PERGAMON International Journal of Multiphase Flow 28 (2002) 1091–1123

International Journal of Multiphase Flow

www.elsevier.com/locate/ijmulflow

Macroscale balance relations for bulk, interfacial and common line systems in multiphase flows through porous media on the basis of molecular considerations

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Received 12 September 2001; received in revised form 5 February 2002

Abstract

A new molecular-based approach is employed to derive balance relations for multiphase flow through porous media. Criteria are prescribed which identify, instant by instant, precisely which molecules are considered to reside in each bulk, interfacial, and contact line phase. Continuum balance relations for mass, momentum and energy are established for each of these phases (which consist of ever-changing molecular populations) at the scale of representative elementary volumes (REVs). All fields in these balance relations are related to space–time averages of molecular quantities, and complete account is taken of molecular transport within and between phases. This is a one-step procedure, as opposed to the two-step approach commonly used in averaging (first going from molecular scale to an intermediate scale, at which common lines, interfaces and pore geometry are manifest, and thence to a macro/REV-scale). In this way consideration of 'excess' quantities is avoided. Simplifications and constitutive considerations are discussed.

Keywords: Porous media; Interfaces; Common lines; Weighted molecular averages

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1. Introduction

Multiphase flows through porous media play an important role in many environmental and engineering contexts. It is well known that such flows are highly sensitive to capillary effects

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0301-9322/02/$ - see front matter
PII: S0301-9322(02)00021-6

associated with the presence of fluid–fluid and fluid–solid interfaces. Their behaviour may also be influenced by the associated three-phase common (also termed 'contact') lines (Platikanov et al., 1980; Miller and Neogi, 1985; Schiegg, 1986; Ivanov et al., 1986). Accordingly, any theory which is to describe flows at a scale large compared with the structural dimensions of a porous body (hereafter termed a 'macroscale') should take into account the *effect* of interfaces and common lines, although these are not explicitly manifest at this scale.

Multiphase systems can be regarded at three distinct scales: the molecular scale, pore scale (also termed 'microscale'), and macroscale. For most applications, governing equations at the macroscale are needed. There is an extensive literature on the derivation of macroscale balance relations by averaging microscale equations over so-called Representative Elementary Volumes (REVs: see Bear, 1972). In turn, microscale balance relations may be obtained by averaging governing equations at the molecular level. Accordingly, a macroscale description on the basis of molecular considerations may be obtained via a two-step procedure, which is now described in more detail.

In the two-step approach, a microscale description may be employed on a scale large compared with nearest-neighbour molecular separations, yet small enough for porous structure to be manifest. From such a perspective the porous body and any bulk phases it contains may be modelled as three-dimensional continua. Interfaces can be described in terms of two-dimensional continua (see, for example, Moeckel, 1975) and common lines regarded as one-dimensional continua (Napolitano, 1979). Since interfaces and common lines actually occupy three-dimensional regions (although, roughly speaking, extremely small in one or two dimensions, respectively), such a continuum description involves selection of model surfaces and curves which lie within the relevant regions. To these surfaces and curves are attributed fields which satisfy balance and constitutive relations adequate to describe behaviour (at the scale in question) of material in the corresponding regions, taking due account of the effects of matter in contiguous regions. It follows that no fields in this approach are attributed to points in interfacial or three-phase common regions which do not lie on the model surfaces or curves. Such points form a region in which there is thus a 'modelling void'. However, if balance relations and constitutive assumptions are to be postulated for interfaces and common lines, then it is necessary to be guided by the extensive literature on interfacial physics (see, for example, Defay et al., 1966; Bikerman, 1970; Slattery, 1990). Following Gibbs (1876), such literature deals with so-called 'excess' quantities which arise as a consequence of the (formal and physically artificial) extension of bulk fields up to interfacial model surfaces. Such extension is effected in such a way that the balance relations satisfied by these fields are preserved. This procedure ensures that there are no points at which fields are undefined: that is, there is no 'modelling void'. Such extra notional material behaviour is compensated by, roughly speaking, subtracting integrated (in a direction normal to the surface) versions of each balance relation for extended fields from the corresponding surface balance for the interfacial region (see, for example, Murdoch, 1990). The resulting surface balance relations involve excess quantities. In this respect it should be noted that 'surface tension' is an excess quantity: (see, for example, Defay et al., 1966, Chapter 1, Section 2). To be consistent, an analogous procedure should be adopted for common lines but would involve much greater geometric complexity. Once balance relations for bulk, interfacial, and common line matter have been established as described above, these may be integrated over REVs to yield corresponding local balances for each material system. Of course, the fields which appear in these final balances are associated with averages taken at the REV scale.

The two-step procedure suffers from two shortcomings. Firstly, the link between macroscopic fields and molecular behaviour is not clearly evident. [1] Secondly, the locations of interfacial surfaces and common lines need to be chosen in a systematic manner. For example, interfacial surfaces are often selected on the basis of having zero excess mass. In such case there will generally be non-zero excess momentum and energy. Further, for multiphase interfaces, the excess mass of a particular phase may be negative, and so create conceptual difficulties. The geometric complexity increases significantly in the case of common lines.

In this work a single upscaling procedure is adopted which is devoid of the aforementioned drawbacks: macroscale balance relations are derived directly from molecular dynamics. The starting point is the identification, instant by instant, of those molecules belonging to each bulk, interfacial, and common line material system. Balance relations appropriate to each of these time-dependent systems are then derived. These relations involve fields defined directly in terms of REV-scale averages of molecular quantities, and full account is taken of molecular migration and interactions between all systems.

While the two-step approach has been implemented in Hassanizadeh and Gray (1979) and Gray and Hassanizadeh (1998), the second, single upscaling, approach has not previously been pursued. It is the purpose of this note to present this second approach, based upon general methodology developed in Murdoch and Bedeaux (1994) and Murdoch (2000) to understand the relationship between continuum equations of balance and molecular behaviour, paying due account to scales of length and time in the averaging procedure. The two approaches are related, since the starting point of the first (delineation of pore geometry, balance and constitutive relations) must be consistent with molecular averaging at a scale small compared with pore size. Accordingly the *result* of the first approach may be regarded as a consequence of two-fold averaging, starting from a molecular model. The second approach effects a direct single-stage averaging procedure to achieve the same ends and hence avoids difficulties in the first approach associated with handling excess quantities for surface and common line systems.

It should be noted that although the system here analysed in detail is composed of one solid and two fluids, the procedure and results are valid for *any* multiphase system.

Of course, once balance relations have been established using either of the foregoing approaches, it is necessary to postulate constitutive relations for certain fields, guided by general aspects of constitutive theory (for example, as in Hassanizadeh and Gray (1990, 1993)). In this respect the complementary natures of the two approaches may be of assistance. Certainly the physical interpretations of fields which appear in balance relations are rendered more transparent as a consequence of their derivations from two different perspectives. This is exemplified by the discussion in the final section.

In Section 2 bulk, interfacial, and common line systems are delineated, for porous bodies containing two immiscible liquids, on the basis of molecular criteria. Densities of mass and momentum are defined in terms of local joint averages, in space (at REV scale) and time, of molecular quantities. Balances of mass, momentum, and energy are derived in Section 3 for these time-dependent systems, with all fields being related to molecular considerations. Simplifications

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[1] This may be an important drawback when considering the effect of surfactants, which can significantly affect macroscopic flows, yet be present in only very small amounts.

are indicated in Section 4, motivated by existing theory for single and two-phase flows. Some constitutive possibilities are discussed. This paper concludes with remarks on the utility and relevance of a molecular perspective in continuum modelling of flows in porous media, indicating topics of particular importance that are elucidated by this viewpoint.

2. Basic molecular considerations

2.1. Delineation of bulk, interfacial, and common line systems

Molecules can always be grouped into individual molecular ‘species’. In the context of multiphase flow through a porous body, it is necessary not only to distinguish the species of each molecule, but also the bulk, interfacial, or common line region in which it is to be found *at any given instant*. Such time-dependence is mandated by the significant molecular migration that occurs between the aforementioned regions.

As a simple example, consider two immiscible liquid phases (oil and water, say) within a porous body. Labelling the liquids ‘O’ and ‘W’, and the solid porous body ‘B’, there will, at any instant, be bulk O, W and B phases, interfacial O–W, W–B and B–O regions, and three-phase W–O–B ‘common’ regions. In order to be precise in what follows it is necessary to define the associated material systems. Assuming there are no chemical reactions, the total material system $\mathscr{M}$ (that is, the total collection of molecules considered) will consist of fixed (that is, time-independent) sets of O, W and B molecules: $\mathscr{M}_{\rm O}$, $\mathscr{M}_{\rm W}$, and $\mathscr{M}_{\rm B}$, respectively. Thus

$$\mathscr{M} = \mathscr{M}_{\rm O} \cup \mathscr{M}_{\rm W} \cup \mathscr{M}_{\rm B}. \tag{2.1}$$

At any instant τ there is a subdivision of each of $\mathscr{M}_{\rm O}$, $\mathscr{M}_{\rm W}$ and $\mathscr{M}_{\rm B}$ into four complementary time-dependent disjoint subsystems. Specifically,

$$\begin{aligned}
\mathscr{M}_{\rm O} &= \mathscr{M}_{\rm O}^{\rm O}(\tau) \cup \mathscr{M}_{\rm O}^{\rm W}(\tau) \cup \mathscr{M}_{\rm O}^{\rm B}(\tau) \cup \mathscr{M}_{\rm O}^{\rm WB}(\tau),\\
\mathscr{M}_{\rm W} &= \mathscr{M}_{\rm W}^{\rm W}(\tau) \cup \mathscr{M}_{\rm W}^{\rm O}(\tau) \cup \mathscr{M}_{\rm W}^{\rm B}(\tau) \cup \mathscr{M}_{\rm W}^{\rm BO}(\tau),\\
\mathscr{M}_{\rm B} &= \mathscr{M}_{\rm B}^{\rm B}(\tau) \cup \mathscr{M}_{\rm B}^{\rm O}(\tau) \cup \mathscr{M}_{\rm B}^{\rm W}(\tau) \cup \mathscr{M}_{\rm B}^{\rm OW}(\tau).
\end{aligned} \tag{2.2}$$

Here $\mathscr{M}_{\rm W}^{\rm W}(\tau)$ consists of those W molecules within a distance [2] δ of each of which only W molecules can be found at instant τ, $\mathscr{M}_{\rm W}^{\rm O}(\tau)$ is the set of W molecules within a distance δ of each of which at least one O molecule (but no B molecule) is to be found at instant τ, $\mathscr{M}_{\rm W}^{\rm B}(\tau)$ is similarly defined (with the roles of O and B molecules interchanged), and $\mathscr{M}_{\rm W}^{\rm BO}(\tau)$ is the set of W molecules

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[2] Here δ is the effective range of molecular interactions. Although δ may vary from system to system, it is a *molecular length* scale which is appropriate for a specific system. Nearest-neighbour separations for bulk phase water molecules are 2–3 Å, and δ is typically of order 10 Å ($= 10^{-9}$ m). For simplicity we take a common, largest value, for all systems here discussed.

