Multi-Scale Modelling IMSE – Continuum Notes

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1 Introduction

In these notes, the governing equations of molecular dynamics and continuum fluid dynamics are introduced. The mathematical link between the two are discussed in the context of matching reference frames, spatial and temporal averaging and definition of equivalent densities, momenta and stresses between both systems.

2 Molecular Dynamics

A molecular dynamics system consists of a number of discrete molecules (N), where each molecule i is located at a point in continuous space denoted by positional vector $\boldsymbol{r}_i$ with velocity vector $\dot{\boldsymbol{r}}_i$. Each molecule in the domain is followed and its evolution is calculated as a function of time - a Lagrangian framework for each molecule. The initial position and velocity of every molecule is the required initial state. Using Newton's second law it should (in principle) be possible to obtain any future state of the N-body system.

2.1 Governing Equations

In its simplest form, MD involves solving Newton's law for each molecule i of the N-molecule system,

$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i \tag{1}$$

where m_i is the mass of molecules i and $\ddot{\boldsymbol{r}}_i$ its acceleration. The force $\boldsymbol{F}_i$ is calculated by adding the contribution from its interaction with the other $N-1$ molecules in the system box. The force on molecule i is given by $\boldsymbol{F}_i = -\boldsymbol{\nabla}\Phi(r)$, where the potential Φ is a function of all the relative molecular positions only. The potential Φ can be expressed as a series of interactions between atomic pairs, triplets, etc,

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = \sum_{i=1}^{N} \Phi(\boldsymbol{r}_i) + \sum_{i=1}^{N}\sum_{j>i}^{N} \Phi(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i=1}^{N}\sum_{j>i}^{N}\sum_{k>j}^{N} \Phi(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k) + \ldots \tag{2}$$

where $\boldsymbol{r}_i$, $\boldsymbol{r}_j$ and $\boldsymbol{r}_k$ are the positions of molecules i, j and k respectively. The $\Phi(\boldsymbol{r}_i)$ is a body term which represents an external field, while higher order terms represent the interactions between two and higher numbers of molecules. The inclusion of pairwise and higher molecular interactions mark the departure from the theory of dilute gas. The greater the density of a fluid, the more terms required from Eq. (2) to model that fluid accurately. A common assumption for molecular dynamics is that the potential, Φ, is dependent on external fields and pair interactions only,

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) \approx \sum_{i=1}^{N} \Phi(\boldsymbol{r}_i) + \sum_{i=1}^{N} \sum_{j>i}^{N} \Phi(\boldsymbol{r}_i, \boldsymbol{r}_j) \equiv \sum_{i=1}^{N} \Phi_i + \sum_{i,j}^{N} \Phi_{ij}. \tag{3}$$

In the interest of being concise, the double sum has been written using a single sum, where i, j denote all pairs and the molecular indices used in the potential's position dependence are expressed by subscripts so $\Phi(\boldsymbol{r}_i, \boldsymbol{r}_j) \equiv \Phi_{ij}$. The forces are then calculated from $\boldsymbol{f}_{ij} = -\partial/\partial \boldsymbol{r}_{ij} \Phi$, with $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ and $\boldsymbol{f}_{iext} = -\partial/\partial \boldsymbol{r}_i \Phi$ so that, the resulting form of Newton's law is,

$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i = \sum_{j \neq i}^{N} \boldsymbol{f}_{ij} + \boldsymbol{F}_{iext}. \tag{4}$$

A common and simple approach is to represent the pairwise potential field using the Lennard-Jones potential (Rahman, 1964), which is commonly used to model liquid argon, but is actually a good representation of more complex fluids,

$$\Phi(\boldsymbol{r}_{ij}) = 4\epsilon \left[\left(\frac{\ell}{\boldsymbol{r}_{ij}} \right)^{12} - \left(\frac{\ell}{\boldsymbol{r}_{ij}} \right)^{6} \right], \quad |\boldsymbol{r}_{ij}| \leq |\boldsymbol{r}_c|. \tag{5}$$

$$\Phi(\boldsymbol{r}_{ij}) = 0 \qquad , \quad |\boldsymbol{r}_{ij}| \geq |\boldsymbol{r}_c|, \tag{6}$$

Although the Lennard-Jones potential describes the interaction of pairs of molecules, it also shows very good agreement to experimental data for real systems which have two and greater molecular interactions (Allen & Tildesley, 1987). This is because Φ in Eqs. (5) and (6) is now an effective pair potential whose parameters incorporate, in a mean field sense, the three body and higher order terms which are formally absent. It therefore represents a good balance between simulation efficiency and accuracy.

In Eq. (5), ℓ is the length scale of the molecular system, usually the atomic diameter and ϵ is a constant specifying the strength of atomic interaction. The term with an exponent of 12 represent the repulsion which becomes stronger as the two atoms move together. The term with the exponent of 6 is the attraction and is greater than repulsion only when $r_{ij} > 2^{1/6}$. The effect of the potential drops off rapidly with distance. For computational reasons, the calculation is often truncated when $r_{ij} > r_c$, a cutoff distance. Instead of an 'all pairs' system with all molecules interacting, the interactions are local and each molecule is only affected by its immediate neighbours. It is assumed the effects of the potential for $r_{ij} > r_c$ are insignificant.

