Control-volume representation of molecular dynamics

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(Dated: Received 13 October 2011; revised manuscript received 2 March 2012; published 22 May 2012)

A Molecular Dynamics (MD) parallel to the Control Volume (CV) formulation of fluid mechanics is developed by integrating the formulas of Irving and Kirkwood, J. Chem. Phys. 18, 817 (1950) over a finite cubic volume of molecular dimensions. The Lagrangian molecular system is expressed in terms of an Eulerian CV, which yields an equivalent to Reynolds’ Transport Theorem for the discrete system. This approach casts the dynamics of the molecular system into a form that can be readily compared to the continuum equations. The MD equations of motion are reinterpreted in terms of a Lagrangian-to-Control-Volume (LCV) conversion function \( \delta_i \), for each molecule \( i \). The LCV function and its spatial derivatives are used to express fluxes and relevant forces across the control surfaces. The relationship between the local pressures computed using the Volume Average (VA, Lutsko, J. Appl. Phys 64, 1152 (1988) ) techniques and the Method of Planes (MOP, Todd et al, Phys. Rev. E 52, 1627 (1995) ) emerges naturally from the treatment. Numerical experiments using the MD CV method are reported for equilibrium and non-equilibrium (start-up Couette flow) model liquids, which demonstrate the advantages of the formulation. The CV formulation of the MD is shown to be exactly conservative, and is therefore ideally suited to obtain macroscopic properties from a discrete system.

DOI: 10.1103/PhysRevE.85.056705 PACS number(s): 05.20.y, 47.11.Mn, 31.15.xv

I. INTRODUCTION

The macroscopic and microscopic descriptions of mechanics have traditionally been studied independently. The former invokes a continuum assumption, and aims to reproduce the large-scale behaviour of solids and fluids, without the need to resolve the micro-scale details. On the other hand, molecular simulation predicts the evolution of individual, but interacting, molecules, which has application in nano and micro-scale systems. Bridging these scales requires a mesoscopic description, which represents the evolution of the average of many microscopic trajectories through phase space. It is advantageous to cast the fluid dynamics equations in a consistent form for both the molecular, mesoscale and continuum approaches. The current work seeks to achieve this objective by introducing a Control Volume (CV) formulation for the molecular system.

The Control Volume approach is widely adopted in continuum fluid mechanics, where Reynolds Transport Theorem relates Newton’s laws of motion for macroscopic fluid parcels to fluxes through a CV. In this form, fluid mechanics has had great success in simulating both fundamental and practical flows. However, when the continuum assumption fails, or when macroscopic constitutive equations are lacking, a molecular-scale description is required. Examples include nano-flows, moving contact lines, solid-liquid boundaries, non-equilibrium fluids, and evaluation of transport properties such as viscosity and heat conductivity.

Molecular Dynamics (MD) involves solving Newton’s equations of motion for an assembly of interacting discrete molecules. Averaging is required in order to compute properties of interest, e.g. temperature, density, pressure and stress, which can vary on a local scale especially out of equilibrium. A rigorous link between mesoscopic and continuum properties was established in the seminal work of Irving and Kirkwood, who related the mesoscopic Liouville equation to the differential form of continuum fluid mechanics. However, the resulting equations at a point were expressed in terms of the Dirac \( \delta \) function — a form which is difficult to manipulate and cannot be applied directly in a molecular simulation. Furthermore, a Taylor series expansion of the Dirac \( \delta \) functions was required to express the pressure tensor. The final expression for pressure tensor is neither easy to interpret nor to compute. As a result, there have been numerous attempts to develop an expression for the pressure tensor for use in MD simulation. Some of these expressions have been shown to be equivalent in the appropriate limit. For example, Heyes et al. demonstrated equivalence between Method of Planes and Volume Average (VA Lutsko ) at a surface.

In order to avoid use of the Dirac \( \delta \) function, the current work adopts a Control Volume representation of the MD system, written in terms of fluxes and surface stresses. This approach is in part motivated by the success of the control volume formulation in continuum fluid mechanics. At a molecular scale, control volume analyses of NEMD simulations can facilitate evaluation of local fluid properties. Furthermore, the CV method also lends itself to coupling schemes between the continuum and molecular descriptions.

The equations of continuum fluid mechanics are presented in Section II A followed by a review of the Irving and Kirkwood procedure for linking continuum and mesoscopic properties in Section II B. In Section III a Lagrangian to Control Volume (LCV) conversion function is used to express the mesoscopic equations for mass and momentum fluxes. Section II C focuses on the stress tensor, and relates the current formulation to established definitions within the literature. In Section IV the CV equations are derived for a single microscopic system, and subsequently integrated in time in order to obtain a form which can be applied in MD simulations. The conservation properties of the CV formulation are demonstrated in NEMD simulations of Couette flow in Section IV C.

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II. BACKGROUND

This section summarizes the theoretical background. First, the macroscopic continuum equations are introduced, followed by the mesoscopic equations which describe the evolution of an ensemble average of systems of discrete molecules. The link between the two descriptions is subsequently discussed.

A. Macroscopic Continuum Equations

The continuum conservation of mass and momentum balance can be derived in an Eulerian frame by considering the fluxes through a Control Volume (CV). The mass continuity equation can be expressed as,

$$\frac{\partial}{\partial t} \int_V \rho dV = -\oint_S \rho \mathbf{u} \cdot d\mathbf{S},$$

(1)

where $\rho$ is the mass density and $\mathbf{u}$ is the fluid velocity. The rate of change of momentum is determined by the balance of forces on the CV,

$$\frac{\partial}{\partial t} \int_V \rho \dot{\mathbf{u}} dV = -\oint_S \rho \mathbf{u} \cdot d\mathbf{S} + \mathbf{F}_{\text{surface}} + \mathbf{F}_{\text{body}}.$$

(2)

The forces are split into those acting on the bounding surfaces, $\mathbf{F}_{\text{surface}}$, and body forces, $\mathbf{F}_{\text{body}}$. Surface forces are expressed in terms of the pressure tensor, $\Pi$, on the CV surfaces,

$$\mathbf{F}_{\text{surface}} = -\oint_S \Pi \cdot d\mathbf{S}. $$

(3)

The rate of change of energy in a CV is expressed in terms of fluxes, the pressure tensor, and a heat flux vector $\mathbf{q}$,

$$\frac{\partial}{\partial t} \int_V \rho \mathbf{E} dV = -\oint_S [\rho \mathbf{E} \mathbf{u} + \Pi \cdot \mathbf{u} + \mathbf{q}] \cdot d\mathbf{S}. $$

(4)

Here the energy change due to body forces is not included. The divergence theorem relates surface fluxes to the divergence within the volume, for a variable $A$,

$$\oint_S A \cdot d\mathbf{S} = \int_V \nabla \cdot A dV.$$

(5)

In addition, the differential form of the flow equations can be recovered in the limit of an infinitesimal control volume $\Delta V$,

$$\nabla \cdot A = \lim_{V \to 0} \frac{1}{V} \oint_S A \cdot d\mathbf{S}. $$

(6)

B. Relationship Between the Continuum and the Mesoscopic Descriptions

A mesoscopic description is a temporal and spatial average of the molecular trajectories, expressed in terms of a probability function, $f$. Irving and Kirkwood established the link between the mesoscopic and continuum descriptions using the Dirac $\delta$ function to define the macroscopic density at a point $\mathbf{r}$ in space,

$$\rho(\mathbf{r}, t) = \sum_{i=1}^{N} \left\langle m_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle f_i.$$

(7)

The angled brackets $\left\langle \alpha; f \right\rangle$ denote the inner product of $\alpha$ with $f$, which gives the expectation of $\alpha$ for an ensemble of systems. The mass and position of a molecule $i$ are denoted $m_i$ and $\mathbf{r}_i$, respectively, and $N$ is the number of molecules in a single system. The momentum density at a point in space is similarly defined by,

$$\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) = \sum_{i=1}^{N} \left\langle \mathbf{p}_i \delta(\mathbf{r}_i - \mathbf{r}) ; f_i \right\rangle.$$

(8)

where the molecular momentum, $\mathbf{p}_i = m_i \dot{\mathbf{r}}_i$. Note that $\mathbf{p}_i$ is the momentum in the laboratory frame, and not the peculiar value $\mathbf{p}$, which excludes the macroscopic streaming term at the location of molecule $i$, $\mathbf{u}(\mathbf{r}_i)$.

$$\mathbf{p}_i = m_i \left( \mathbf{p}_i - \mathbf{u}(\mathbf{r}_i) \right).$$

(9)

The present treatment uses $\mathbf{p}_i$ in the lab frame. A discussion of translating CV and its relationship to the peculiar momentum is given in Appendix A.

Finally, the energy density at a point in space is defined by

$$\rho(\mathbf{r}, t) \mathbf{E}(\mathbf{r}, t) = \sum_{i=1}^{N} \left\langle e_i \delta(\mathbf{r}_i - \mathbf{r}) ; f_i \right\rangle.$$

(10)

where the energy of the $i^{th}$ molecule is defined as the sum of the kinetic energy and the inter-molecular interaction potential $\phi_{ij}$,

$$e_i = \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{j \neq i}^{N} \phi_{ij}.$$

(11)

It is implicit in this definition that the potential energy of an interatomic interaction, $\phi_{ij}$, is divided equally between the two interacting molecules, $i$ and $j$.

As phase space is bounded, the evolution of a property, $\alpha$, in time is governed by the equation,

$$\frac{\partial}{\partial t} \left\langle \alpha; f \right\rangle = \sum_{i=1}^{N} \left\langle \mathbf{F}_i \cdot \frac{\partial \alpha}{\partial \mathbf{p}_i} + \mathbf{p}_i \cdot \frac{\partial \alpha}{\partial \mathbf{r}_i} \right\rangle f_i.$$

(12)

where $\mathbf{F}_i$ is the force on molecule $i$, and $\alpha = \alpha(\mathbf{r}_i(t), \mathbf{p}_i(t))$ is an implicit function of time. Using Eq. (12), Irving and Kirkwood derived the time evolution of the mass (from Eq. 1), momentum density (from Eq. 8), and energy density (from Eq. 10) for a mesoscopic system. A comparison of the resulting equations to the continuum counterpart provided a term-by-term equivalence. Both the mesoscopic and continuum equations were valid at a point; the former expressed in terms of Dirac $\delta$ and the latter in differential form. In the current work, the mass and momentum densities are recast within the CV framework which avoids use of the Dirac $\delta$ functions directly, and attendant problems with their practical implementation.

