i),$$

with $m_i\ddot{\boldsymbol{u}}_i=\boldsymbol{f}_i$ being the total force on i. Equation (2.3) can be rewritten as

$$\frac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{\sigma}(\boldsymbol{r},t)=\sum_i\boldsymbol{f}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i). \tag{4.2}$$

After Fourier transform, equation (4.2) has the form

$$\begin{aligned}\mathrm{i}\boldsymbol{k}\cdot\hat{\boldsymbol{\sigma}}(\boldsymbol{k},t)&=-\sum_i\boldsymbol{f}_i\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}\\&=-\sum_i\sum_{j\,(\neq i)}\boldsymbol{f}_{ij}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}\\&=-\frac{1}{2}\sum_i\sum_{j\,(\neq i)}(\boldsymbol{f}_{ij}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}+\boldsymbol{f}_{ji}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j})\\&=\mathrm{i}\boldsymbol{k}\cdot\frac{1}{2}\sum_i\sum_{j\,(\neq i)}\boldsymbol{r}_{ij}\otimes\boldsymbol{f}_{ij}\frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}-\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j}}{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ji}},\end{aligned} \tag{4.3}$$

where $\mathrm{i}=\sqrt{-1}$, $\boldsymbol{k}$ is the wavenumber, $\hat{\boldsymbol{\sigma}}(\boldsymbol{k},t)=\int_V\boldsymbol{\sigma}(\boldsymbol{r},t)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\,\mathrm{d}V$ and use has been made of the fact that $\boldsymbol{f}_i=\sum_{j\neq i}\boldsymbol{f}_{ij}$ when external forces do not exist (e.g. the body is infinite). It is important to point out that the derivation and conclusion here also apply to finite systems with external (body) forces. The result would be the same. The only difference is that the analysis would use an argument similar to that in § 1 concerning the interpretation of (1.6) to show that the body force does not affect the physically significant part of the stress function solution.

To carry out the inverse transform of

$$\boldsymbol{\sigma}(\boldsymbol{r},t)=\frac{1}{(2\pi)^3}\int_{V^{\boldsymbol{k}}}\hat{\boldsymbol{\sigma}}(\boldsymbol{k},t)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\,\mathrm{d}V^{\boldsymbol{k}}$$

($V^{\boldsymbol{k}}$ being the transformed space), we use the technique of Cormier *et al.* (2001) by noting that

$$\frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}-\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j}}{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ji}}=\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j}\int_0^1\mathrm{e}^{(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ji})s}\,\mathrm{d}s,$$

where $0\leqslant s\leqslant 1$ is a scalar variable independent of the relevant quantities. Under this notation,

$$\begin{aligned}\boldsymbol{\sigma}(\boldsymbol{r},t)&=\frac{1}{2}\sum_i\sum_{j\,(\neq i)}\boldsymbol{r}_{ij}\otimes\boldsymbol{f}_{ij}\left\{\int_0^1\left[\frac{1}{(2\pi)^3}\int_{V^{\boldsymbol{k}}}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_{ji}s+\boldsymbol{r}_j-\boldsymbol{r})}\,\mathrm{d}V^{\boldsymbol{k}}\right]\mathrm{d}s\right\}\\&=\frac{1}{2}\sum_i\sum_{j\,(\neq i)}\boldsymbol{r}_{ij}\otimes\boldsymbol{f}_{ij}\left\{\int_0^1\delta[\boldsymbol{r}-(\boldsymbol{r}_{ji}s+\boldsymbol{r}_j)]\,\mathrm{d}s\right\}\\&=\frac{1}{2}\sum_i\sum_{j\,(\neq i)}\boldsymbol{r}_{ij}\otimes\boldsymbol{f}_{ij}\delta[\boldsymbol{r}-(\boldsymbol{r}_{ji}\ell+\boldsymbol{r}_j)],\end{aligned}\tag{4.4}$$

where $0\leqslant\ell\leqslant 1$. The third equality reflects the singular nature of the delta function and the meaning of the integral on the right-hand side of the second equal sign. Although written in a slightly different form, the above expression is exactly the same as the second term in (1.6). In particular, $\delta[\boldsymbol{r}-(\boldsymbol{r}_{ji}\ell+\boldsymbol{r}_j)]$ is singular along the line segment between $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ and is zero elsewhere. The same physical arguments associated with (1.6) and (1.7) can be used to show that the physically significant interpretation of this mathematical solution in the context of discrete atomic systems is

$$\boldsymbol{\sigma}(\boldsymbol{r})=\frac{1}{2}\sum_i\sum_{j\,(\neq i)}\boldsymbol{r}_{ij}\otimes\boldsymbol{f}_{ij}\delta(\boldsymbol{r}-\boldsymbol{r}_i).\tag{4.5}$$

This singular expression for Cauchy stress can be used to obtain the average stress over any region of an atomistic ensemble. For a region with volume Ω around atom i, the average stress is

$$\bar{\boldsymbol{\sigma}}=\frac{1}{2\Omega}\sum_i\sum_{j\,(\neq i)}\boldsymbol{r}_{ij}\otimes\boldsymbol{f}_{ij}.\tag{4.6}$$

This stress has all the physical meanings of the average Cauchy stress over Ω. Recognizing the relationship between stress, deformation and internal strain energy, Huang (1950) and Born & Huang (1988) used an elastic energy approach to evaluate the stress in lattices. Their result is identical to that in (4.6), confirming the concurrence that stress is a continuum measure of the internal interactions between material points and does not depend on the motion of atoms or mass transfer.

It is worthwhile to note that many authors (see, for example, Egami *et al.* 1980; Srolovitz *et al.* 1981*a*, *b*; Alber *et al.* 1992; Horstemeyer & Baskes 1999, among others) have indeed correctly stated and used (4.6) as the measure for atomic level stress. Some of these uses may have been out of the belief that at 0 K the kinetic-energy term in the virial formula vanishes. This paper has shown that their expressions hold, in

general, at finite temperatures as well. Equation (4.6) is not a special case of (1.1). Equation (4.6) defines the Cauchy stress in general for fully dynamic conditions and (1.1) defines a momentum flux tensor in general for fully dynamic conditions. Furthermore, equation (1.1) does not define a mechanical stress in any sense.

Equations (1.1), (4.3), (4.5) and (4.6) show that

$$\boldsymbol{\Pi} = -\sum_i m_i \dot{\boldsymbol{u}}_i \otimes \dot{\boldsymbol{u}}_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) + \boldsymbol{\sigma} \quad \text{and} \quad \bar{\boldsymbol{\Pi}} = -\frac{1}{\Omega} m_i \dot{\boldsymbol{u}}_i \otimes \dot{\boldsymbol{u}}_i + \bar{\boldsymbol{\sigma}}. \tag{4.7}$$

Indeed, the first equation of (4.7) is exactly (19.12) in Zubarev (1974). This quantity has been widely referred to as 'stress' in the literature; we have shown that it is not mechanical stress. The combination of terms on the right-hand side does not assign any physical significance to $\boldsymbol{\Pi}$ and renders it in violation of Newton's second law *if it is interpreted as the Cauchy stress*. Its significance is as a tensor that measures the momentum flux in space, as can be seen from (2.5) and has been pointed out in § 2 *b*. In particular, it is obvious that the components of $\boldsymbol{\Pi}$ are not measures for mechanical force components in the current configuration. Equation (4.1) and the fact that $\boldsymbol{\Pi}$ is evaluated for fixed spatial surface S^e characterize the virial stress as a stress-like quantity that measures the time rate of change of the total momentum contained in spatial region V^e. This is strictly a geometric interpretation. In contrast, the Cauchy stress $\boldsymbol{\sigma}$ measures the material time derivative of momentum possessed by material mass which happens to occupy spatial region V^e with surface S^e at time t. It is explicatory to note that, in discrete particle dynamics where mass is lumped at mathematical points (or rigid-body dynamics where mass density is constant at all points and at all times), a direct relation exists between momentum flux through an isolated mass point and the total force on that point of mass (not spatial location), making it possible to evaluate the force directly from momentum flux. In deformable body continuum mechanics, however, the continuous convection of mass or change in mass density due to deformation prevents a *direct* relation from being established between force (stress) and momentum flow over a spatial region alone. Instead, mass transfer must be accounted for, as indicated by (4.1) as well as (2.3). This is necessitated by the reality that mass is not conserved, in general, within fixed spatial regions.

As a side note, $\boldsymbol{\Pi}$ can be used to evaluate the momentum flow across a spatial surface S^e, as pointed out by Lutsko (1988). Specifically, equation (1.4) yields

$$\frac{\partial}{\partial t} \int_{S^e} \boldsymbol{n} \cdot \boldsymbol{p} \, \mathrm{d}S = \int_{V^e} \frac{\partial}{\partial \boldsymbol{r}} \cdot \left(\frac{\partial}{\partial \boldsymbol{r}} \cdot \boldsymbol{\Pi} \right) \mathrm{d}V.$$

Again, this is simply a geometric interpretation concerning momentum flow in space. It must also be pointed out that the momentum flow across a spatial surface is not a measure or indication of any mechanical force. Detailed discussions on this are given in § 4 *b*.

Having clarified the true meaning of the virial stress (derived by solving (1.4)) as a measure for spatial momentum flow and the fact that it is distinctly different from the Cauchy stress, we now turn our attention to the question of whether or not (1.3) can be a valid representation of balance of linear momentum in terms of stress on a non-deforming reference (Lagrangian) configuration. In a reference configuration, the mass density ρ_0 (mass per unit reference volume) is only a function of initial

material point location $\boldsymbol{r}_0$ and not a function of time. On such a configuration, the balance of momentum is expressed as (Malvern 1969)

$$\frac{\partial}{\partial \boldsymbol{r}_0} \cdot \boldsymbol{S}(\boldsymbol{r}_0) = \rho_0(\boldsymbol{r}_0)\ddot{\boldsymbol{u}}[\boldsymbol{r}(\boldsymbol{r}_0, t), t] = \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{p}_0(\boldsymbol{r}_0, t), \tag{4.8}$$

where $\boldsymbol{S}$ is the non-symmetric first Piola–Kirchhoff stress and $\boldsymbol{p}_0$ is the momentum possessed by materials contained in unit *initial* volume at location $\boldsymbol{r}_0$ *in the reference configuration*. Equation (1.3) bears resemblance to (4.8) in that neither equation involves a mass-transfer term like that in (2.3). However, for (1.3) to be regarded as being written on the reference configuration and interpreted as (4.8), one must require that the discussion and calculations in both (1.3) and (1.5) are carried out consistently on the reference configuration. This is clearly not the case, nevertheless. First of all, the interatomic forces $\boldsymbol{f}_{ij}$ depend on $\boldsymbol{r}_{ij}$, the current interatomic distances. Also, the tensor product in (1.1) and (1.7) and the volume averaging in (1.1) use dimensions in the current configuration. Note also that $\boldsymbol{\Pi}$ is symmetric and, in general, $\boldsymbol{S}$ is not. Most importantly, atomic position rearrangement during deformation, in general, makes it impossible to define a valid (positive-definite) deformation mapping between the current configuration and any fixed reference configuration. This difficulty results from a fundamental difference between discrete particle models and continuum models. Specifically, particle rearrangement renders the determinant of the deformation gradient $\boldsymbol{F}$ to be non-positive ($\det \boldsymbol{F} \leqslant 0$); a situation not permitted in continuum mechanics. Therefore, it is not possible, in general, to define stress in the reference configuration for a discrete system and (1.3) is not a valid representation of balance of momentum in a reference configuration. Consequently, $\boldsymbol{\Pi}$ cannot be identified as the first Piola–Kirchhoff stress $\boldsymbol{S}$ either.

In summary, the use of (1.3) for an atomic system is not justified regardless of the choice of configuration (reference or current). If (1.3) is interpreted as being written in the current configuration, the term $\dot{\rho}\dot{\boldsymbol{u}}$ in (2.3) is not correctly accounted for. As a result, it cannot be used to assign the quantity $\boldsymbol{\Pi}$ (and therefore $\bar{\boldsymbol{\Pi}}$) any physical meaning. The only possible derivation and interpretation for $\boldsymbol{\Pi}$ (and $\bar{\boldsymbol{\Pi}}$) (as far as Lutsko's approach is concerned) is through (1.4) and (2.5), giving it the geometric meaning of a measure for momentum change in space. This spatial nature of Lutsko's analysis adds the kinetic-energy term to the virial expression in (1.7) and (1.1). The inclusion of this kinetic-energy term is inconsistent with the continuum definition of mechanical (Cauchy) stress and the requirements of *material* balance of momentum. Stress is a measure of the *internal mechanical force* interactions *between material points*. Mass transport through geometrical surfaces in space (Gibbs dividing surfaces) should have no part in any definition of stress, since it neither contributes to the mechanical interaction between material points nor induces mechanical interaction between external planes and material particles, as clearly illustrated by the example in figure 4.