within a distance δ of each of which at least one B and one O molecule can be found at instant τ. $\mathscr{M}^{\mathrm{O}}_{\mathrm{O}}(\tau), \ldots, \mathscr{M}^{\mathrm{OW}}_{\mathrm{B}}(\tau)$ are similarly defined. Thus [3]

$$\mathscr{I}_{\mathrm{WO}}(\tau) := \mathscr{M}^{\mathrm{W}}_{\mathrm{O}}(\tau) \cup \mathscr{M}^{\mathrm{O}}_{\mathrm{W}}(\tau) \tag{2.3}$$

consists of molecules which, at time τ, reside in W–O interfaces but not in W–O–B common lines. Similarly (omitting τ-dependency for brevity),

$$\mathscr{I}_{\mathrm{OB}} := \mathscr{M}^{\mathrm{B}}_{\mathrm{O}} \cup \mathscr{M}^{\mathrm{O}}_{\mathrm{B}} \quad \text{and} \quad \mathscr{I}_{\mathrm{BW}} := \mathscr{M}^{\mathrm{B}}_{\mathrm{W}} \cup \mathscr{M}^{\mathrm{W}}_{\mathrm{B}} \tag{2.4}$$

represent matter in O–B and B–W interfacial regions, respectively. System

$$\mathscr{T}_{\mathrm{WOB}} := \mathscr{M}^{\mathrm{OB}}_{W} \cup \mathscr{M}^{\mathrm{BW}}_{\mathrm{O}} \cup \mathscr{M}^{\mathrm{WO}}_{\mathrm{B}} \tag{2.5}$$

is comprised of those W, O and B molecules which instantaneously constitute W–O–B common lines. Summarising, the total material system at any instant may be expressed as the union of seven mutually disjoint, time-dependent, material subsystems:

$$\mathscr{M} = \mathscr{M}^{\mathrm{O}}_{\mathrm{O}} \cup \mathscr{M}^{\mathrm{W}}_{\mathrm{W}} \cup \mathscr{M}^{\mathrm{B}}_{\mathrm{B}} \cup \mathscr{I}_{\mathrm{WO}} \cup \mathscr{I}_{\mathrm{OB}} \cup \mathscr{I}_{\mathrm{BW}} \cup \mathscr{T}_{\mathrm{WOB}}. \tag{2.6}$$

Of course, $\mathscr{M}^{\mathrm{O}}_{\mathrm{O}}$, $\mathscr{M}^{\mathrm{W}}_{\mathrm{W}}$ and $\mathscr{M}^{\mathrm{B}}_{\mathrm{B}}$ represent the instantaneous O, W and B 'pure' bulk phases, respectively, $\mathscr{I}_{\mathrm{WO}}$, $\mathscr{I}_{\mathrm{OB}}$ and $\mathscr{I}_{\mathrm{BW}}$ the (binary) interfacial systems, and $\mathscr{T}_{\mathrm{WOB}}$ the (ternary) common line system.

Remark 1. Delineation of instantaneous molecular populations of liquid–vapour interfacial systems is more subtle than identifying immiscible liquid–liquid interfacial matter, since the former may involve just a single molecular species. However, once a criterion is adopted for characterising interfacial phases the methodology and forms of balance here obtained apply without modification. For example, for liquid–vapour H_2O interfaces a rough criterion would be to classify a molecule as instantaneously in gaseous, interfacial, or liquid phase according to whether, within a distance of 3 Å therefrom, there are, respectively, fewer than two other such molecules, between two and five such molecules, and six or greater such molecules.

Remark 2. Suppose a third liquid, L say, is present in the porous body, and mixes with neither W nor O molecules. In such a case there may be subsets of W, O, L and B molecules characterised at any instant by the property that, within a distance δ of each W, O, L and B molecules therein, are to be found molecules of each of the other three species. Such subsets delineate regions the span of each of which is of order δ. Accordingly, from the macroscopic viewpoint, these regions are modelled as *common points* (see Gray and Hassanizadeh, 1998). For brevity and simplicity, situations involving more than two immiscible liquids are not here discussed. However, the methodology applies directly to material in four-phase common points.

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[3] Symbol ':=' is to be read as 'is defined to be' or 'defined to be'.

2.2. Outline of the averaging procedure

Let $\mathscr{S}$ denote one of the seven time-dependent subsets of $\mathscr{M}$ in (2.6). Suppose that $\mathscr{M}$ consists of N molecules, modelled as a system of point masses P_i $(i = 1, 2, \dots, N)$. The mass, together with the location and velocity at instant τ, of P_i will be denoted by m_i, $\mathbf{x}_i(\tau)$ and $\mathbf{v}_i(\tau)$, respectively. For each P_i, membership or otherwise of $\mathscr{S}(\tau)$ at instant τ is described in terms of function e_i, where

$$e_i(\tau) = \begin{cases} 1 & \text{if } P_i \in \mathscr{S}(\tau) \text{ at instant } \tau, \\ 0 & \text{if } P_i \notin \mathscr{S}(\tau) \text{ at instant } \tau. \end{cases} \tag{2.7}$$

The *total* mass and *total* momentum associated with $\mathscr{S}$ *at instant* τ are thus, respectively,

$$m(\tau) := \sum_{i=1}^{N} m_i e_i(\tau) \quad \text{and} \quad \mathbf{p}(\tau) := \sum_{i=1}^{N} m_i \mathbf{v}_i(\tau) e_i(\tau). \tag{2.8}$$

Remark 3. For simplicity of notation no distinction has been made between the three time-*independent* molecular species $\mathscr{M}_\mathrm{O}$, $\mathscr{M}_\mathrm{W}$ and $\mathscr{M}_\mathrm{B}$ (see (2.1)). Accordingly there will be molecules P_i for which e_i is always zero. For example, if $\mathscr{S}$ is chosen to be $\mathscr{I}_\mathrm{WO}$ then e_i will vanish identically for all $P_i \in \mathscr{M}_\mathrm{B}$. The utility of the membership function e_i is that in what follows all sums are taken over the *fixed* set of molecules which constitute $\mathscr{M}$.

Local spatial densities ρ_w and $\mathbf{p}_w$ of mass and momentum for $\mathscr{S}$, evaluated at a geometrical point $\mathbf{x}$ and instant τ, are defined by

$$\begin{aligned} \rho_w(\mathbf{x}, \tau) &:= \sum_{i=1}^{N} m_i e_i(\tau) w(\mathbf{x}_i(\tau) - \mathbf{x}), \\ \mathbf{p}_w(\mathbf{x}, \tau) &:= \sum_{i=1}^{N} m_i \mathbf{v}_i(\tau) e_i(\tau) w(\mathbf{x}_i(\tau) - \mathbf{x}). \end{aligned} \tag{2.9}$$

Here w is a *weighting-function*. That is, w is a real-valued function, defined for all displacements, which assigns greater emphasis to contributions from molecules near $\mathbf{x}$ to those far from $\mathbf{x}$, has physical dimension L^{-3}, and is normalised; that is

$$\int_{\text{all displacements}} w = 1. \tag{2.10}$$

Remark 4. The simplest choice of w is a 'mollified' (that is, *smoothed*) version of $\hat{w}$, where for any displacement $\mathbf{d}$,

$$\hat{w}(\mathbf{d}) = \begin{cases} \frac{3}{4\pi\epsilon^3} & \text{if } |\mathbf{d}| < \epsilon, \\ 0 & \text{if } |\mathbf{d}| \geqslant \epsilon. \end{cases} \tag{2.11}$$

Choice $w = \hat{w}$ yields $\rho_w(\mathbf{x}, \tau)$ as the total mass of all molecules of $\mathscr{S}(\tau)$ at instant τ which lie within a sphere of radius ϵ centred at $\mathbf{x}$, divided by the volume of this sphere. Similarly, $\mathbf{p}_w(\mathbf{x}, \tau)$ is the momentum density associated with these molecules at instant τ. Mollification can be undertaken on a very short scale compared with ϵ, so that replacing $\hat{w}$ by its smoothed version does not alter, for practical purposes, the interpretations of ρ_w and $\mathbf{p}_w$. Averaging over an REV may be accomplished by simple generalisation of the foregoing. Let V denote the volume of the REV and define, for any pair of points $\mathbf{x}$ and $\mathbf{y}$, $\tilde{w}(\mathbf{y}-\mathbf{x})$ to be V^{-1}, or 0, according to whether $\mathbf{y}$ lies, or does not lie, within that REV with centroid at $\mathbf{x}$. Again w may be chosen to be a mollified version of $\tilde{w}$: this is discussed in detail in Murdoch and Kubik (1995, Section 2.3). The need for mollification arises because w will be differentiated in what follows, yet choices $\hat{w}$ and $\tilde{w}$ in the foregoing are discontinuous on the surface of the sphere and REV, respectively.

In order to take full account of molecular migration between (time-dependent) material systems it proves necessary to define continuum field values in terms of space–*time* averages. Of course, this accords with the identification of particular field values with measurements: no measurement is ever truly instantaneous or localised at a geometrical point. The *Δ-time average of a function f of time at instant t* is

$$f_\Delta(t) := \frac{1}{\Delta}\int_{t-\Delta}^{t} f(\tau)\,\mathrm{d}\tau. \tag{2.12}$$

It follows that if f is continuous, then

$$\dot{f}_\Delta(t) := \frac{\mathrm{d}}{\mathrm{d}t}\{f_\Delta(t)\} = \frac{1}{\Delta}\{f(t) - f(t-\Delta)\}. \tag{2.13}$$

The Δ-time averaged counterparts of ρ_w and $\mathbf{p}_w$ are

$$\rho_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\int_{t-\Delta}^{t} \rho_w(\mathbf{x},\tau)\,\mathrm{d}\tau = \frac{1}{\Delta}\sum_{i=1}^{N} m_i \int_{t-\Delta}^{t} e_i(\tau) w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau \tag{2.14}$$

and

$$\mathbf{p}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\int_{t-\Delta}^{t} \mathbf{p}_w(\mathbf{x},\tau)\,\mathrm{d}\tau = \frac{1}{\Delta}\sum_{i=1}^{N} m_i \int_{t-\Delta}^{t} \mathbf{v}_i(\tau) e_i(\tau) w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau. \tag{2.15}$$

Remark 5. The integrands in (2.14) and (2.15) are not continuous, and hence result (2.13) cannot be invoked in respect of fields $\rho_{w,\Delta}$ and $\mathbf{p}_{w,\Delta}$. However, for each molecule P_i, an instantaneous transition between membership of $\mathscr{S}$ to non-membership (or vice versa), as described by e_i in (2.7), may be mollified over an arbitrarily small time interval (for definiteness 10^{-20} s). Accordingly, transitions may be treated in what follows as if instantaneous, yet result (2.13) is applicable to $\rho_{w,\Delta}$ and $\mathbf{p}_{w,\Delta}$.