III. THE CONTROL VOLUME FORMULATION

In order to cast the governing equations for a discrete system in CV form, a ‘selection function’ $\psi_i$ is introduced, which isolates those molecules within the region of interest. This function is obtained by integrating the Dirac $\delta$ function, $\delta(\mathbf{r}_i - \mathbf{r})$, over a cuboid in space, centered at $\mathbf{r}$ and of side length $\Delta \mathbf{r}$ as illustrated in figure 1(a) [37]. Using
FIG. 1. (Color online) The CV function and its derivative applied to a system of molecules. The figures were generated using the VMD visualization package. From left to right, (a) Schematic of \( \partial_i \) which selects only the molecules within a cube, (b) Location of cube center \( \mathbf{r} \) and labels for cube surfaces, (c) Schematic of \( \partial_i / \partial x \) which selects only molecules crossing the \( x^+ \) and \( x^- \) surface planes.

\[
\delta(\mathbf{r} - \mathbf{r}_i) = \delta(x_i - x)\delta(y_i - y)\delta(z_i - z),
\]

the resulting triple integral is,

\[
\partial_i \equiv \int \int \int \delta(x_i - x)\delta(y_i - y)\delta(z_i - z)dx\,dy\,dz
\]

\[
= \left[ \left[ H(x_i - x)H(y_i - y)H(z_i - z) \right] \right] x^+ y^+ z^+
\]

\[
\times \left[ \left[ H(x_i - x)H(y_i - y)H(z_i - z) \right] \right] x^- y^- z^-.
\]

(13)

where \( H \) is the Heaviside function, and the limits of integration are defined as, \( r^- \equiv \mathbf{r} - \frac{dS^i}{dx^+} \) and \( r^+ \equiv \mathbf{r} + \frac{dS^i}{dx^-} \), for each direction (see Fig. 1(b)). Note that \( \partial_i \) can be interpreted as a Lagrangian-to-Control-Volume conversion function (LCV) for molecule \( i \). It is unity when molecule \( i \) is inside the cuboid, and equal to zero otherwise, as illustrated in Fig. 1(a).

Using L’Hôpital’s rule and defining, \( \Delta V \equiv \Delta x \Delta y \Delta z \), the LCV function for molecule \( i \) reduces to the Dirac \( \delta \) function in the limit of zero volume,

\[
\delta(\mathbf{r} - \mathbf{r}_i) = \lim_{\Delta V \to 0} \frac{\partial_i}{\Delta V}.
\]

The spatial derivative in the \( x \) direction of the LCV function for molecule \( i \) is,

\[
\frac{\partial \partial_i}{\partial x} = \frac{\partial \partial_i}{\partial x_i} = \left[ \delta(x^+ - x_i) - \delta(x^- - x_i) \right] S_{x_i},
\]

(14)

where \( S_{x_i} \) is

\[
S_{x_i} \equiv \left[ H(y^+ - y_i) - H(y^- - y_i) \right] \left[ H(z^+ - z_i) - H(z^- - z_i) \right].
\]

(15)

Eq. (14) isolates molecules on a 2D rectangular patch in the \( yz \) plane. The derivative \( \partial \partial_i / \partial x \) is only non-zero when molecule \( i \) is crossing the surfaces marked in Fig. 1(c) normal to the \( x \) direction. The contribution of the \( i^{th} \) molecule to the net rate of mass flux through the control surface is expressed in the form, \( p_i \cdot \partial S_i \). Defining for the right \( x \) surface,

\[
dS_{x^+}^i \equiv \delta(x^+ - x_i)S_{x_i},
\]

(16)

and similarly for the left surface, \( dS_{x^-}^i \), the total flux Eq. (14) in any direction \( \mathbf{r} \) is then,

\[
\frac{\partial \partial_i}{\partial \mathbf{r}} = dS_{x^+}^i - dS_{x^-}^i \equiv dS_i.
\]

(17)

The LCV function is key to the derivation of a molecular-level equivalent of the continuum CV equations, and it will be used extensively in the following sections. The approach in sections IIIA, IIIB, and IIID shares some similarities with the work of Serrano and Español [38] which considers the time evolution of Voronoi characteristic functions. However the LCV function has precisely defined extents which allows the development of conservation equations for a microscopic system. In the following treatment, the CV is fixed in space (i.e., \( \mathbf{r} \) is not a function of time). The extension of this treatment to an advecting CV is made in Appendix A.

A. Mass Conservation for a Molecular CV

In this section, a mesoscopic expression for the mass in a cuboidal CV is derived. The time evolution of mass within a CV is shown to be equal to the net mass flux of molecules across its surfaces.

The mass inside an arbitrary CV at the molecular scale can be expressed in terms of the LCV as follows,

\[
\int_V \rho(\mathbf{r}, t)dV = \int_V \sum_{i=1}^{N} \left\langle m_i \delta(\mathbf{r}_i - \mathbf{r})|f| \right\rangle dV
\]

\[
= \sum_{i=1}^{N} \int_{x^- y^- z^-} \left\langle m_i \delta(\mathbf{r}_i - \mathbf{r})|f| \right\rangle dV
\]

\[
= \sum_{i=1}^{N} \left\langle m_i \partial_i|f| \right\rangle.
\]

(18)

Taking the time derivative of Eq. (13) and using Eq. (12),

\[
\frac{\partial}{\partial t} \int_V \rho(\mathbf{r}, t)dV = \frac{\partial}{\partial t} \sum_{i=1}^{N} \left\langle m_i \partial_i|f| \right\rangle
\]

\[
= \sum_{i=1}^{N} \left\langle p_i \cdot \partial \mathbf{r}_i|f| + F_i \cdot \frac{\partial}{\partial p_i} m_i \partial_i|f| \right\rangle.
\]

(19)

The term \( \partial m_i / \partial p_i = 0 \), as \( \partial_i \) is not a function of \( p_i \).

Therefore,

\[
\frac{\partial}{\partial t} \int_V \rho dV = - \sum_{i=1}^{N} \left\langle p_i \cdot \partial \mathbf{r}_i|f| \right\rangle.
\]

(20)
where the equality, \( \partial \theta_i / \partial r_i = - \partial \theta_j / \partial r \) has been used. From the continuum mass conservation given in Eq. (11), the macroscopic and mesoscopic fluxes over the surfaces can be equated,
\[
\sum_{faces} \int_{S_f} \rho u \cdot dS_f = \sum_{i=1}^{N} \left\langle p_i \cdot dS_i; f \right\rangle. \tag{21}
\]
The mesoscopic equation for evolution of mass in a control volume is given by,
\[
\frac{\partial}{\partial t} \sum_{i=1}^{N} \left\langle m_i \theta_i; f \right\rangle = - \sum_{i=1}^{N} \left\langle p_i \cdot dS_i; f \right\rangle. \tag{22}
\]
Appendix B shows that the surface mass flux yields the Irving and Kirkwood \(^{10}\) expression for divergence as the CV tends to a point (i.e. \( V \to 0 \)), in analogy to Eq. (6).

### B. Momentum Balance for a Molecular CV

In this section, a mesoscopic expression for time evolution of momentum within a CV is derived. The starting point is to integrate the momentum at a point, given in Eq. (20), over the CV,
\[
\int_V \rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) dV = \sum_{i=1}^{N} \left\langle p_i \theta_i; f \right\rangle. \tag{23}
\]
Following a similar procedure to that in section IIIA the formula (12) is used to obtain the time evolution of the momentum within the CV,
\[
\frac{\partial}{\partial t} \int_V \rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) dV = \frac{\partial}{\partial t} \sum_{i=1}^{N} \left\langle p_i \theta_i; f \right\rangle = \sum_{i=1}^{N} \left\langle \frac{p_i}{m_i} \frac{\partial}{\partial r_i} p_i \theta_i + \mathbf{F}_i \cdot \frac{\partial}{\partial p_i} p_i \theta_i; f \right\rangle, \tag{24}
\]
where the terms \( K_T \) and \( C_T \) are the kinetic and configurational components, respectively. The kinetic part is,
\[
K_T = \sum_{i=1}^{N} \left\langle \frac{p_i}{m_i} \frac{\partial}{\partial r_i} p_i \theta_i; f \right\rangle = \sum_{i=1}^{N} \left\langle \mathbf{p}_i \mathbf{p}_i \cdot \frac{\partial \theta_i}{\partial r_i}; f \right\rangle, \tag{25}
\]
where \( \mathbf{p}_i \mathbf{p}_i \) is the dyadic product. For any surface of the CV, here \( x^+ \), the molecular flux can be equated to the continuum convection and pressure on that surface,
\[
\int_{S_x^+} \rho(x^+, y, z, t) u(x^+, y, z, t) u_x(x^+, y, z, t) dydz + \int_{S_x^+} K_T^+ dydz = \sum_{i=1}^{N} \left\langle \frac{p_i \mathbf{p}_i}{m_i} dS^+_x; f \right\rangle,
\]
where \( K_T^+ \) is the kinetic part of the pressure tensor due to molecular transgressions across the \( x^+ \) CV surface. The average molecular flux across the surface is then,
\[
\{\rho u u_x\}^+ + K_T^+ = \frac{1}{\Delta A_x} \sum_{i=1}^{N} \left\langle \frac{p_i \mathbf{p}_i}{m_i} dS^+_x; f \right\rangle. \tag{26}
\]
where the continuum expression \( \{\rho u u_x\}^+ \) is the average flux through a flat region in space with area \( \Delta A_x^2 = \Delta y \Delta z \). This kinetic component of the pressure tensor is discussed further in Section IIIC.

The configurational term of Eq. (24) is,
\[
C_T = \sum_{i=1}^{N} \left\langle \mathbf{F}_i \cdot \frac{\partial}{\partial p_i} p_i \theta_i; f \right\rangle = \sum_{i=1}^{N} \left\langle \mathbf{F}_i \theta_i; f \right\rangle, \tag{27}
\]
where the total force \( \mathbf{F}_i \) on particle \( i \) is the sum of pairwise-additive interactions with potential \( \phi_{ij} \), and from an external potential \( \psi_i \).
\[
\mathbf{F}_i = \sum_{j \neq i} \phi_{ij} \frac{\partial \psi_i}{\partial r_i} + \mathbf{F}_{ext} = \mathbf{F}_{ext}. \tag{28}
\]

It is commonly assumed that the potential energy of an interatomic interaction, \( \phi_{ij} \), can be divided equally between the two interacting molecules, \( i \) and \( j \), such that,
\[
\mathbf{F}_i = \frac{1}{2} \sum_{j \neq i} \left[ \frac{\partial \phi_{ij}}{\partial r_i} + \frac{\partial \phi_{ji}}{\partial r_j} \right]. \tag{29}
\]
where the notation \( \sum_{i,j}^N = \sum_{i=1}^{N} \sum_{j \neq i}^{N} \) has been introduced for conciseness. Therefore, the configurational term can be expressed as,
\[
C_T = \frac{1}{2} \sum_{i,j}^N \left\langle \mathbf{f}_{ij} \theta_{ij}; f \right\rangle + \sum_{i=1}^{N} \left\langle \mathbf{f}_{ext} \theta_i; f \right\rangle, \tag{29}
\]
where \( \mathbf{f}_{ij} = - \frac{\partial \phi_{ij}}{\partial r_i} = \frac{\partial \phi_{ji}}{\partial r_j} \) and \( \mathbf{f}_{ext} = - \frac{\partial \psi_i}{\partial r_i} \). The notation, \( \theta_{ij} \equiv \theta_i - \theta_j \), is introduced, which is non-zero only when the force acts over the surface of the CV, as illustrated in Fig. 2.