(*b*) *Conceptual flaws in the generalization of the virial theorem for gas pressure to stress*

This section focuses on the first and the second conceptual errors in the historic development of the virial stress referred to in § 1. The virial stress in (1.1) is not a valid measure for *internal* material interactions. Further, the components of $\boldsymbol{\Pi}$ are

not the traction components applied on fixed *spatial* planes that are parallel to coordinate planes and run through the location of interest, contrary to assertions in the literature (see, for example, Tsai 1979). First, it must be pointed out that there is no force interaction between material particles and imagined spatial planes. Note also that the mechanical interactions of atomic particles with each other (internal interactions) and the interactions with external (physical) surfaces occur only through atomic forces for real materials with mass. The motion of a particle (mass transfer) does not *directly* cause mechanical forces to be applied on other particles or surfaces. Instead, the motion (velocity) has an *indirect* effect on the forces. Specifically, the higher the velocities of the particles, the closer they may come within each other or relative to external walls. This is considered 'collision' and this process simply *increases* the maximum and mean values of interparticle forces or forces between particles and external surfaces, since atomic forces depend on interatomic distances. Other than affecting the values of the interatomic forces, this process does not induce *additional* forces of any kind. The virial approach or virial theorem (Clausius 1870), as applied to gas systems in the evaluation of external pressure (not virial stress) strictly in the *statistical* average sense over many atoms, correctly captures this effect (an elaboration follows below). The key is that the pressure represents external forces between an atomic system and a container. In contrast, stress represents internal forces between particles inside a body. When individual atomic positions, particle velocities and atomic forces are *explicitly* considered, the atomic forces and the *indirect* effect of particle motion (velocity and position) on atomic forces must be distinguished. Specifically, a distinction must be made between internal interatomic forces (forces between atomic particles within a system) and external atomic forces (forces between particles in the system and agents external to the system). The internal forces give rise to the stresses and the external forces give rise to surface and body forces for the continuum permeating the spatial region occupied by the discrete atomic particle system. As an example, for a gas system that is in a statistically 'steady' motion (see, for example, Jeans 1967), the external forces manifest through the statistical pressure tensor

$$\begin{aligned} \boldsymbol{p} &= \frac{1}{3V}\left\langle \sum_i m_i|\dot{\boldsymbol{u}}_i|^2 - \frac{1}{2}\sum_i \sum_{j\,(\neq i)} \boldsymbol{r}_{ij}\cdot\boldsymbol{f}_{ij}\right\rangle \boldsymbol{I} \\ &= \frac{1}{V}\left\langle NkT - \frac{1}{6}\sum_i \sum_{j\,(\neq i)} \boldsymbol{r}_{ij}\cdot\boldsymbol{f}_{ij}\right\rangle \boldsymbol{I}, \end{aligned} \tag{4.9}$$

where N is the total number of particles in volume V, k is Boltzmann's constant, T is temperature, $\boldsymbol{I}$ is the identity tensor and $\langle\cdot\rangle$ denotes the average over a sufficient duration of time. Derived directly from the virial theorem, this relation contains both a kinetic-energy part and an internal-force part. The second term in the brackets is called the 'internal virial' of a system. Equation (4.9) correctly describes the *macroscopic* pressure of a gas system under three conditions.

(i) The system is in steady motion, i.e. the system is in statistical equilibrium and no pressure waves (disturbances) reverberate in the molecular system (mathematically, this is can be written as $\langle(\mathrm{d}^2/\mathrm{d}t^2)(\sum_i \boldsymbol{r}_i\cdot\boldsymbol{r}_i)\rangle = 0$ (see, for example, Jeans 1967).

(ii) The pressure is to be interpreted in a time-averaged, as well as volume-averaged, sense, i.e. fluctuations at the molecular level are assumed to average out over time and space.

(iii) The pressure $\boldsymbol{p}$ must be recognized as the average force per unit area on the wall of a physical container holding the gas system. It is also the amount of force applied on the atoms in the gas system by a unit area of the container wall. In other words, $\boldsymbol{p}$ is only defined as the average *external* force between the container and the atomic system.

It is under these conditions that the macroscopic average pressure is defined. The third condition is especially important, since atomic systems are intrinsically dynamic. The pressure $\boldsymbol{p}$, as defined in (4.9), is an effective measure for the structural interaction between the gas system and the external wall. This statistical measure is calculated through the combination of a kinetic-energy term and an internal-force term. Apparently, this combination of terms and the similarity of stress to pressure led Tsai (1979) and Rowlinson & Widom (1982), among others, to conclude that the atomic stress depends on mass transport as well as on interatomic forces. It is because of this analogy, and the fact that (4.9) is derived from the virial theorem, that $\bar{\boldsymbol{\Pi}}$ is called the virial stress. However, this analogy, and, more importantly, the resulting notion that stress must also consist of a kinetic-energy part and an internal-force (virial) part at the *atomic level* when an explicit and *time-resolved* account of atomic positions, velocities and interatomic forces is taken, turns out to be in violation of balance of momentum, as is shown in § 4 *a*. One of the causes for this flawed concept is that the definition of the virial stress at the individual atom level disregards the three fundamental conditions (specified above) under which (4.9) holds. These conditions do not hold at the atomic level with which the virial stress is applied in many contemporary papers. Even though the system as a whole may be in steady-state, the fully dynamic non-equilibrium conditions at the atomic level must be recognized. Under such dynamic conditions at the atomic level, the internal forces between material particles and the external forces from agents outside the atomic system are not in equilibrium and are not equal. They can even be varied independently of each other in an instantaneous sense (external forces can be 'turned on' instantly; however, it takes time to change interatomic distances and interatomic forces). Consequently, stress, as a measure for internal forces, cannot be conceptually equated with pressure which is a measure for external forces. It must also be pointed out that, for an atomic ensemble not in equilibrium, pressure is *only* defined at the interface between the system and a physically existing external surface. Without the physical interaction of atoms and an external wall, external pressure cannot be defined. In the interior of the system where a physical wall does not exist, the only quantity that can be defined is the stress tensor and it must be defined in accordance with balance of momentum and conservation of internal work rate. Detailed discussions on this topic are given in §§ 4 *a* and 5. Because of the intrinsic dynamic nature of the atomic system, the statistical average of the Cauchy stress (see (4.6) above) for a gas system (which is sometimes called the internal pressure)

$$\langle \boldsymbol{\sigma} \rangle = \frac{1}{6V} \left\langle \sum_i \sum_{j\,(\neq i)} \boldsymbol{r}_{ij} \cdot \boldsymbol{f}_{ij} \right\rangle \boldsymbol{I} \tag{4.10}$$

is not equal to $-\boldsymbol{p}$, as pointed out by Jeans (1967) and contrary to Newton's belief (Newton 1999). Equality $\langle\boldsymbol{\sigma}\rangle = -\boldsymbol{p}$ exists only when atomic level static equilibrium occurs, at absolute zero when all atomic motions cease.

Is it possible to view the virial stress in a statistical sense as a measure for mechanical interactions? To rephrase the question, if an average is taken both in space and time, does the virial stress converge to the Cauchy stress such that the kinetic-energy term averages out to zero? The question is a reasonable one, since, in many cases, atomic motions are local and oscillatory around their equilibrium positions. The answer, however, is negative. Since $-m_i\dot{\boldsymbol{u}}_i \otimes \dot{\boldsymbol{u}}_i = -m_i(-\dot{\boldsymbol{u}}_i) \otimes (-\dot{\boldsymbol{u}}_i)$, this tensor quantity always has three non-positive eigenvalues of $-m_i|\dot{\boldsymbol{u}}_i|^2$, 0 and 0; with the negative eigenvalue being associated with the directions of $\pm\dot{\boldsymbol{u}}_i$. Because of this reason, the time average

$$-\langle m_i\dot{\boldsymbol{u}}_i \otimes \dot{\boldsymbol{u}}_i\rangle = -\tfrac{1}{3}\langle m_i|\dot{\boldsymbol{u}}_i|^2\rangle\boldsymbol{I}$$

for an atom and the statistical average

$$-\frac{1}{V}\left\langle \sum_i m_i\dot{\boldsymbol{u}}_i \otimes \dot{\boldsymbol{u}}_i \right\rangle = -\frac{1}{3V}\left\langle \sum_i m_i|\dot{\boldsymbol{u}}_i|^2 \right\rangle\boldsymbol{I}$$

for the system will always have negative eigenvalues and, therefore, cannot be the null tensor, except at 0 K when all atomic motions stop. This demonstrates that the virial stress cannot be a valid measure for stress in the statistical sense either.

Having pointed out the conceptual errors in the generalization of the virial theorem for pressure to stress, we refocus our attention on the theoretical interpretation of the virial stress from the perspective of balance of momentum in § 4 *a*. Put together, these discussions clarify the exact meaning of the virial stress and have shown why it cannot be a measure for stress in any sense.

(*c*) *Version of virial stress involving fluctuation velocity*

Equation (1.1) is the most commonly used version of the virial stress. Once the true nature of (1.1) is understood, it becomes straightforward to explain the meaning of the version of the virial stress formula involving only the fluctuation part of the atomic velocities.

Perhaps, in an effort to avoid the erroneous interpretation related to the problem in figure 4 for fluid flows, Irving & Kirkwood (1950), Evans & Morriss (1990) and Todd *et al.* (1995) stated that the stress is (Evans & Morriss (1990) and Todd *et al.* (1995) called $-\boldsymbol{\Pi}$ the pressure tensor)

$$\boldsymbol{\Pi} = \sum_i \left[-m_i(\dot{\boldsymbol{u}}_i - \dot{\tilde{\boldsymbol{u}}}) \otimes (\dot{\boldsymbol{u}}_i - \dot{\tilde{\boldsymbol{u}}})\delta(\boldsymbol{r} - \boldsymbol{r}_i) + \frac{1}{2}\sum_{j\,(\neq i)} \boldsymbol{r}_{ij} \otimes \boldsymbol{O}_{ij}\boldsymbol{f}_{ij} \right], \tag{4.11}$$

where $\dot{\tilde{\boldsymbol{u}}}$ is called the 'streaming velocity', whose choice is not clearly defined (although it can be chosen to be $\dot{\boldsymbol{u}}_0$ in figure 4), and

$$\begin{aligned} \boldsymbol{O}_{ij}\boldsymbol{f}_{ij} &= [\delta(\boldsymbol{r} - \boldsymbol{r}_i) - \delta(\boldsymbol{r} - \boldsymbol{r}_j)]\boldsymbol{f}_{ij} \\ &= \boldsymbol{f}_{ij} - \frac{1}{2!}\boldsymbol{r}_{ij} \cdot \frac{\partial}{\partial \boldsymbol{r}}\boldsymbol{f}_{ij} + \cdots + \frac{1}{n!}\left(-\boldsymbol{r}_{ij} \cdot \frac{\partial}{\partial \boldsymbol{r}}\right)^{n-1}\boldsymbol{f}_{ij} + \cdots . \end{aligned} \tag{4.12}$$

For a reference frame fixed in space, this expression has neither physical meaning nor geometrical meaning. It violates the balance of momentum due to two mathematical errors in its derivation (Irving & Kirkwood 1950, pp. 822–828; Evans & Morriss 1990, pp. 67, 68). Each error alone or the combination of both renders (4.11) meaningless. The first error relates to the first term in (4.11). Specifically, the authors neglected the term

$$-\frac{\partial}{\partial \boldsymbol{r}} \cdot \sum_i m_i(\dot{\boldsymbol{u}}_i \otimes \dot{\bar{\boldsymbol{u}}} + \dot{\bar{\boldsymbol{u}}} \otimes \dot{\boldsymbol{u}}_i)\delta(\boldsymbol{r} - \boldsymbol{r}_i)$$

in their texts (Irving & Kirkwood 1950, eqn (5.7); Evans & Morriss 1990, eqn (3.116)). This term is not zero (even if a time average is taken) in general and cannot be and should not have been dropped from their derivations. If this error is corrected, the first term in (4.11) will be the same as that in (1.1).

> Although it is not at all suggested in these references, we can regard their analyses as being carried out relative to a frame moving at velocity $\dot{\bar{\boldsymbol{u}}}$. In such a scenario, the first term in (4.11) would represent momentum flow due to atomic motion relative to this moving frame. This would assign the velocity fluctuation term a geometric meaning, not a meaning for a contribution to stress. More discussions on this aspect are given in association with figures 5, 10 and 11.

The second error concerns the second term, which is incorrect since it is not equal to the second term in (1.7). This is due to an improper treatment of the delta functions involved. The particular serial expansion is unnecessary and is not mathematically defined. However, this aspect is of no consequence to the topic of this paper.

In another attempt to obtain consistency in situations similar to that in the example in figure 4, Yasui *et al.* (1999) and Nakane *et al.* (2000) stated that

$$\bar{\boldsymbol{\Pi}} = \frac{1}{\Omega}\sum_i \left[-m_i(\dot{\boldsymbol{u}}_i - \dot{\bar{\boldsymbol{u}}}) \otimes (\dot{\boldsymbol{u}}_i - \dot{\bar{\boldsymbol{u}}}) + \frac{1}{2}\sum_{j\,(\neq i)} (\boldsymbol{r}_{ij} \otimes \boldsymbol{f}_{ij})\right], \tag{4.13}$$

where only the fluctuation part $(\dot{\boldsymbol{u}}_i - \dot{\bar{\boldsymbol{u}}})$ of the total velocity $\dot{\boldsymbol{u}}_i$ is used. Just like (1.1), this expression does not measure mechanical stress in any sense. It has a geometric meaning as noted below. The derivation of this relation as a mechanical stress measure is flawed and incorrect because it involves a mixed use of the spatial balance of momentum (2.5) and the material balance of momentum (2.3). The error is subtle but significant. It falls into the third type of the three types of errors outlined in § 1 of this paper. Specifically, note that *eqns (14)–(22) in Yasui et al. (1999)* are based on a *spatial* analysis of balance of momentum. To state it differently, the integration in (14) in their paper is over fixed spatial volume v and fixed spatial surface a (in the notation used by Yasui *et al.*). As a result, *eqn (18) in that paper* is *spatial* in nature (the same as (2.5) in this paper, *except that (18) in Yasui et al. is written for a reference frame moving at velocity* $\dot{\bar{\boldsymbol{u}}}$). In contrast, *eqn (23) in that paper* is *material* in nature (the same as (2.3) in this paper) *because the authors insisted that the stress in that equation is the Cauchy stress.* The authors obtained their result by equating the spatial equation of balance of momentum to the material equation of balance of momentum. This is unjustifiable and incorrect. If the authors correct this oversight and compare *their (18)* with the spatial equation of balance of momentum

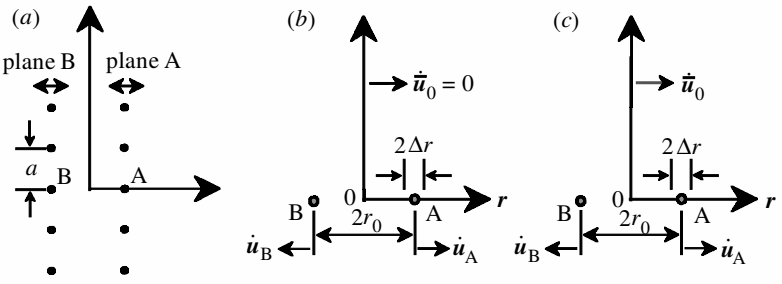

Figure 5. Oscillatory motion of a two-atom system.

(equation (2.5) in this paper) *written in a reference frame that travels with the local streaming velocity* $\dot{\bar{\boldsymbol{u}}}$, it is then clear that (4.13) defines a quantity that measures the momentum change relative to a reference frame that *travels with the local streaming velocity* $\dot{\bar{\boldsymbol{u}}}$. This is purely a geometric interpretation. It is not surprising, since (1.1) defines a measure for momentum change in space relative to a frame that is fixed in space. Another way to look at their result is to note the difference and the relationship between the Cauchy stress and the 'virial stress' as given in (4.7); their result will be the same as (4.6) in this paper as far as the Cauchy stress is concerned, directly confirming the conclusion of the current paper.