3. Balance relations

3.1. Mass balance

From (2.13) and (2.14)

$$\begin{aligned}\frac{\partial \rho_{w,\varDelta}}{\partial t}(\mathbf{x},t) &= \frac{1}{\varDelta}\{\rho_w(\mathbf{x},t) - \rho_w(\mathbf{x},t-\varDelta)\}\\ &= \frac{1}{\varDelta}\sum_{i=1}^{N} m_i\{e_i(t)w(\mathbf{x}_i(t)-\mathbf{x}) - e_i(t-\varDelta)w(\mathbf{x}_i(t-\varDelta)-\mathbf{x})\}.\end{aligned} \tag{3.1}$$

Further, from (2.15),

$$\begin{aligned}(\operatorname{div}\mathbf{p}_{w,\varDelta})(\mathbf{x},t) &= \frac{1}{\varDelta}\sum_{i=1}^{N} m_i \int_{t-\varDelta}^{t} \operatorname{div}_{\mathbf{x}}\{\mathbf{v}_i(\tau)e_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})\}\,\mathrm{d}\tau\\ &= \frac{1}{\varDelta}\sum_{i=1}^{N} m_i \int_{t-\varDelta}^{t} \mathbf{v}_i(\tau)e_i(\tau)\cdot\nabla_{\mathbf{x}}w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau\\ &= -\frac{1}{\varDelta}\sum_{i=1}^{N} m_i \int_{t-\varDelta}^{t} \mathbf{v}_i(\tau)e_i(\tau)\cdot\nabla w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau\\ &= -\frac{1}{\varDelta}\sum_{i=1}^{N} m_i \int_{t-\varDelta}^{t} e_i(\tau)\frac{\mathrm{d}}{\mathrm{d}\tau}\{w(\mathbf{x}_i(\tau)-\mathbf{x})\}\,\mathrm{d}\tau.\end{aligned} \tag{3.2}$$

Appreciation of the last sum is best obtained by considering some simple possibilities, noting that P_i may belong to $\mathscr{S}$ for only part of the time interval $t-\varDelta < \tau < t$, if at all. If $P_i \in \mathscr{S}$ at time $t-\varDelta$, remains therein until $\tau = t_1 < t$, and does not return before time t, then the contribution to the last sum in (3.2) reduces to

$$-\frac{1}{\varDelta}m_i\int_{t-\varDelta}^{t_1}\frac{\mathrm{d}}{\mathrm{d}\tau}\{w(\mathbf{x}_i(\tau)-\mathbf{x})\}\,\mathrm{d}\tau = -\frac{1}{\varDelta}m_i\{w(\mathbf{x}_i(t_1)-\mathbf{x}) - w(\mathbf{x}_i(t-\varDelta)-\mathbf{x})\}. \tag{3.3}$$

Similarly, if $P_i \notin \mathscr{S}$ for $t-\varDelta < \tau < t_0$, and $P_i \in \mathscr{S}$ for $t_0 \leqslant \tau \leqslant t$, then the contribution is

$$-\frac{1}{\varDelta}m_i\{w(\mathbf{x}_i(t)-\mathbf{x}) - w(\mathbf{x}_i(t_0)-\mathbf{x})\}. \tag{3.4}$$

More generally, if $P_i \in \mathscr{S}$ only for times

$$\tau \in [t_{i_1}, t_{i_2}] \cup [t_{i_3}, t_{i_4}] \cup \cdots \cup [t_{i_{2r-1}}, t_{i_{2r}}],$$

where

$$t-\varDelta \leqslant t_{i_1} < t_{i_2} < t_{i_3} < \cdots < t_{i_{2r}} \leqslant t,$$

then the contribution is

$$\begin{aligned}-\frac{1}{\varDelta}m_i\big\{&[w(\mathbf{x}_i(t_{i_2})-\mathbf{x}) + w(\mathbf{x}_i(t_{i_4})-\mathbf{x}) + \cdots + w(\mathbf{x}_i(t_{i_{2r}})-\mathbf{x})]\big\}\\ &- \big\{[w(\mathbf{x}_i(t_{i_1})-\mathbf{x}) + w(\mathbf{x}_i(t_{i_3})-\mathbf{x}) + \cdots + w(\mathbf{x}_i(t_{i_{2r-1}})-\mathbf{x})]\big\}.\end{aligned} \tag{3.5}$$

It follows from (3.2), and consideration of all migratory possibilities such as (3.3)–(3.5), that

$$\big(\operatorname{div}\mathbf{p}_{w,\Delta}\big)(\mathbf{x},t) = -\frac{1}{\Delta}\left\{\sum_{i=1}^{N} m_i e_i(t) w(\mathbf{x}_i(t)-\mathbf{x}) - \sum_{i=1}^{N} m_i e_i(t-\Delta) w(\mathbf{x}_i(t-\Delta)-\mathbf{x})\right\} - \mathscr{G}^{\text{out}}_{w,\Delta}(\mathbf{x},t) + \mathscr{G}^{\text{in}}_{w,\Delta}(\mathbf{x},t), \tag{3.6}$$

where

$$\mathscr{G}^{\text{out}}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_j} m_i w\big(\mathbf{x}_i(t_{i_j}) - \mathbf{x}\big) \tag{3.7}$$

and

$$\mathscr{G}^{\text{in}}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_k} m_i w(\mathbf{x}_i(t_{i_k}) - \mathbf{x}). \tag{3.8}$$

In (3.7) the i_j sum is taken over all times t_{i_j} in the interval $(t-\Delta, t)$ at which P_i leaves $\mathscr{S}$, and the i_k sum in (3.8) is taken over all times in $(t-\Delta, t)$ at which P_i joins $\mathscr{S}$. There are no contributions from particles P_i which do not migrate into or out of $\mathscr{S}$ during interval $[t-\Delta, t]$. Quantity

$$\mathscr{G}_{w,\Delta} := \mathscr{G}^{\text{in}}_{w,\Delta} - \mathscr{G}^{\text{out}}_{w,\Delta} \tag{3.9}$$

represents the net local rate of mass density increase associated with REVs and time intervals of duration Δ. That is, $\mathscr{G}_{w,\Delta}$ is the *net local mass supply rate density* at the space–time scales corresponding to REV dimensions and Δ-time intervals.

From (3.1) and (3.6)

$$\frac{\partial\rho_{w,\Delta}}{\partial t} + \operatorname{div}\mathbf{p}_{w,\Delta} = \mathscr{G}_{w,\Delta}. \tag{3.10}$$

The appropriate velocity field is

$$\mathbf{v}_{w,\Delta} := \mathbf{p}_{w,\Delta}/\rho_{w,\Delta}, \tag{3.11}$$

which yields from (3.10) the mass balance for $\mathscr{S}$ as

$$\frac{\partial\rho_{w,\Delta}}{\partial t} + \operatorname{div}(\rho_{w,\Delta}\mathbf{v}_{w,\Delta}) = \mathscr{G}_{w,\Delta}. \tag{3.12}$$

Remark 6. Field $\mathbf{v}_{w,\Delta}$ is the natural kinematic variable in terms of which the concepts of 'motion', 'deformation', and 'material point' may be derived (see Murdoch, 1998, Section 3.1). This is the reverse of the usual viewpoint (see, for example, Truesdell and Noll, 1965) in which the primitive concepts are material point and deformation. Let B_t denote the common spatial domain of $\rho_{w,\Delta}$ and $\mathbf{p}_{w,\Delta}$ at time t. Then the *motion relative to the situation at time* t_0 is the solution $\boldsymbol{\chi}_0^{w,\Delta}$ to the initial-value problem defined for each $\mathbf{X} \in B_{t_0}$ by

$$\dot{\boldsymbol{\chi}}_0^{w,\Delta}(\mathbf{X},t) = \mathbf{v}_{w,\Delta}\big(\boldsymbol{\chi}_0^{w,\Delta}(\mathbf{X},t),t\big), \tag{3.13}$$

where

$$\boldsymbol{\chi}_0^{w,\Delta}(\mathbf{X},t_0) = \mathbf{X}.$$

With each $\mathbf{X} \in B_{t_0}$ may be identified a material point X: $\boldsymbol{\chi}_0^{w,\Delta}(\mathbf{X}, t)$ is regarded to be the location of X at time t. Accordingly it is seen that the notion of material point is scale-dependent, and is a mathematical construct based upon the fundamental physical quantities $\rho_{w,\Delta}$ and $\mathbf{p}_{w,\Delta}$. Further, such notion is independent of whether or not the material system in question is time-dependent.

Remark 7. Relation (3.10), together with subsequent balance relations for momentum, moment of momentum, and energy, hold for averages of molecular quantities computed at the arbitrary length scale (ϵ say) associated with w, and the arbitrary time scale Δ. Of course, such balances need to be supplemented by constitutive assumptions which involve relations between ϵ and Δ – scale averages: for example, the manner in which force density representing the resistance to flow of one fluid due to its interaction with the porous body depends upon the velocity of the fluid relative to the porous body. It is at the stage of making such constitutive assumptions that specific scales become crucial. While the *sine qua non* for spatial scales is the assumption of an REV, the time scale Δ is not usually discussed. At a fundamental level, Δ must be large compared with appropriate molecular time scales. Small molecules have typical mass centre average speeds of 10^3 ms^{-1} (at standard temperature and pressure), with condensed phase separations of order 3 Å ($= 3 \times 10^{-10}$ m), and the relevant *molecular* time scale is 3×10^{-13} s. Macromolecular liquids have longer time scales, but the choice $\Delta = 10^{-6}$ s will in general suffice. From a practical standpoint, continuum field values must be related to measurement values which are (in the context of deterministic modelling) reproducible to within some tolerance of variation. Measurement values are associated with monitoring the system at specific length and time scales. (No measurement is either entirely 'local' in space or 'instantaneous' but has associated scales of length and time.) It follows that the ultimate criteria for relevant ϵ, Δ values in any specific context are:

(i) the specific phenomenon/flow in question,
(ii) the length/time scales of the measurements made, and
(iii) the tolerance of variation admitted which results in reproducible behaviour at the scales of (ii), as evidenced by measurement.

These considerations were discussed in more detail in Section 2.2.1 of Murdoch and Bedeaux (1996).

Remark 8. In the foregoing discussion of molecular migration, no account was taken of the material system from or to which $\mathscr{S}$ molecules came or went. For example, if $\mathscr{S}$ is $\mathscr{I}_{\mathrm{WO}}$ then a W molecule can enter from $\mathscr{M}_{\mathrm{W}}^{\mathrm{W}}$, $\mathscr{M}_{\mathrm{W}}^{\mathrm{B}}$, or $\mathscr{T}_{\mathrm{WOB}}$, while an O molecule can enter from $\mathscr{M}_{\mathrm{O}}^{\mathrm{O}}$, $\mathscr{M}_{\mathrm{O}}^{\mathrm{B}}$, or $\mathscr{T}_{\mathrm{WOB}}$. Similarly, W or O molecules can leave $\mathscr{I}_{\mathrm{WO}}$ for these same systems. Taking account of such detailed book-keeping would seem to be a priori desirable.

Remark 9. In itemising separate contributions to the exchange term $\mathscr{G}_{w,\Delta}$ it should be noted that certain migrations are highly unlikely. For example, for a W → WOB transition to occur at some instant, a W molecule must *simultaneously* 'encounter' an O molecule *and* a B molecule in the sense of being distant *exactly* δ from each at this instant. In what follows such transitions will be assumed to yield negligible contributions to migratory quantities. Specifically terms associated with W → WOB, WOB → W, B → WOB, WOB → B, O → WOB, WOB → O, BW → WO, WO → BW, BW → BO, BO → BW transitions will be neglected. The foregoing reasoning was based solely upon the definitions of the relevant material systems in terms of purely molecular considerations. While it may be helpful to visualise regions 'occupied' by such systems (for example, interfacial regions), such a viewpoint corresponds to a continuum description at a scale at which pore geometry is manifest, and is *not* adopted here. Indeed, it is the prime objective of this work to derive balance relations which involve REV-scale field values directly from a molecular perspective.