Typically, the molecular representation is non-dimensionalised using length scale ℓ, mass m and energy ϵ (Rapaport, 2004), resulting in the equation of motion 7 being in terms of these MD units,

$$\ddot{\boldsymbol{r}}_i = 48 \sum_{j \neq i}^{N} \left(r_{ij}^{-12} - \frac{1}{2} r_{ij}^{-6} \right) \boldsymbol{r}_{ij}. \tag{7}$$

Therefore, the variables in the above equation are non-dimensionalised by the molecular parameters.

2.2 Statistical Mechanics

The aim of this section is to introduce the mesoscopic framework which links the discrete microscopic and the continuum macroscopic descriptions.

A molecular system can be described in three dimensions in terms of three molecular positions $\boldsymbol{r}(t)$ and three momenta $\boldsymbol{p}(t)$ for every one of the N molecules at a time t. A convenient framework to consider this system is a $6N$ dimensional phase space in which each combination of molecule position and velocity has a unique value. Consider a probability function f which describes how likely a given point in phase space is to contain a molecule.

$$f = f(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N, \boldsymbol{p}_1, \boldsymbol{p}_2, ..., \boldsymbol{p}_N, t). \tag{8}$$

This can be normalised to unity over the whole of phase space,

$$\underbrace{\int \cdots \int}_{6N} f(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N, \boldsymbol{p}_1, \boldsymbol{p}_2, ..., \boldsymbol{p}_N, t) d\boldsymbol{r}_1 d\boldsymbol{p}_1 ... d\boldsymbol{r}_N d\boldsymbol{p}_N = 1, \tag{9}$$

which, in this form, represents the canonical ensemble formulation of statistical mechanics. It is based on the idea of an average over an arbitrary number of independent molecular systems (an ensemble). This average is used as a probability f of finding a molecule at a point in phase space. In other words, for a given $\boldsymbol{r}$ and $\boldsymbol{p}$ how likely it is to find a molecule with these properties in any of the ensemble of different systems. This is called a mesoscopic system as it is not based on the macroscopic continuum hypothesis and does not follow individual microscopic discrete molecules. The requirement is that a statistically significant number of molecules exist across the arbitrary number of systems. The evolution in time of f is governed by the Liouville equations of statistical mechanics. This is derived in an analogous way to the conservation equations of fluid mechanics but using a volume in phase space (Evans & Morriss, 2007),

$$\frac{\partial f}{\partial t} = \sum_{i=1}^{N} \left[\boldsymbol{F}_i \cdot \frac{\partial f}{\partial \boldsymbol{p}_i} - \frac{\boldsymbol{p}_i}{m_i} \cdot \frac{\partial f}{\partial \boldsymbol{r}_i} \right]. \tag{10}$$

The Liouville equation in the form of Eq. (10) contains all the complexity of the averaged MD systems, including the internal structure. The Liouville equation can be simplified to obtain the Boltzmann equation by assuming a statistical model of pair collisions (a truncation of the BBGKY hierarchy (Succi, 2001)). The key difference between the equation obtained by Boltzmann and a MD approach comes from replacing the all pairs calculation in MD with the assumption of uncorrelated collisions. This means that although both approaches model the streaming and collision of molecules (albeit statistically vs. explicitly), the Boltzmann equation does not model the microscopic structure of the fluid. For this reason, the Boltzmann equation, especially in the form of the lattice Boltzmann method, is easily applied to macroscopic flows. The Boltzmann equation can also be shown to yield the Navier-Stokes and other continuum conservation equations through low Knudsen number expansion (Chapman &

Cowling, 1970). However, there has been limited success applying Boltzmann based equations to problems modelling smaller scales. The use of mean field theory where an N-molecule system is approximated as one molecule with a force applied to model the $N-1$ other molecules cannot capture the full underlying complexities of a dense fluid. It is for this reason that molecular dynamics is essential in capturing the effects of microscopic phenomena and, through coupling to the continuum, the effect on the macroscopic flow properties.

For a property α, the expectation value of α can be obtained by evaluating the inner product of Eq. (9) with the probability function defined by Eq. (8),

$$\left\langle \alpha; f \right\rangle \equiv \underbrace{\int \cdots \int}_{6N} \alpha(\boldsymbol{r}_1, .., \boldsymbol{r}_N, \boldsymbol{p}_1, .., \boldsymbol{p}_N) f(\boldsymbol{r}_1, .., \boldsymbol{r}_N, \boldsymbol{p}_1, .., \boldsymbol{p}_N, t) d\boldsymbol{r}_1 d\boldsymbol{p}_1 .. d\boldsymbol{r}_N d\boldsymbol{p}_N, \tag{11}$$

where angled bracket notation $\langle \alpha; f \rangle$ is introduced to define the ensemble average. Here α is any dynamic variable expressed as a function of position and velocity (although not time explicitly). Assuming phase space is bounded, the evolution in time of the expected value of a property, α, is,

$$\frac{\partial}{\partial t} \left\langle \alpha; f \right\rangle = \sum_{i=1}^{N} \left\langle \boldsymbol{F}_i \cdot \frac{\partial \alpha}{\partial \boldsymbol{p}_i} + \frac{\boldsymbol{p}_i}{m_i} \cdot \frac{\partial \alpha}{\partial \boldsymbol{r}_i}; f \right\rangle, \tag{12}$$

which is obtained by Irving & Kirkwood (1950) from the Liouville Eq. (10). This equation is the key to deriving the evolution in time of molecular properties. In a molecular dynamics simulation, which is the micro-canonical ensemble, a property is found by averaging in time and space. Sufficient measurements in time and space must be taken to ensure the results are statistically significant and representative of the system. The ergodic hypothesis is used to link the canonical ensemble, based on independent systems, to the micro-canonical ensemble based on one system. That is, sufficient time must has passed for the successive measurements being averaged to become uncorrelated (Allen & Tildesley, 1987). The same result can be obtained in the micro-canonical molecular simulation using.

$$\left\langle \alpha; f \right\rangle \approx \frac{1}{\Delta t} \int\limits_{t_0}^{t_0 + \Delta t} \alpha(\boldsymbol{r}, \boldsymbol{p}) dt \approx \frac{1}{\Delta t} \sum_{t=t_0}^{t_0 + \Delta t} \alpha(\boldsymbol{r}, \boldsymbol{p}), \tag{13}$$

where the first equality follows from the ergodic hypothesis.