To illustrate the meaning of (4.13), we consider the harmonic oscillation of a system consisting of two planes of atoms, as shown in figure 5*a*. Assume that the motions of all atoms in each plane are identical and synchronous. It is sufficient to analyse the simplified two-atom system as shown in figure 5*b* whose centre of mass O is stationary and the two-atom system in figure 5*c* whose centre of mass O has velocity $\dot{\bar{\boldsymbol{u}}}_0$. In both parts (*a*) and (*b*) of figure 5, $\dot{\boldsymbol{u}}_\mathrm{A}$ and $\dot{\boldsymbol{u}}_\mathrm{B}$ denote the *fluctuation velocities of atom A and atom B relative to the centre of mass O*, respectively. We stipulate that the oscillation is symmetric, so that $\dot{\boldsymbol{u}}_\mathrm{A} = -\dot{\boldsymbol{u}}_\mathrm{B}$. Here, for simplicity, without loss of generality, we assume that lattice constants a (in the y direction, figure 5*a*) and b (in the z direction, not shown) are both greater than the cut-off radius of the interatomic potential. Therefore, the only non-zero interatomic force between particle A and particle B is $\mathrm{d}U/\mathrm{d}r$, with U being the potential function (energy) for each atom. Equation (4.6) indicates that the Cauchy stresses in parts (*b*) and (*c*) of figure 5 are equal. That is, in both cases,

$$\bar{\sigma}_{11} = \frac{1}{ab}\frac{\mathrm{d}U}{\mathrm{d}r}. \tag{4.14}$$

However, an interpretation using (4.13) shows the virial stress to be

$$\bar{\Pi}_{11} = \frac{1}{abr}\left(-m|\dot{\boldsymbol{u}}_\mathrm{A}|^2 + r\frac{\mathrm{d}U}{\mathrm{d}r}\right) = \frac{1}{abr}\left(-m|\dot{\boldsymbol{u}}_\mathrm{B}|^2 + r\frac{\mathrm{d}U}{\mathrm{d}r}\right), \tag{4.15}$$

for both parts (*b*) and (*c*) of figure 5. This is clearly not the stress in the system. First, it is not equal to the correct stress interpretation in (4.14). It is important to point out that the kinetic-energy term in (4.15) will never average out to zero in time or in space, since it is never positive. Note that an integration of (4.14) over one cycle of motion yields

$$\int_t^{t+t_0} \bar{\sigma}_{11}\,\mathrm{d}t = \frac{1}{ab}\int_t^{t+t_0}\frac{\mathrm{d}U}{\mathrm{d}r}\,\mathrm{d}t = \frac{1}{ab}\int_t^{t+t_0} m\ddot{\boldsymbol{u}}_\mathrm{A}\,\mathrm{d}t = \frac{1}{ab}m(\dot{\boldsymbol{u}}_\mathrm{A})|_t^{t+t_0} = 0, \tag{4.16}$$

where t_0 is the time period for the cyclic oscillation. This is expected, since the oscillation is harmonic and no external forces exist. In contrast, an integration of (4.15) shows that

$$\int_t^{t+t_0} \bar{\Pi}_{11}\,\mathrm{d}t = -\frac{1}{ab}\int_t^{t+t_0} \frac{1}{r} m|\dot{\boldsymbol{u}}_{\mathrm{A}}|^2\,\mathrm{d}t < 0. \tag{4.17}$$

This observation shows that the expression in (4.13) represents neither the instantaneous stress in the time-resolved (dynamic) sense nor the average stress in the statistical sense.

The fact that (4.15) does not define mechanical stress can also be shown through a consideration of stress work rate and work conjugacy. Note that the rate-of-deformation tensor is

$$\boldsymbol{D} = \begin{pmatrix} \dot{r}/r & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{4.18}$$

giving a strain rate of $D_{11} = \dot{r}/r$. The stress work for deformation between positions $2r_1$ and $2r_2$ (assume that $2r_1$ is the separation between the particles at an arbitrary time t_1) is

$$2\int_{t_1}^{t_2} \bar{\sigma}_{11} D_{11}\,\mathrm{d}t = \frac{2}{ab}\int_{t_1}^{t_2} r\frac{\mathrm{d}U}{\mathrm{d}r}\frac{\dot{r}}{r}\,\mathrm{d}t = \frac{2}{ab}\int_{r_1}^{r_2}\frac{\mathrm{d}U}{\mathrm{d}r}\,\mathrm{d}r = \frac{2}{ab}U(r)|_{r_1}^{r_2}. \tag{4.19}$$

This is equal to the internal work done by the interatomic force. Apparently, the stress work over one cycle of motion is 0. This is, again, fully expected and correct. The vibration of the system in figure 5 is a process of interchange of kinetic and potential energy. The process is fully conservative and no potential (or kinetic) energy is gained or lost in one cycle of deformation. In the continuum sense, the elastic deformation and stress must preserve the conservative nature of the process. The work done by stress over one cyclic of strain must be zero, as is the case in (4.19). Indeed,

$$\bar{\sigma}_{11} D_{11} = \dot{r}\left(\frac{1}{ab}\frac{\mathrm{d}U}{\mathrm{d}r}\right)$$

represents (velocity) $\times$ (force per unit area) for the system and is the mechanical work rate of the internal force. However, this is not the case for $\bar{\Pi}_{11}$ in (4.15), since

$$\bar{\Pi}_{11} D_{11} = -\frac{1}{ab}\frac{\dot{r}}{r} m|\ddot{\boldsymbol{u}}_{\mathrm{A}}|^2$$

has no meaning whatsoever. Furthermore, $\bar{\Pi}_{11}$ is not work conjugate to any other measure of strain or strain rate. Specifically,

$$2\int_{t_1}^{t_2} \bar{\Pi}_{11} D_{11}\,\mathrm{d}t = -\frac{2}{ab}\int_{t_1}^{t_2} \frac{\dot{r}}{r} m|\dot{\boldsymbol{u}}_{\mathrm{A}}|^2\,\mathrm{d}t \neq \frac{2}{ab}U(r)|_{r_1}^{r_2} \tag{4.20}$$

shows that $\bar{\boldsymbol{\Pi}}$ cannot not be a valid measure for mechanical stress, since it does not possess work conjugacy required for a valid measure of stress. The fact that, by coincidence,

$$2\int_t^{t+t_0} \bar{\Pi}_{11} D_{11}\,\mathrm{d}t = -\frac{2}{ab}\int_t^{t+t_0} \frac{\dot{r}}{r} m|\dot{\boldsymbol{u}}_{\mathrm{A}}|^2\,\mathrm{d}t = 0$$

does not assign any physical significance to $\bar{\Pi}_{11}$!

On a separate but related note, the virial expression in (1.1) yields

$$\bar{\Pi}_{11} = \frac{1}{abr}\left(-m|\dot{\boldsymbol{u}}_{\mathrm{A}} + \dot{\bar{\boldsymbol{u}}}_0|^2 - m|-\dot{\boldsymbol{u}}_{\mathrm{A}} + \dot{\bar{\boldsymbol{u}}}_0|^2 + r\frac{\mathrm{d}U}{\mathrm{d}r}\right) \tag{4.21}$$

for figure 5*c*. We note that the quantities in (4.15) and (4.21) have separate geometric meanings, as shown earlier in this section. The quantity in (4.15) measures the rate of change of momentum flow as seen by an observer travelling with the centre of mass O of the system at velocity $\dot{\bar{\boldsymbol{u}}}_0$. The quantity in (4.21) measures the rate of change of momentum flow as seen by an observer that remains fixed in space at all times. These quantities are not stress, do not measure force and are not work conjugate to the rate of deformation (or any other measure of strain rate) as discussed above.

After seeing the incorrect predications for stress given by (1.1) and (4.13) in the preceding paragraphs and after pointing out the misconceptions in the references already cited, we note that a formula similar to (4.13) was given by Hardy (1982). The derivation there is also spatial in nature. Also, in (4.1) of Hardy (1982), a frame moving with local velocity $\dot{\bar{\boldsymbol{u}}}(\boldsymbol{r}, t)$ is used. The tensor quantity he obtained is clearly a measure of momentum change relative to that coordinate system, and, consequently, the same as that in (4.13). It is not a measure for mechanical stress in any sense.

The geometric meaning of (4.13) and its irrelevance to mechanical stress are further illustrated by the examples in figure 10 of § 6 and figure 11 of § 7. Note that there is no system level average velocity due to symmetry in those examples, and therefore $\dot{\bar{\boldsymbol{u}}} = 0$. The result is the same regardless of whether one uses (1.1) or (4.13). These expressions yield a 'stress tensor' that increases with coordinates x and y in figure 10. This is apparently not consistent with the fact that the deformation is uniform throughout and strain and therefore *stress must be uniform*.

5. Work conjugacy and EC

It is worthwhile to point out that the singular Cauchy stress and average Cauchy stress in (4.5) and (4.6) have not been associated with a work-conjugate continuum deformation field *in general* (for arbitrary conditions of deformation) to allow the internal and external mechanical work rates of the system to be evaluated. To overcome the lack of work conjugacy, to provide a systematic approach toward the continuum analysis of discrete molecular systems and to further demonstrate the irrelevance of the mass-transfer terms in (1.1) and (1.7) to stress evaluation, we introduce the concept of the EC for dynamically deforming atomic particle systems. This framework of analysis is based on a systematic delineation of the internal and external atomic forces. The objective is not only to evaluate work-conjugate continuum stress and deformation fields, but also to specify all other work- and momentum-preserving kinetic quantities (external traction and external body force) and mass distribution for the EC. The continuum is equivalent to its corresponding discrete atomic particle system in that, at all times, it preserves the linear and angular momenta of the particle system, it conserves the internal and external mechanical work rates and it has an equal amount of kinetic energy and contains the same amount of mass as the particle system. The momentum and work equivalence is achieved by virtue of the principle of virtual work for fully dynamic conditions. This equivalence should hold for the entire system and for volume elements defined by any subset of particles in the system, therefore averaging and characterization across different length-scales

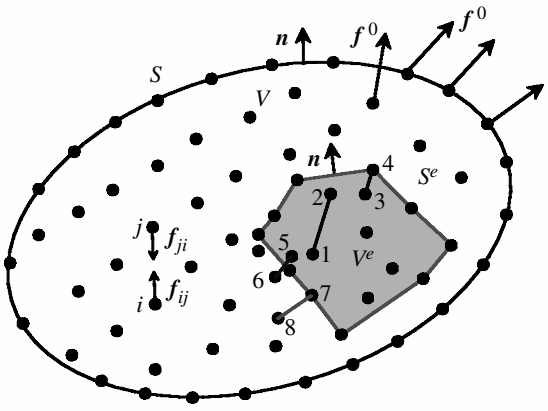

Figure 6. Particle system and EC.

are possible and size-scale effects can be explicitly analysed. The discussion below concerns central-force atomic particle systems. A more general discussion in the context of micropolar systems with both interatomic forces and interatomic moments is given in Zhou & McDowell (2002).

It is important to point out that, usually in higher-scale continuum theories, kinetic energy is only associated with the 'macroscopic' deformation or motion that can be explicitly resolved at the size- and time-scales of an analysis. The part of the atomic motion at high frequencies that cannot be resolved at a certain practical level is considered heat or thermal energy and is accounted for phenomenologically. Ultimately, in the context of multiscale modelling and characterization of material behaviour 'from the ground up' (from ab initial, first principle, MD to micro, meso and macroscopic continuum models), the thermal part and the structural dynamic part of the atomic kinetic energy must be delineated as one approaches higher length-scales. The EC theory developed here is a nanoscale mechanical theory. Just like in the MD model, the EC represents, the kinetic energy of the EC developed here includes both the 'thermal' part and the 'structural' dynamic part. In this sense, the EC is a fully faithful continuum form representation of the MD model. By faithful here, we mean time-resolved explicit equivalence in all work rates, kinetic energy, mass and deformation fields. Just like MD models explicitly track the absolute particle motion and the total kinetic energy, the EC model here does the same by explicitly following the motion of the particles in a fully time-resolved manner. The EC development can be, and, perhaps, should be, regarded as the 'continuumization' of discrete models, which offers a high degree of fidelity to the discrete description. Following this initial step, further development could involve scaling in time and space. One important element of that process should be the delineation of thermal energy in the form of atomic vibrations and kinetic energy associated with structural deformation. This partitioning is inherently scale dependent and should be the topic of future research.

(*a*) *Continuum-particle system equivalence*

Consider a dynamically deforming system of N particles that occupies space V and has an envelope of surface S as illustrated in figure 6. At time t, particle i has position $\boldsymbol{r}_i$, displacement $\boldsymbol{u}_i$ and velocity $\dot{\boldsymbol{r}}_i = \dot{\boldsymbol{u}}_i$. The force on particle i due to

atoms or agents that are *external* to the system under consideration is $\boldsymbol{f}_i^0$. The total force on i is

$$\boldsymbol{f}_i = \sum_j \boldsymbol{f}_{ij} + \boldsymbol{f}_i^0 = \boldsymbol{f}_i^{\mathrm{int}} + \boldsymbol{f}_0^{\mathrm{ext}}. \tag{5.1}$$

Here, the summation is over those particles inside the system of N particles that interact directly with particle i. It is worthwhile to point out that due to non-local interactions external force can exist for particles both in the interior of V and on the surface S. Note that the concepts of internal and external forces are specific to the particular sub-volume V^e of V considered. So, in general, $\boldsymbol{f}_0^{\mathrm{int}} \neq \sum_j \boldsymbol{f}_{ij}$ and $\boldsymbol{f}_0^{\mathrm{ext}} \neq \boldsymbol{f}_0^0$, except for $V^e = V$. For example, for the volume element V^e illustrated in figure 6, the forces between atoms 1 and 2 ($\boldsymbol{f}_{12}$, $\boldsymbol{f}_{21}$), as well as those between atoms 3 and 4 ($\boldsymbol{f}_{34}$, $\boldsymbol{f}_{43}$), are internal; while the forces between atoms 5 and 6 ($\boldsymbol{f}_{56}$, $\boldsymbol{f}_{65}$) and those between atoms 7 and 8 ($\boldsymbol{f}_{78}$, $\boldsymbol{f}_{87}$) are external. Note that all of these forces are internal when the system is considered as a whole.