Paying attention to Remarks 8 and 9, the local forms of mass balance for the time-dependent systems considered are, upon suppressing dependence upon w and Δ for brevity, as follows:

$$\mathscr{M}^{\mathrm{W}}_{\mathrm{W}}: \quad \frac{\partial \rho_{\mathrm{W}}}{\partial t} + \operatorname{div} \rho_{\mathrm{W}} \mathbf{v}_{\mathrm{W}} = \mathscr{G}^{\mathrm{WO}\to\mathrm{W}} + \mathscr{G}^{\mathrm{BW}\to\mathrm{W}} - \mathscr{G}^{\mathrm{W}\to\mathrm{WO}} - \mathscr{G}^{\mathrm{W}\to\mathrm{BW}}, \tag{3.14}$$

$$\mathscr{M}^{\mathrm{O}}_{\mathrm{O}}: \quad \frac{\partial \rho_{\mathrm{O}}}{\partial t} + \operatorname{div} \rho_{\mathrm{O}} \mathbf{v}_{\mathrm{O}} = \mathscr{G}^{\mathrm{WO}\to\mathrm{O}} + \mathscr{G}^{\mathrm{OB}\to\mathrm{O}} - \mathscr{G}^{\mathrm{O}\to\mathrm{WO}} - \mathscr{G}^{\mathrm{O}\to\mathrm{OB}}, \tag{3.15}$$

$$\mathscr{M}^{\mathrm{B}}_{\mathrm{B}}: \quad \frac{\partial \rho_{\mathrm{B}}}{\partial t} + \operatorname{div} \rho_{\mathrm{B}} \mathbf{v}_{\mathrm{B}} = \mathscr{G}^{\mathrm{OB}\to\mathrm{B}} + \mathscr{G}^{\mathrm{BW}\to\mathrm{B}} - \mathscr{G}^{\mathrm{B}\to\mathrm{OB}} - \mathscr{G}^{\mathrm{B}\to\mathrm{BW}}, \tag{3.16}$$

$$\begin{aligned}\mathscr{I}_{\mathrm{WO}}: \quad & \frac{\partial \rho_{\mathrm{WO}}}{\partial t} + \operatorname{div} \rho_{\mathrm{WO}} \mathbf{v}_{\mathrm{WO}} \\ & = \mathscr{G}^{\mathrm{O}\to\mathrm{WO}} + \mathscr{G}^{\mathrm{W}\to\mathrm{WO}} + \mathscr{G}^{\mathrm{WOB}\to\mathrm{WO}} - \mathscr{G}^{\mathrm{WO}\to\mathrm{O}} - \mathscr{G}^{\mathrm{WO}\to\mathrm{W}} - \mathscr{G}^{\mathrm{WO}\to\mathrm{WOB}},\end{aligned} \tag{3.17}$$

$$\begin{aligned}\mathscr{I}_{\mathrm{BW}}: \quad & \frac{\partial \rho_{\mathrm{BW}}}{\partial t} + \operatorname{div} \rho_{\mathrm{BW}} \mathbf{v}_{\mathrm{BW}} \\ & = \mathscr{G}^{\mathrm{B}\to\mathrm{BW}} + \mathscr{G}^{\mathrm{W}\to\mathrm{BW}} + \mathscr{G}^{\mathrm{WOB}\to\mathrm{BW}} - \mathscr{G}^{\mathrm{BW}\to\mathrm{B}} - \mathscr{G}^{\mathrm{BW}\to\mathrm{W}} - \mathscr{G}^{\mathrm{BW}\to\mathrm{WOB}},\end{aligned} \tag{3.18}$$

$$\begin{aligned}\mathscr{I}_{\mathrm{OB}}: \quad & \frac{\partial \rho_{\mathrm{OB}}}{\partial t} + \operatorname{div} \rho_{\mathrm{OB}} \mathbf{v}_{\mathrm{OB}} \\ & = \mathscr{G}^{\mathrm{O}\to\mathrm{OB}} + \mathscr{G}^{\mathrm{B}\to\mathrm{OB}} + \mathscr{G}^{\mathrm{WOB}\to\mathrm{OB}} - \mathscr{G}^{\mathrm{OB}\to\mathrm{O}} - \mathscr{G}^{\mathrm{OB}\to\mathrm{B}} - \mathscr{G}^{\mathrm{OB}\to\mathrm{WOB}},\end{aligned} \tag{3.19}$$

$$\begin{aligned}\mathscr{T}_{\mathrm{WOB}}: \quad & \frac{\partial \rho_{\mathrm{WOB}}}{\partial t} + \operatorname{div} \rho_{\mathrm{WOB}} \mathbf{v}_{\mathrm{WOB}} \\ & = \mathscr{G}^{\mathrm{OB}\to\mathrm{WOB}} + \mathscr{G}^{\mathrm{BW}\to\mathrm{WOB}} + \mathscr{G}^{\mathrm{WO}\to\mathrm{WOB}} - \mathscr{G}^{\mathrm{WOB}\to\mathrm{OB}} - \mathscr{G}^{\mathrm{WOB}\to\mathrm{BW}} - \mathscr{G}^{\mathrm{WOB}\to\mathrm{WO}}.\end{aligned} \tag{3.20}$$

Here ρ_{W}, ρ_{O}, ρ_{B}, ρ_{WO}, ρ_{BW}, ρ_{OB} and ρ_{WOB} denote the mass densities for systems $\mathscr{M}^{\mathrm{W}}_{\mathrm{W}}$, $\mathscr{M}^{\mathrm{O}}_{\mathrm{O}}$, $\mathscr{M}^{\mathrm{B}}_{\mathrm{B}}$, $\mathscr{I}_{\mathrm{WO}}$, $\mathscr{I}_{\mathrm{BW}}$, $\mathscr{I}_{\mathrm{OB}}$ and $\mathscr{T}_{\mathrm{WOB}}$, respectively, with corresponding velocity fields written as $\mathbf{v}_{\mathrm{W}}$, $\mathbf{v}_{\mathrm{O}}$, $\mathbf{v}_{\mathrm{B}}$, $\mathbf{v}_{\mathrm{WO}}$, $\mathbf{v}_{\mathrm{BW}}, \mathbf{v}_{\mathrm{OB}}$ and $\mathbf{v}_{\mathrm{WOB}}$. Term $\mathscr{G}^{\mathrm{WO}\to\mathrm{W}}$ denotes the mass supply rate density associated with migration of W molecules from $\mathscr{I}_{\mathrm{WO}}$ into $\mathscr{M}^{\mathrm{W}}_{\mathrm{W}}$, and $-\mathscr{G}^{\mathrm{W}\to\mathrm{WO}}$ the corresponding (negative, of course) density corresponding to migration of W molecules out of $\mathscr{M}^{\mathrm{W}}_{\mathrm{W}}$ into $\mathscr{I}_{\mathrm{WO}}$. Similar interpretations attach to $\mathscr{G}^{\mathrm{BW}\to\mathrm{W}}$, $-\mathscr{G}^{\mathrm{W}\to\mathrm{BW}}$, etc. while $\mathscr{G}^{\mathrm{WOB}\to\mathrm{WO}}$ and $-\mathscr{G}^{\mathrm{WO}\to\mathrm{WOB}}$ take care of migration of W and O molecules between $\mathscr{T}_{\mathrm{WOB}}$ and $\mathscr{I}_{\mathrm{WO}}$, etc.

3.2. Linear momentum balance

In an inertial frame the motion of P_i is governed by

$$\sum_{\substack{\ell=1\\ \ell\neq i}}^{N} \mathbf{f}_{i\ell} + \mathbf{b}_i = m_i\dot{\mathbf{v}}_i, \tag{3.21}$$

where $\mathbf{f}_{i\ell}$ denotes the force exerted upon P_i by another point mass P_ℓ, $\mathbf{b}_i$ represents the resultant force on P_i due to all agencies other than $\mathscr{M}$ (including, of course, the effect of gravitation), and $\dot{\mathbf{v}}_i := \mathrm{d}\mathbf{v}_i/\mathrm{d}t$. Multiplication of all terms in (3.21) at time τ by $e_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})$, and summing over all particles, yield

$$\sum_{i=1}^{N}\sum_{\substack{\ell=1\\ \ell\neq i}}^{N} \mathbf{f}_{i\ell}(\tau)e_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x}) + \sum_{i=1}^{N}\mathbf{b}_i(\tau)e_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x}) = \sum_{i=1}^{N} m_i e_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})\dot{\mathbf{v}}_i(\tau). \tag{3.22}$$

The presence of factor $e_i(\tau)$ throughout means that (3.22) is a relation pertaining to system $\mathscr{S}$ (see (2.6)), while common factor $w(\mathbf{x}_i(\tau)-\mathbf{x})$ for each $i = 1,2,\ldots,N$ indicates the equation involves only spatial densities localised at the geometrical point $\mathbf{x}$. The separate contributions of $\mathscr{S}$ and non-$\mathscr{S}$ molecules to relation (3.22) may be distinguished by decomposition of the first term:

$$\sum_{i=1}^{N}\sum_{\substack{\ell=1\\ \ell\neq i}}^{N} \mathbf{f}_{i\ell}(\tau)e_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x}) = \mathbf{f}_w^{\mathrm{int}}(\mathbf{x},\tau) + \mathbf{f}_w^{\mathrm{ext}}(\mathbf{x},\tau), \tag{3.23}$$

where

$$\mathbf{f}_w^{\mathrm{int}}(\mathbf{x},\tau) := \sum_{i=1}^{N}\sum_{\substack{\ell=1\\ \ell\neq i}}^{N} \mathbf{f}_{i\ell}(\tau)e_i(\tau)e_\ell(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x}) \tag{3.24}$$

and

$$\mathbf{f}_w^{\mathrm{ext}}(\mathbf{x},\tau) := \sum_{i=1}^{N}\sum_{\substack{\ell=1\\ \ell\neq i}}^{N} \mathbf{f}_{i\ell}(\tau)e_i(\tau)(1-e_\ell(\tau))w(\mathbf{x}_i(\tau)-\mathbf{x}). \tag{3.25}$$

The only non-zero terms in sum (3.24) are those for which both $e_i(\tau)$ and $e_\ell(\tau)$ equal to 1 (see (2.6)), so $\mathbf{f}_w^{\mathrm{int}}$ involves only $\mathscr{S}$–$\mathscr{S}$ molecular interactions. In (3.25) only terms for which $e_i(\tau) = 1$ and $e_\ell(\tau) = 0$ contribute, whence $\mathbf{f}_w^{\mathrm{ext}}$ delivers the effect of non-$\mathscr{S}$ molecules upon $\mathscr{S}$ molecules.

The Δ-time average of the left-hand side of (3.22) at time t yields

$$\mathbf{f}_{w,\Delta}^{\mathrm{int}}(\mathbf{x},t) + \mathbf{f}_{w,\Delta}^{\mathrm{ext}}(\mathbf{x},t) + \mathbf{b}_{w,\Delta}(\mathbf{x},t), \tag{3.26}$$

where

$$\mathbf{f}^{\mathrm{int}}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\int_{t-\Delta}^{t} \mathbf{f}^{\mathrm{int}}(\mathbf{x},\tau)\,\mathrm{d}\tau, \quad \mathbf{f}^{\mathrm{ext}}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\int_{t-\Delta}^{t} \mathbf{f}^{\mathrm{ext}}_{w}(\mathbf{x},\tau)\,\mathrm{d}\tau \tag{3.27}$$

and

$$\mathbf{b}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\int_{t-\Delta}^{t} \mathbf{b}_i(\tau)e_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau. \tag{3.28}$$

Remark 10. Force density $\mathbf{f}^{\mathrm{int}}_{w,\Delta}(\mathbf{x},t)$ is a local space–time average associated with the effect of $\mathscr{S}$ molecules *anywhere* upon $\mathscr{S}$ molecules within that REV centred at $\mathbf{x}$. Pairwise equilibration of molecular interactions (that is, $\mathbf{f}_{i\ell}+\mathbf{f}_{\ell i}=\mathbf{0}$ for *any* P_i, P_ℓ) implies that this force density is actually the effect of $\mathscr{S}$ molecules *outside* the REV upon $\mathscr{S}$ molecules *inside* the REV.