![FIG. 2. (Color online) A section through the CV to illustrate the role of \( \partial_{ij} \) in selecting only the \( i \) and \( j \) interactions that cross the bounding surface of the control volume. Due to the limited range of interactions, only the forces between the internal (red) molecules \( i \) and external (blue) molecules \( j \) near the surfaces are included.](image-url)
Substituting the kinetic \((K_T)\) and configurational \((C_T)\) terms, from Eqs. (25) and (29) into Eq. (24), the time evolution of momentum within the CV at the mesoscopic scale is,

\[
\frac{\partial}{\partial t} \sum_{i=1}^{N} \left( \frac{\mathbf{p}_i}{m_i} \right) = \frac{1}{2} \sum_{i,j} \left( \mathbf{f}_{ij} \delta_{ij} \right) + \sum_{i=1}^{N} \left( \mathbf{f}_{ext,i} \right).
\]

(30)

Equations (22) and (30) describe the evolution of mass and momentum respectively within a CV averaged over an ensemble of representative molecular systems. As proposed by Evans and Morriss [8], it is possible to develop microscopic evolution equations that do not require ensemble averaging. Hence, the equivalents of Eqs. (22) and (30) are derived for a single trajectory through phase space in section IV A integrated in time in section IV B and tested numerically using molecular dynamics simulation in section IV C.

The link between the macroscopic and mesoscopic treatments is given by equating their respective momentum Eqs. (2) and (30),

\[
- \int_{S} \rho \mathbf{u} \cdot d \mathbf{S} + \mathbf{F}_{\text{surface}} + \mathbf{F}_{\text{body}} = \frac{1}{2} \sum_{i=1}^{N} \left( \frac{\mathbf{p}_i}{m_i} \right) \cdot d \mathbf{S}_{i} + \sum_{i=1}^{N} \left( \mathbf{f}_{ext,i} \right).
\]

(31)

As can be seen, each term in the continuum evolution of momentum has an equivalent term in the mesoscopic formulation.

The continuum momentum Eq. (2) can be expressed in terms of the divergence of the pressure tensor, \(\Pi\), in the control volume from,

\[
\frac{\partial}{\partial t} \int_{V} \rho dV = - \int_{S} \rho \mathbf{u} \cdot d \mathbf{S} + \mathbf{F}_{\text{surface}} + \mathbf{F}_{\text{body}} = \frac{1}{2} \sum_{i=1}^{N} \left( \frac{\mathbf{p}_i}{m_i} \right) \cdot d \mathbf{S}_{i} + \sum_{i=1}^{N} \left( \mathbf{f}_{ext,i} \right).
\]

(32a)

\[
\frac{\partial}{\partial t} \int_{V} \rho dV = \frac{1}{2} \sum_{i=1}^{N} \left( \frac{\mathbf{p}_i}{m_i} \right) \cdot d \mathbf{S}_{i} + \sum_{i=1}^{N} \left( \mathbf{f}_{ext,i} \right). \quad (32b)
\]

In the following subsection, the right hand side of Eq. (31) is recast first in divergence form as in Eq. (32b) and then in terms of surface pressures as in Eq. (32a).

C. The Pressure Tensor

The average molecular pressure tensor ascribed to a control volume is conveniently expressed in terms of the \(\text{LCV}\) function. This is shown \textit{inter alia} to lead to a number of literature definitions of the local stress tensor. In the first part of this section, the techniques of Irving and Kirkwood [8] are used to express the divergence of the stress (as with the right hand side of Eq. (32b)) in terms of intermolecular force. Secondly, the CV pressure tensor is related to the Volume Average (VA) formula \((14,17)\) and, by consideration of the interactions across the surfaces, to the Method Of Planes (MOP) \(13,14\). Finally, the molecular CV Eq. (30) is written in analogous form to the macroscopic Eq. (32b).

The pressure tensor, \(\Pi\), can be decomposed into a kinetic \(\kappa\) term, and a configurational stress \(\sigma\). In keeping with the engineering literature, the stress and pressure tensors have opposite signs,

\[
\Pi = \kappa - \sigma. \quad (33)
\]

The separation into kinetic and configurational parts is made to accommodate the debate concerning the inclusion of kinetic terms in the molecular stress \([9,39,40]\).

In order to avoid confusion, the stress, \(\sigma\), is herein defined to be due to the forces only (surface tractions). This, combined with the kinetic pressure term \(\kappa\), yields the total pressure tensor \(\Pi\) first introduced in Eq. (3).

1. Irving Kirkwood Pressure Tensor

The virial expression for the stress cannot be applied locally as it is only valid for a homogeneous system \([1,2]\). The Irving and Kirkwood [8] technique for evaluating the non-equilibrium, locally-defined stress resolves this issue, and is herein extended to a CV. To obtain the stress, \(\sigma\), the intermolecular force term of Eq. (31) is defined to be equal to the divergence of stress,

\[
\int_{V} \frac{\partial}{\partial r} \cdot \sigma dV = \frac{1}{2} \sum_{i,j} \left( \mathbf{f}_{ij} \delta_{ij} \right).
\]

(34)

Irving and Kirkwood [8] used a Taylor expansion of the Dirac \(\delta\) functions to express the pair force contribution in the form of a divergence,

\[
\mathbf{f}_{ij} \left[ \delta(\mathbf{r}_i - \mathbf{r}) - \delta(\mathbf{r}_j - \mathbf{r}) \right] = - \frac{1}{2} \mathbf{r}_{ij} \mathbf{O}_{ij} \mathbf{d}(\mathbf{r}_i - \mathbf{r}),
\]

where \(\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j\), and \(\mathbf{O}_{ij}\) is an operator which acts on the Dirac \(\delta\) function,

\[
\mathbf{O}_{ij} \equiv \left( 1 - \frac{1}{2} \mathbf{r}_{ij} \frac{\partial}{\partial \mathbf{r}_i} + \ldots - \frac{1}{n!} \left( \mathbf{r}_{ij} \frac{\partial}{\partial \mathbf{r}_i} \right)^{n-1} + \ldots \right).
\]

(35)

Equation (34) can therefore be rewritten,

\[
\int_{V} \frac{\partial}{\partial r} \cdot \sigma dV = - \frac{1}{2} \sum_{i,j} \int \frac{\partial}{\partial r_i} \mathbf{f}_{ij} \mathbf{r}_{ij} \mathbf{O}_{ij} \delta(\mathbf{r}_i - \mathbf{r})dV. \quad (36)
\]

The Taylor expansion in Dirac \(\delta\) functions is not straightforward to evaluate. This operation can be bypassed by integrating the position of the molecule \(i\) over phase space \([11]\), or by replacing the Dirac \(\delta\) with a similar but finite-valued function of compact support \([15,18,19,21]\). In the current treatment, the \(\text{LCV}\) function, \(\vartheta\), is used, which is advantageous because it explicitly defines both the extent of the CV and its surface fluxes. The pressure tensor can be written in terms of the \(\text{LCV}\) function by exploiting the following identities (see Appendix of Ref. [8]).

\[
\mathbf{O}_{ij} \delta(\mathbf{r}_i - \mathbf{r}_j) = \int \frac{1}{0} \left( \delta(\mathbf{r} - \mathbf{r}_i + \mathbf{s}_{ij}) \right) d\mathbf{s}. \quad (37)
\]
Equation (36) can therefore be written as,
\[
\int_V \frac{\partial}{\partial r} \cdot \sigma \, dV = - \int_V \frac{1}{2} \sum_{i,j} \left\langle \frac{\partial}{\partial r} \cdot f_{ij} r_{ij} \right\rangle + \frac{1}{2} \sum_{i,j} \left\langle f_{ij} r_{ij} \right\rangle \int_0^1 \delta(r - r_i + s r_{ij}) ds \, f \, dV.
\]
Equation Eq. (38) leads to the VA and MOP definitions of the pressure tensor.

2. VA Pressure Tensor

The definition of the stress tensor of Lutsko [16] and Cormier et al. [17] can be obtained by rewriting Eq. (38) as,
\[
\frac{\partial}{\partial r} \int_V \sigma \, dV = - \frac{\partial}{\partial r} \int_V \frac{1}{2} \sum_{i,j} \left\langle f_{ij} r_{ij} \right\rangle + \frac{1}{2} \sum_{i,j} \left\langle f_{ij} r_{ij} \right\rangle \int_0^1 \delta(r - r_i + s r_{ij}) ds \, f \, dV.
\]
Swapping the order of integration and evaluating the integral of the Dirac \(\delta\) function over \(\Delta V\) gives a different form of the \(\mathcal{LCV}\) function, \(\vartheta_s\),
\[
\vartheta_s \equiv \int_V \delta(r - r_i + s r_{ij}) dV = \left[ H(x^+ - x_i + x s_{ij}) - H(x^- - x_i + x s_{ij}) \right] \times \left[ H(y^+ - y_i + y s_{ij}) - H(y^- - y_i + y s_{ij}) \right] \times \left[ H(z^+ - z_i + z s_{ij}) - H(z^- - z_i + z s_{ij}) \right],
\]
which is non-zero if at any point on the line between the two molecules, \(r_i - s r_{ij}\), is inside the cubic region (c.f. \(r_i\) with \(\vartheta_l\)). Substituting the definition, \(\vartheta_s\) (Eq. [41]), into Eq. (40) gives,
\[
\frac{\partial}{\partial r} \int_V \sigma \, dV = - \frac{1}{2\Delta V} \sum_{i,j} \left\langle f_{ij} r_{ij} \right\rangle l_{ij} \int_0^1 \vartheta_s ds \, f = \frac{\partial}{\partial r} \int_V \frac{1}{2} \sum_{i,j} \left\langle f_{ij} r_{ij} \right\rangle l_{ij} \int_0^1 \vartheta_s ds \, f \, dV.
\]
where \(l_{ij}\) is the integral from \(r_i\) (\(s = 0\)) to \(r_j\) (\(s = 1\)) of the \(\vartheta_s\) function,
\[
l_{ij} \equiv \int_0^1 \vartheta_s ds.
\]
Therefore, \(l_{ij}\) is the fraction of interaction length between \(i\) and \(j\) which lies within the CV, as illustrated in Fig. 3. The definition of the configurational stress in Eq. (42) is the same as in the work of Lutsko [18] and Cormier et al. [17]. The microscopic divergence theorem given in Appendix A can be applied to obtain the volume averaged kinetic component of the pressure tensor, \(\mathcal{K}_T\), in Eq. (25).

\[
\sum_{i=1}^N \left( \frac{\mathbf{p}_i \cdot \mathbf{m}_i}{m_i} \cdot dS_i f \right) = \frac{\partial}{\partial r} \sum_{i=1}^N \left( \frac{\mathbf{p}_i \cdot \mathbf{m}_i}{m_i} \vartheta_i f \right).
\]
Note that the expression inside the divergence includes both the advection, \{ \(\rho uu\) \}, and kinetic components of the pressure tensor. The VA form \{ \(\rho uu\) \} is obtained by combining the above expression with the configurational stress \(\sigma\).
\[
\frac{\partial}{\partial r} \left( \sum_{i=1}^N \left( \frac{\mathbf{p}_i \cdot \mathbf{m}_i}{m_i} \vartheta_i f \right) \right) + \frac{\mathbf{VA}}{\mathcal{K}_T} = \vartheta_s \left( \sum_{i=1}^N \left( \frac{\mathbf{p}_i \cdot \mathbf{m}_i}{m_i} \vartheta_i f \right) \right) = \frac{\mathbf{VA}}{\mathcal{K}_T} + \frac{\mathbf{VA}}{\mathcal{K}_T} - \frac{\mathbf{VA}}{\sigma} = \vartheta_s \left( \sum_{i=1}^N \left( \frac{\mathbf{p}_i \cdot \mathbf{m}_i}{m_i} \vartheta_i f \right) \right) + \frac{\mathbf{VA}}{\mathcal{K}_T}. \quad (43)
\]
In contrast to the work of Cormier et al. [17], the advection term in the above expression is explicitly identified, in order to be compatible with the right hand side of Eq. (22b) and definition of the pressure tensor, \(\Pi\).