The continuum equivalent to the particle ensemble has volume V and surface S. A material point in the continuum initially at $\boldsymbol{x}_0$ has position $\boldsymbol{x}$ (or $\boldsymbol{r}$) in the current configuration, so that the displacement and velocity functions are, respectively, $\boldsymbol{u} = \boldsymbol{x} - \boldsymbol{x}_0$ and $\dot{\boldsymbol{x}} = \dot{\boldsymbol{u}}$. The stress tensor $\boldsymbol{\sigma}$ is related to the surface traction $\boldsymbol{t}$ through $\boldsymbol{t} = \boldsymbol{n} \cdot \boldsymbol{\sigma}$, where $\boldsymbol{n}$ is the outward unit normal to any internal surface S^e or surface envelope of the body S. Body forces can result from non-local effects of atoms or agents external to the system under consideration. Let $\boldsymbol{b}$ denote the densities of the continuum body forces in V. In the following analyses, all kinetic and kinematic quantities are evaluated on the current deformed configuration. Also, the continuum has mass density $\rho(\boldsymbol{x})$ in the current configuration. The continuum we seek to occupy V should be dynamically equivalent to the particle system. This requires that, at all times, (i) the stress field over the continuum defined by a discrete particle ensemble has the same work rate as the *internal* interatomic force field, (ii) the body-force and surface-traction fields produce the same external work rate as that of the external interatomic force fields, and (iii) the kinetic energy of the continuum be the same as that of the discrete atomic ensemble. The first requirement ensures that the contribution of the continuum stress field to the motion and deformation of continuum (or the particle system) is the same as that of the original inter-particle force field. The second requirement ensures that the continuum external force field provides the same input to the motion and deformation of the continuum (or the particle system) as the discrete particle forces due to external atoms and agents. The third requirement ensures that the contributions of material inertia to motion and deformation are the same for the EC and the particle system. These separate requirements for the internal and external work rates and kinetic energy can be satisfied through the dynamic principle of virtual work, allowing definition of work-preserving fields of continuum stress ($\boldsymbol{\sigma}$), work-preserving continuum surface traction and body force ($\boldsymbol{t}$ and $\boldsymbol{b}$) and continuum mass density $\rho(\boldsymbol{x})$.

For the entire ensemble with N particles, the above requirements can be written in terms of the dynamic principle of virtual work, i.e.

$$\begin{aligned} -\int_V \boldsymbol{\sigma} : \delta \boldsymbol{D}\, \mathrm{d}V + \int_V \boldsymbol{b} \cdot \delta \dot{\boldsymbol{u}}\, \mathrm{d}V + \int_S \boldsymbol{t} \cdot \delta \dot{\boldsymbol{u}}\, \mathrm{d}S \\ = \sum_{i=1}^N \boldsymbol{f}_i \cdot \delta \dot{\boldsymbol{u}}_i = \int_V \rho \ddot{\boldsymbol{u}} \cdot \delta \dot{\boldsymbol{u}}\, \mathrm{d}V = \sum_{i=1}^N m_i \ddot{\boldsymbol{u}}_i \cdot \delta \dot{\boldsymbol{u}}_i, \end{aligned} \tag{5.2}$$

where the symbol δ in $\delta\boldsymbol{D}$, $\delta\dot{\boldsymbol{u}}$ and $\delta\dot{\boldsymbol{r}}_i$ denotes any kinematically admissible functional representations of the corresponding quantities. Superimposed double dots represent second-order material time derivative, i.e. $\ddot{\boldsymbol{u}} = \mathrm{d}^2\boldsymbol{u}/\mathrm{d}t^2$; $\boldsymbol{D}$ is the symmetric continuum rate of deformation and $\boldsymbol{\sigma} : \delta\boldsymbol{D} = \sigma_{\alpha\beta}\delta D_{\beta\alpha}$ ($\alpha, \beta = 1, 2, 3$, summation over repeated indices α and β is implied).

Note that balance of momentum must be satisfied by a system as a whole and by any portion of the system. Internal and external forces are fundamentally different. If two systems are to be equivalent and balance of momentum is to be satisfied at any size scale, their internal-force work rate, external-force work rate and inertial work rate must be equivalent.

To develop a scalable representation of the EC, consider a sub-volume element $V^e \subset V$ with closed surface S^e associated with a subset of M (less than or equal to N) particles in the ensemble. Assume that M_S out of the M particles ($M_S \leqslant M$) are on surface S^e, therefore defining it. The remaining $M - M_S$ particles are in the interior of V^e and are considered as internal particles for V^e. To define the momentum- and work-conserving stress $\boldsymbol{\sigma}^{(e)}$, surface traction $\boldsymbol{t}^{(e)}$, body force $\boldsymbol{b}^{(e)}$ and mass density $\rho^{(e)}(\boldsymbol{x})$ over V^e, the variational principle of is applied to this portion of the system, yielding

$$
\begin{aligned}
&-\int_{V^e} \boldsymbol{\sigma}^{(e)} : \delta\boldsymbol{D}^{(e)}\,\mathrm{d}V + \int_{V^e} \boldsymbol{b}^{(e)} \cdot \delta\dot{\boldsymbol{u}}^{(e)}\,\mathrm{d}V + \int_{S^e} \boldsymbol{t}^{(e)} \cdot \delta\dot{\boldsymbol{u}}^{(e)}\,\mathrm{d}S \\
&\qquad = \sum_{I=1}^{M} \boldsymbol{f}_I^{\mathrm{int}} \cdot \delta\dot{\boldsymbol{u}}_I + \sum_{I=1}^{M} \boldsymbol{f}_I^{\mathrm{ext}} \cdot \delta\dot{\boldsymbol{u}}_I = \int_{V^e} \rho^{(e)}\ddot{\boldsymbol{u}}^{(e)} \cdot \delta\dot{\boldsymbol{u}}^{(e)}\,\mathrm{d}V = \sum_{I=1}^{M} \varsigma_I m_I \ddot{\boldsymbol{r}}_I \cdot \delta\dot{\boldsymbol{u}}_I.
\end{aligned}
\tag{5.3}
$$

Here, a capital subscript 'I' denotes particle index *internal* to the volume element V^e ($1 \leqslant I \leqslant M$). Each atom inside V^e is given two indices, one is the local index I ($1 \leqslant I \leqslant M$) and the other is its global index i ($1 \leqslant i \leqslant N$), as the atom is also part of the complete system V. Since a unique correspondence between I and its global counterpart i can be established, we use them interchangeably here for convenience of discussion. Under this notation, '$j \neq I$' and '$j = I$' should be interpreted, respectively, as '$j \neq i$' and '$j = i$'. For example, '$j = I$' should be read as 'the particle with global index j and the particle with local index I (and therefore global index i) are the same particle'.

This notation is used here to delineate the total force $\boldsymbol{f}_I^{\mathrm{int}}$ on atom I in V^e exerted by other atoms *also inside* V^e (either in the interior of V^e or on surface S^e) and the force $\boldsymbol{f}_I^{\mathrm{ext}}$ exerted by atoms or agents *outside* V^e. A distinction must be made between these internal and external interactions. Note that the total force on I is $\boldsymbol{f}_I = \boldsymbol{f}_I^{\mathrm{int}} + \boldsymbol{f}_I^{\mathrm{ext}}$, and

$$
\boldsymbol{f}_I^{\mathrm{int}} = \sum_{J \neq I}^{M} \eta_{IJ}\boldsymbol{f}_{IJ}, \qquad \boldsymbol{f}_I^{\mathrm{ext}} = \sum_{j\,(J \neq 1,2,\ldots M)}^{N} \boldsymbol{f}_{Ij} + \boldsymbol{f}_I^0. \tag{5.4}
$$

Here, η_{IJ} is the fraction of the atomic bond that is spatially within element V^e. It pertains to the bond between atoms I and J that are both inside V^e. In general, when atoms are randomly distributed (as in amorphous materials), η_{IJ} is determined by the dihedral angle of the element as a fraction of the sum of such angles

(less than or equal to 360°) of all elements associated with the particular bond. Specifically, $\eta^e_{IJ} = \phi^e_{IJ} / \sum_e^k \phi^e_{IJ}$, with ϕ^e_{IJ} being the dihedral angle in element (e) associated with the bond between atoms I and J, and k being the number of elements connected to the bond. Consider, for example, the BCC lattice in figure 7. The bond between atoms 1 and 3 is shared by four tetrahedral cells (each of the four tetrahedral cells is considered a volume element V^e with $M = 4$). Therefore, for the tetrahedral element defined by atoms 1, 2, 3 and 4 (and for each of the other three cells) $\eta = 90°/360° = 0.25$ for this bond. For bonds on surface S^e (both atoms of the bond are on S^e), the sum of such angles is less than 360°. ς_I in (5.3) is the fraction of atom I that is attributed to element V^e. For example, atom 1 in figure 7 is shared by 24 tetrahedral elements, therefore, $\varsigma = \frac{1}{24}$ for each element. For periodic and amorphous structures alike, ς can be defined through $\varsigma^e_I = \varphi^e / \sum_e^k \varphi^e$, with φ^e being the solid angle (three dimensions) or angle (two dimensions) subtended by an element and k being the number of elements connected to an atom.

The continuum quantities $\boldsymbol{\sigma}^{(e)}$, $\boldsymbol{t}^{(e)}$, $\boldsymbol{b}^{(e)}$, $\dot{\boldsymbol{u}}^{(e)}$, $\boldsymbol{D}^{(e)}$ and $\rho^{(e)}$ in (5.3) are associated with element V^e. The use of $V^e < V$ has two clear benefits. One is that it allows size effects to be analysed. The other is that the analysis with a smaller V^e is more computationally efficient, and simpler shape functions can be used.

With the above notation, the requirements that the virtual work rates of internal, external and inertial forces are equal can then be written as

$$\left.\begin{aligned} -\int_{V^e} \boldsymbol{\sigma}^{(e)} : \delta \boldsymbol{D}^{(e)} \,\mathrm{d}V &= \sum_{I=1}^{M} \boldsymbol{f}_I^{\mathrm{int}} \cdot \delta \dot{\boldsymbol{u}}_I, \\ \int_{S^e} \boldsymbol{t}^{(e)} \cdot \delta \dot{\boldsymbol{u}}^{(e)} \,\mathrm{d}S &= \sum_{I=1}^{M_S} (1-\kappa_I) \boldsymbol{f}_I^{\mathrm{ext}} \cdot \delta \dot{\boldsymbol{u}}_I, \\ \int_{V^e} \boldsymbol{b}^{(e)} \cdot \delta \dot{\boldsymbol{u}}^{(e)} \,\mathrm{d}V &= \sum_{I=1}^{M} \kappa_I \boldsymbol{f}_I^{\mathrm{ext}} \cdot \delta \dot{\boldsymbol{u}}_I, \\ \int_{V^e} \rho^{(e)} \ddot{\boldsymbol{u}}^{(e)} \cdot \delta \dot{\boldsymbol{u}}^{(e)} \,\mathrm{d}V &= \sum_{I=1}^{M} \varsigma_I m_I \ddot{\boldsymbol{u}}_I \cdot \delta \dot{\boldsymbol{u}}_I. \end{aligned}\right\} \tag{5.5}$$

The breakup of (5.3) into the above component equations or the requirement of strict term-to-term satisfaction of (5.3) fully reflects the dynamics of the system. It ensures the satisfaction of balance of momentum and full dynamic equivalence between the EC and the particle system at any size scale. The associations of internal forces to internal stress only and external forces to body force and surface traction only are strictly required by balance of momentum and conservation of energy. Otherwise, if one allows internal forces to generate external traction and/or body forces, a system (or part of a system) would accelerate and gain momentum and energy *by the effect of its internal forces alone*. This would violate balance of momentum and balance of energy. Similarly, if a part of the external forces is used to generate internal stress but not external traction (or body force), part of the momentum and work from the external forces would vanish, again causing violation of balance of momentum and balance of energy.

The first relation pertains to stress. The second relation concerns the surface traction. The corresponding summation is over only the M_s particles on surface S^e.

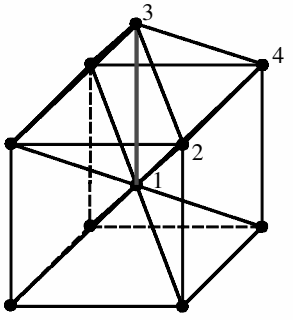

Figure 7. Atomic bonds shared by neighbouring cells.

The third relation concerns the body force due to external forces. External forces on atoms *in the interior* of V^e contribute only to the body-force density $\boldsymbol{b}^{(e)}$, and therefore factor κ_I is always taken as unity ($\kappa_I = 1$) for atoms in the interior of V^e. The external forces exerted on atoms on surface S^e are considered to contribute solely to surface traction $\boldsymbol{t}^{(e)}$, and therefore $\kappa_I = 0$ for atoms on S^e. This partition is somewhat arbitrary and, indeed, any choice $0 \leqslant \kappa_I \leqslant 1$ for surface atoms (along with $\kappa_I = 1$ for interior atoms) will allow external work rate to be preserved. However, the choice of $\kappa_I = 0$ for surface atoms (along with $\kappa_I = 1$ for interior atoms) has the clear advantage of yielding zero body-force density as non-local external forces become zero. This outcome is consistent with local continuum theories.

The above delineation of external forces and moments is related to non-local interatomic interactions and is important for the definition of $\boldsymbol{\sigma}^{(e)}$, $\boldsymbol{b}^{(e)}$ and $\boldsymbol{t}^{(e)}$. It allows the length-scale dependence of nanoscale atomic behaviour due to non-local interatomic interactions to be quantified as the size of V^e (and therefore the number of atoms M contained) is increased or decreased.