From (3.22), expression (3.26) is to be equated with

$$\frac{1}{\Delta}\sum_{i=1}^{N} m_i \int_{t_\Delta}^{t} e_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})\frac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}\tau}\,\mathrm{d}\tau. \tag{3.29}$$

Now

$$w(\mathbf{x}_i(\tau)-\mathbf{x})\frac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}\tau} = \frac{\mathrm{d}}{\mathrm{d}\tau}\{w(\mathbf{x}_i(\tau)-\mathbf{x})\mathbf{v}_i(\tau)\} - \frac{\mathrm{d}}{\mathrm{d}\tau}\{w(\mathbf{x}_i(\tau)-\mathbf{x})\}\mathbf{v}_i(\tau) \tag{3.30}$$

and

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\tau}\{w(\mathbf{x}_i(\tau)-\mathbf{x})\}\mathbf{v}_i(\tau) &= (\nabla w(\mathbf{x}_i(\tau)-\mathbf{x})\cdot\mathbf{v}_i(\tau))\mathbf{v}_i(\tau)\\ &= (\mathbf{v}_i(\tau)\otimes\mathbf{v}_i(\tau))\nabla w(\mathbf{x}_i(\tau)-\mathbf{x})\\ &= -\mathrm{div}_{\mathbf{x}}\{\mathbf{v}_i(\tau)\otimes\mathbf{v}_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})\}.\end{aligned} \tag{3.31}$$

Here the tensor product of two vectors has been introduced: if $\mathbf{a},\mathbf{b}$ are vectors then $\mathbf{a}\otimes\mathbf{b}$ is that linear transformation which acts upon any vector $\mathbf{v}$ to yield vector $(\mathbf{b}\cdot\mathbf{v})\mathbf{a}$. [In Cartesian tensor notation $(\mathbf{a}\otimes\mathbf{b})_{ij}=a_ib_j$.] Use has also been made of the identity

$$\mathrm{div}\{\phi\mathbf{A}\} = \phi\,\mathrm{div}\,\mathbf{A} + \mathbf{A}\nabla\phi,$$

where ϕ is a scalar field and $\mathbf{A}$ is a linear transformation field: here $\phi = w$ and $\mathbf{A}$ is the position-independent tensor $\mathbf{v}_i\otimes\mathbf{v}_i$ (so $\mathrm{div}\,\mathbf{A}=\mathbf{0}$). From (3.30) and (3.31) expression (3.29) may be written as

$$\frac{1}{\Delta}\sum_{i=1}^{N} m_i \int_{t-\Delta}^{t} e_i(\tau)\frac{\mathrm{d}}{\mathrm{d}\tau}\{w(\mathbf{x}_i(\tau)-\mathbf{x})\mathbf{v}_i(\tau)\}\,\mathrm{d}\tau + \mathrm{div}\,\mathbf{B}, \tag{3.32}$$

where

$$\mathbf{B}(\mathbf{x},t) := \frac{1}{\Delta}\int_{t-\Delta}^{t}\sum_{i=1}^{N}\{e_i(\tau)m_i\mathbf{v}_i(\tau)\otimes\mathbf{v}_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})\}\,\mathrm{d}\tau. \tag{3.33}$$

Contributions to $\mathbf{B}(\mathbf{x},t)$ derive solely from particles located near $\mathbf{x}$ at times close to t. In this respect it proves helpful to introduce the *notional diffusive velocity of* P_i *with respect to location* $\mathbf{x}$ *and time* t as

$$\hat{\mathbf{v}}_i(\tau;\mathbf{x},t) := \mathbf{v}_i(\tau) - \mathbf{v}_{w,\Delta}(\mathbf{x},t). \tag{3.34}$$

Whenever P_i is near to $\mathbf{x}$ at a time τ close to t, the *notional* diffusive velocity of P_i at time τ with respect to $(\mathbf{x},t)$ approximates the actual *diffusive velocity* $\tilde{\mathbf{v}}_i(\tau) := \mathbf{v}_i(\tau) - \mathbf{v}_{w,\Delta}(\mathbf{x}_i(\tau),\tau)$ of P_i at time τ.

From (2.14), (2.15) and (3.11),

$$\frac{1}{\Delta}\int_{t-\Delta}^{t}\sum_{i=1}^{N} e_i(\tau)m_i\hat{\mathbf{v}}_i(\tau;\mathbf{x},t)w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau = \mathbf{0}. \tag{3.35}$$

Accordingly, using (3.34) to express $\mathbf{v}_i$ in terms of $\hat{\mathbf{v}}_i$ and $\mathbf{v}_{w,\Delta}$ in the definition (3.33) of $\mathbf{B}$, and invoking (3.35), it follows that

$$\mathbf{B} = \hat{\mathbf{D}}_{w,\Delta} + \rho_{w,\Delta}\mathbf{v}_{w,\Delta}\otimes\mathbf{v}_{w,\Delta}, \tag{3.36}$$

where the *diffusive stress tensor*

$$\hat{\mathbf{D}}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\int_{t-\Delta}^{t}\sum_{i=1}^{N} e_i(\tau)m_i\hat{\mathbf{v}}_i(\tau;\mathbf{x},t)\otimes\hat{\mathbf{v}}_i(\tau;\mathbf{x},t)w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau. \tag{3.37}$$

The first expression in (3.32) may be treated as the sum in (3.2): consideration of all migratory possibilities yields for this expression

$$\begin{aligned}&\frac{1}{\Delta}\sum_{i=1}^{N} m_i\{e_i(t)\mathbf{v}_i(t)w(\mathbf{x}_i(t)-\mathbf{x}) - e_i(t-\Delta)\mathbf{v}_i(t-\Delta)w(\mathbf{x}_i(t-\Delta)-\mathbf{x})\}\\ &\qquad + \mathbf{P}^{\mathrm{out}}_{w,\Delta}(\mathbf{x},t) - \mathbf{P}^{\mathrm{in}}_{w,\Delta}(\mathbf{x},t),\end{aligned} \tag{3.38}$$

where

$$\mathbf{P}^{\mathrm{out}}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_j} m_i\mathbf{v}_i(t_{i_j})w(\mathbf{x}_i(t_{i_j})-\mathbf{x}) \tag{3.39}$$

and

$$\mathbf{P}^{\mathrm{in}}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_k} m_i\mathbf{v}_i(t_{i_k})w(\mathbf{x}_i(t_{i_k})-\mathbf{x}). \tag{3.40}$$

The sums in (3.39) and (3.40) are precisely those sums which appear in (3.7) and (3.8), respectively. Term $\mathbf{P}^{\mathrm{out}}_{w,\Delta}$ ($\mathbf{P}^{\mathrm{in}}_{w,\Delta}$) represents a local time rate of change of momentum density associated with molecules leaving (entering) $\mathscr{S}$. The sum in (3.38) is, using (2.13) with $f(\tau) = \mathbf{p}_w(\mathbf{x},\tau)$, $(\partial\mathbf{p}_{w,\Delta}/\partial t)(\mathbf{x},t)$ (see $(2.8)_2$ and (2.15)). This observation, together with (3.22), (3.26), (3.29), (3.32), (3.36) and (3.38), yield the local form of linear momentum balance for $\mathscr{S}$ as (upon suppressing suffices w,Δ and arguments $\mathbf{x},t$)

$$\mathbf{f}^{\text{int}} + \mathbf{f}^{\text{ext}} + \mathbf{P}^{\text{in}} - \mathbf{P}^{\text{out}} + \mathbf{b} = \frac{\partial}{\partial t}\{\rho\mathbf{v}\} + \operatorname{div}\{\hat{\mathbf{D}} + \rho\mathbf{v}\otimes\mathbf{v}\}. \tag{3.41}$$

The effectively short-range nature of molecular interactions enables Noll's Theorem (first introduced by Noll, 1955) to be used to exhibit the existence (and explicit form) of the *$\mathscr{S}$–$\mathscr{S}$ interaction stress tensor* $\mathbf{T}^{-}_{w,\Delta}$ such that

$$\mathbf{f}^{\text{int}}_{w,\Delta} = \operatorname{div}\mathbf{T}^{-}_{w,\Delta}. \tag{3.42}$$

(See Murdoch and Bedeaux, 1994 or Murdoch and Kubik, 1995 for details.) It follows that (3.41) may be expressed in the form

$$\operatorname{div}\mathbf{T} + \mathbf{f}^{\text{ext}} + \mathbf{P}^{\text{in}} - \mathbf{P}^{\text{out}} + \mathbf{b} = \frac{\partial}{\partial t}\{\rho\mathbf{v}\} + \operatorname{div}\{\rho\mathbf{v}\otimes\mathbf{v}\}, \tag{3.43}$$

where the *$\mathscr{S}$–$\mathscr{S}$ stress tensor*

$$\mathbf{T} := \mathbf{T}^{-} - \hat{\mathbf{D}}. \tag{3.44}$$

Equivalently, invoking mass balance (3.12),

$$\operatorname{div}\mathbf{T} + \mathbf{f}^{\text{ext}} + \mathbf{P} + \mathbf{b} = \rho\dot{\mathbf{v}} + \mathscr{G}\mathbf{v}, \tag{3.45}$$

where the material time derivative

$$\dot{\mathbf{v}} := \partial\mathbf{v}/\partial t + (\nabla\mathbf{v})\mathbf{v} \tag{3.46}$$

denotes the acceleration field appropriate to system $\mathscr{S}$, and

$$\mathbf{P} := \mathbf{P}^{\text{in}} - \mathbf{P}^{\text{out}} \tag{3.47}$$

represents the *net* momentum density supply rate due to $\mathscr{S}$ molecular migration. An alternative form of (3.45) is

$$\operatorname{div}\mathbf{T} + \mathbf{f}^{\text{ext}} + \mathbf{I} + \mathbf{b} = \rho\dot{\mathbf{v}}, \tag{3.48}$$

where

$$\mathbf{P} - \mathscr{G}\mathbf{v} =: \mathbf{I} = \mathbf{I}^{\text{in}} - \mathbf{I}^{\text{out}}, \tag{3.49}$$

with (see (3.7), (3.8), (3.39) and (3.40))

$$\mathbf{I}^{\text{in}}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_k} m_i\hat{\mathbf{v}}_i(t_{i_k};\mathbf{x},t)w(\mathbf{x}_i(t_{i_k}) - \mathbf{x}) \tag{3.50}$$

and

$$\mathbf{I}^{\text{out}}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_j} m_i\hat{\mathbf{v}}_i(t_{i_j};\mathbf{x},t)w(x_i(t_{i_j}) - \mathbf{x}). \tag{3.51}$$

Remark 11. Fields $\hat{\mathbf{D}}$, $\mathbf{I}^{\text{in}}$ and $\mathbf{I}^{\text{out}}$ are defined in terms of molecular *notional* diffusive velocities. The actual diffusive velocity of P_i (at REV spatial, and Δ-time, scales) in the foregoing is $\tilde{\mathbf{v}}_i := \mathbf{v}_i(\tau) - \mathbf{v}_{w,\Delta}(\mathbf{x}_i(\tau),\tau)$, which is, for $(\mathbf{x}_i(\tau),\tau)$ near $(\mathbf{x},t)$, well-approximated by $\hat{\mathbf{v}}_i(\tau;\mathbf{x},t)$. Since average molecular velocities in solids or fluids are large compared with REV-scale velocities of any system here considered, fields $\hat{\mathbf{D}}$, $\mathbf{I}^{\text{in}}$ and $\mathbf{I}^{\text{out}}$ are essentially of thermal character. The kinetic energy $\sum_{i=1}^{N} e_i m_i \tilde{\mathbf{v}}_i^2/2$ is the heat energy instantaneously possessed by system $\mathscr{S}$: this is precisely the kinetic theory of heat (see, for example, Brush, 1986).