3. MOP Pressure Tensor

The stress in the CV can also be related to the tractions over each surface. In analogy to prior use of the molecular \(\mathcal{LCV}\) function, \(\vartheta_s\), to evaluate the flux, the stress \(\mathcal{LCV}\) function, \(\vartheta_s\), can be differentiated to give the tractions over each surface. These surface tractions are the ones used in the formal definition of the continuum Cauchy stress tensor. The surface traction (i.e., force per unit area) and the kinetic pressure on a surface combined give the MOP expression for the pressure tensor [13].
In the context of the CV, the forces and fluxes on the six bounding surfaces are required to obtain the pressure inside the CV. It is herein shown that each face takes the form of the Han and Lee [14] localization of the MOP pressure components. The divergence theorem is used to express the left hand side of Eq. (38) in terms of stress across the six faces of the cube. The mesoscopic right hand side of Eq. (38) can also be expressed as surface stresses by starting with the LCV function $\vartheta_s$,

$$\sum_{\text{faces}} \int_{S_f} \sigma \cdot dS_f = - \frac{1}{2} \sum_{i,j} N \left\langle f_{ij} \left[ \text{sgn}(x^+ - x_j) \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \r
vector is the sum of all forces acting over the surface,
\[ T_x^+ = -\frac{1}{4\Delta x^2} \sum_{i,j} \left\langle f_{ij} [\text{sgn}(x^+ - x_j) - \text{sgn}(x^+ - x_i)] S_{xij}^+ ; f \right\rangle, \]  
which satisfies the definition,
\[ T_x^+ = \sigma \cdot n_x^+, \]
of the Cauchy traction \[ ^{42\text{ }} \]. A similar relationship can be written for both the kinetic and total pressures,
\[ K_x^+ = \kappa \cdot n_x^+, \]
\[ P_x^+ = \Pi \cdot n_x^+, \]
where \( n_x^+ = [\pm 1 \ 0 \ 0]^T \).

The time evolution of the molecular momentum within a CV (Eq. \[ ^{30\text{ }} \]), can be expressed in a similar form to the Navier-Stokes equations of continuum fluid mechanics. Dividing both sides of Eq. \[ ^{30\text{ }} \] by the volume, the following form can be obtained; note that this step requires Eqs. Eq. \[ ^{26\text{ }} \], Eq. \[ ^{45\text{ }} \] and Eq. \[ ^{47\text{ }} \].

\[ \frac{1}{\Delta V} \frac{\partial}{\partial t} \sum_{i=1}^{N} \left\langle \rho_{\alpha i} \dot{\vartheta}_i ; f \right\rangle + \frac{\rho_{\alpha u} u_{\beta}}{\Delta r_{\beta}} = -\frac{K_{\alpha \beta}^+ - K_{\alpha \beta}^-}{\Delta r_{\beta}} + \frac{T_{\alpha \beta}^+ - T_{\alpha \beta}^-}{\Delta r_{\beta}} + \frac{1}{\Delta V} \sum_{i=1}^{N} \left\langle f_{\alpha i \text{vol}} \dot{\vartheta}_i ; f \right\rangle, \]

where index notation has been used (e.g. \( T_x^+ = T_{xx}^+ \)) with the Einstein summation convention.

In the limit of zero volume, each expression would be similar to a term in the differential continuum equations (although the pressure term would be the divergence of a tensor and not the gradient of a scalar field as is common in fluid mechanics). The Cauchy stress tensor, \( \sigma \), is defined in the limit that the cube’s volume tends to zero, so that \( T^+ \) and \( T^- \) are related by an infinitesimal difference. This is used in continuum mechanics to define the unique nine component Cauchy stress tensor, \( d\sigma / dx \equiv \lim_{\Delta x \to 0} [T^+ - T^-] / \Delta x \). This limit is shown in Appendix \[ ^{3\text{ }} \] to yield the Irving and Kirkwood \[ ^{8\text{ }} \] stress in terms of the Taylor expansion in Dirac \( \delta \) functions.

Rather than defining the stress at a point, the tractions can be compared to their continuum counterparts in a fluid mechanics control volume or a solid mechanics finite elements (FE) method. Computational Fluid Dynamics (CFD) is commonly formulated using CV and in discrete simulations, Finite Volume \[ ^{4\text{ }} \]. Surface forces are ideal for coupling schemes between MD and CFD. Building on the pioneering work of O’Connell and Thompson \[ ^{23\text{ }} \], there are many MD to CFD coupling schemes — see the review paper by Mohamed and Mohamad \[ ^{43\text{ }} \]. More recent developments for coupling to fluctuating hydrodynamics are covered in a review by Delgado-Buscacioni \[ ^{43\text{ }} \]. A discussion of coupling schemes is outside the scope of this work, however finite volume algorithms have been used extensively in coupling methods \[ ^{31\text{–}44\text{–}47\text{}} \] together with equivalent control volumes defined in the molecular region. An advantage of the herein proposed molecular CV approach is that it ensures conservation laws are satisfied when exchanging fluxes over cell surfaces — an important requirement for accurate unsteady coupled simulations as outlined in the finite volume coupling of Delgado-Buscacioni and Coveney \[ ^{45\text{}} \]. For solid coupling schemes, \[ ^{30\text{}} \], the principle of virtual work can be used with tractions on the element corners (the MD CV) to give the state of stress in the element \[ ^{48\text{}} \].

\[ \int_V \sigma \cdot \nabla N_a dV = \int_S N_a T dS, \]

where \( N_a \) is a linear shape function which allows stress to be defined as a continuous function of position. It will be demonstrated numerically in the next section, \[ ^{14\text{}} \] that the CV formulation is exactly conservative; the surface tractions and fluxes entirely define the stress within the volume. The tractions and stress in Eq. \[ ^{50\text{}} \] are connected by the weak formulation and the form of the stress tensor results from the choice of shape function \( N_a \).

\[ \int_{\Omega} \sigma_{ij} \cdot \epsilon_{ij} d\Omega = \int_{\partial \Omega} T_i dS_i, \]

\[ \int_{\Omega} \sigma_{ij} \cdot \epsilon_{ij} d\Omega = \int_{\partial \Omega} T_i dS_i. \]

where \( \Delta V \) is the finite volume. The principle of virtual work can be used with tractions on the element corners (the MD CV) to give the state of stress in the element \[ ^{48\text{}} \]. For solid coupling schemes, \[ ^{30\text{}} \], the principle of virtual work can be used with tractions on the element corners (the MD CV) to give the state of stress in the element \[ ^{48\text{}} \].
The right hand side of this equation is equated to the right hand side of the continuum energy Eq. \([43]\):

\[
\begin{align*}
\text{energy flux} & \quad - \int_S \rho \mathbf{e} \cdot d\mathbf{S} - \int_S \mathbf{q} \cdot d\mathbf{S} - \int_S \mathbf{f} \cdot d\mathbf{S} = - \sum_{i=1}^{N} \left( e_i \mathbf{p}_i / m_i \right) \cdot d\mathbf{S}_i \quad \text{(53)}
\end{align*}
\]

where the energy due to the external (body) forces is neglected. The \(f_{ij}\) force has been re-expressed in terms of surface tractions, \(s_{ij} \cdot d\mathbf{S}_{ij}\), using the analysis of the previous section. In its current form, the microscopic equation does not delineate the contribution due to energy flux, heat flux and pressure heating. To achieve this division, the notion of the peculiar momentum at the molecular location, \(\mathbf{u}(\mathbf{r}_i)\) is used together with the velocity at the CV surfaces \(\mathbf{u}(\mathbf{r}^\pm)\), following a similar process to Evans and Morriss \([7]\).

IV. IMPLEMENTATION

In this section, the CV equation for mass, momentum and energy balance, Eqs. \((32), \(40)\) and \((53)\), will be proved to apply and demonstrated numerically for a microscopic system undergoing a single trajectory through phase space.

A. The Microscopic System

Consider a single trajectory of a set of molecules through phase space, defined in terms of their time dependent coordinates \(\mathbf{r}_i\) and momentum \(\mathbf{p}_i\). The LC\(\mathcal{V}\) function depends on molecular coordinates, the location of the center of the cube, \(\mathbf{r}\), and its side length, \(\Delta \mathbf{r}\), i.e., \(\vartheta_i = \vartheta_i(\mathbf{r}_i(t), \mathbf{r}, \Delta \mathbf{r})\). The time evolution of the mass within the molecular control volume is given by,

\[
\frac{d}{dt} \sum_{i=1}^{N} m_i \vartheta_i = \sum_{i=1}^{N} m_i \frac{\partial \vartheta_i}{\partial t} = \sum_{i=1}^{N} m_i \mathbf{p}_i \cdot d\mathbf{S}_i, \quad \text{(54)}
\]

using, \(\mathbf{p}_i = m_i \mathbf{d}r_i / dt\). The time evolution of momentum in the molecular control volume is,

\[
\frac{\partial}{\partial t} \sum_{i=1}^{N} \mathbf{p}_i = \sum_{i=1}^{N} \mathbf{p}_i \vartheta_i = \sum_{i=1}^{N} \mathbf{p}_i \cdot d\mathbf{S}_i = \sum_{i=1}^{N} \mathbf{p}_i \cdot d\mathbf{S}_i, \quad \text{as } \mathbf{d}p_i / dt = \mathbf{F}_i.
\]

As, \(\mathbf{d}p_i / dt = \mathbf{F}_i\), then,

\[
\frac{\partial}{\partial t} \sum_{i=1}^{N} \mathbf{p}_i = \sum_{i=1}^{N} \left[ \mathbf{p}_i \cdot d\mathbf{S}_i + \mathbf{F}_i \vartheta_i \right] = - \sum_{i=1}^{N} \mathbf{p}_i \cdot d\mathbf{S}_i + \sum_{i=1}^{N} \frac{\mathbf{p}_i \mathbf{p}_i}{m_i} \cdot d\mathbf{S}_i + \sum_{i=1}^{N} \mathbf{f}_i \vartheta_i, \quad \text{(55)}
\]

where the total force on molecule \(i\) has been decomposed into surface and ‘external’ or body terms. The time evolution of energy in a molecular control volume is obtained by evaluating,

\[
\frac{\partial}{\partial t} \sum_{i=1}^{N} e_i \vartheta_i = \sum_{i=1}^{N} e_i \frac{\partial \vartheta_i}{\partial t} = \sum_{i=1}^{N} e_i \vartheta_i \cdot d\mathbf{S}_i + \sum_{i=1}^{N} \frac{\mathbf{p}_i \mathbf{p}_i}{m_i} \vartheta_i + \sum_{i=1}^{N} \mathbf{f}_i \vartheta_i, \quad \text{(55)}
\]

The right hand side of this equation is equated to the right hand side of the continuum energy Eq. \([43]\).

\[
\begin{align*}
\text{energy flux} & \quad - \int_S \rho \mathbf{e} \cdot d\mathbf{S} - \int_S \mathbf{q} \cdot d\mathbf{S} - \int_S \mathbf{f} \cdot d\mathbf{S} = - \sum_{i=1}^{N} \left( e_i \mathbf{p}_i / m_i \right) \cdot d\mathbf{S}_i \quad \text{(53)}
\end{align*}
\]