(*b*) *Stress field*

We first focus the discussion on internal work rate and the first equation of (5.5) for stress. To evaluate the continuum version of the virtual work, an interpolation for the virtual velocity of atoms in V^e is needed. Many possible methods for the interpolation are available. One uses the shape functions of finite elements, i.e.

$$\delta\dot{\boldsymbol{u}}^{(e)}(\boldsymbol{x}) = \sum_{I=1}^{M} N_I(\boldsymbol{x})\delta\dot{\boldsymbol{u}}_I, \tag{5.6}$$

where $N_I(\boldsymbol{x})$ are the shape functions and should be interpreted as $N_I^{(e)}(\boldsymbol{x})$. The superscript '$(e)$' is omitted for brevity. Details regarding these shape functions can be found in finite-element method texts. The corresponding virtual velocity gradient is

$$\frac{\partial\delta\dot{\boldsymbol{u}}^{(e)}}{\partial\boldsymbol{x}} = \sum_{I=1}^{M} \delta\dot{\boldsymbol{u}}_I \otimes \frac{\partial N_I}{\partial\boldsymbol{x}} = \sum_{I=1}^{M} \delta\dot{\boldsymbol{u}}_I \otimes \boldsymbol{B}_I. \tag{5.7}$$

Here, $\boldsymbol{B}_I = \partial N_I(\boldsymbol{x})/\partial \boldsymbol{x}$ are gradients of the shape functions and $\otimes$ denotes the tensor product of two vectors. The virtual rate of deformation is

$$\delta \boldsymbol{D}^{(e)} = \frac{1}{2}\left[\frac{\partial \delta \dot{\boldsymbol{u}}^{(e)}}{\partial \boldsymbol{x}} + \left(\frac{\partial \delta \dot{\boldsymbol{u}}^{(e)}}{\partial \boldsymbol{x}}\right)^{\mathrm{T}}\right] = \frac{1}{2}\sum_{I=1}^{M}(\delta \dot{\boldsymbol{u}}_I \otimes \boldsymbol{B}_I + \boldsymbol{B}_I \otimes \delta \dot{\boldsymbol{u}}_I). \tag{5.8}$$

The virtual work of the stress tensor with respect to the virtual rate of deformation is given by

$$\int_{V^e} \boldsymbol{\sigma}^{(e)} : \delta \boldsymbol{D}^{(e)}\, \mathrm{d}V = \int_{V^e} \boldsymbol{\sigma}^{(e)} : \sum_{I=1}^{M}(\boldsymbol{B}_I \otimes \delta \dot{\boldsymbol{u}}_I)\, \mathrm{d}V = \sum_{I=1}^{M}\int_{V^e} (\boldsymbol{\sigma}^{(e)} \cdot \boldsymbol{B}_I) \cdot \delta \dot{\boldsymbol{u}}_I\, \mathrm{d}V. \tag{5.9}$$

Since $\delta \dot{\boldsymbol{u}}_I$ are completely arbitrary and independent degrees of freedom, $(5.5)_1$ and (5.9) lead to

$$\int_{V^e} \boldsymbol{\sigma}^{(e)} \cdot \boldsymbol{B}_I\, \mathrm{d}V = -\boldsymbol{f}_I^{\mathrm{int}}. \tag{5.10}$$

Since $\boldsymbol{f}_I^{\mathrm{int}}$ are internal forces, Newton's third law implies that

$$\sum_{I=1}^{M} \boldsymbol{f}_I^{\mathrm{int}} = 0 \quad \text{and} \quad \sum_{I=1}^{M} \boldsymbol{r}_I \times \boldsymbol{f}_I^{\mathrm{int}} = 0. \tag{5.11}$$

Note that one of the basic requirements for shape functions is $\sum_{I=1}^{M} N_I = 1$, and therefore $\sum_{I=1}^{M} \boldsymbol{B}_I = \boldsymbol{0}$. In general, for an element V^e with M atoms, equation (5.10) yields $3M - 6$ independent equations. Since the number of independent components in $\boldsymbol{\sigma}^{(e)}$ is six, the problem of finding a *constant spatially non-varying average* $\boldsymbol{\sigma}^{(e)}$ is overspecified for any choice of M greater than four. Consequently, it is impossible to find a *constant spatially non-varying average* work-equivalent stress over the volume associated with an arbitrary subset of the particle ensemble. It important to point out that this is *not* to say that work-conjugate stress field cannot be found on an arbitrary size scale in general. Of course, properly formulated *spatially varying* $\boldsymbol{\sigma}^{(e)}$ can always be found for an element at any scale. More discussions on this follow in the next paragraph. Because of this reason, the average stress in (4.6) cannot be, in general, associated with a work-conjugate deformation field. Although it may be desirable to do so, such a task is not possible because of the disparate number of degrees of freedom (DoF) for the discrete particle subset and the fixed dimensional order of the stress tensor. Parity in the DoF and the order of the stress tensor occurs (six equations and six unknown stress components) only for the simplest three-dimensional cell, the tetrahedron which is associated with four particles. In two dimensions, triangles associated with three atoms are the only possible choice (three equations and three independent unknown stress components). This particular level of continuum characterization is very useful because it fully recognizes the effects of heterogeneities and steep gradients at the scale of individual atoms. This process of establishing dynamical equivalence between the continuum and MD formulations, although performed at interatomic scales, is also very important because it yields the lowest-scale continuum fields that may be subsequently subjected to various treatments of continuum averaging, including those of statistical mechanics.

It is important to point out that for $M > 4$ in three dimensions and $M > 3$ in two dimensions, equation (5.10) requires, in general, spatially varying stress fields

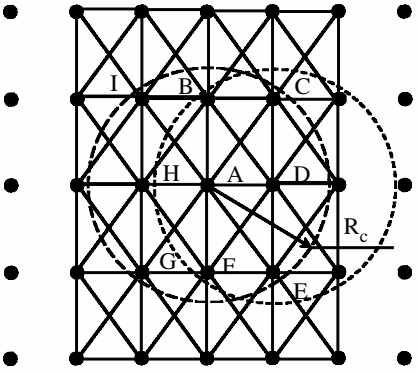

Figure 8. Superposition of stress subfields in overlapping elements.

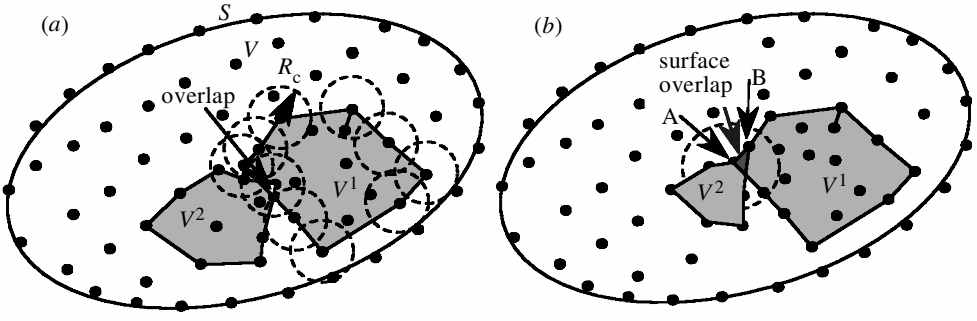

Figure 9. Size scale of element overlapping. (*a*) Volume overlap. (*b*) Surface overlap.

with proper choice of integration points in V^e for the relevant numbers of unknowns. Although somewhat more computationally involved, such a pursuit would be quite useful and important since it permits scaling and allows size effects to be quantified through the variation of the size of V^e.

Different volume elements V^e chosen for stress calculation occupy different spatial regions. In general, due to multiple and non-local atomic interactions, these elements partly overlap. A two-dimensional illustration of this issue is given in figures 8 and 9. In figure 8, assume the cut-off radius for the material is R_c. For atom A, interactions with eight other atoms must be considered. Specifically, forces on A due to atoms B, C and D give rise to elements ABC and ACD among other elements (note that only a portion of the forces may be considered in each triangle, as indicated in (5.4)). For atom D, a similar cut-off circle must be drawn and triangles DAB and DBC must be analysed among others. Since these four elements partly overlap and do not coincide, the superposition of the stress subfields varies for each spatial location in V. This issue necessitates proper superposition of these elemental quantities to obtain the total fields for $\boldsymbol{\sigma}$, $\boldsymbol{t}$, $\boldsymbol{b}$, $\dot{\boldsymbol{u}}$, $\boldsymbol{D}$ and ρ, since the summation for the virtual work in (5.2) must be performed over all interatomic bonds ($i = 1, 2, \ldots, N$) on the discrete side and over all elements on the continuum side to ensure equality of virtual work. To state it simply, the need for superposition of elemental fields to obtain system-level fields is due to a combination of two factors. The first factor is that overlap of elements occurs because of the non-local nature of atomic interactions. The second factor is the requirement that, at the system level, the continuum fields yield the

same momentum, work rates and mass as the discrete fields. The elemental stress $\boldsymbol{\sigma}^{(e)}(\boldsymbol{x})$ contributions at a position $\boldsymbol{x}$ combine to give rise to $\boldsymbol{\sigma}(\boldsymbol{x})$ as

$$\boldsymbol{\sigma}(\boldsymbol{x}) = \sum_e \boldsymbol{\sigma}^{(e)}(\boldsymbol{x}), \tag{5.12}$$

where the superposition is carried out for each $\boldsymbol{x}$ with all elements that contain that point.

The rate-of-deformation work-conjugate to the stress field in (5.12) is

$$D_{\beta\alpha} = \frac{\sum_e \sigma^{(e)}_{\alpha\beta} D^{(e)}_{\beta\alpha}}{\sum_e \sigma^{(e)}_{\alpha\beta}}, \tag{5.13}$$

where summation is *not* implied over repeated indices α and β. Note, however, that in the limit in which $V^e = V$, there is only one element and $\boldsymbol{\sigma}^{(e)}(\boldsymbol{x}) = \boldsymbol{\sigma}(\boldsymbol{x})$ and $(\partial \dot{\boldsymbol{u}}/\partial \boldsymbol{x})^{(e)} = \partial \dot{\boldsymbol{u}}/\partial \boldsymbol{x}$; therefore no superposition is needed.

The detection of overlap is primarily a computational issue. It could be quite complicated, in terms of a systematic algorithm. The easiest way to approach this issue is to (a) formulate all elements in a computational implementation and calculate all elemental fields, (b) construct a uniform spatial grid that is fine enough for the problem at hand, and (c) calculate the stress at each point by checking how many elements actually contain that location and therefore contributing stress to it.

(*c*) *Traction and body force*

An illustration of surface overlap is given in figure 9*b*. To obtain the traction over the surface area S^e of V^e, consider a surface element $\Delta S \subset S^e$ defined by L particles. The virtual velocity over ΔS is

$$\delta \dot{\boldsymbol{u}}^{(e)}(\boldsymbol{x}) = \sum_{I=1}^{L} N_I(\boldsymbol{x}) \delta \dot{\boldsymbol{u}}_I. \tag{5.14}$$

Substitution into the second equation of (5.5) yields

$$\sum_{I=1}^{L} \int_{\Delta S} N_I(\boldsymbol{x}) t^{(e)}(\boldsymbol{x})\, \mathrm{d}S \cdot \delta \dot{\boldsymbol{u}}_I = \sum_{I=1}^{L} \xi_I (1-\kappa_I) \boldsymbol{f}^{\mathrm{ext}}_I \cdot \delta \dot{\boldsymbol{u}}_I, \tag{5.15}$$

where ξ_I is the fraction of $(1-\kappa_I)\boldsymbol{f}^{\mathrm{ext}}_I$ that can be attributed to ΔS, since ΔS may be only a portion of S^e and particle I may be on the boundary of ΔS (shared by the rest of S^e). ξ_I can be defined through $\xi^i_I = (\Delta S)^i_I / \sum_i^k (\Delta S)^i_I$, with k being the number of surface areas connected to atom I. Again, the arbitrariness of $\delta \dot{\boldsymbol{u}}_I$ requires that

$$\int_{\Delta S} N_I(\boldsymbol{x}) \boldsymbol{t}^{(e)}(\boldsymbol{x})\, \mathrm{d}S = \xi_I (1-\kappa_I) \boldsymbol{f}^{\mathrm{ext}}_I, \tag{5.16}$$

with $I = 1, 2, \ldots, L$. The solution to the above is

$$\boldsymbol{t}^{(e)}(\boldsymbol{x}) = \sum_{J=1}^{L} N_J(\boldsymbol{x}) \boldsymbol{\lambda}_J, \tag{5.17}$$

where $\boldsymbol{\lambda}_J$ are vector solutions of the linear system of equations in the form

$$\sum_{J=1}^{L} c_{IJ}\boldsymbol{\lambda}_J = \xi_I(1-\kappa_I)\boldsymbol{f}_I^{\text{ext}}. \tag{5.18}$$

In the above equations, $c_{IJ} = \int_{\Delta S} N_I(\boldsymbol{x})N_J(\boldsymbol{x})\,\mathrm{d}S$, with $I, J = 1, 2, \ldots, L$. The simplest case is that of triangular surface areas with $L = 3$.

If ΔS resides on the surfaces of two or more elements, the total traction is

$$\boldsymbol{t}(\boldsymbol{x}) = \sum_e \boldsymbol{t}^{(e)}. \tag{5.19}$$

The equations for the body-force density $\boldsymbol{b}$ resulting from the third equation in (5.5) are

$$\boldsymbol{b}^{(e)}(\boldsymbol{x}) = \sum_{J=1}^{M} N_J(\boldsymbol{x})\boldsymbol{\nu}_J, \tag{5.20}$$

where $\boldsymbol{\nu}_J$ are the vector solutions of the linear system of equations in the form of

$$\sum_{J=1}^{M} d_{IJ}\boldsymbol{\nu}_J = \kappa_I \boldsymbol{f}_I^{\text{ext}}. \tag{5.21}$$

In the above relations, $d_{IJ} = \int_{V^e} N_I(\boldsymbol{x})N_J(\boldsymbol{x})\,\mathrm{d}V$, with $I, J = 1, 2, \ldots, M$, $\kappa_I = 1$ for atoms in the interior of V^e and $\kappa_I = 0$ for particles on the surface S^e of V^e.

The elemental body-force contributions obtained above combine to yield the total body-force density as

$$\boldsymbol{b}(\boldsymbol{x}) = \sum_e \boldsymbol{b}^{(e)}(\boldsymbol{x}). \tag{5.22}$$

The velocity field work-conjugate to this is

$$\dot{u}_\alpha = \frac{\sum_e b_\alpha^{(e)}\dot{u}_\alpha^{(e)}}{\sum_e b_\alpha^{(e)}}, \tag{5.23}$$

where summation is *not* implied over repeated index α. It must be pointed out that if no body force exists, the total velocity is simply the average of the elemental velocities involved. This will allow the null work rate of the null body-force field to be preserved.