Recalling Remarks 8 and 9, details of the separate contributions to $\mathbf{f}^{\text{ext}}$ and $\mathbf{P}$ from each system distinct from $\mathscr{S}$ can be made explicit. The balances of linear momentum for the seven systems considered are, upon indicating such book-keeping, as follows:

$$\begin{aligned}\mathscr{M}_{\mathrm{W}}^{\mathrm{W}}:\quad & \operatorname{div}\mathbf{T}_{\mathrm{W}} + \mathbf{f}_{\mathrm{W}}^{\mathrm{WO}} + \mathbf{f}_{\mathrm{W}}^{\mathrm{BW}} + \mathbf{f}_{\mathrm{W}}^{\mathrm{WOB}} + \mathbf{b}_{\mathrm{W}} + \mathbf{P}^{\mathrm{WO}\to\mathrm{W}} - \mathbf{P}^{\mathrm{W}\to\mathrm{WO}} + \mathbf{P}^{\mathrm{BW}\to\mathrm{W}} - \mathbf{P}^{\mathrm{W}\to\mathrm{BW}} \\ & = \frac{\partial}{\partial t}\{\rho_{\mathrm{W}}\mathbf{v}_{\mathrm{W}}\} + \operatorname{div}\{\rho_{\mathrm{W}}\mathbf{v}_{\mathrm{W}} \otimes \mathbf{v}_{\mathrm{W}}\},\end{aligned} \tag{3.52}$$

$$\begin{aligned}\mathscr{M}_{\mathrm{O}}^{\mathrm{O}}:\quad & \operatorname{div}\mathbf{T}_{\mathrm{O}} + \mathbf{f}_{\mathrm{O}}^{\mathrm{WO}} + \mathbf{f}_{\mathrm{O}}^{\mathrm{OB}} + \mathbf{f}_{\mathrm{O}}^{\mathrm{WOB}} + \mathbf{b}_{\mathrm{O}} + \mathbf{P}^{\mathrm{WO}\to\mathrm{O}} - \mathbf{P}^{\mathrm{O}\to\mathrm{WO}} + \mathbf{P}^{\mathrm{OB}\to\mathrm{O}} - \mathbf{P}^{\mathrm{O}\to\mathrm{OB}} \\ & = \frac{\partial}{\partial t}\{\rho_{\mathrm{O}}\mathbf{v}_{\mathrm{O}}\} + \operatorname{div}\{\rho_{\mathrm{O}}\mathbf{v}_{\mathrm{O}} \otimes \mathbf{v}_{\mathrm{O}}\},\end{aligned} \tag{3.53}$$

$$\begin{aligned}\mathscr{M}_{\mathrm{B}}^{\mathrm{B}}:\quad & \operatorname{div}\mathbf{T}_{\mathrm{B}} + \mathbf{f}_{\mathrm{B}}^{\mathrm{OB}} + \mathbf{f}_{\mathrm{B}}^{\mathrm{BW}} + \mathbf{f}_{\mathrm{B}}^{\mathrm{WOB}} + \mathbf{b}_{\mathrm{B}} + \mathbf{P}^{\mathrm{OB}\to\mathrm{B}} - \mathbf{P}^{\mathrm{B}\to\mathrm{OB}} + \mathbf{P}^{\mathrm{BW}\to\mathrm{B}} - \mathbf{P}^{\mathrm{B}\to\mathrm{BW}} \\ & = \frac{\partial}{\partial t}\{\rho_{\mathrm{B}}\mathbf{v}_{\mathrm{B}}\} + \operatorname{div}\{\rho_{\mathrm{B}}\mathbf{v}_{\mathrm{B}} \otimes \mathbf{v}_{\mathrm{B}}\},\end{aligned} \tag{3.54}$$

$$\begin{aligned}\mathscr{I}^{\mathrm{WO}}:\quad & \operatorname{div}\mathbf{T}_{\mathrm{WO}} + \mathbf{f}_{\mathrm{WO}}^{\mathrm{W}} + \mathbf{f}_{\mathrm{WO}}^{\mathrm{O}} + \mathbf{f}_{\mathrm{WO}}^{\mathrm{BO}} + \mathbf{f}_{\mathrm{WO}}^{\mathrm{BW}} + \mathbf{f}_{\mathrm{WO}}^{\mathrm{WOB}} + \mathbf{b}_{\mathrm{WO}} + \mathbf{P}^{\mathrm{O}\to\mathrm{WO}} - \mathbf{P}^{\mathrm{WO}\to\mathrm{O}} \\ & + \mathbf{P}^{\mathrm{W}\to\mathrm{WO}} - \mathbf{P}^{\mathrm{WO}\to\mathrm{W}} + \mathbf{P}^{\mathrm{WOB}\to\mathrm{WO}} - \mathbf{P}^{\mathrm{WO}\to\mathrm{WOB}} \\ & = \frac{\partial}{\partial t}\{\rho_{\mathrm{WO}}\mathbf{v}_{\mathrm{WO}}\} + \operatorname{div}\{\rho_{\mathrm{WO}}\mathbf{v}_{\mathrm{WO}} \otimes \mathbf{v}_{\mathrm{WO}}\},\end{aligned} \tag{3.55}$$

$$\begin{aligned}\mathscr{I}^{\mathrm{BW}}:\quad & \operatorname{div}\mathbf{T}_{\mathrm{BW}} + \mathbf{f}_{\mathrm{BW}}^{\mathrm{B}} + \mathbf{f}_{\mathrm{BW}}^{\mathrm{W}} + \mathbf{f}_{\mathrm{BW}}^{\mathrm{OB}} + \mathbf{f}_{\mathrm{BW}}^{\mathrm{WO}} + \mathbf{f}_{\mathrm{BW}}^{\mathrm{WOB}} + \mathbf{b}_{\mathrm{BW}} + \mathbf{P}^{\mathrm{B}\to\mathrm{BW}} - \mathbf{P}^{\mathrm{BW}\to\mathrm{B}} \\ & + \mathbf{P}^{\mathrm{W}\to\mathrm{BW}} - \mathbf{P}^{\mathrm{BW}\to\mathrm{W}} + \mathbf{P}^{\mathrm{WOB}\to\mathrm{BW}} - \mathbf{P}^{\mathrm{BW}\to\mathrm{WOB}} \\ & = \frac{\partial}{\partial t}\{\rho_{\mathrm{BW}}\mathbf{v}_{\mathrm{BW}}\} + \operatorname{div}\{\rho_{\mathrm{BW}}\mathbf{v}_{\mathrm{BW}} \otimes \mathbf{v}_{\mathrm{BW}}\},\end{aligned} \tag{3.56}$$

$$\begin{aligned}\mathscr{I}^{\mathrm{OB}}:\quad & \operatorname{div}\mathbf{T}_{\mathrm{OB}} + \mathbf{f}_{\mathrm{OB}}^{\mathrm{O}} + \mathbf{f}_{\mathrm{OB}}^{\mathrm{B}} + \mathbf{f}_{\mathrm{OB}}^{\mathrm{BW}} + \mathbf{f}_{\mathrm{OB}}^{\mathrm{WO}} + \mathbf{f}_{\mathrm{OB}}^{\mathrm{WOB}} + \mathbf{b}_{\mathrm{OB}} + \mathbf{P}^{\mathrm{O}\to\mathrm{OB}} - \mathbf{P}^{\mathrm{OB}\to\mathrm{O}} + \mathbf{P}^{\mathrm{B}\to\mathrm{OB}} \\ & - \mathbf{P}^{\mathrm{OB}\to\mathrm{B}} + \mathbf{P}^{\mathrm{WOB}\to\mathrm{OB}} - \mathbf{P}^{\mathrm{OB}\to\mathrm{WOB}} \\ & = \frac{\partial}{\partial t}\{\rho_{\mathrm{OB}}\mathbf{v}_{\mathrm{OB}}\} + \operatorname{div}\{\rho_{\mathrm{OB}}\mathbf{v}_{\mathrm{OB}} \otimes \mathbf{v}_{\mathrm{OB}}\},\end{aligned} \tag{3.57}$$

$$\begin{aligned}\mathscr{T}^{\mathrm{WOB}}:\quad & \operatorname{div}\mathbf{T}_{\mathrm{WOB}} + \mathbf{f}_{\mathrm{WOB}}^{\mathrm{W}} + \mathbf{f}_{\mathrm{WOB}}^{\mathrm{O}} + \mathbf{f}_{\mathrm{WOB}}^{\mathrm{B}} + \mathbf{f}_{\mathrm{WOB}}^{\mathrm{WO}} + \mathbf{f}_{\mathrm{WOB}}^{\mathrm{OB}} + \mathbf{f}_{\mathrm{WOB}}^{\mathrm{BW}} + \mathbf{b}_{\mathrm{WOB}} \\ & + \mathbf{P}^{\mathrm{WO}\to\mathrm{WOB}} - \mathbf{P}^{\mathrm{WOB}\to\mathrm{WO}} + \mathbf{P}^{\mathrm{OB}\to\mathrm{WOB}} - \mathbf{P}^{\mathrm{WOB}\to\mathrm{OB}} + \mathbf{P}^{\mathrm{BW}\to\mathrm{WOB}} - \mathbf{P}^{\mathrm{WOB}\to\mathrm{BW}} \\ & = \frac{\partial}{\partial t}\{\rho_{\mathrm{WOB}}\mathbf{v}_{\mathrm{WOB}}\} + \operatorname{div}\{\rho_{\mathrm{WOB}}\mathbf{v}_{\mathrm{WOB}} \otimes \mathbf{v}_{\mathrm{WOB}}\}.\end{aligned} \tag{3.58}$$