In this section, the microscopic molecular dynamics equations in terms of Newton's laws were outlined, followed by the variational principles of classical mechanics. The mesoscopic statistical mechanical description was also introduced which is an intermediate between the discrete system of molecular dynamics and continuum mechanics. The next section considers the macroscopic continuum formulation of mechanics.

3 Continuum Fluid Dynamics

This section introduces the equations used in continuum fluid dynamics.

The continuum assumption states that the material being considered is continuous in space and time, allowing calculus to be freely applied. It is widely assumed that the continuum assumption is reasonable given the length scales of the problem are much larger than the mean free path of the individual molecules, $i.e.$ there are enough molecules in the smallest length scale that the material still acts like a continuum. This continuum assumption underpins the vast majority of engineering simulations.

3.1 Governing 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,

$$\frac{\partial}{\partial t}\int_V \rho dV = -\oint_S \rho \boldsymbol{u}\cdot d\mathbf{S}, \tag{14}$$

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

$$\frac{\partial}{\partial t}\int_V \rho \boldsymbol{u} dV = -\oint_S \rho \boldsymbol{u}\boldsymbol{u}\cdot d\mathbf{S} + \mathbf{F}_{\text{surface}} + \mathbf{F}_{\text{body}}. \tag{15}$$

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

$$\mathbf{F}_{\text{surface}} = -\oint_S \mathbf{\Pi}\cdot d\mathbf{S}. \tag{16}$$

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

$$\frac{\partial}{\partial t}\int_V \rho \mathcal{E} dV = -\oint_S \left[\rho\mathcal{E}\boldsymbol{u} + \mathbf{\Pi}\cdot\boldsymbol{u} + \boldsymbol{Q}\right]\cdot d\mathbf{S}, \tag{17}$$

which has been obtained by neglecting the term for the energy change due to body forces.

In order to express the CV equations in differential form, the divergence theorem is used This relates surface fluxes to the divergence within the volume, $e.g.$ for a variable A,

$$\oint_S \boldsymbol{A}\cdot d\mathbf{S} = \int_V \boldsymbol{\nabla}\cdot\boldsymbol{A} dV. \tag{18}$$

which in the limit of an infinitesimal control volume (Borisenko & Tarapov, 1979) defines the differential form,

$$\boldsymbol{\nabla}\cdot\boldsymbol{A} = \lim_{V\to 0}\frac{1}{V}\oint_S \boldsymbol{A}\cdot d\mathbf{S}. \tag{19}$$

Therefore, taking the zero volume limit of the conservation of mass through a control volume, Eq. (14), results in the differential continuity equation,

$$\frac{\partial \rho}{\partial t} + \nabla_\beta(\rho u_\beta) = 0. \tag{20}$$

Index notation has been used with the Einstein summation convention. Subscript and bold notations are used interchangeably to describe tensors throughout.

The differential momentum balance equation is obtained from the zero volume limits of the CV momentum balance equation Eq. (15),

$$\frac{\partial \rho u_\alpha}{\partial t} + \nabla_\beta \left[\rho u_\alpha u_\beta - \Pi_{\alpha\beta} \right] + F_{\alpha ext} = 0. \tag{21}$$

with surface forces, $\mathbf{F}_{\text{surface}}$, expressed in terms of pressure using Eq. (16). Effects due to external forces $F_{\alpha ext}$ (body forces, $\mathbf{F}_{\text{body}}$, at a point) are usually not considered and will be neglected in the following treatment. Finally for energy ($\mathcal{E}$) conservation at a point is derived from Eq. (17) as,

$$\frac{\partial}{\partial t} \rho \mathcal{E} = -\nabla_\beta \left[\rho \mathcal{E} u_\beta + \Pi_{\alpha\beta} u_\alpha + Q_\beta \right], \tag{22}$$

The pressure tensor, $\Pi_{\alpha\beta}$, can be further subdivided into the equilibrium pressure from kinetic theory, P, and solid mechanics concept of stress $\sigma_{\alpha\beta}$ acting on the control volume,

$$\Pi_{\alpha\beta} = -P \delta_{\alpha\beta} + \sigma_{\alpha\beta}, \tag{23}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta. The decomposition is arbitrary and it is only the total stress tensor $\Pi_{\alpha\beta}$ that has any physical meaning, as it satisfies the definition of an infinitesimal force acting on an infinitesimal area (Evans & Morriss, 2007). The term, $\sigma_{\alpha\beta}$, is the Cauchy stress widely measured in solid mechanics. The pressure term, P, does not typically appear in the solid mechanics formulation as the solid is assumed to be initially undeformed (gauge of zero). In a fluid, P can vary throughout the domain. The convective term is unique to liquids as it describes transport resulting from the actual movement of fluid through the control volume.