(*d*) *Mass distribution*

The equality of the continuum virtual work and atomic virtual work associated with inertia forces in the last equation of (5.5) specifies the distribution of mass of the EC. We can express these elemental densities in terms of the shape functions as

$$\rho^{(e)}(\boldsymbol{x}) = \sum_{K=1}^{M} N_K(\boldsymbol{x})g_K, \tag{5.24}$$

where g_K $(K = 1, 2, \ldots, M)$ are solutions of

$$\sum_{K=1}^{M} g_K\boldsymbol{\chi}_{IK} = \varsigma_I m_I\ddot{\boldsymbol{u}}_I, \tag{5.25}$$

with

$$\boldsymbol{\chi}_{IK} = \int_{V^e} N_I(\boldsymbol{x}) N_K(\boldsymbol{x}) \ddot{\boldsymbol{u}}^e \, \mathrm{d}V \quad \text{and} \quad \ddot{\boldsymbol{u}}^e = \sum_{I=1}^{M} N_I(\boldsymbol{x}) \ddot{\boldsymbol{u}}_I.$$

Note that the requirement of conservation of mass must be satisfied by (5.24) and (5.25). The solution for (5.24) must be carefully constructed.

Accounting for contributions from overlapping elements at a location $\boldsymbol{x}$, the total mass density is

$$\rho(\boldsymbol{x}) = \sum_e \rho^{(e)}(\boldsymbol{x}). \tag{5.26}$$

The acceleration field that is work conjugate to this mass distribution and the velocity field in (5.23) is

$$\ddot{u}_\alpha = \frac{\sum_e \rho^{(e)} \ddot{u}_\alpha^{(e)} \dot{u}_\alpha^{(e)}}{\dot{u}_\alpha(\boldsymbol{x}) \rho(\boldsymbol{x})}, \tag{5.27}$$

where summation is *not* implied over repeated index α.

We note that, in general, for areas where overlap of elements occurs, the deformation field quantities from (5.13), (5.23) and (5.27) do not satisfy $\boldsymbol{D} = \operatorname{sym} \partial \dot{\boldsymbol{u}} / \partial \boldsymbol{x}$, even though at the element level $\boldsymbol{D}^{(e)} = \operatorname{sym} \partial \dot{\boldsymbol{u}}^{(e)} / \partial \boldsymbol{x}$ is indeed satisfied. This situation results from the weighted averaging used to maintain the work conjugacy of the stress, body force and surface traction. The lack of full consistency with the continuum differential requirement occurs only on the size scale of the cut-off radius of the material. Such overlap affects only the boundary region of V^e inside S^e that has a thickness smaller than or equal to R_c (see figure 9 for the size of overlapping zone between elements V^1 and V^2). Locations in the interior of V^e that have distances from S^e greater than R_c are not affected by the overlap. As the size of V^e is increased, the effect of this lack of differential smoothness decreases. Full consistency is achieved in the limit of $V^e = V$. Full consistency is also maintained when elemental stresses $\boldsymbol{\sigma}^{(e)}$ and body-force densities $\boldsymbol{b}^{(e)}$ are the same in overlapping elements. It is worthwhile to point out that the use of such superimposed deformation quantities can also be avoided completely by always placing the locations of interest fully in the non-overlapping interior of an element. It will be shown in § 5 *e* that the benefit of this weighted averaging is that the conservation of internal and external work rates, conservation of linear and angular momenta and conservation of mass are achieved between the EC and the discrete particle system.

(*e*) *Work conjugacy and balance of momenta*

To demonstrate the global equivalence of work rates, we replace $\delta \dot{\boldsymbol{u}}$ in (5.2) and (5.5) by the actual velocity $\dot{\boldsymbol{u}}$. These equations then become, respectively,

$$\begin{aligned} -\int_V \boldsymbol{\sigma} : \boldsymbol{D} \, \mathrm{d}V + \int_V \boldsymbol{b} \cdot \dot{\boldsymbol{u}} \, \mathrm{d}V + \int_S \boldsymbol{t} \cdot \dot{\boldsymbol{u}} \, \mathrm{d}S \\ = \sum_{i=1}^{N} \boldsymbol{f}_i \cdot \dot{\boldsymbol{u}}_i = \int_V \rho \ddot{\boldsymbol{u}} \cdot \dot{\boldsymbol{u}} \, \mathrm{d}V = \sum_{i=1}^{N} m_i \ddot{\boldsymbol{u}}_i \cdot \dot{\boldsymbol{u}}_i, \end{aligned} \tag{5.28}$$

$$-\int_V \boldsymbol{\sigma} : \boldsymbol{D} \, \mathrm{d}V = \sum_{i=1}^{N} \boldsymbol{f}_i^{\mathrm{int}} \cdot \dot{\boldsymbol{u}}_i \tag{5.29}$$

and

$$\int_V \boldsymbol{b}\cdot\dot{\boldsymbol{u}}\,\mathrm{d}V + \int_S \boldsymbol{t}\cdot\dot{\boldsymbol{u}}\,\mathrm{d}S = \sum_{i=1}^{N} \boldsymbol{f}_i^{\mathrm{ext}}\cdot\dot{\boldsymbol{u}}_i. \tag{5.30}$$

These relations show that the EC indeed has the same internal, external and inertial work rates as the discrete particle system.

The EC also has the same global linear and angular momenta as the original particle system. It can be shown that (5.19), (5.22) and (5.26) satisfy

$$\left.\begin{aligned} \int_S \boldsymbol{t}\,\mathrm{d}S + \int_V \boldsymbol{b}\,\mathrm{d}V &= \sum_{i=1}^{N} \boldsymbol{f}_i^{\mathrm{ext}} = \sum_{i=1}^{N} \boldsymbol{f}_i = \int_V \rho\ddot{\boldsymbol{u}}\,\mathrm{d}V = \sum_{i=1}^{N} m_i\ddot{\boldsymbol{u}}_i, \\ \int_S \boldsymbol{r}\times\boldsymbol{t}\,\mathrm{d}S + \int_V \boldsymbol{r}\times\boldsymbol{b}\,\mathrm{d}V &= \sum_{i=1}^{N} \boldsymbol{r}_i\times\boldsymbol{f}_i^{\mathrm{ext}} = \sum_{i=1}^{N} \boldsymbol{r}_i\times\boldsymbol{f}_i \\ &= \int_V \rho\boldsymbol{r}\times\ddot{\boldsymbol{u}}\,\mathrm{d}V = \sum_{i=1}^{N} m_i\boldsymbol{r}_i\times\ddot{\boldsymbol{u}}_i. \end{aligned}\right\} \tag{5.31}$$

Therefore, using the dynamic principle of virtual work, we have defined an EC that is dynamically consistent with atomic ensembles in MD idealizations. The consistency is in the conservation of internal work rate, external work rate and work rate due to inertial forces. The fields of work-conserving stress, surface traction, body-force density and mass density are determined along with a work-conjugate deformation field. The continuum-particle assembly work equality and momentum equivalency ensures that the continuum interpretation of the discrete force field maintains the physical effects of the particle system at all times. It is important to point out that the continuum fields defined here reflect an interpretation of the particle force and deformation over the entire spatial region and surface occupied by the particle system. The advantage is that regular continuum averaging, scaling and interpretation are fully allowed. Furthermore, the equivalence of work rates, kinetic energy, linear momentum and angular momentum holds for any finite volume element V^e, as well as for the entire system. The formulation, algorithm and results allow a consistent transition from the MD framework to the continuum framework. The length-scale effects due to non-local interatomic interactions can be accounted for in this framework of analysis. Since full fields of all fundamental kinetic and kinematic quantities are given, scaling and averaging can be carried out.

6. Example: uniform tension of a rectangular lattice

In order to illustrate the work conjugacy of the Cauchy stress in (4.6) and (5.10) and to further illustrate the irrelevance of mass transfer to stress, we consider the uniform tension under external forces $\boldsymbol{f}_x^0$ and $\boldsymbol{f}_y^0$ of a lattice in figure 10. Because of symmetry, only the first quadrant of the system is shown. The initial lattice constants are a_0 and b_0. The deformed lattice has dimensions a and b in the horizontal and vertical directions, respectively. The material is homogeneous and the mass of each atom is m. For simplicity, assume the cut-off radius R_{c} is such that $a < R_{\mathrm{c}} < 2a$ and $b < R_{\mathrm{c}} < 2b$, and therefore non-local interactions do not occur. The calculation for

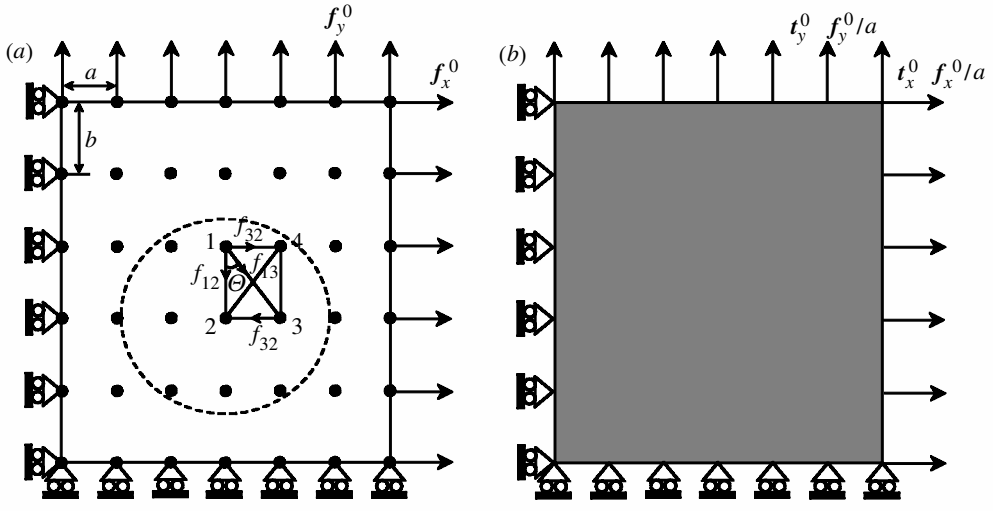

Figure 10. Uniform tension of a two-dimensional lattice and continuum equivalent.

Table 1. *EC stress and deformation fields for a lattice in uniform tension*

element	stress and rate-of-deformation fields
1-2-3	$\boldsymbol{\sigma}^{(e)} = \begin{pmatrix} (\frac{1}{2}f_{32} + f_{13}\sin\Theta)/b & -f_{13}\sin\Theta/a \\ -f_{13}\sin\Theta/a & (\frac{1}{2}f_{12} + f_{13}\cos\Theta)/a \end{pmatrix}$, $\boldsymbol{D}^{(e)} = \begin{pmatrix} \dot{a}/a & 0 \\ 0 & \dot{b}/b \end{pmatrix}$
1-3-4	$\boldsymbol{\sigma}^{(e)} = \begin{pmatrix} (\frac{1}{2}f_{32} + f_{13}\sin\Theta)/b & -f_{13}\sin\Theta/a \\ -f_{13}\sin\Theta/a & (\frac{1}{2}f_{12} + f_{13}\cos\Theta)/a \end{pmatrix}$, $\boldsymbol{D}^{(e)} = \begin{pmatrix} \dot{a}/a & 0 \\ 0 & \dot{b}/b \end{pmatrix}$
1-2-4	$\boldsymbol{\sigma}^{(e)} = \begin{pmatrix} (\frac{1}{2}f_{32} + f_{13}\sin\Theta)/b & -f_{13}\sin\Theta/a \\ -f_{13}\sin\Theta/a & (\frac{1}{2}f_{12} + f_{13}\cos\Theta)/a \end{pmatrix}$, $\boldsymbol{D}^{(e)} = \begin{pmatrix} \dot{a}/a & 0 \\ 0 & \dot{b}/b \end{pmatrix}$
2-3-4	$\boldsymbol{\sigma}^{(e)} = \begin{pmatrix} (\frac{1}{2}f_{32} + f_{13}\sin\Theta)/b & -f_{13}\sin\Theta/a \\ -f_{13}\sin\Theta/a & (\frac{1}{2}f_{12} + f_{13}\cos\Theta)/a \end{pmatrix}$, $\boldsymbol{D}^{(e)} = \begin{pmatrix} \dot{a}/a & 0 \\ 0 & \dot{b}/b \end{pmatrix}$
overall	$\boldsymbol{\sigma} = \begin{pmatrix} (f_{32} + 2f_{13}\sin\Theta)/b & 0 \\ 0 & (f_{12} + 2f_{13}\cos\Theta)/a \end{pmatrix}$, $\boldsymbol{D} = \begin{pmatrix} \dot{a}/a & 0 \\ 0 & \dot{b}/b \end{pmatrix}$
	stress work rate $\boldsymbol{\sigma} : \boldsymbol{D} = (1/ab)(f_{32}\dot{a} + f_{12}\dot{b} + 2f_{13}\dot{r})$

the EC here uses two-dimensional linear shape functions. Results of the continuum interpretation of the interatomic potential solutions are listed in table 1. The problem considered is dynamic; therefore, the interatomic forces can vary with time (i.e. $f_{12} = f_{12}(a(t), b(t))$, $f_{13} = f_{13}(a(t), b(t))$ and $f_{32} = f_{32}(a(t), b(t))$) while they are uniform in space due to the fact that the deformation is uniform. At the upper boundary, $\boldsymbol{t} = \boldsymbol{f}_y^0/a$, consistent with the continuum solution of traction at the boundary and the continuum expectation of uniform stress in the horizontal direction. Similarly, at the right-hand boundary $\boldsymbol{t} = \boldsymbol{f}_x^0/b$. The rate of deformation and stress work rate in table 1 are also in complete agreement with continuum mechanics expectations.