Remark 12. In line with the considerations of Remark 9, terms associated with direct *molecular exchange* between bulk phases and common lines, and between different interfacial phases, have been considered negligible in relations (3.52)–(3.58). However, corresponding *interaction* terms are not necessarily negligible. Here the criterion is the range of molecular interactions. In general (see, for example, Hirschfelder, 1967) such interactions are effectively small at separations of 10 Å. This was the motivation behind choice $\delta \sim 10$ Å in the definition of the distinct material systems considered. It follows that force densities which derive from interactions between molecules in different *bulk* phases are to be expected to be negligible, since such molecules are by definition at least a distance δ apart. (For example, $\mathbf{f}_{\mathrm{W}}^{\mathrm{O}}$ is the force density associated with the effect on bulk phase W molecules due to bulk phase O molecules. However, only W molecules are to be found within a distance δ of any bulk phase W molecule, by definition, so that all contributions to $\mathbf{f}_{\mathrm{W}}^{\mathrm{O}}$ stem from W–O molecular pairs separated by a distance of at least δ.) Thus force densities $\mathbf{f}_{\mathrm{W}}^{\mathrm{O}}$, $\mathbf{f}_{\mathrm{W}}^{\mathrm{B}}$, $\mathbf{f}_{\mathrm{O}}^{\mathrm{B}}$, $\mathbf{f}_{\mathrm{O}}^{\mathrm{W}}$ $(= -\mathbf{f}_{\mathrm{W}}^{\mathrm{O}})$, $\mathbf{f}_{\mathrm{B}}^{\mathrm{W}}$ $(= -\mathbf{f}_{\mathrm{W}}^{\mathrm{B}})$ and $\mathbf{f}_{\mathrm{B}}^{\mathrm{O}}$ $(= -\mathbf{f}_{\mathrm{O}}^{\mathrm{B}})$ are expected to be negligible. On the other hand $\mathbf{f}_{\mathrm{W}}^{\mathrm{WOB}}$ is not a priori negligible, but represents a body force density associated with the effect upon bulk liquid W by liquid W in the common line system $\mathscr{T}_{\mathrm{WOB}}$. Similar remarks apply to bulk–interfacial force densities. For example, a W molecule of $\mathscr{M}_{\mathrm{W}}^{\mathrm{W}}$ will be further than distance δ from an O molecule of $\mathscr{I}_{\mathrm{WO}}$, and hence density $\mathbf{f}_{\mathrm{W}}^{\mathrm{WO}}$ will derive essentially from W–W interactions, as also must $\mathbf{f}_{\mathrm{WO}}^{\mathrm{W}}$ $(= -\mathbf{f}_{\mathrm{W}}^{\mathrm{WO}})$. Further, interface–interface force densities essentially involve only interactions between molecules of the same species. Specifically, $\mathbf{f}_{\mathrm{WO}}^{\mathrm{BW}}$ $(= -\mathbf{f}_{\mathrm{BW}}^{\mathrm{WO}})$derives from W–W interactions, $\mathbf{f}_{\mathrm{WO}}^{\mathrm{OB}}$ $(= -\mathbf{f}_{\mathrm{OB}}^{\mathrm{WO}})$ from O–O interactions, and $\mathbf{f}_{\mathrm{OB}}^{\mathrm{BW}}$ $(= -\mathbf{f}_{\mathrm{BW}}^{\mathrm{OB}})$ from B–B interactions. The foregoing observations indicate that in any interfacial balance certain terms can be grouped together. For example, in (3.55), $\mathbf{f}_{\mathrm{WO}}^{\mathrm{W}} + \mathbf{f}_{\mathrm{WO}}^{\mathrm{BW}} + \mathbf{P}^{\mathrm{W}\to\mathrm{WO}} - \mathbf{P}^{\mathrm{WO}\to\mathrm{W}}$ represents an effective force density associated solely with W molecules, $\mathbf{f}_{\mathrm{WO}}^{\mathrm{O}} + \mathbf{f}_{\mathrm{WO}}^{\mathrm{BO}} + \mathbf{P}^{\mathrm{O}\to\mathrm{WO}} - \mathbf{P}^{\mathrm{WO}\to\mathrm{O}}$ a density involving only O molecules, and $\mathbf{f}_{\mathrm{WO}}^{\mathrm{WOB}} + \mathbf{P}^{\mathrm{WOB}\to\mathrm{WO}} - \mathbf{P}^{\mathrm{WO}\to\mathrm{WOB}}$ a density involving both W and O molecules. (The adjective 'effective' is employed since the time-averaged momentum exchange terms such as $\mathbf{P}^{\mathrm{W}\to\mathrm{WO}}$ are not strictly force densities.)

Remark 13. The above relations may be summarised by denoting any material system of interest by $\mathscr{S}$, with corresponding mass density, velocity, stress and body force density $\rho_{\mathscr{S}}$, $\mathbf{v}_{\mathscr{S}}$, $\mathbf{T}_{\mathscr{S}}$ and $\mathbf{b}_{\mathscr{S}}$, respectively. Then momentum balance for $\mathscr{S}$ is

$$\operatorname{div}\mathbf{T}_{\mathscr{S}} + \sum_{\mathscr{S}'\neq\mathscr{S}} \left\{\mathbf{f}_{\mathscr{S}}^{\mathscr{S}\prime} + \mathbf{P}^{\mathscr{S}\prime\to\mathscr{S}} - \mathbf{P}^{\mathscr{S}\to\mathscr{S}\prime}\right\} + \mathbf{b}_{\mathscr{S}} = \frac{\partial}{\partial t}\{\rho_{\mathscr{S}}\mathbf{v}_{\mathscr{S}}\} + \operatorname{div}\{\rho_{\mathscr{S}}\mathbf{v}_{\mathscr{S}} \otimes \mathbf{v}_{\mathscr{S}}\}. \tag{3.59}$$

Here the sums are taken over all material systems $\mathscr{S}'$ in $\mathscr{M}$ with the exception of $\mathscr{S}$ itself, $\mathbf{f}_{\mathscr{S}}^{\mathscr{S}'}$ denotes the force density associated with the action of $\mathscr{S}'$ upon $\mathscr{S}$, and $\mathbf{P}^{\mathscr{S}\to\mathscr{S}'}$ (respectively, $\mathbf{P}^{\mathscr{S}'\to\mathscr{S}}$) the momentum density supply rate corresponding to migration of molecules from $\mathscr{S}(\mathscr{S}')$ into $\mathscr{S}'(\mathscr{S})$. The alternative form of balance (3.48) is expressible in this format as

$$\operatorname{div}\mathbf{T}_{\mathscr{S}} + \sum_{\mathscr{S}'\neq\mathscr{S}} \{\mathbf{f}_{\mathscr{S}}^{\mathscr{S}'} + \mathbf{I}^{\mathscr{S}'\to\mathscr{S}} - \mathbf{I}^{\mathscr{S}\to\mathscr{S}'}\} + \mathbf{b}_{\mathscr{S}} = \rho_{\mathscr{S}}\dot{\mathbf{v}}_{\mathscr{S}}. \tag{3.60}$$

In the same way, mass balance relations (3.14)–(3.20) can be summarised as

$$\frac{\partial\rho_{\mathscr{S}}}{\partial t} + \operatorname{div}\rho_{\mathscr{S}}\mathbf{v}_{\mathscr{S}} = \sum_{\mathscr{S}'\neq\mathscr{S}} \{\mathscr{G}^{\mathscr{S}'\to\mathscr{S}} - \mathscr{G}^{\mathscr{S}\to\mathscr{S}'}\}, \tag{3.61}$$

where $\mathscr{G}^{\mathscr{S}'\to\mathscr{S}}$ (respectively $\mathscr{G}^{\mathscr{S}\to\mathscr{S}'}$) represents the mass supply rate density associated with migration from $\mathscr{S}'(\mathscr{S})$ into $\mathscr{S}(\mathscr{S}')$.

Of course, as discussed in Remarks 9 and 12, certain terms in the above balances are to be expected to be negligible.

3.3. Energy balance

Consider the result of scalar multiplication of (3.21) by $\Delta^{-1}e_i w(\mathbf{x}_i - \mathbf{x})\mathbf{v}_i$, integration of the resulting relation over time interval $t - \Delta \leqslant \tau \leqslant t$, and then summation over all molecules $P_i \in \mathscr{M}$. The first term may be written as

$$\frac{1}{\Delta}\sum_{i=1}^{N}\sum_{\substack{\ell=1\\ \ell\neq i}}^{N}\int_{t-\Delta}^{t}\{\mathbf{f}_{i\ell}(\tau)e_i(\tau)e_\ell(\tau) + \mathbf{f}_{i\ell}(\tau)e_i(\tau)(1 - e_\ell(\tau))\}\cdot\mathbf{v}_i(\tau)w(\mathbf{x}_i(\tau) - \mathbf{x})\,\mathrm{d}\tau. \tag{3.62}$$

From (3.34) this expression reduces to (see (3.26) and (3.27))

$$\left(\mathsf{q}^{\mathrm{int}}_{w,\Delta} + \mathbf{f}^{\mathrm{int}}_{w,\Delta}\cdot\mathbf{v}_{w,\Delta} + \mathsf{q}^{\mathrm{ext}}_{w,\Delta} + \mathbf{f}^{\mathrm{ext}}_{w,\Delta}\cdot\mathbf{v}_{w,\Delta}\right)(\mathbf{x}, t), \tag{3.63}$$

where

$$\mathsf{q}^{\mathrm{int}}_{w,\Delta}(\mathbf{x}, t) := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{\substack{\ell=1\\ \ell\neq i}}^{N}\int_{t-\Delta}^{t} e_i(\tau)e_\ell(\tau)\mathbf{f}_{i\ell}(\tau)\cdot\hat{\mathbf{v}}_i(\tau; \mathbf{x}, t)w(\mathbf{x}_i(\tau) - \mathbf{x})\,\mathrm{d}\tau, \tag{3.64}$$

and

$$\mathsf{q}^{\mathrm{ext}}_{w,\Delta} := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{\substack{\ell=1\\ \ell\neq i}}^{N}\int_{t-\Delta}^{t} e_i(\tau)(1 - e_\ell(\tau))\mathbf{f}_{i\ell}(\tau)\cdot\hat{\mathbf{v}}_i(\tau; \mathbf{x}, t)w(\mathbf{x}_i(\tau) - \mathbf{x})\,\mathrm{d}\tau. \tag{3.65}$$

Remark 14. Fields $\mathsf{q}^{\mathrm{int}}_{w,\Delta}$ and $\mathsf{q}^{\mathrm{ext}}_{w,\Delta}$ are of a thermal nature: their definitions involve the diffusive (‘random’ or ‘thermal’) velocities $\hat{\mathbf{v}}_i$ (see Remark 11). Density $\mathsf{q}^{\mathrm{int}}_{w,\Delta}$ represents a local rate of self-heating of $\mathscr{S}$ molecules while $\mathsf{q}^{\mathrm{ext}}_{w,\Delta}$ denotes a local rate of heating density for $\mathscr{S}$ molecules stemming from interactions with non-$\mathscr{S}$ molecules of $\mathscr{M}$: the latter is thus a *conductive heat supply rate density* associated with interactions.

The second term in (3.21) yields

$$\frac{1}{\Delta}\sum_{i=1}^{N}\int_{t-\Delta}^{t} e_i(\tau)\mathbf{b}_i(\tau)\cdot\{\mathbf{v}_{w,\Delta}(\mathbf{x}, t) + \hat{\mathbf{v}}_i(\tau; \mathbf{x}, t)\}w(\mathbf{x}_i(\tau) - \mathbf{x})\,\mathrm{d}\tau = (\mathbf{b}_{w,\Delta}\cdot\mathbf{v}_{w,\Delta} + r_{w,\Delta})(\mathbf{x}, t), \tag{3.66}$$

where

$$r_{w,\Delta}(\mathbf{x}, t) := \frac{1}{\Delta}\sum_{i=1}^{N}\int_{t-\Delta}^{t} e_i(\tau)\mathbf{b}_i(\tau)\cdot\hat{\mathbf{v}}_i(\tau; \mathbf{x}, t)w(\mathbf{x}_i(\tau) - \mathbf{x}) \tag{3.67}$$

represents the density associated with the local rate of heat supply to $\mathscr{S}$ molecules due to agencies outwith system $\mathscr{M}$ (evaluated at $(\mathbf{x}, t)$). This term is usually identified with the (external) radiative heat supply rate density.