The average of many such trajectories defined through Eqs. \((54), \(55)\) and \((56)\) over the time interval \([0, \tau]\) enables these equations to be usable in a molecular simulation. For the conservation of mass term,

\[
\sum_{i=1}^{N} m_i \left[ \vartheta_i(\tau) - \vartheta_i(0) \right] = - \int_{0}^{\tau} \sum_{i=1}^{N} \mathbf{p}_i \cdot d\mathbf{S}_i dt, \quad \text{(57)}
\]

The surface crossing term, \(d\mathbf{S}_i\), defined in Eq. \([16]\), involves a Dirac \(\delta\) function and therefore cannot be evaluated directly. Over the time interval \([0, \tau]\), molecule \(i\) passes through a given point \(x\) position at times, \(t_{x_i,k}\), where \(k = 1, 2, ..., N_{tg}\) \([49]\). The positional Dirac \(\delta\) can be expressed as,

\[
\delta(x_i(t) - x) = \sum_{k=1}^{N_{tg}} \delta(t - t_{x_i,k}) / |x_i(t_{x_i,k})|, \quad \text{(58)}
\]

where \(|x_i(t_{x_i,k})|\) is the magnitude of the velocity in the \(x\) direction at time \(t_{x_i,k}\). Equation Eq. \((58)\) is used to rewrite \(d\mathbf{S}_i\) in Eq. \((57)\) in the form,

\[
\begin{align*}
d\mathbf{S}_{a_i,k} &= \left[ \text{sgn}(t_{a_i,k}^+ - \tau) - \text{sgn}(t_{a_i,k}^- - \tau) \right] S_{a_i,k}^+(t_{a_i,k}^+) - \left[ \text{sgn}(t_{a_i,k}^- - \tau) - \text{sgn}(t_{a_i,k}^+ - \tau) \right] S_{a_i,k}^-(t_{a_i,k}^-), \quad \text{(59)}
\end{align*}
\]

where \(\alpha = \{x, y, z\}\), and the fluxes are evaluated at times, \(t_{a_i,k}^+\) and \(t_{a_i,k}^-\) for the right and left surfaces of the cube, respectively. Using the above expression, the time integral in Eq. \((57)\) can be expressed as the sum of all molecule cross-
ings, \( N_t = N_{tx} + N_{ty} + N_{tz} \) over the cube’s faces,
\[
\sum_{i=1}^{N} \frac{m_i}{\alpha|\alpha|} [\partial_i(\tau) - \partial_i(0)] = -\sum_{i=1}^{N} \sum_{k=1}^{N} \frac{m_i}{\alpha|\alpha|} \frac{P_{\alpha \alpha}}{P_{\alpha \alpha}} dS_{\alpha i,k}.
\]
(Advection)
\[
\sum_{i=1}^{N} \frac{m_i}{\alpha|\alpha|} [\partial_i(\tau) - \partial_i(0)] = -\sum_{i=1}^{N} \sum_{k=1}^{N} \frac{m_i}{\alpha|\alpha|} \frac{P_{\alpha \alpha}}{P_{\alpha \alpha}} dS_{\alpha i,k}.
\]
(60)

In other words, the mass in a CV at time \( t = \tau \) minus its initial value at \( t = 0 \) is the sum of all molecules that cross its surfaces during the time interval.

The momentum balance equation Eq. (55), can also be written in time-integrated form,
\[
\sum_{i=1}^{N} \frac{m_i}{\alpha|\alpha|} [\partial_i(\tau) - \partial_i(0)] = -\int_0^\tau \sum_{i=1}^{N} \frac{m_i}{\alpha|\alpha|} \frac{P_{\alpha \alpha}}{P_{\alpha \alpha}} dS_i - \frac{1}{2} \sum_{i,j} f_{ij} \partial_{ij} - \sum_{i=1}^{N} f_{\text{ext}} \partial_i dt,
\]
and using identity (59),
\[
\sum_{i=1}^{N} \frac{m_i}{\alpha|\alpha|} [\partial_i(\tau) - \partial_i(0)] = \sum_{i,j} \int_0^\tau f_{ij}(t) dt + \sum_{i=1}^{N} f_{\text{ext}} \partial_i dt.
\]
(61)

The integral of the forcing term can be rewritten as the sum,
\[
\int_0^\tau f_{ij}(t) dt \approx \Delta t \sum_{n=1}^{N_T} f_{ij} (t_n) \partial_{ij} (t_n),
\]
where \( N_T \) is the number time steps. Equation (61) can be rearranged as follows,
\[
\sum_{i=1}^{N} \frac{m_i}{\alpha|\alpha|} [\partial_i(\tau) - \partial_i(0)] = -\sum_{i=1}^{N} \sum_{k=1}^{N} \frac{m_i}{\alpha|\alpha|} \frac{P_{\alpha \alpha}}{P_{\alpha \alpha}} dS_{\alpha i,k}.
\]
(Advection)
\[
\sum_{i=1}^{N} \frac{m_i}{\alpha|\alpha|} [\partial_i(\tau) - \partial_i(0)] = \sum_{i,j} \int_0^\tau f_{ij}(t) dt + \sum_{i=1}^{N} f_{\text{ext}} \partial_i dt.
\]
(61)

The integral of the forcing term can be approximated by the sum,
\[
\int_0^\tau f_{ij}(t) dt \approx \Delta t \sum_{n=1}^{N_T} f_{ij} (t_n) \partial_{ij} (t_n),
\]
where \( N_T \) is the number of time steps.

In the next section, the elements, Accumulation, Advection and Forcing in the above equations are computed individually in an MD simulation to confirm Eqs. (62), (63) and (64) numerically.

C. Results and Discussion

Molecular Dynamics (MD) simulations in 3D are used in this section to validate numerically, and explore the statistical convergence of, the CV formalism for three test cases. The first investigation was to confirm numerically the conservation properties of an arbitrary control volume. The second simulation compares the value of the scalar pressure obtained from the molecular CV formulation with that of the virial expression for an equilibrium system in a periodic domain. The final test is a Non Equilibrium Molecular Dynamics (NEMD) simulation of the start-up of Couette flow initiated by translating the top wall in a slit channel geometry. The NEMD system is analyzed using the CV expressions Eqs. (60), (61) and (64), and the shear pressure was
computed by the VA and CV routes. Newton’s equations of motion were integrated using the half-step leap-frog Verlet algorithm. \[50\]. The repulsive Lennard-Jones (LJ) or Weeks-Chandler-Anderson (WCA) potential \[51\].

\[
\Phi(r_{ij}) = 4\epsilon \left( \frac{\ell}{r_{ij}} \right)^{12} - \left( \frac{\ell}{r_{ij}} \right)^{6} + \epsilon, \quad r_{ij} \leq r_c, \quad (65)
\]

was used for the molecular interactions, which is the Lennard-Jones potential shifted upwards by \(\epsilon\) and truncated at the minimum in the potential, \(r_{ij} = r_c \equiv 2^{1/6}\ell\). The potential is zero for \(r_{ij} > r_c\). The energy scale is set by \(\epsilon\), the length scale by \(\ell\) and molecular mass by \(m\). The results reported here are given in terms of \(\ell, \epsilon\) and \(m\). A timestep of 0.005 was used for all simulations. The domain size in the first two simulations was 13.68, which contained \(N = 2048\) molecules, the density was \(\rho = 0.8\) and the reduced temperature was set to an initial value of \(T = 1.0\). Test cases 1 and 2 described below are for equilibrium systems, and therefore did not require thermostatting. Case 3 is for a non-equilibrium system and required removal of generated heat, which was achieved by thermostatting the wall atoms only.

1. Case 1

In case 1, the periodic domain simulates a constant energy ensemble. The separate terms of the integrated mass, momentum and energy equations given in \[40, 61\] and \[64\] were evaluated numerically for several sizes of CV. The mass conservation can readily be shown to be satisfied as it simply requires tracking the number of molecules in the CV. The momentum and energy balance equations are conveniently checked for compliance at all times by evaluating the residual quantity,

\[
\text{Residual} = \text{Accumulation} - \text{Forcing} + \text{Advection}, \quad (66)
\]

which must be equal to zero at all times for the CV equations to be satisfied. This was demonstrated to be the case, as may be seen in Figs. 5(a) and 5(b) for a cubic CV of side length 1.52 in the absence of body forces. The evolution of momentum inside the CV is shown numerically to be exactly equal to the integral of the surface forces until a molecule crosses the CV boundary. Such events give rise to a momentum flux which must be equal to zero at all times for the CV equations to be satisfied. This was demonstrated to be the case, as may be seen in Figs. 5(a) and 5(b) for a cubic CV of side length 1.52 in the absence of body forces. The evolution of momentum inside the CV is shown numerically to be exactly equal to the integral of the surface forces until a molecule crosses the CV boundary. Such events give rise to a momentum flux which must be equal to zero at all times for the CV equations to be satisfied.
in Fig. 6 to converge towards the same value with increasing time. The simulation is started from an FCC lattice with a short range potential (WCA) so the initial configurational stress is zero. It is the evolution of the pressure from this initial state that is compared in Fig. 6. The virial kinetic pressure makes use of the instantaneous values of the domain molecule’s velocities at every time step. In contrast, the CV kinetic part of the pressure is due to molecular surface crossings only, which may explain its slower convergence to the limiting value than the kinetic part of the virial expression. To quantify this difference in convergence for the two measures of the pressure, the standard deviation, SD, is evaluated, ensuring decorrelation [47] using block averaging [51]. For the kinetic virial, SD(\(\sigma_{vir}\)) = 0.0056, and configurational, SD(\(\sigma_{vir}\)) = 0.0619. For the kinetic CV pressure SD(\(\kappa_{CV}\)) = 0.4549 and configurational SD(\(\kappa_{CV}\)) = 0.2901. The CV pressure, which makes use of the MOP formula, would therefore require more samples to converge to a steady state value. However, the MOP pressures are generally more efficient to calculate than the VA. More usefully, from an evaluation of only the interactions over the outer CV surface, the pressure in a volume of arbitrary size can be determined.

Figure 7 is a log-log plot of the Percentage Discrepancy (PD) between the two (\(PD = \frac{\delta(100\times|\Pi_{CV} - \Pi_{vir}|/\Pi_{vir})}{\Pi_{vir}}\)). After 10 million timesteps or a reduced time of \(\frac{5 \times 10^5}{t}\), the percentage discrepancy in the configurational part has decreased to 0.01%, and the kinetic part of the pressure matches the virial (and kinetic theory) to within 0.1%. The total pressure value agrees to within 0.1% at the end of this averaging period. The simulation average temperature was 65 K, and the kinetic part of the CV pressure was statistically the same as the kinetic theory formula prediction, \(\kappa_{CV} = \frac{1}{2}k_BT = 0.52\) [51]. The VA formula for the pressure in a volume the size of the domain is by definition formally the same as that of the virial pressure. The next test case compares the CV and VA formulas for the shear stress in a system out of equilibrium.