The stress tensor can be expanded as a power series in strain rate. Generally it is assumed to be a linear function of strain rate (not assuming this will lead to the Burnett or super Burnett equations depending on the order of the relationship). A fourth order tensor is the simplest linear relation between stress and strain (i.e. a relation linking each of the 9 stress components linearly to each of the 9 strain components needs 81 components).

$$\sigma_{\alpha\beta} = C_{\alpha\beta\gamma\zeta} \varepsilon_{\gamma\zeta}. \tag{24}$$

The assumed symmetry of the stress and strain tensors ($C_{\alpha\beta\gamma\zeta} = C_{\beta\alpha\gamma\zeta}$ and $C_{\alpha\beta\gamma\zeta} = C_{\alpha\beta\zeta\gamma}$) along with the requirement that work done by deformation be zero ($C_{\alpha\beta\gamma\zeta} = C_{\gamma\zeta\alpha\beta}$) allows the 81 components to be reduced . The following relationship results between just second order tensors with only two unknown coefficients, λ and μ,

$$C_{\alpha\beta\gamma\zeta} = \lambda \delta_{\alpha\beta} \delta_{\gamma\zeta} + \mu (\delta_{\beta\gamma} \delta_{\alpha\zeta} + \delta_{\alpha\gamma} \delta_{\beta\zeta}), \tag{25}$$

The fluid is assumed to be physically and structurally isotropic meaning it can only deform by shear and bulk deformation. The equation linking stress and strain takes the form,

$$\sigma_{\alpha\beta} = \lambda \delta_{\alpha\beta} \varepsilon_{\gamma\gamma} + \mu (\varepsilon_{\gamma\zeta} + \varepsilon_{\zeta\gamma}). \tag{26}$$

Using the definition of small strains for $\varepsilon_{\alpha\beta} = \nabla_\beta u_\alpha + \nabla_\alpha u_\beta$, the equation for $\Pi_{\alpha\beta}$ can be written (in vector notation) as,

$$\boldsymbol{\Pi} = P\boldsymbol{\delta} - \mu(\boldsymbol{\nabla}\boldsymbol{u} + (\boldsymbol{\nabla}\boldsymbol{u})^T - \boldsymbol{\nabla}\cdot\boldsymbol{u}\boldsymbol{\delta}) - \lambda\boldsymbol{\nabla}\cdot\boldsymbol{u}\boldsymbol{\delta}. \tag{27}$$

The Stokes hypothesis relates the two co-efficients μ and λ which is exactly true for a monatomic gas but a good approximation for most gases. The coefficient μ is often called the shear viscosity coefficient and is the same form as the one in Newton's law of viscosity. The bulk viscosity coefficient is $(\lambda - \frac{2}{3}\mu\ )$ (Hoover, 1991), although some textbooks incorrectly describe λ itself as the bulk viscosity. It is the bulk or compressional viscosity which is zero under Stokes' hypothesis, i.e. $\lambda = \frac{2}{3}\mu$. A bulk viscosity of zero is an approximation not correct for fluids with internal structures (Gad-el Hak, 1995). Molecular dynamics explicitly incorporates the effect of finite bulk viscosity.

Using the assumption of incompressibility, the continuity Eq. (20) reduces to $\boldsymbol{\nabla}\cdot\boldsymbol{u} = 0$ and Eq. (21) can be simplified to

$$\frac{\partial\boldsymbol{u}}{\partial t} + (\boldsymbol{u}\cdot\boldsymbol{\nabla})\,\boldsymbol{u} = -\frac{1}{\rho}\boldsymbol{\nabla}P + \nu\nabla^2\boldsymbol{u}, \tag{28}$$

where $\boldsymbol{u}(\boldsymbol{x},t)$ is the fluid velocity and $P(\boldsymbol{x},t)$ pressure, at each spatial position $\boldsymbol{x}$ and time t. The fluid is assumed to have a uniform density ρ and viscosity $\nu = \rho/\mu$. Non-dimensionalising using a length scale L, a characteristic velocity U and time of U/L with the definition of the Reynolds number $Re = UL/\nu$, Eq. (28) becomes,

$$\frac{\partial\boldsymbol{u}}{\partial t} + (\boldsymbol{u}\cdot\boldsymbol{\nabla})\,\boldsymbol{u} = -\boldsymbol{\nabla}P + \frac{1}{Re}\nabla^2\boldsymbol{u}, \tag{29}$$

where the variables shown are non-dimensional for the continuum scale.

4 Towards a Consistent Mathematical Framework

This section outlines the mathematical relationship between the discrete framework of molecular dynamics and the equations of continuum mechanics. First the difference in reference frame used in the Eulerian fluid mechanics and the many Lagrangian molecules is discussed. The link between these is provided by the seminal work of Irving & Kirkwood (1950) through the Dirac delta functional. Using the Dirac delta, a number of localised 'state' properties are defined including density, momentum, temperature and energy. The time derivatives of these state properties can be used to obtain the fluxes (again following Irving & Kirkwood (1950)). The fluxes include advection of momentum (convection) and the notion of the stress tensor in a molecular system. A consistent stress definition is essential to flux coupling schemes, however, the exact definition of the molecular stress is a controversial area. The various issues associated with the molecular stress tensor are discussed in this section.