The displacement and velocity fields for the system are, respectively,

$$\boldsymbol{u}_i(\boldsymbol{x}, t) = l_x^i(a - a_0)\boldsymbol{e}_x + l_y^i(b - b_0)\boldsymbol{e}_y \quad \text{and} \quad \dot{\boldsymbol{u}}_i(\boldsymbol{x}, t) = l_x^i\dot{a}\boldsymbol{e}_x + l_y^i\dot{b}\boldsymbol{e}_y. \tag{6.1}$$

In (6.1), $l_x^i = 0, 1, 2 \ldots, N_x$ and $l_y^i = 0, 1, 2 \ldots, N_y$ denote the column and row

numbers, respectively, of i in the lattice; N_x and N_y are the total number of columns and total number of rows, respectively, and $\boldsymbol{e}_x$ and $\boldsymbol{e}_y$ are unit base vectors in the x and y directions, respectively. Under this deformation, the first term in (1.1) has the form

$$-\frac{1}{\Omega}m_i\dot{\boldsymbol{u}}_i\otimes\dot{\boldsymbol{u}}_i=-\frac{1}{\Omega}m_i\begin{pmatrix}l_x^il_x^i\dot{a}\dot{a} & l_x^il_y^i\dot{a}\dot{b}\\ l_x^il_y^i\dot{a}\dot{b} & l_y^il_y^i\dot{b}\dot{b}\end{pmatrix}. \tag{6.2}$$

This quantity varies with the positions of the atoms in the array, leading to a virial stress tensor that increases in the x direction as well as in the y direction. This is not in accord with the uniform strain and uniform rate of deformation in the forms of

$$\boldsymbol{\varepsilon}=\begin{pmatrix}(a-a_0)/a_0 & 0\\ 0 & (b-b_0)/b_0\end{pmatrix}\quad\text{and}\quad\boldsymbol{D}=\begin{pmatrix}\dot{a}/a & 0\\ 0 & \dot{b}/b\end{pmatrix}. \tag{6.3}$$

This apparent contradiction to the deformation and loading reality is, again, a manifestation of the irrelevance of $\boldsymbol{\Pi}$ and $\bar{\boldsymbol{\Pi}}$ to the concept of continuum stress and their lack of physical significance theoretically shown in §§ 2 and 4.

The calculation of the Cauchy stress in (5.10) does not involve ad hoc specification of a relevant volume. The evaluation of the stress in (4.6) for any set of atoms requires the identification of a proper Ω whose extent is not always obvious. Under conditions of arbitrary and inhomogeneous deformations, the identification of Ω is ambiguous and somewhat uncertain. In the example of figure 10, the overall deformation is homogeneous across different unit cells and periodicity of the lattice is maintained. In addition, locality of interatomic forces is assumed through the choice of the relatively small cut-off radius. Therefore, Ω can be taken as the volume of the unit cell, i.e. $\Omega=ab$. Under this condition, the mechanical stress in (4.6) (or the mechanical part (second term) of the virial stress in (1.1)) for the problem in figure 10*a* is

$$\frac{1}{2\Omega}\sum_{j\,(\neq i)}\boldsymbol{r}_{ij}\otimes\boldsymbol{f}_{ij}=\begin{pmatrix}(f_{32}+2f_{13}\sin\Theta)/b & 0\\ 0 & (f_{12}+2f_{13}\cos\Theta)/a\end{pmatrix}. \tag{6.4}$$

This coincides with the Cauchy stress $\boldsymbol{\sigma}$ in table 1. This agreement occurs because of the simple geometry of the problem, the uniformity of loading and the absence of non-local interactions. A proper perspective is in order here. The stresses in (4.6) and (5.10) are different representations of the Cauchy stress. The stress field in (5.10) has a work-conjugate deformation field (equations (5.6) and (5.13)) and always makes the same work contribution to deformation as the interparticle force system over any finite volume element. The stress in (4.6) does not have a work-conjugate deformation field identified for it. Indeed, it is defined without regard to any possible work-conjugate deformation field. However, under the conditions of uniform deformation, equations (4.6) and (5.10) yield identical results that have work conjugacy with respect to the deformation field.

An account of stress work rate and work equivalence between the EC and the atomic system in figure 10 can provide further insight here. First, note that, since deformation and stress are uniform, analysis of stress work rate for a unit cell is representative for the whole specimen. Specifically, the results in table 1 yield that

$$\int_V\boldsymbol{\sigma}:\boldsymbol{D}\,\mathrm{d}V=N_{\mathrm{c}}(f_{32}\dot{a}+f_{12}\dot{b}+2f_{13}\dot{r})=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1\,(\neq i)}^{N}\boldsymbol{f}_{ij}\cdot\dot{\boldsymbol{r}}_{ij}=\sum_{i=1}^{N}\boldsymbol{f}_i^{\mathrm{int}}\cdot\dot{\boldsymbol{u}}_i, \tag{6.5}$$

where $N_c = N_x N_y$ is the total number of unit cells in the specimen in figure 10, N is the total number of atoms in the system as before, $f_{32}\dot{a} + f_{12}\dot{b} + 2f_{13}\dot{r}$ is the work rate of interatomic forces in a rectangular unit cell and $r = \sqrt{a^2 + b^2}$. This equation shows that the EC stress field in table 1 indeed has the same internal work rate as the atomic force system in figure 10 and (5.29) is satisfied.

It is important to point out that the virial stress $\bar{\boldsymbol{\Pi}}$ in (1.1) for the problem in figure 10 combines contributions from both (6.2) and (6.4). It cannot and does not satisfy the work conjugacy requirement in (6.5). In fact, $\bar{\boldsymbol{\Pi}} : \boldsymbol{D}$ and $\int_V \bar{\boldsymbol{\Pi}} : \boldsymbol{D}\, \mathrm{d}V$ have no meaning whatsoever. This example provides another direct illustration of the fact that the virial stress is not a measure of stress. It does not measure mechanical force. It cannot yield stress work.

7. Discussion and conclusions

The analyses in this paper have reiterated and reaffirmed the interpretation of the virial stress as a measure for momentum change in space, confirming the understanding in the literature. With regard to the mechanical stress tensor at the scale of individual atoms or small sets of atoms, it has been shown that the kinetic-energy term in the virial stress leads to violation of balance of momentum and loss of physical significance as a measure for mechanical interaction between material points. This conclusion points out that the 'virial stress' is not the Cauchy stress or any other form of mechanical stress. For the simple conditions of rigid-system translation, uniform tension and harmonic atomic oscillations, the virial stress has been shown to yield apparently erroneous interpretations of the loading conditions. Although the kinetic-energy term is usually small compared with the interatomic force term for solids, it may be the dominant term for gases. This term is neither related to internal interactions between particles in a system nor related to forces between particles and agents external to the system (such as an external wall) in general. Therefore, this term is irrelevant to the concept of stress. This conclusion holds true both at the individual atom level and at the system level in the dynamic time-resolved sense. It also holds at the system level in the time- and space-averaged statistical sense, in general. The virial stress in the form of (1.1), *averaged over time and over the whole system for a system within a rigid non-deforming container*, may be related to the statistical average of the external forces between the system and the container. Even for this extremely narrow interpretation, the formula does not provide a measure for stress in any sense, since, for intrinsically dynamic systems (temperature above 0 K), internal forces (stress) and external forces are not equal. The virial stress as defined in (1.1) and (1.7) has the geometric interpretation of being a measure for the momentum change in a fixed spatial region. This interpretation does not assign any physical significance to the virial stress as a possible measure of mechanical interaction. The preceding discussions focused on the analytical error and the conceptual flaw in the historic derivations of the virial stress that essentially resolve around the improper use of the equation for spatial balance of momentum. The results demonstrate that the interatomic force term of the virial stress alone constitutes a valid stress measure and can be identified with the Cauchy stress.

It must noted here that some authors have argued that only the fluctuation part of the atomic velocity (rather than the total absolute velocity) should be used in

the virial formula (1.1). This version of the virial stress (4.13) has been put forth by Irving & Kirkwood (1950), Hardy (1982), Yasui *et al.* (1999) and Nakane *et al.* (2000), among others. It has been shown that this version does not represent a measure for mechanical stress either. Instead, it measures momentum flow in space relative to a moving frame, as opposed to a fixed frame for (1.1).

By definition, stress is the mechanical force between material mass points in a continuum per unit area. A review of the definition in figure 1 (see also, for example, Malvern 1969, fig. 3.2, p. 69) makes this clear. First, we make a cut through a point in a body. This is a material cut which moves with the material point under consideration. Note that the definition is for all conditions, fully dynamic as well as static. It is not necessary to know what the velocity at the point of interest is. This is because, by definition, the cut always follows the mass point. The force between the two sides (or between the mass points on the two sides of the material cut) per unit area gives the internal traction or Cauchy stress components. It is obvious in this definition that stress has nothing to do with velocity. Another way to look at this issue is through balance of momentum. Note the material description of balance of momentum in figure 3. By definition, S^e is the *deforming surface* of the fixed amount of mass Δm, and therefore there is no mass convection through S^e. The Cauchy stress tensor gives the traction (force) on S^e through $\boldsymbol{t} = \boldsymbol{n} \cdot \boldsymbol{\sigma}$. This definition clearly states that stress has nothing to do with mass convection. In other words, stress is a measure of the effect of pure force on momentum change associated with a fixed amount of mass (not change in momentum contained in a spatial region). In contrast, the 'virial stress' is defined using a spatial cut which is fixed in space. This definition is very clearly reflected in many papers. Specifically, the 'virial stress' components are the components of the momentum vector passing through a unit area of a fixed spatial plane in a unit amount of time (see example in figure 4 and (3.2) for an illustration). This definition is very similar to the definition of Cauchy stress using the material description of balance of momentum. Apparently, momentum change in space is not just due to force alone. Momentum can transfer in space purely by the force-free kinetic motion of mass. This definition of the 'virial stress' is very clear in figure 3 and (2.4), (2.5) and (4.1). In summary, the term 'virial stress' is, in a way, a misnomer. It does not measure stress. It is very much a stress-like quantity in that (i) it has the unit of force/area, and (ii) it satisfies the spatial equation of balance of momentum in a way similar to the Cauchy stress satisfying the material equation of balance of momentum. Apparently, it is these aspects that may have been the source of confusion in the literature. Does the 'virial stress' somehow measure a force per unit area between a flowing mass system and a pure non-physical spatial plane? The answer is no. This is exactly one of the misconceptions some hold (see, for example, Cheung & Yip 1991), as is pointed out and discussed in § 4 *b*. Mechanical force cannot and does not exist between mass and space. Force is the mechanical interaction between mass points. If one still insists that force can be applied on a pure spatial plane and a pure spatial plane can apply a force on mass, one would be forced to conclude, according to Newton's third law, that the free-flowing system in figure 4 would 'experience' a resistance to its motion due to pure space and slow down as a consequence. We know this is totally false. The virial stress is not the Cauchy stress or some other 'mysterious' form of mechanical stress.

This conclusion demonstrates that, for gas systems in macroscopic steady-state, the statistical average of the Cauchy stress tensor $\langle \boldsymbol{\sigma} \rangle$ over time and space is an

isotropic tensor and is not equal to the negative of the macroscopic pressure tensor $(-\boldsymbol{p})$ for the system. This is contrary to Newton's belief given in *Principia* and is a reflection of the fundamental difference between an intrinsically dynamic system in steady-state and a system in static equilibrium. The isotropic statistical average of the internal stress tensor $\langle\boldsymbol{\sigma}\rangle$ is equal to the negative of external (macroscopic) pressure tensor only at absolute zero when all molecular motions cease.

In order to see why and how this confusion about stress and pressure can occur, let us use the phrase 'external stress' to denote the average *external* force per unit area for a material system (gases, solids and fluids). This external stress (traction) is applied on the atomic system by, for example, the wall of a container in contact with the atomic system. For intrinsically dynamic systems (temperature above absolute zero), this external stress (or traction) is not equal to the *internal stress* (often called stress) in the body. This is the key. If one uses Newton's second law, one can show that the external stress (pressure) and the internal stress (stress) differ and are not equal. This paper has shown that the stress (internal) has nothing to do with velocity and the virial formula for this stress concept is incorrect.

For solids, the external and internal stress tensors are fully populated and are not diagonal. The internal stress is what causes solids to, for example, fracture. We are not very interested in the *external stress* for solids, since it does not measure the internal material interaction and is inconsequential as far as deformation and fracture are concerned (externally applied stress 'causes' fracture to occur *only by inducing 'internal stress' between mass points*).

For gases (and fluids), on the other hand, we, most of the time, are interested in the *external stress* (often called pressure because it is an isotropic tensor). The reason is gases do not fracture; gas deformation does not cause irreversible internal material structure changes such as fracture from a macroscopic perspective. In this sense, internal stress is relatively 'inconsequential' for gases and fluids. Instead, it is the pressure effect of gases on the external surroundings that we are more often concerned with. Therefore, although we do not often explicit say it, the term 'gas pressure' implies the meaning of external pressure. This pressure, *when defined as* a measure for *external* force interactions between particles, indeed has a velocity term. *Its precise meaning is that the external pressure is the sum of the internal pressure (stress) and a kinetic-energy term. Note that the three strict conditions under which the gas pressure formula (4.9) can be used must be explicitly understood and cannot be neglected.* One must realize that stress (internal) and pressure (when defined as external force per unit area) are *fundamentally different and not equal.* They are related through the kinetic-energy (velocity) term in (4.9). Most of the time, we do not need to use (4.10) for gases. This fact and *the confusion that stress and pressure are equal or the same* for gases lead people to think stress in gases depends on velocity. This misconception also has led many to think stress for solids has to do with velocity (or kinetic energy).

Since a very significant of amount of research has been conducted using (1.1), it is essential to quantify the relative magnitudes of the two terms in these equations. In general, the kinetic-energy term is dominant for gases (the error is 100% for ideal gases, since, by definition, they do not have interatomic force interactions). For fluids, the kinetic-energy term is large. Therefore, extreme care must be taken in such cases when *stress* or *internal pressure* is calculated using (1.1). Significant errors may exist *if the calculated result is interpreted as a measure for the force interaction*

between material points inside a system. This interpretation does not always happen since the internal interaction in gases and fluids are not always the quantity causing consequences in cases involving fluids and gases. Instead, the calculated pressure is often *correctly* interpreted as a measure for the force (structural) interaction between the system and an external wall. For solids, the situation is different. It is generally believed and expected that the kinetic-energy term is small compared with the interatomic force term. However, detailed molecular dynamics calculations conducted for copper nanowires by Liang & Zhou (2003) show that the numerical error can be very significant when (1.1) is used instead of (4.6). Specifically, under conditions of tensile deformations at an initial temperature of 300 K and strain rates between 10^7 and 10^9 s^{-1}, the ratio between the magnitudes for the components of the two terms in (1.1) in the loading direction (kinetic-energy component divided by the force component) can be up to or more than 100%. Since these calculations are carried out using symmetric velocity loading conditions, there is no system-level translation. The ratio is indeed very small (up to 4–5%) for deformation up to the yield point. However, after the onset of plastic deformation, the kinetic-energy term can be as high as 35% of the interatomic force term. Under conditions of thermal vibrations without external loading (residual stress after specimen fractures, for example), the velocity term can be equal to or even higher than the interatomic force term. Note that stresses are not equal to zero even if no external mechanical loading is applied. This is because at finite temperatures atomic systems are intrinsically dynamic, and therefore external and internal forces are not equal in general. It is very important to point out that correct stress calculation is essential for solids since internal stress causes failure in solids and internal stresses actually carried by solids at yielding or fracture are the only correct and true measures of strength.