3. Case 3

In this simulation study, Couette flow was simulated by entraining a model liquid between two solid walls. The top wall was set in translational motion parallel to the bottom (stationary) wall and the evolution of the velocity profile towards the steady-state Couette flow limit was followed. The velocity profile, and the derived CV and VA shear stresses are compared with the analytical solution of the unsteady diffusion equation. Four layers of tethered molecules were used to represent each wall, with the top wall given a sliding velocity of, \(U_0 = 1.0\) at the start of the simulation, time \(t = 0\). The temperature of both walls was controlled by applying the Nosé-Hoover (NH) thermostat to the wall atoms [52]. The two walls were thermostatted separately, and the equations of motion of the wall atoms were,

\[
\dot{r}_i = \frac{\vec{p}_i}{m_i} + U_0 n_x^+ , \tag{69a}
\]

\[
\dot{\vec{p}}_i = F_i + r_{ext} - \xi \vec{p}_i , \tag{69b}
\]

\[
r_{ext} = r_{i0} \left( 4k_4 r_{i0}^2 + 6k_6 r_{i0}^4 \right) , \tag{69c}
\]

\[
\xi = \frac{1}{Q_\xi} \sum_{n=1}^{N} \left[ \frac{\vec{p}_n \cdot \vec{p}_n}{m_n} - 3T_0 \right] , \tag{69d}
\]

where \(n_x^+\) is a unit vector in the \(x\)-direction, \(m_n \equiv m\), and \(r_{ext}\) is the tethered atom force, using the formula of Petravic and Harrowell [53] \((k_4 = 5 \times 10^2, k_6 = 5 \times 10^6)\). The vector, \(r_{i0} = r_i - r_0\), is the displacement of the tethered atom, \(i\), from its lattice site coordinate, \(r_0\). The Nosé-Hoover thermostat dynamical variable is denoted by \(\xi\), \(T_0 = 1.0\) is the target temperature of the wall, and the effective time constant or damping coefficient, in Eq. (69c), was given the value, \(Q_\xi = N \Delta t\). The simulation was carried out for a cubic domain of sidelength 27.40, of which the fluid region extent was 20.52 in the \(y\)-direction. Periodic boundaries were used.
in the streamwise ($x$) and spanwise ($z$) directions. The results presented are the average of eight simulation trajectories starting with a different set of initial atom velocities. The lattice contained 16384 molecules and was at a density of $\rho = 0.8$. The molecular simulation domain was sub-divided into 4096 (16$^3$) control volumes, and the average velocity and shear stress was determined in each of them. A larger single CV encompassing all of the liquid region of the domain, shown bounded by the thick line in Fig. 8 was also considered.

The continuum solution for this configuration is considered now. Between two plates, there are no body forces and the flow eventually becomes fully developed, so that Eq. (2) can be simplified and after applying the divergence theorem from Eq. (5) it becomes,

$$ \frac{\partial}{\partial t} \int_V \rho u dV = - \int_V \nabla \cdot \Pi dV, $$


which is valid for any arbitrary volume in the domain and must be valid at any point for a continuum. The shear pressure in the fluid, $\Pi_{xy}(y)$, drives the time evolution,

$$ \frac{\partial \rho u_x}{\partial t} = - \frac{\partial \Pi_{xy}}{\partial y}. $$

For a Newtonian liquid with viscosity, $\mu$, Eq. (54),

$$ \Pi_{xy} = - \mu \frac{\partial u_x}{\partial y}, $$


(70)

this gives the 1D diffusion equation,

$$ \frac{\partial u_x}{\partial t} = \frac{\mu}{\rho} \frac{\partial^2 u_x}{\partial y^2}, $$


(71)

assuming the liquid to be incompressible. This can be solved for the boundary conditions,

$$ u_x(0,t) = 0 \quad u_x(L,t) = U_0 \quad u_x(y,0) = 0, $$

where the bottom and top wall-liquid boundaries are at $y = 0$ and $y = L$, respectively. The Fourier series solution of these equations with inhomogeneous boundary conditions is,

$$ u_x(y,t) = \begin{cases} 
U_0 \sum_{n=1}^{\infty} u_n(t) \sin \left( \frac{n\pi y}{L} \right) & 0 < y < L \\
0 & y = 0
\end{cases} $$


(72)

where $\lambda_n = (n\pi/L)^2$ and $u_n(t)$ is given by,

$$ u_n(t) = \frac{2U_0(-1)^n}{n\pi} \left[ \exp \left( - \frac{\lambda_n \mu t}{\rho} \right) - 1 \right]. $$

The velocity profile resolved at the control volume level is compared with the continuum solution in Fig. 9. There were 16 cubic NEMD CV of side length 1.72 spanning the system in the $y$ direction, with each data point on the figure being derived from a local time average of 0.5 time units. The analytic continuum solution was evaluated numerically from Eq. (72) with $n = 1000$ and $\mu = 1.6$, the latter a literature value for the WCA fluid shear viscosity at $\rho = 0.8$ and $T = 1.0$, 55]. There is mostly very good agreement between the analytic and NEMD velocity profiles at all times, although some effect of the stacking of molecules near the two walls can be seen in a slight blunting of the fluid velocity profile very close to the tethered walls (located by the horizontal two squares on the far left and right of the figure) which is an aspect of the molecular system that the continuum treatment is not capable of reproducing.

The VA and CV shear pressure, given by Eqs. (43) and (45), are compared at time $t = 10$ in Fig. 10. The comparison is for a single simulation trajectory resolved into 16 cubic volumes of size 1.72 in the $y$–direction, with averaging in the $x$ and $z$ directions and over 0.5 in reduced time. The figure shows the shear pressure on the faces of the
shows that there
to confirm Eq. (74) numerically. The time evolution of
\( \lambda \), is written as,
which is valid for the entire domain
CV. Inside the CV, the pressure was assumed to vary linearly,
and the value at the midpoint is shown to be comparable
that the three methods exhibit good agreement within the
CV . Inside the CV , the pressure was assumed to vary linearly,
but a linear pressure relationship is assumed for CV to obtain
the pressure tensor value corresponding to the center of the CV.

The continuum analytical \( xy \) pressure tensor component can be derived analytically using the same Fourier series
approach for \( \partial u_x/\partial y \), [55].
\[
\Pi_{xy}(y,t) = -\frac{\mu U_0}{L} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-\frac{\lambda n y}{L}} \cos \left( \frac{n \pi y}{L} \right) \right],
\]
which is valid for the entire domain \( 0 \leq y \leq L \).

A statistically meaningful comparison between the CV,
VA and continuum analytic shear pressure profiles requires more averaging of the simulation data than for the streaming
velocity. [57], and eight independent simulation trajectories over 5 reduced
time units were used. Figure 11 shows that the three methods exhibit good agreement within the
simulation statistical uncertainty.

As a final demonstration of the use of the CV equations,
the control volume is now chosen to encompass the entire
liquid domain (see Fig. 8), and therefore the external forces
arise from interactions with the wall atoms only. The
momentum equation, Eq. (55), is written as,
\[
\frac{\partial}{\partial t} \sum_{i=1}^{N} \mathbf{p}_i \mathbf{v}_i = - \frac{1}{N} \sum_{i=1}^{N} \mathbf{f}_i \mathbf{v}_i + \sum_{i=1}^{N} \mathbf{f}_{ext} \mathbf{v}_i,
\]
which can be simplified as follows. For term, \( 1 \) in the
above equation, the fluxes across the CV boundaries in the
streamwise and spanwise directions cancel due to the periodic
boundary conditions. Fluxes across the \( xz \) boundary
surface are zero as the tethered wall atoms prevent such crossings.
The force term, \( 2 \), also vanishes because across the
periodic boundary, \( \mathbf{f}_{ij} dS_{xij}^+ = -\mathbf{f}_{ij} dS_{xij}^- \) (similarly for \( z \)).
The external force term, \( 3 \), is zero because all the forces
in the system result from interatomic interactions. The sum of the \( \mathbf{f}_{ij} \) force components across the horizontal boundaries
will be equal and opposite, and by symmetry the two \( f_{xij} \) terms in \( 4 \) will be zero on average. The above equation
therefore reduces to,
\[
\frac{\partial}{\partial t} \sum_{i=1}^{N} \mathbf{p}_i \mathbf{v}_i = - \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \left[ \mathbf{f}_{xij} dS_{yij}^+ - \mathbf{f}_{xij} dS_{yij}^- \right].
\]
As the simulation approaches steady state, the rate of change of momentum in the control volume tends to zero because
the difference between the shear stresses acting across the
top and bottom walls vanishes. The forces on the \( xz \) plane boundary and momentum inside the CV are plotted in Fig.
12 to confirm Eq. (74) numerically. The time evolution of
these molecular momenta and surface stresses are compared.
FIG. 12. The evolution of surface forces and momentum change for a molecular CV from Eq. (74), (points) and analytical solution for the continuum (Eqs. (77), (78) and (76), presented as lines on the figure. The Residual, defined in Eq. (66), is also given. Each point represents the average over an ensemble of eight independent systems and 40 timesteps.

to the analytical continuum solution for the CV,

$$\frac{\partial}{\partial t} \int_V \rho u_x dV = - \left[ \int_{S_f^+} \Pi_{xy} dS_f^+ - \int_{S_f^-} \Pi_{xy} dS_f^- \right].$$

(75)

The normal components of the pressure tensor are non-zero in the continuum, but exactly balance across opposite CV faces, i.e. $\Pi_{xx}^+ = \Pi_{xx}^-$. By appropriate choice of the gauge pressure, $\Pi_{xx}$ does not appear in the governing Eq. (75). The left hand side of the above equation is evaluated from the analytic expression for $u_x$,

$$\frac{\partial}{\partial t} \int_V \rho u_x dV = 2 \Delta x \Delta z \frac{\mu U_0}{L} \sum_{n=1}^{\infty} \left[ 1 - (-1)^n \right] e^{-\frac{n \lambda \mu t}{\rho}}.$$

(76)

The right hand side is obtained from the analytic continuum expression for the shear stress, for the bottom surface at $y = 0$,

$$\int_{S_f^+} \Pi_{xy} dS_f^+ = -2 \Delta x \Delta z \frac{\mu U_0}{L} \sum_{n=1}^{\infty} e^{-\frac{n \lambda \mu t}{\rho}},$$

(77)

and for the top $y = L$,

$$\int_{S_f^-} \Pi_{xy} dS_f^- = -2 \Delta x \Delta z \frac{\mu U_0}{L} \sum_{n=1}^{\infty} (-1)^n e^{-\frac{n \lambda \mu t}{\rho}}.$$

(78)

In Fig 12, the momentum evolution on the left hand side of Eq. (74) is compared to Eq. (76). Equations (77) and (78) are also given for the shear stresses acting across the top and bottom of the molecular control volume (right hand side of Eq. (74)). The scatter seen in the MD data reflects the thermal fluctuations in the forces and molecular crossings of the CV boundaries. The average response nevertheless agrees well with the analytic solution, bearing in mind the element of uncertainty in the matching state parameter values. This example demonstrates the potential of the CV approach applied on the molecular scale, as it can be seen that computation of the forces across the CV boundaries determines completely the average molecular microhydrodynamic response of the system contained in the CV. In fact, the force on only one of the surfaces is all that was required, as the force terms for the opposite surface could have been obtained from Eq. (74).