4.1 Lagrangian and Eulerian frameworks

Both the continuum and molecular systems are classical systems, entirely governed by Newton's law. It should therefore be possible to express the time

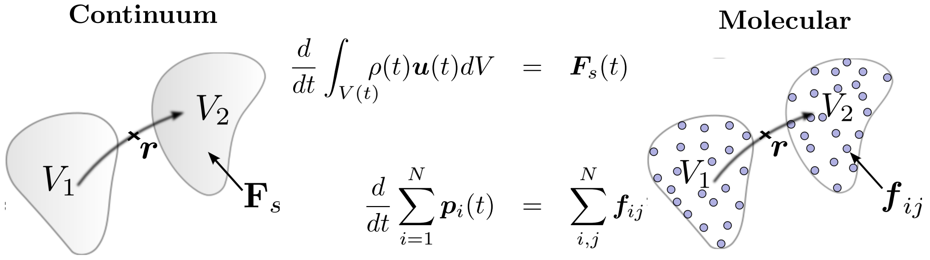

Figure 1: An equivalent Lagrangian element for the continuum and discrete system with corresponding forms of Newton's law. An arbitrary fixed point $\boldsymbol{r}$ on the path of evolution represents an infinitesimal Eulerian frame. The equations of motion in the Eulerian frame are given by expressing the flow through this infinitesimal control volume in the continuum or application of the Dirac delta function in the discrete system.

evolution of both in an equivalent manner. This is achieved in this subsection, by considering an arbitrary and equivalent Lagrangian element in both systems. The link to the Eulerian formulation for both systems is then discussed.

Newton formulated his law based on the evolution of discrete objects, subject to impressed forces [1]. The equation resulting from Newton's second law,

$$m\frac{d^2\boldsymbol{r}}{dt^2} = \boldsymbol{F},$$

relates a particle's mass m and second temporal derivative of its position $\boldsymbol{r}$ to the forces it experiences, $\boldsymbol{F}$. The application of Newton's law to a continuous substance requires the division of that substance into arbitrary interacting regions. These "discrete elements" are often called particles, although to avoid confusion, this term is here reserved for discrete molecules and the term element is used instead.

A Lagrangian continuum element is defined to be an arbitrary and fixed quantity of continuous media with a time evolving volume $V = V(t)$ contained inside a bounding surface S. The temporal evolution of this volume and the momentum inside is governed by the forces acting over its bounding surface $\boldsymbol{F}_s$. Figure 1 shows this continuum element and the form of Newton's law which governs its evolution.

In order to link the two, a similar element can be defined in the molecular system, containing a fixed number of molecules N (*c.f.* the fixed quantity of continuous media) and surrounded by a bounding surface S. The volume $V = V(t)$ of this molecular element is given by the shape enclosing the positions of all N molecules and its evolution is governed by the sum of all inter-molecular forces acting over the surface $\boldsymbol{f}_{ij}$. Note by following an 'element' of molecules, the sum over all i and j is the surface forces, as internal interactions between molecules inside the element cancel (Newton's 3rd law).

These two element in both system are equivalent; both advancing due to Newton's law, following a fixed collection of substance and evolving as a result

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[1] "*An impressed force is an action exerted upon a body, in order to change its state, either of rest, or of moving uniformly forward in a right line.*" Newton (1726) from definition IV, page 3 in the translation by Motte (1729).

of external forces due to interactions with substance outside the element. In this form, the equations represent the Lagrangian formulation of mechanics (see Figure 1), in which the evolution of a fixed quantity of substance is followed through time. However, fluid mechanics is almost always written in the Eulerian reference frame, which considers the flow past a fixed point in space. For this reason, the coupling strategies employed in the solid mechanics literature (Curtin & Miller, 2003) are generally not applicable to fluid system. The continuum can be written in an Eulerian frame using Reynolds Transport Theorem (Reynolds, 1903)

$$\frac{d}{dt}\int_V \rho \boldsymbol{u} dV = \int_V \frac{\partial \left(\rho \boldsymbol{u}\right)}{\partial t} dV + \oint_S \left(\rho \boldsymbol{u}\boldsymbol{u}\right) \cdot d\mathbf{S}.$$

The use of the Dirac delta function provides a way to write the molecular systems in an Eulerian framework. This is due to the property of the Dirac delta that,

$$h(\boldsymbol{r}) = \int_{-\infty}^{\infty} \delta(\boldsymbol{r}_i - \boldsymbol{r}) h(\boldsymbol{r}_i) d\boldsymbol{r}_i, \tag{31}$$

here, $\boldsymbol{r}$ is a location in space (of the Eulerian reference) and $\boldsymbol{r}_i$ the location of molecule i. Consider the point $\boldsymbol{r}$ in Figure 1, which includes molecules only as they pass through point $\boldsymbol{r}$. As the Dirac delta is defined only at a infinitesimal position in space, the molecular system is effectively considered only at the location $\boldsymbol{r}$. Regardless of the shape or size of the element, the Dirac delta only considers the properties as they move past $\boldsymbol{r}$. The analysis of Irving & Kirkwood (1950) provides the link between the ensemble averaged microscopic variables and the macroscopic density, momentum and energy at a fixed Eulerian point in space as discussed in the next subsection. The reader is referred to Irving & Kirkwood (1950) for a full justification of the Dirac delta function as a link between macroscopic and mesoscopic descriptions.