An EC for dynamically deforming atomistic particle systems is defined. The systematic delineation of internal and external interactions, the continuum-MD system equivalence, and the resulting Cauchy stress field along with its work-conjugate deformation field established here have further illustrated the irrelevance of mass transfer to the evaluation of stress. The equivalence of the continuum to discrete atomic systems includes (i) preservation of linear and angular momenta, (ii) conservation of internal, external and inertial work rates, (iii) conservation of mass, and (iv) preservation of kinetic energy. It has been shown that the work- and momentum-preserving Cauchy stress defined here and the mechanical part of the virial stress coincide under conditions of uniform deformation. However, in addition to its work conjugacy not shared by the mechanical part of the virial stress, the Cauchy stress field defined avoids possible ambiguities in the determination of the exact volume necessary in the evaluation of the mechanical part of the virial stress for a specific set of atoms. We note that the EC stress field defined here, along with other fields, is also computationally intensive to obtain. In contrast, the mechanical stress in (4.6) permits direct and expeditious computation.

The continuum fields for the EC can be piecewise continuous, leading to potentially large fluctuations from atom to atom. This is a reflection of the effects of atomic scale material heterogeneities under dynamic equivalence at interatomic scales. The resolution of such interatomic features is important for problems involving heterogeneities and steep gradients of fields, such as interfaces and crack tips. The fields obtained permit continuum treatments, including averaging across length-scales. The continuum fields obtained allowed other derivative field quantities to be obtained.

In particular, since the mass density and velocity fields are already explicitly given, the momentum density is simply the product of the mass-density function and the velocity function. All field quantities for the EC are regular continuum quantities, the momentum density for the EC should also be interpreted in the regular continuum sense.

It is worthwhile to note that the approach taken here fully admits non-local atomistic interactions. The continuum fields obtained reflect the non-local characteristics of the MD solutions. Because of this reason, the superposed solution embodied in (5.12), (5.13), (5.19), (5.22), (5.23), (5.26) and (5.27) and the solution obtained by taking $V = V^e$ are not identical except for conditions of uniform deformation or uniform loading. The former preserves global work rates and momenta but lacks general differential compatibility of the kinematic quantities. The latter fully preserves the global work rates and momenta and satisfies the requirements of kinematic differential compatibility. Moreover, such full consistency is also achieved for the V^e defined by any subset of an atomistic system. This consistency at any scale allows the effects of non-locality and scaling to be quantified using a continuum framework.

To achieve the dynamic equivalence between the continuum and the particle system on any size scale, the analysis involves a systematic delineation of internal and external interatomic interactions, delineation of surface and body forces, sharing of a bond by neighbouring elements and distribution of atomic mass to elements connected to an atom. These processes use parameters ς (equation (5.3)), η (equation (5.4)), κ (equation (5.5)) and ξ (equation (5.15)). It is important to point out that values for these parameters are independent of the dynamic principle of virtual work (PVW), and therefore cannot be determined by the PVW beyond the extent that the sum of each of these parameters be unity for the corresponding bond or atom. Any value in the ranges given earlier for these parameters will allow the work and momentum equivalence to be maintained. Realistic determination of the values should depend on material structure, symmetry, quantum mechanical description of the spatial shape of the interatomic bonds and consistency with continuum mechanics expectations at higher scales. In general, for example, η for an element can be determined by the dihedral angle in that element as a fraction of the sum of all such angles associated with the bond. For periodic and amorphous structures alike, ς can be defined through $\varsigma_I^e = \varphi^e / \sum_e^k \varphi^e$, with φ^e being the solid angle (three dimensions) or angle (two dimensions) subtended by an element and k being the number of elements connected to an atom. The determination of ξ should use a similar consideration for uniform traction distributions on planar surfaces for the type of shape functions used. Considerations for the determination of κ are fully given in § 5. It is important to point out that in the limit of $V^e = V$ and $S^e = S$, ς, η and ξ become unnecessary and irrelevant.

It is useful to point out that §§ 2 and 4 have reiterated the interpretation of the virial stress as a measure for momentum flux in space. It has been pointed out that the virial stress must not be confused for, and must not be used as a measure for, mechanical stress. Instead, the interatomic force term in the virial formula fully and correctly defines the Cauchy stress. Section 5 has provided a new framework for transitioning from MD descriptions to continuum descriptions. This framework goes beyond the evaluation of stress. The conclusions of the two parts on stress are consistent with each other and reinforce each other.

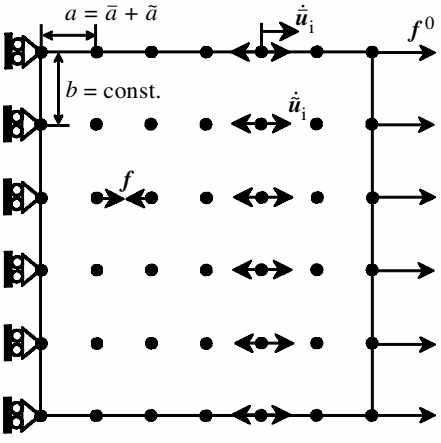

Figure 11. One-dimensional tensile deformation of a lattice with thermal fluctuations.

Finally, a discussion is in order concerning the effect of atomic thermal fluctuations on stress. MD models offer fully dynamic explicit resolution of the absolute atomic motions. The velocity of a particle can be decomposed into a structural dynamic part and a thermal fluctuation part, i.e. $\dot{\boldsymbol{u}}_i = \dot{\bar{\boldsymbol{u}}}_i + \dot{\tilde{\boldsymbol{u}}}_i$, where $\dot{\tilde{\boldsymbol{u}}}_i$ is the high-frequency thermal velocity which is not explicitly resolved at the size and time-scales of most continuum models. In these models, only the structural deformation part, $\dot{\bar{\boldsymbol{u}}}_i$, is explicitly resolved. This decomposition allows the (higher-scale) continuum kinetic energy and the thermal part of the kinetic energy to be treatment separately. This partitioning of motion at higher scales could be a source of confusion, leading to a perception that, somehow, mass transfer in space relative to a certain reference frame may contribute to stress. A full analysis of this issue using the EC framework presented in this paper would by itself be a significant development and constitute a separate publication. However, a relatively simple discussion can be pursued here to illustrate that this issue should not be confused with the calculation of stress or be construed as to giving rise to a dependence of stress on mass transfer. To this effect, we consider the one-dimensional tensile deformation with thermal fluctuation of a lattice as shown in figure 11. For simplicity, without loss of generality, we assume that the particle motions are only in the x direction, and therefore the lattice parameter b remains constant throughout the deformation. Furthermore, we assume there is no interatomic force in the y direction due to the fact that the interatomic distance b is greater than the cut-off radius of the atomic potential. Note that the lattice parameter a can be decomposed into a structural deformation part and a thermal vibration part as $a(t) = \bar{a}(t) + \tilde{a}(t)$. Usually, $\tilde{a}(t)$ is a small perturbation around the 'equilibrium' value $\bar{a}(t)$ (for thermal fluctuation), i.e. $|\tilde{a}(t)| \ll \bar{a}(t)$. We also assume that the macroscopic motion of the system is such that $\bar{a}(t)$ is uniform everywhere. The direct stress analysis in § 4 *a* and the EC theory in § 5 give the same stress interpretation for this example. This consistency is both at the absolute atomic scale and at the continuum scale. Specifically, according to (4.6) and (5.10) the atomic level fully time-resolved stress is

$$\sigma_{11}(t) = \frac{f(a(t))}{b}, \tag{7.1}$$

where atomic force $f(a(t)) = \mathrm{d}U/\mathrm{d}a$, with U being the potential energy of a unit cell. Since the thermal fluctuation $\tilde{a}(t)$ is outside the purview of an observer at the continuum scale, equations (4.6) and (5.10) indicate that continuum level stress based on the structural deformation is

$$\bar{\sigma}_{11}(t) = \frac{f(\bar{a}(t))}{b}. \tag{7.2}$$

Note that $\sigma_{11}(t)$ oscillates around $\bar{\sigma}_{11}(t)$ at the high frequency of thermal fluctuations. Since the thermal oscillation of the atomic force $f(a(t))$ around $f(\bar{a}(t))$ at $\bar{a}$ is small and harmonic,

$$\bar{\sigma}_{11}(t) = \frac{1}{\tau}\int_{t}^{t+t_0} \sigma_{11}(\tau)\,\mathrm{d}\tau, \tag{7.3}$$

where t_0 is the time period of the thermal oscillation. The fully time-resolved strain rate and the macroscopic strain rate are, respectively, $D_{11} = \dot{a}/a$ and $\bar{D}_{11} = \dot{\bar{a}}/\bar{a}$. Consequently, the stress work in a unit cell associated with one cycle of thermal motion is

$$\int_{t}^{t+t_0} ab\sigma_{11}(\tau)D_{11}(\tau)\,\mathrm{d}\tau = \int_{t}^{t+t_0} f(a)\dot{a}\,\mathrm{d}\tau = U(a)|_{\tilde{a}}^{\tilde{a}} = 0. \tag{7.4}$$

The stress work over the macroscopic deformation from lattice size $\bar{a}(t_1) = \bar{a}_1$ to size $\bar{a}(t_2) = \bar{a}_2$ is

$$\int_{t_1}^{t_2} \bar{a}b\bar{\sigma}_{11}(t)\bar{D}_{11}(t)\,\mathrm{d}t = \int_{t_1}^{t_2} f(\bar{a})\dot{\bar{a}}\,\mathrm{d}t = U(\bar{a})|_{\bar{a}_1}^{\bar{a}_2}.$$

These thermal and structural stress works are equal to the respective mechanical works done by the interatomic force in each unit cell, establishing work conjugacy of the above stress measures. They also establish a direct work equivalence between the continuum stress interpretations (from both (4.6) and (5.10)) and the original atomic force field. They clearly demonstrate that stress has nothing to do with mass transfer *at both the explicit time-resolved atomic level and at the macroscopic continuum level where thermal fluctuations are accounted for separately from the structural deformation of an atomic system.*

On the other hand, the virial stress from (1.1) is

$$\mathit{\Pi}_{11}(t) = -\frac{m|\dot{\boldsymbol{u}}_i|^2}{ab} + \frac{f(a(t))}{b} \tag{7.5}$$

at the fully time-resolved atomic level, and

$$\bar{\mathit{\Pi}}_{11}(t) = -\frac{m|\dot{\bar{\boldsymbol{u}}}_i|^2}{\bar{a}b} + \frac{f(\bar{a}(t))}{b} \tag{7.6}$$

at the macroscopic structural level. Note that (7.6) is a strict interpretation of (1.1) at the macroscopic level, since the thermal velocity $\dot{\tilde{\boldsymbol{u}}}_i$ is outside the purview of the macroscopic observer and he simply does not 'see' the thermal fluctuations. It is clear that, unlike $\bar{\sigma}_{11}(t)$ in (7.3),

$$\bar{\mathit{\Pi}}_{11}(t) \neq \frac{1}{\tau}\int_{t}^{t+t_0} \mathit{\Pi}_{11}(\tau)\,\mathrm{d}\tau. \tag{7.7}$$

This is inconsistent with the cyclic nature of stress variation due to thermal oscillations. Additionally, since, in general,

$$\int_{t_1}^{t_2} ab\Pi_{11}(\tau)D_{11}(\tau)\,\mathrm{d}\tau \neq \int_{t_1}^{t_2} f(a)\dot{a}\,\mathrm{d}\tau, \tag{7.8}$$

$\Pi_{11}(\tau)$ is not work conjugate to the deformation and does not yield stress work. This aspect is also clearly seen at the structural deformation level since, in general,

$$\int_{t_1}^{t_2} \bar{a}b\bar{\Pi}_{11}(t)\bar{D}_{11}(t)\,\mathrm{d}t \neq \int_{t_1}^{t_2} f(\bar{a})\dot{\bar{a}}\,\mathrm{d}t \tag{7.9}$$

cannot represent stress work in any sense.

To summarize, the Cauchy stress in (4.6) and (5.10) correctly measures the mechanical interaction and internal mechanical work rate at both the scale of a fully time-resolved analysis and the scale of a macroscopic continuum analysis. In contrast, the virial stress does not yield meaningful interpretation for stress and mechanical work at either scale. This simple example illustrates that even under the conditions of higher-scale thermal-mechanical analyses, mass transfer must not enter into the expression for stress.

To end this paper, we again note that some authors have presented an alternate version of the virial stress formula that involves the use of the fluctuation velocity $\dot{\boldsymbol{u}}_i$ in (1.1) rather than the absolute velocity $\boldsymbol{\dot{u}}_i$ (cf. Irving & Kirkwood 1950; Hardy 1982; Yasui *et al*. 1999; Nakane *et al*. 2000). An interpretation using their formulae yields

$$\tilde{\Pi}_{11}(t) = -\frac{m|\dot{\boldsymbol{u}}_i|^2}{ab} + \frac{f(a(t))}{b}. \tag{7.10}$$

While (7.5) and (7.6) are written for an observer fixed in space (with two different time resolutions for his analysis), equation (7.10) can be regarded as being written from the perspective of an observer travelling with the 'streaming' velocity of $\dot{\boldsymbol{u}}_i$. Obviously, just like (7.5) and (7.6), equation (7.10) cannot represent stress or provide stress work in any sense, since

$$\tilde{\Pi}_{11}(t) \neq \frac{1}{\tau}\int_{t}^{t+t_0} \Pi_{11}(\tau)\,\mathrm{d}\tau, \qquad \tilde{\Pi}_{11}(t) \neq \frac{1}{\tau}\int_{t}^{t+t_0} \sigma_{11}(\tau)\,\mathrm{d}\tau \tag{7.11}$$

and

$$\int_{t_1}^{t_2} ab\tilde{\Pi}_{11}(\tau)D_{11}(\tau)\,\mathrm{d}\tau \neq \int_{t_1}^{t_2} f(a)\dot{a}\,\mathrm{d}\tau. \tag{7.12}$$

These inequalities show that $\tilde{\Pi}_{11}(t)$ provides inconsistent interpretations of the loading conditions and interatomic mechanical work in the atomic system at hand. It is obvious that (7.5), (7.6) and (7.10) represent momentum transfer in space from the perspectives of their respective frames of reference with specific levels of resolution. They must not be regarded as stress in any sense.

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