V. CONCLUSIONS

In analogy to continuum fluid mechanics, the evolution equations for a molecular systems has been expressed within a Control Volume (CV) in terms of fluxes and stresses across the surfaces. A key ingredient is the definition and manipulation of a Lagrangian to Control Volume conversion function, $\vartheta$, which identifies molecules within the CV. The final appearance of the equations has the same form as Reynolds’ Transport Theorem applied to a discrete system. The equations presented follow directly from Newton’s equation of motion for a system of discrete particles, requiring no additional assumptions and therefore sharing the same range of validity.

Using the $\mathcal{L}CV$ function, the relationship between Volume Average (VA) [16, 17] and Method Of Planes (MOP) pressure [13, 14] has been established, without Fourier transformation. The two definitions of pressure are shown numerically to give equivalent results away from equilibrium and, for homogeneous systems, shown to equal the virial pressure.

A Navier–Stokes-like equation was derived for the evolution of momentum within the control volume, expressed in terms of surface fluxes and stresses. This provides an exact mathematical relationship between molecular fluxes/pressures and the evolution of momentum and energy in a CV. Numerical evaluations of the terms in the conservation of mass, momentum and energy equations demonstrated consistency with theoretical predictions.

The CV formulation is general, and can be applied to derive conservation equations for any fluid dynamical property localised to a region in space. It can also facilitate the derivation of conservative numerical schemes for MD, and the evaluation of the accuracy of numerical schemes. Finally, it allows for accurate evaluation of macroscopic flow properties, in a manner consistent with the continuum conservation laws.

Appendix A: Discrete form of Reynolds’ Transport Theorem and the Divergence Theorem

In this appendix, both Reynolds’ Transport Theorem and the Divergence Theorem for a discrete system are derived. The relationship between an advecting and fixed control volume is shown using the concept of peculiar momentum.

The microscopic form of the continuous Reynolds’ Transport Theorem \cite{4} is derived for a property $\chi = \chi(\mathbf{r}, \mathbf{p}, t)$ which could be mass, momentum or the pressure tensor. The $\mathcal{L}CV$ function, $\vartheta_i$, is dependent on the molecule’s coordinate; the location of the cube center, $\mathbf{r}$, and side length, $\Delta \mathbf{r}$, which are all a function of time. The time evolution of the CV is
The velocity of the moving volume is defined as \( \mathbf{u} = \frac{d\mathbf{r}}{dt} \), which can be different to the macroscopic velocity \( \mathbf{u} \). Surface translation or deformation of the cube, \( \partial \mathbf{u}/\partial \mathbf{r} \), can be included in the expression for velocity \( \mathbf{u} \). The above analysis is for a microscopic system, although a similar process for a mesoscopic system can be applied and includes terms for CV movement in Eq. (12).

Hence Reynolds treatment of a continuous medium is extended here to a discrete molecular system,

\[
\frac{d}{dt} \sum_{i=1}^{N} \chi(t) v_i(t) \mathbf{r}_i(t), \Delta \mathbf{r}(t) = \sum_{i=1}^{N} \left[ \frac{d\chi}{dt} \mathbf{v}_i + \chi \left( \mathbf{u}_m - \mathbf{p}_i \right) \cdot dS_i \right].
\]

(A1)

The conservation equation for the mass, \( \chi = m_i \), in a moving reference frame is,

\[
\frac{d}{dt} \sum_{i=1}^{N} m_i \mathbf{v}_i = \sum_{i=1}^{N} \left[ m_i \left( \mathbf{u}_m - \mathbf{p}_i \right) \cdot dS_i \right].
\]

(A2)

In a Lagrangian reference frame, the translational velocity of CV surface must be equal to the molecular streaming velocity, \( i.e., \mathbf{u}(r^+) = \mathbf{u}(r_1) \), so that,

\[
\sum_{i=1}^{N} \left[ m_i \left( \mathbf{u} - \frac{\mathbf{p}_i}{m_i} \right) \cdot dS_i \right] = - \sum_{i=1}^{N} \mathbf{F}_i \cdot dS_i.
\]

The evolution of the peculiar momentum, \( \chi = \mathbf{p}_i \), in a moving reference frame is,

\[
\frac{d}{dt} \sum_{i=1}^{N} \mathbf{p}_i \mathbf{v}_i = \sum_{i=1}^{N} \left[ \mathbf{F}_i \mathbf{v}_i + \mathbf{p}_i \left( \mathbf{u} - \frac{\mathbf{p}_i}{m_i} \right) \cdot dS_i \right] = \sum_{i=1}^{N} \left[ \mathbf{F}_i \mathbf{v}_i + \mathbf{p}_i \mathbf{F}_i \cdot dS_i \right].
\]

Here an inertial reference frame has been assumed so that \( \partial \mathbf{p}_i/dt = \partial \mathbf{p}_i/dt = \mathbf{F}_i \). For a simple case (e.g. one dimensional flow) it is possible to utilize a Lagrangian description by ensuring, \( \mathbf{u}(r^+) = \mathbf{u}(r_1) \), throughout the time evolution. In more complicated cases, this is not always possible and the Eulerian description is generally adopted.

Next, a microscopic analogue to the macroscopic divergence theorem is derived for the generalized function, \( \chi \),

\[
\int_V \sum_{i=1}^{N} \frac{\partial}{\partial \mathbf{r}} \left[ \chi(\mathbf{r}, \mathbf{p}_i, t) \delta(\mathbf{r}_i - \mathbf{r}) \right] dV = \int_V \sum_{i=1}^{N} \chi(\mathbf{r}_i, \mathbf{p}_i, t) \cdot \frac{\partial}{\partial \mathbf{r}} \delta(\mathbf{r}_i - \mathbf{r}) dV.
\]

The vector derivative of the Dirac \( \delta \) followed by the integral over volume results in,

\[
\int_V \frac{\partial}{\partial \mathbf{r}} (x_i - x) \delta(y_i - y) \delta(z_i - z) dV = \left[ \frac{\partial}{\partial x} H(y_i - y) H(z_i - z) \right]_V \left[ \frac{\partial}{\partial x} H(y_i - y) H(z_i - z) \right]_V = \left[ \frac{\partial}{\partial x} (y_i - y) \delta(y_i - y) \delta(z_i - z) \right]_V = \left[ \frac{\partial}{\partial x} (z_i - z) \delta(z_i - z) \right]_V = dS_i,
\]

where the limits of the cuboidal volume are \( r^+ = r + \Delta r \) and \( r^- = r^- \Delta r \). The mesoscopic equivalent of the continuum divergence theorem (Eq. (3)) is therefore,

\[
\int_V \frac{\partial}{\partial \mathbf{r}} \sum_{i=1}^{N} \chi(\mathbf{r}_i - \mathbf{r}) dV = \sum_{i=1}^{N} \chi \cdot dS_i.
\]

**Appendix B: Relation between Control Volume and Description at a Point**

This Appendix proves that the Irving and Kirkwood expression for the flux at a point is the zero volume limit of the CV formulation. As in the continuum, the control volume equations at a point are obtained using the gradient operator in Eq. (6), the flux at a point can be shown by taking the zero volume limit of the gradient operator of Eq. (6). Assuming the three side lengths of the control volume, \( \Delta x, \Delta y, \Delta z \), tend to zero and hence the evaluation, \( \Delta V \), tends to zero,

\[
\nabla \cdot \rho \mathbf{u} = \lim_{\Delta x \rightarrow 0} \lim_{\Delta y \rightarrow 0} \lim_{\Delta z \rightarrow 0} \frac{1}{\Delta x \Delta y \Delta z} \times \sum_{i=1}^{N} \left( \rho_i \frac{\partial \mathbf{v}_i}{\partial x} + \rho_i \frac{\partial \mathbf{v}_i}{\partial y} + \rho_i \frac{\partial \mathbf{v}_i}{\partial z} \mathbf{f} \right).
\]

(B1)

from Eq. (21). For illustration, consider the \( x \) component above, where

\[
\frac{\partial \mathbf{v}_i}{\partial x} = \left[ \delta(x^+ - x) - \delta(x^- - x) \right] S_{xi}.
\]

(B2)

Using the definition of the Dirac \( \delta \) function as the limit of two slightly displaced Heaviside functions,

\[
\delta(\xi) = \lim_{\Delta \xi \rightarrow 0} \frac{H(\xi + \Delta \xi) - H(\xi - \Delta \xi)}{2 \Delta \xi},
\]

the limit of the \( S_{xi} \) term is,

\[
\lim_{\Delta y \rightarrow 0, \Delta \xi \rightarrow 0} S_{xi} = \delta(y_i - y) \delta(z_i - z).
\]

The \( \Delta x \rightarrow 0 \) limit for \( x_{face} \) (defined in Eq. (12)) can be evaluated using L'Hôpital's rule, combined with the property of the \( \delta \) function,

\[
\frac{\partial}{\partial \Delta \xi} \delta(\xi - \Delta \xi) = \frac{1}{2} \frac{\partial}{\partial \xi} \delta(\xi - \Delta \xi),
\]