4.2 State Variable, Density Velocity and Temperature

In this subsection, an equivalent definition for state properties (density, momentum, energy and temperature) is obtained for a fixed Eulerian point in space in both the molecular and continuum system. Recall from section 2.2, that the expectation value of any variable $\alpha = \alpha(\boldsymbol{r}_1, ..., \boldsymbol{r}_N, \boldsymbol{p}_1, ..., \boldsymbol{p}_N, t)$ is given by the inner product with the probability density function,

$$\Big\langle \alpha; f \Big\rangle = \int \cdots \int_{6N} \alpha f(\boldsymbol{r}_1, ..., \boldsymbol{r}_N, \boldsymbol{p}_1, ..., \boldsymbol{p}_N, t) d\boldsymbol{r}_1 d\boldsymbol{p}_1 ... d\boldsymbol{r}_N d\boldsymbol{p}_N.$$

By letting α be the Dirac delta function, Irving & Kirkwood (1950) provided the link between the Lagrangian and Eulerian descriptions. The macroscopic density definition follows from $\alpha = \sum_{i=1}^{N} m_i \delta(\boldsymbol{r}_i - \boldsymbol{r})$, giving,

$$\rho(\boldsymbol{r}, t) \equiv \Big\langle \sum_{i=1}^{N} m_i \delta(\boldsymbol{r}_i - \boldsymbol{r}); f \Big\rangle. \tag{32}$$

This returns the possible configurations of the system in phase space which satisfy the criterion that a molecule is located at a point $\boldsymbol{r}$. This is the definition of average density of mass located at $\boldsymbol{r}$ for an ensemble of molecular systems. The momentum density at a point in space is similarly defined by,

$$\rho(\boldsymbol{r},t)\boldsymbol{u}(\boldsymbol{r},t) \equiv \sum_{i=1}^{N} \left\langle \boldsymbol{p}_i \delta(\boldsymbol{r}_i - \boldsymbol{r}); f \right\rangle, \tag{33}$$

where the momentum of molecule i is $\boldsymbol{p}_i = m_i \dot{\boldsymbol{r}}_i$. Note that $\boldsymbol{p}_i$ is the momentum in the laboratory frame, and not the peculiar value $\overline{\boldsymbol{p}}_i$, which excludes the macroscopic streaming term at the location of molecule i, $\boldsymbol{u}(\boldsymbol{r}_i)$, (Evans & Morriss, 2007). The laboratory frame and peculiar momentum are related through,

$$\overline{\boldsymbol{p}}_i \equiv m_i \left(\frac{\boldsymbol{p}_i}{m_i} - \boldsymbol{u}(\boldsymbol{r}_i) \right). \tag{34}$$

The energy density at a point in space is defined by

$$\rho(\boldsymbol{r},t)\mathcal{E}(\boldsymbol{r},t) \equiv \sum_{i=1}^{N} \left\langle e_i \delta(\boldsymbol{r}_i - \boldsymbol{r}); f \right\rangle, \tag{35}$$

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

$$e_i \equiv \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{j \neq i}^{N} \phi_{ij}.$$

It is implicit in this definition that the potential energy of an interatomic interaction, ϕ_{ij}, is arbitrarily divided equally between the two interacting molecules, i and j. The factor of 1/2 in the last term of the above equation is therefore included to avoid double counting. Related to the energy is the definition of temperature, which can be defined at a point in terms of the peculiar momentum,

$$T(\boldsymbol{r},t) = \frac{1}{3k_B(N-1)} \sum_{i=1}^{N} \left\langle \frac{\overline{p}_i^2}{m_i} \delta(\boldsymbol{r}_i - \boldsymbol{r}); f \right\rangle. \tag{36}$$

The time evolution of these state properties provides the fluxes in the next section.

4.3 Momentum Fluxes and the Pressure Tensor

The fluxes are obtained by evaluating the time evolution of state properties using the Irving & Kirkwood (1950) time evolution equation (12). The link to the equations in this section will be obtained in the limiting case of zero volume. The reader is also referred to the original work of Irving & Kirkwood (1950) for the full derivation of the equations presented in this section.

The time evolution of mass is obtained by taking the time derivative of both sides of Eq. (32) and applying Eq. (12),

$$\frac{\partial}{\partial t}\rho(\boldsymbol{r},t) = \frac{\partial}{\partial t}\sum_{i=1}^{N}\left\langle m_i\delta(\boldsymbol{r}_i-\boldsymbol{r});f\right\rangle$$

$$= -\frac{\partial}{\partial \boldsymbol{r}}\cdot\sum_{i=1}^{N}\left\langle \boldsymbol{p}_i\delta(\boldsymbol{r}_i-\boldsymbol{r});f\right\rangle = -\frac{\partial}{\partial \boldsymbol{r}}\cdot\rho(\boldsymbol{r},t)\boldsymbol{u}(\boldsymbol{r},t), \tag{37}$$

which results in the divergence of momentum given in Eq. (33). This circumvents the process of defining the momentum in Eq. (33) and also results in a form of momentum which is not unique (the gauge can be set by adding an arbitrary constant).

The time evolution of momentum is obtained by taking the time derivative of both sides of Eq. (33) and applying Eq. (12),

$$\frac{\partial}{\partial t}\rho(\boldsymbol{r},t)\boldsymbol{u}(\boldsymbol{r},t) = \frac{\partial}{\partial t}\sum_{i=1}^{N}\left\langle \boldsymbol{p}_i\delta(\boldsymbol{r}_i-\boldsymbol{r});f\right\rangle$$

$$= \frac{\partial}{\partial \boldsymbol{r}}\cdot\rho(\boldsymbol{r},t)\boldsymbol{u}(\boldsymbol{r},t)\boldsymbol{u}(\boldsymbol{r},t) + \frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{\Pi}(\boldsymbol{r},t),$$

which results in the molecular flux and stress at a point in space. The resulting stress tensor, known as the IK stress tensor, is of the form,

$$\boldsymbol{\Pi} = \sum_{i=1}^{N}\left\langle m_i\left(\frac{\boldsymbol{p}_i}{m_i}-\boldsymbol{u}\right)\left(\frac{\boldsymbol{p}_i}{m_i}-\boldsymbol{u}\right)\delta(\boldsymbol{r}_i-\boldsymbol{r}) + \frac{1}{2}\sum_{j\neq i}^{N}\boldsymbol{f}_{ij}\boldsymbol{r}_{ij}O_{ij}\delta(\boldsymbol{r}_i-\boldsymbol{r});f\right\rangle. \tag{38}$$

The O_{ij} term is the Irving & Kirkwood (1950) operator resulting from a Taylor expansion of two Dirac delta functionals, *i.e.*

$$\delta(\boldsymbol{r}_i-\mathbf{r})-\delta(\boldsymbol{r}_j-\boldsymbol{r}) = -\boldsymbol{r}_{ij}\cdot\frac{\partial}{\partial \boldsymbol{r}}O_{ij}\delta(\boldsymbol{r}_i-\boldsymbol{r}),$$

where the so-called IK operator is,

$$O_{ij} = \left(1-\frac{1}{2}\boldsymbol{r}_{ij}\cdot\frac{\partial}{\partial \boldsymbol{r}_i}+\ldots+\frac{1}{n!}(-\boldsymbol{r}_{ij}\cdot\frac{\partial}{\partial \boldsymbol{r}_i})^{n-1}+\ldots\right). \tag{39}$$

It is instructive to compare the continuum momentum equations Eq. (21) (with $\boldsymbol{\Pi} = P\boldsymbol{I}-\sigma$) and the mesoscopic Eq. (38) obtained by Irving & Kirkwood (1950),

$$\begin{array}{rcl}\dfrac{\partial}{\partial t}\rho\boldsymbol{u}+\boldsymbol{\nabla}\cdot\rho\boldsymbol{u}\boldsymbol{u} & = & \boldsymbol{\nabla}\cdot\left[\; P\boldsymbol{I} \qquad\qquad - \qquad\qquad \sigma \qquad\qquad\right] \\ \displaystyle\sum_{i=1}^{N}\left\langle\frac{\partial}{\partial t}\boldsymbol{p}_i\delta(\boldsymbol{r}_i-\boldsymbol{r});f\right\rangle+\boldsymbol{\nabla}\cdot\rho\boldsymbol{u}\boldsymbol{u} & = & \displaystyle\boldsymbol{\nabla}\cdot\sum_{i=1}^{N}\left\langle\frac{\overline{\boldsymbol{p}}_i\overline{\boldsymbol{p}}_i}{m_i}\delta(\boldsymbol{r}_i-\boldsymbol{r})+\frac{1}{2}\sum_{j\neq i}^{N}\boldsymbol{f}_{ij}\boldsymbol{r}_{ij}O_{ij}\delta(\boldsymbol{r}_i-\boldsymbol{r});f\right\rangle.\end{array}$$

It is clear from this comparison that time evolution of momentum is equal to the divergence of kinetic pressure P, Cauchy stress $\boldsymbol{\sigma}$ and fluid convection $\rho\boldsymbol{u}\boldsymbol{u}$. The IK pressure of Eq. (38) is a formally exact definition valid at a point in space. It can be simplified to yield the kinetic theory (ideal gas) pressure as well as the virial pressure (Parker, 1954).

The kinetic pressure is obtained by assuming a homogeneous dilute gas (with $\phi_{ij}(r) = 0$) in a closed volume V (Chapman & Cowling, 1970); Eq. (38) simplifies to,

$$\overset{KT}{\mathbf{\Pi}} = \frac{1}{V}\sum_{i=1}^{N}\left\langle \frac{\boldsymbol{p}_i\boldsymbol{p}_i}{m_i}; f \right\rangle, \tag{40}$$

which is the ideal gas kinetic theory definition of the pressure tensor. Note that a single value is taken for the whole system and there is no local $\boldsymbol{u}$ ($\overline{\boldsymbol{p}}_i = \boldsymbol{p}_i$). With no internal interactions, the pressure tensor is entirely due to the 'stress like' movement of momentum by microscopic fluctuations. This also appears to be consistent with the common definition of P in the continuum literature (Potter & Wiggert, 2002).

The virial pressure is obtained from Eq. (38) in a closed volume V and taking only the first term in the IK operator of Eq. (39), known as the IK1 approximation, so that $\delta(\boldsymbol{r}_i - \boldsymbol{r}) = 1$ and $O_{ij}\delta(\boldsymbol{r}_i - \boldsymbol{r}) = 1$. The result is the well-known tensorial form of the virial pressure (Parker, 1954),

$$\overset{VIRIAL}{\mathbf{\Pi}} = \frac{1}{V}\sum_{i=1}^{N}\left\langle \frac{\boldsymbol{p}_i\boldsymbol{p}_i}{m_i} + \frac{1}{2}\sum_{i\neq j}^{N}\boldsymbol{f}_{ij}\boldsymbol{r}_{ij}; f \right\rangle.$$

The virial form of pressure is the most widely used in the molecular dynamics literature due to its simplicity. However, the virial can only be used to provide a single pressure tensor for an entire isolated system. Using the virial pressure locally is incorrect, as interactions with the surrounding fluid are not included (Tsai, 1978). This is a consequence of neglecting terms of higher order in Eq. (39). As a result, the effects of local inhomogeneity in the fluid are lost. Away from equilibrium a localised description is required and the full Eq. (39) expression must be retained.