so that,

\[
\lim_{\Delta x \rightarrow 0} x_{face} = \frac{\partial}{\partial x} \delta(x - x_i).
\]
Therefore, the limit of $\partial \theta_i / \partial x$ as the volume approaches zero is,
\[
\lim_{\Delta V \to 0} \lim_{0 \to \Delta y} \lim_{0 \to \Delta z} \left. \frac{\partial \theta_i}{\partial x} \right|_0 = \frac{\partial}{\partial x} \delta (r_i - r),
\]
Taking the limits for the $x$, $y$, and $z$ terms in Eq. (31) yields the expected Irving and Kirkwood [3] definition of the divergence at a point,
\[
\nabla \cdot \rho u = \sum_{i=1}^{N} \left( \frac{\partial}{\partial r_i} \cdot p_i \delta (r_i - r)\right) : f.
\]
This zero volume limit of the CV surface fluxes shows that the divergence of a Dirac $\delta$ function represents the flow of molecules over a point in space. The advection and kinetic pressure at a point is, from Eq. (25),
\[
\nabla \cdot [\rho uu + \kappa] = \sum_{i=1}^{N} \left( \frac{\partial}{\partial r_i} \cdot p_i p_i \delta (r_i - r)\right) : f.
\]
The same limit of zero volume for the surface tractions defines the Cauchy stress. Using Eq. (8) and taking the limit of Eq. (49), written in terms of tractions,
\[
\nabla \cdot \sigma = \lim_{\Delta V \to 0} \frac{1}{\Delta V} \sum_{j=1}^{N} \int_{S_f} \sigma \cdot dS_f = \lim_{\Delta x \to 0} \lim_{\Delta y \to 0} \lim_{\Delta z \to 0} \left[ \frac{T_x^+ - T_x^-}{\Delta r_x} + \frac{T_y^+ - T_y^-}{\Delta r_y} + \frac{T_z^+ - T_z^-}{\Delta r_z} \right].
\]
For the $r_x^+$ surface, and taking the limits of $\Delta y$ and $\Delta z$ using L'Hôpital's rule,
\[
\lim_{\Delta V \to 0} \frac{T_x^+}{\Delta r_x} = -\lim_{\Delta r_x \to 0} \frac{1}{2} \sum_{i,j} \sum_{f} \int_{S_f} \sigma_{ij} \frac{\partial \omega_{xyz}}{\partial r} ds : f.
\]
where $\omega$ is
\[
\omega_{\beta \gamma \eta}^+ \equiv \left[ H(r_{\beta}^+ - r_{\beta}^+) - H(r_{\beta}^- - r_{\beta}^-) \right] \times \delta (r_{\kappa} - r_{\kappa}^- - r_{\beta}^+) \frac{r_{\kappa}^- - r_{\beta}^+}{r_{\beta}^- - r_{\beta}^-} + \delta (r_{\gamma} - r_{\gamma}^- - r_{\beta}^+) \frac{r_{\gamma} - r_{\beta}^-}{r_{\beta}^- - r_{\beta}^-}.
\]
The indices $\beta$, $\kappa$, and $\gamma$ can be $x$, $y$ or $z$ and $\dagger$ denotes the top surface (+ superscript), bottom surface (− superscript) or CV center (no superscript). The $\omega$ selecting function includes only the contribution to the stress when the line of interaction between $i$ and $j$ passes through the point $r^1$ in space. The difference between $T_x^+$ and $T_x^-$ tends zero on taking the limit $\Delta r_x \to 0$, so that L'Hôpital's rule can be applied. Using the property,
\[
\frac{\partial}{\partial (\Delta \xi)} \delta (\xi - 1/2 \Delta \xi) H (\xi - 1/2 \Delta \xi) = -\frac{1}{2} \frac{\partial}{\partial \xi} \delta (\xi - 1/2 \Delta \xi) H (\xi - 1/2 \Delta \xi),
\]
then,
\[
\lim_{\Delta V \to 0} \frac{T_x^+ - T_x^-}{\Delta r_x} = -\frac{1}{2} \sum_{i,j} \sum_{f} \int_{S_f} \sigma_{ij} \frac{\partial \omega_{xyz}}{\partial r} ds : f.
\]
where $r^+ \to r$ and $r^- \to r$. The $\omega_{\beta \gamma \eta}$ function is the integral between two molecules introduced in Eq. (57),
\[
\int_0^1 \delta (r - r_i + sr_{ij}) ds = \delta (r - r_i + sr_{ij}) ds : f.
\]
As the choice of shifting direction is arbitrary, use of $r_y$ or $r_z$ in the above treatment would result in $\omega_{xzy}$ and $\omega_{xyz}$, respectively. Therefore, Eq. (35), without the volume integral, can be expressed as,
\[
\frac{1}{2} \sum_{i,j} \sum_{f} \int_{S_f} \sigma_{ij} \frac{\partial \omega_{xyz}}{\partial r} ds : f = \frac{1}{2} \sum_{i,j} \sum_{f} \int_{S_f} \sigma_{ij} \frac{\partial \omega_{xzy}}{\partial r} ds : f.
\]
As Eq. (35) is equivalent to the Irving and Kirkwood [3] stress of Eq. (86), the Irving Kirkwood stress is recovered in the limit that the CV tends to zero volume. This Appendix has proved therefore that in the limit of zero control volume, the molecular CV Eqs. (23) and (49) recover the description at a point in the same limit that the continuum CV Eqs. (1) and (2) tend to the differential continuum equations. This demonstrates that the molecular CV equations presented here are the molecular scale equivalent of the continuum CV equations.

Appendix C: Relationship between Volume Average and Method Of Planes Stress

This Appendix gives further details of the derivation of the Method Of Planes form of stress from the Volume Average form. Starting from Eq. (35) written in terms of the CV function for an integrated volume,
\[
-\sum_{f} \int_{S_f} \sigma \cdot dS_f = \frac{1}{2} \sum_{i,j} \int_{S_f} \frac{\partial \omega_{\xi_{ij}}}{\partial r} ds : f
\]
\[
= \frac{1}{2} \sum_{i,j} \int_{S_f} \frac{\partial \omega_{xyz}}{\partial r} ds : f.
\]
Taking only the $x$ derivative above,
\[
\frac{x_{ij}}{\partial r_{ij}} = x_{ij} \left[ \frac{\delta (x^+ - x_i + sx_{ij})}{x^- - x_i + sx_{ij}} \right] G(s)
\]

where \( G(s) \) is,
\[
G(s) \equiv \left[ H(y^+ - y_i + sy_{ij}) - H(y^- - y_i + sy_{ij}) \right] \\
\times \left[ H(z^+ - z_i + sz_{ij}) - H(z^- - z_i + sz_{ij}) \right].
\]

As \( \delta(ax) = \frac{\delta(x)}{|a|} \) the \( x_{ij} x_{face}^+ G(s) \) term in Eq. (C2) can be expressed as,
\[
x_{ij} x_{face}^+ G(s) = \frac{x_{ij}}{|x_{ij}|} \delta \left( \frac{x - x_{ij}}{x_{ij}} + s \right) G(s). \quad (C3)
\]
The integral can be evaluated using the sifting property of the Dirac function \( \delta(x) \) as follows,
\[
\int_0^1 x_{ij} x_{face}^+ G(s) ds = \frac{x_{ij}}{|x_{ij}|} \int_0^1 \delta \left( \frac{x - x_{ij}}{x_{ij}} + s \right) G(s) ds = sgn(x_{ij}) \left[ H \left( \frac{x - x_{ij}}{x_{ij}} \right) - H \left( \frac{x - x_{ij}}{x_{ij}} \right) \right] S_{x_{ij}}^+.
\]
where the signum function, \( sgn(x_{ij}) \equiv x_{ij}/|x_{ij}|. \) The \( S_{x_{ij}}^+ \) term is the value of \( s \) on the cube surface,
\[
S_{x_{ij}}^+ = \left( s = \frac{x - x_{ij}}{x_{ij}} \right) \quad \text{which is,}
\]
\[
S_{x_{ij}}^+ \equiv \left[ H \left( y^+ - y_i - \frac{y_{ij}}{x_{ij}} (x - x_i) \right) - H \left( y^- - y_i - \frac{y_{ij}}{x_{ij}} (x - x_i) \right) \right] \times \left[ H \left( z^+ - z_i - \frac{z_{ij}}{x_{ij}} (x - x_i) \right) - H \left( z^- - z_i - \frac{z_{ij}}{x_{ij}} (x - x_i) \right) \right]. \quad (C4)
\]
The definition \( S_{x_{ij}}^+ \) (analogous to \( S_{x_{ij}} \)) has been introduced as it filters out those \( ij \) terms where the point of intersection of line \( r_{ij} \) and plane \( x^+ \) has \( y \) and \( z \) components between the limits of the cube surfaces. The corresponding terms, \( S_{x_{ij}}^- \), are defined for \( \alpha = \{ y, z \} \). Taking \( H(0) = \frac{1}{2} \), the Heaviside function can be rewritten as \( H(ax) = \frac{1}{2} (sgn(a)sgn(x) - 1) \), and,
\[
H \left( \frac{x^+ - x_i}{x_{ij}} \right) - H \left( \frac{x^+ - x_i}{x_{ij}} \right) = \frac{1}{2} sgn \left( \frac{1}{x_{ij}} \right) [ sgn(x^+ - x_i) - sgn(x^- - x_i) ],
\]
so the expression, \( x_{ij} x_{face}^+ G(s) \) in Eq. (C2) becomes,
\[
x_{ij} \int_0^1 x_{face}^+ G(s) ds = \frac{1}{2} sgn(x_{ij}) sgn \left( \frac{1}{x_{ij}} \right) \times [ sgn(x^+ - x_i) - sgn(x^- - x_i) ] S_{x_{ij}}^+.
\]
The signum function, \( sgn \left( \frac{1}{x_{ij}} \right) \), cancels the one obtained from integration along \( s \), \( sgn(x_{ij}) \). The expression for the \( x^+ \) face is therefore,
\[
- \int_{S_x^+} \sigma \cdot dS = \frac{1}{2} \sum_{i,j} \left\langle f_{ij} x_{ij} \right\rangle \int_0^1 x_{face}^+ G(s) ds f \]
\[
= \frac{1}{4} \sum_{i,j} \left\langle f_{ij} \right\rangle \left[ sgn(x^+ - x_i) - sgn(x^- - x_i) \right] S_{x_{ij}}^+ f.
\]
Repeating the same process for the other faces allows Eq. (C1) to be expressed as,
\[
\sum_{faces} \int_{S_f} \sigma \cdot dS = -\frac{1}{2} \sum_{i,j} \left\langle f_{ij} r_{ij} \right\rangle \int_0^1 \frac{\partial s_{ij}}{\partial r} ds f
\]
\[
= -\frac{1}{4} \sum_{i,j} \left\langle f_{ij} \right\rangle \left[ S_{x_{ij}}^+ - S_{x_{ij}}^- \right] f,
\]
where \( dS_{x_{ij}}^\pm = \left\{ \frac{sgn(r_{ij} - r_{ij}) - sgn(r_{ij} - r_{ij})}{2} \right\} S_{x_{ij}}^\pm \) and \( n_{ij} \equiv sgn(r_{ij}) sgn \left( \frac{1}{r_{ij}} \right) = [1 1 1]. \) This is the force over the CV surfaces, Eq. (46), in section III C.

To verify the interpretation of \( S_{x_{ij}}^+ \) used in this work, consider the vector equation for the point of intersection of a line and a plane in space. The equation for a vector \( r \) between \( r_i \) and \( r_j \) is defined as \( r = r_i - s \frac{r_{ij}}{|r_{ij}|}. \)

The plane containing the positive face of a cube is defined by \( (r^+ - p) \cdot n \) where \( p \) is any point on the plane and \( n \) is normal to that plane. By setting \( a = p \) and upon rearrangement of \( (r^+ - r_i + s \frac{r_{ij}}{|r_{ij}|}) \cdot n \) the value of \( s \) at the point of intersection with the plane is,
\[
s = -\left( \frac{r_i - r_j}{|r_{ij}|} \right) \cdot n.
\]
The point on line \( a \) located on the plane is,
\[
a_p^+ = r_i + r_{ij} \left( \frac{(r^+ - r_i) \cdot n}{r_{ij} \cdot n} \right).
\]
Taking \( n \) as the normal to the \( x \) surface, i.e. \( n \rightarrow n_x = [1, 0, 0] \), then,
\[
\begin{align*}
x_{ap}^+ &= \left( \frac{x_{ap}^+}{x_{ap}^+} \right) = \left( \frac{y_i + \frac{y_{ij}}{x_{ij}} (x^+ - x_i)}{z_i + \frac{z_{ij}}{x_{ij}} (x^+ - x_i)} \right)
\end{align*}
\]
written using index notation with \( \alpha = \{ x, y, z \} \). The vector \( x_{ap}^+ \) is the point of intersection of line \( a \) with the \( x^+ \) plane. A function to check if the point \( x_{ap}^+ \) on the plane is located on the region between \( y^+ \) and \( z^+ \) would use Heaviside functions and is similar to the form of Eq. (15).
\[
S_{x_{ij}}^+ = \left[ H \left( y^+ - x_{ap}^+ \right) - H \left( y^- - x_{ap}^+ \right) \right] \times \left[ H \left( z^+ - x_{ap}^+ \right) - H \left( z^- - x_{ap}^+ \right) \right],
\]
which is the form obtained in the text by direct integration of the expression for stress, i.e. Eq. (C4).
[37] The cuboid is chosen as the most commonly used shape in continuum mechanic simulations on structured grids, although the process could be applied to any arbitrary shape.
[41] The resulting equality satisfies Eq. (39) and both sides are equal to within an arbitrary constant (related to choosing the gauge).
[58] V. Thankoppan, Quantum Mechanics, 1st ed. (New Age pub, New Delhi, 1985).