The IK form of pressure in Eq. (39) is formally exact and equal to the pointwise continuum description. The Dirac delta function is defined in the infinitely thin, infinitely large limit which is exactly the same limit in which the continuum infinitesimal is defined. However, in practice the Dirac delta function cannot be implemented in a molecular system as no molecule will ever be exactly at point $\boldsymbol{r}$. Therefore, some relaxation of the Dirac delta is required and a number of possibilities are discussed in the literature.

4.4 Energy Equations

The final type of flux expression is for energy, which includes the definition of the stress tensor. The molecular equivalents of various terms from the energy evolution, Eq. (42), can be defined as follows,

$$\begin{aligned}
\rho\mathcal{E}\boldsymbol{u} &= \sum_{i=1}^{N}\Big\langle e_i\boldsymbol{u}\,\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right);f\Big\rangle, & \text{(41a)}\\
\boldsymbol{\Pi}\cdot\boldsymbol{u} &= \sum_{i=1}^{N}\Bigg\langle\left[\frac{\overline{\boldsymbol{p}}_i\,\overline{\boldsymbol{p}}_i}{m_i}-\frac{1}{2}\sum_{j\neq i}^{N}\boldsymbol{f}_{ij}\boldsymbol{r}_{ij}O_{ij}\right]\cdot\boldsymbol{u}\,\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right);f\Bigg\rangle, & \text{(41b)}\\
\boldsymbol{Q} &= \sum_{i=1}^{N}\Big\langle\overline{e}_i\frac{\overline{\boldsymbol{p}}_i}{m_i}\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right)-\frac{1}{2}\sum_{j\neq i}^{N}\frac{\overline{\boldsymbol{p}}_i}{m_i}\cdot\boldsymbol{f}_{ij}\boldsymbol{r}_{ij}O_{ij}\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right);f\Big\rangle,
\end{aligned}$$

where the peculiar momentum and energy are defined by,

$$\frac{\overline{\boldsymbol{p}}_i}{m_i}\equiv\left(\frac{\boldsymbol{p}_i}{m_i}-\boldsymbol{u}\right);\quad e_i\equiv\frac{p_i^2}{2m_i}+\frac{1}{2}\sum_{j\neq i}^{N}\phi_{ij}\quad\text{and}\quad\overline{e}_i\equiv\frac{\overline{p}_i^2}{2m_i}+\frac{1}{2}\sum_{j\neq i}^{N}\phi_{ij}.$$

The energy equation at a point in space is therefore,

$$\begin{aligned}
\frac{\partial}{\partial t}\rho\mathcal{E} = -\boldsymbol{\nabla}\cdot\sum_{i=1}^{N}\Bigg\langle e_i\boldsymbol{u}\,\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right)+\left[\frac{\overline{\boldsymbol{p}}_i\,\overline{\boldsymbol{p}}_i}{m_i}-\frac{1}{2}\sum_{j\neq i}^{N}\boldsymbol{f}_{ij}\boldsymbol{r}_{ij}O_{ij}\right]\cdot\boldsymbol{u}\,\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right)\\
+\overline{e}_i\frac{\overline{\boldsymbol{p}}_i}{m_i}\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right)-\frac{1}{2}\sum_{j\neq i}^{N}\frac{\overline{\boldsymbol{p}}_i}{m_i}\cdot\boldsymbol{f}_{ij}\boldsymbol{r}_{ij}O_{ij}\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right);f\Big\rangle\Bigg),
\end{aligned}\tag{42}$$

It is possible to take the IK1 form of the energy, with $O_{ij}\delta(\boldsymbol{r}-\boldsymbol{r}_i)=1$ from Eq. (39) and averaging over the Dirac delta function,

$$\begin{aligned}
\rho\mathcal{E}\boldsymbol{u} &= \sum_{i=1}^{N}\Big\langle e_i\boldsymbol{u}\Big\rangle, & \text{(43a)}\\
\boldsymbol{\Pi}\cdot\boldsymbol{u} &= \sum_{i=1}^{N}\Bigg\langle\left(\frac{\overline{\boldsymbol{p}}_i\,\overline{\boldsymbol{p}}_i}{m_i}-\frac{1}{2}\sum_{j\neq i}^{N}\boldsymbol{f}_{ij}\boldsymbol{r}_{ij}\right)\cdot\boldsymbol{u}\Bigg\rangle, & \text{(43b)}\\
\boldsymbol{Q} &= \sum_{i=1}^{N}\Big\langle\overline{e}_i\frac{\overline{\boldsymbol{p}}_i}{m_i}-\frac{1}{2}\sum_{j\neq i}^{N}\frac{\overline{\boldsymbol{p}}_i}{m_i}\cdot\boldsymbol{f}_{ij}\boldsymbol{r}_{ij}\Big\rangle, & \text{(43c)}
\end{aligned}$$

this is the most commonly used form of energy equation in the coupling literature due to it simplicity. Many of the issues associated with the definition of the stress tensor also apply to the energy equations and the heat flux $\boldsymbol{Q}$.

The equations presented in this section provide a direct mathematical link between state properties: mass, momentum, temperature and energy in the continuum and molecular system. The linking of the flux properties, *i.e.* convection, energy advection, pressures and heat flux have also been discussed.

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