The right-hand side of (3.21) yields (via operations similar to those employed in (3.30) and (3.31))

$$\frac{1}{\Delta}\sum_{i=1}^{N}\int_{t-\Delta}^{t} e_i(\tau)\frac{\mathrm{d}}{\mathrm{d}\tau}\left\{\frac{1}{2}m_i\mathbf{v}_i^2(\tau)\right\}w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau = (A_{w,\Delta}+B_{w,\Delta})(\mathbf{x},t), \tag{3.68}$$

where

$$A_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\int_{t-\Delta}^{t} e_i(\tau)\frac{\mathrm{d}}{\mathrm{d}\tau}\left\{\frac{1}{2}m_i\mathbf{v}_i^2(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})\right\}\mathrm{d}\tau \tag{3.69}$$

and

$$B_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\int_{t-\Delta}^{t} \mathrm{div}_{\mathbf{x}}\left\{\frac{1}{2}m_i e_i(\tau)\mathbf{v}_i^2(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})\mathbf{v}_i(\tau)\right\}\mathrm{d}\tau. \tag{3.70}$$

Considering all migratory possibilities (cf. (3.2) and (3.28)),

$$\begin{aligned}A_{w,\Delta}(\mathbf{x},t) = {} & \frac{1}{\Delta}\sum_{i=1}^{N}\frac{m_i}{2}\{e_i(t)\mathbf{v}_i^2(t)w(\mathbf{x}_i(t)-\mathbf{x}) - e_i(t-\Delta)\mathbf{v}_i^2(t-\Delta)w(\mathbf{x}_i(t-\Delta)-\mathbf{x})\}\\ & + \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_j}\frac{1}{2}m_i\mathbf{v}_i^2(t_{ij})w(\mathbf{x}_i(t_{i_j})-\mathbf{x}) - \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_k}\frac{1}{2}m_i\mathbf{v}_i^2(t_{i_k})w(\mathbf{x}_i(t_{i_k})-\mathbf{x}),\end{aligned} \tag{3.71}$$

where times t_{i_j} and t_{i_k} are precisely those which appear in (3.7), (3.8), (3.39), (3.40), (3.50) and (3.51). Using decomposition (3.34) and noting result (3.35), the first half of expression (3.71) for $A_{w,\Delta}(\mathbf{x},t)$ becomes

$$\frac{\partial}{\partial t}\left\{\rho_{w,\Delta}\left[h_{w,\Delta}+\frac{1}{2}\mathbf{v}_{w,\Delta}^2\right](\mathbf{x},t)\right\}. \tag{3.72}$$

Here

$$(\rho_{w,\Delta}h_{w,\Delta})(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\int_{t-\Delta}^{t} e_i(\tau)\frac{m_i}{2}\hat{\mathbf{v}}_i^2(\tau;\mathbf{x},t)w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau \tag{3.73}$$

is the local *heat content density*: from (3.37) this is precisely one-half the trace of tensor $\hat{\mathbf{D}}_{w,\Delta}(\mathbf{x},t)$.

Decomposition (3.34) yields, for the second half of the expression (3.71) for $A_{w,\Delta}(\mathbf{x},t)$,

$$\left(K_{w,\Delta}^{\mathrm{out}} - K_{w,\Delta}^{\mathrm{in}} + \left(\mathbf{I}_{w,\Delta}^{\mathrm{out}} - \mathbf{I}_{w,\Delta}^{\mathrm{in}}\right)\cdot\mathbf{v}_{w,\Delta} + \frac{1}{2}\left(\mathscr{G}_{w,\Delta}^{\mathrm{out}} - \mathscr{G}_{w,\Delta}^{\mathrm{in}}\right)\mathbf{v}_{w,\Delta}^2\right)(\mathbf{x},t), \tag{3.74}$$

where

$$K_{w,\Delta}^{\mathrm{out}}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_j}\frac{1}{2}m_i\hat{\mathbf{v}}_i^2(t_{i_j};\mathbf{x},t)w(\mathbf{x}_i(t_{i_j})-\mathbf{x}) \tag{3.75}$$

and

$$K^{\mathrm{in}}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\sum_{i_k}\frac{1}{2}m_i\hat{\mathbf{v}}_i^2(t_{i_k};\mathbf{x},t)w(\mathbf{x}_i(t_{i_k})-\mathbf{x}). \tag{3.76}$$

Term $K^{\mathrm{out}}_{w,\Delta}$ (respectively $K^{\mathrm{in}}_{w,\Delta}$) represents the local density of the loss (gain) of heat as a consequence of molecular migration out of $\mathscr{S}$ (into $\mathscr{S}$).

From (3.71), (3.72) and (3.74), upon suppressing suffices w,Δ and arguments $\mathbf{x},t$,

$$A = \frac{\partial}{\partial t}\left\{\rho\left[h+\frac{1}{2}\mathbf{v}^2\right]\right\} + K^{\mathrm{out}} - K^{\mathrm{in}} + \left(\mathbf{I}^{\mathrm{out}}-\mathbf{I}^{\mathrm{in}}\right)\cdot\mathbf{v} + \frac{1}{2}(\mathscr{G}^{\mathrm{out}}-\mathscr{G}^{\mathrm{in}})\mathbf{v}^2. \tag{3.77}$$

For later comparison with (3.45) it should be noted that (see (3.49), (3.47) and (3.9))

$$\mathbf{I}\cdot\mathbf{v} + \frac{1}{2}\mathscr{G}\mathbf{v}^2 = \mathbf{P}\cdot\mathbf{v} - \frac{1}{2}\mathscr{G}\mathbf{v}^2. \tag{3.78}$$

Writing (3.70) in the form

$$B_{w,\Delta}(\mathbf{x},t) = \mathrm{div}_{\mathbf{x}}\left\{\frac{1}{\Delta}\sum_{i=1}^{N}\int_{t-\Delta}^{t}\frac{m_i}{2}e_i(\tau)w(\mathbf{x}_i(\tau)-\mathbf{x})(\mathbf{v}_i(\tau)\otimes\mathbf{v}_i(\tau))\mathbf{v}_i(\tau)\,\mathrm{d}\tau\right\}, \tag{3.79}$$

using (3.34) and (3.35) it follows (upon suppressing suffices and arguments) that

$$B = \mathrm{div}\left\{\mathbf{k} + \rho h\mathbf{v} + \hat{\mathbf{D}}\mathbf{v} + \frac{1}{2}\rho\mathbf{v}^2\mathbf{v}\right\}. \tag{3.80}$$

Here

$$\mathbf{k}_{w,\Delta}(\mathbf{x},t) := \frac{1}{\Delta}\sum_{i=1}^{N}\int_{t-\Delta}^{t}\frac{m_i}{2}e_i(\tau)\hat{\mathbf{v}}_i^2(\tau;\mathbf{x},t)\hat{\mathbf{v}}_i(\tau;\mathbf{x},t)w(\mathbf{x}_i(\tau)-\mathbf{x})\,\mathrm{d}\tau. \tag{3.81}$$

denotes the *diffusive heat flux vector field.*

Energy balance, from (3.63), (3.66), (3.68), (3.72), (3.74) and (3.80), takes the form

$$\begin{aligned} &r + \mathsf{q}^{\mathrm{int}} + \mathsf{q}^{\mathrm{ext}} + \left(\mathbf{f}^{\mathrm{int}} + \mathbf{f}^{\mathrm{ext}} + \mathbf{b} + \mathbf{I}^{\mathrm{in}} - \mathbf{I}^{\mathrm{out}}\right)\cdot\mathbf{v} + K^{\mathrm{in}} - K^{\mathrm{out}} + \frac{1}{2}(\mathscr{G}^{\mathrm{in}}-\mathscr{G}^{\mathrm{out}})\mathbf{v}^2 \\ &\quad = \frac{\partial}{\partial t}\left\{\rho\left(h+\frac{1}{2}\mathbf{v}^2\right)\right\} + \mathrm{div}\left\{\mathbf{k} + \rho h\mathbf{v} + \hat{\mathbf{D}}\mathbf{v} + \frac{1}{2}\rho\mathbf{v}^2\mathbf{v}\right\}. \end{aligned} \tag{3.82}$$

This balance simplifies, upon invoking balances (3.12) and (3.45) of mass and linear momentum, to

$$-\mathrm{div}\,\mathbf{k} + r + \mathsf{q}^{\mathrm{int}} + \mathsf{q}^{\mathrm{ext}} + K^{\mathrm{in}} - K^{\mathrm{out}} - \hat{\mathbf{D}}\cdot\mathbf{L} = \rho\dot{h} + (\mathscr{G}^{\mathrm{in}}-\mathscr{G}^{\mathrm{out}})h. \tag{3.83}$$

Here

$$\dot{h} := \partial h/\partial t + \nabla h\cdot\mathbf{v} \tag{3.84}$$

denotes the material time derivative of h and

$$\mathbf{L} := \nabla\mathbf{v} \tag{3.85}$$

represents the velocity gradient. (In Cartesian tensor notation $L_{ij} = v_{i,j}$.)

Remark 15. Noll's theorem can again be used to show (see Murdoch and Bedeaux, 1994, Section 7, for full details) that there exists an *$\mathscr{S}$–$\mathscr{S}$ interaction heat flux vector* $\mathbf{q}^-$ such that

$$\mathsf{q}^{\mathrm{int}} = -\mathrm{div}\,\mathbf{q}^- + \mathsf{q}^+, \tag{3.86}$$

where q^+ is the local *$\mathscr{S}$–$\mathscr{S}$ self-heating density* (or *net internal radiative heat supply density*). This enables the first three terms in (3.83) to be re-expressed as

$$r - \mathrm{div}\ \mathbf{q} + \mathsf{q}^+, \tag{3.87}$$

where the *$\mathscr{S}$–$\mathscr{S}$ heat flux vector*

$$\mathbf{q} := \mathbf{q}^- + \mathbf{k}. \tag{3.88}$$

Term q^+ is usually considered to be negligible and will henceforth be omitted.

Balance (3.83) constitutes an evolution equation for the heat content per unit mass h. The balance of *total* energy is obtained from (3.82) using (3.42), (3.44), (3.86) and (3.88). These relations yield

$$\begin{aligned} & r + \mathsf{q}^{\mathrm{ext}} + \mathrm{div}\{\mathbf{T}^{\mathrm{T}}\mathbf{v} - \mathbf{q}\} - \mathbf{T}^- \cdot \mathbf{L} + K^{\mathrm{in}} - K^{\mathrm{out}} + \{\mathbf{f}^{\mathrm{ext}} + \mathbf{b} + \mathbf{I}^{\mathrm{in}} - \mathbf{I}^{\mathrm{out}}\} \cdot \mathbf{v} \\ & \quad = \rho(\dot{h} + \dot{\widehat{\mathbf{v}^2}}/2) + (\mathscr{G}^{\mathrm{in}} - \mathscr{G}^{\mathrm{out}})h. \end{aligned} \tag{3.89}$$

Let β be the solution (see Remark 17 below) to

$$\rho\dot{\beta} + \mathscr{G}\beta = \mathbf{T}^- \cdot \mathbf{L}, \tag{3.90}$$

and define

$$\mathscr{K} := K^{\mathrm{in}} - K^{out} + (\mathbf{I}^{\mathrm{in}} - \mathbf{I}^{\mathrm{out}}) \cdot \mathbf{v} + (\mathscr{G}^{\mathrm{in}} - \mathscr{G}^{\mathrm{out}})\mathbf{v}^2/2. \tag{3.91}$$

Then (3.89) becomes

$$\mathrm{div}\{\mathbf{T}^{\mathrm{T}}\mathbf{v} - \mathbf{q}\} + r + \mathsf{q}^{\mathrm{ext}} + \mathscr{K} + \{\mathbf{f}^{\mathrm{ext}} + \mathbf{b}\} \cdot \mathbf{v} = \rho(\dot{e} + \dot{\widehat{\mathbf{v}^2}}/2 + (\mathscr{G}^{\mathrm{in}} - \mathscr{G}^{\mathrm{out}})(e + \mathbf{v}^2/2)), \tag{3.92}$$

where

$$e := \beta + h \tag{3.93}$$

denotes the total internal energy density per unit mass and a superposed dot '$\cdot$' denotes the material time derivative (see (3.46) and (3.89)). Term β represents the *interaction energy density per unit mass*.

Remark 16. From definitions (3.7), (3.8), (3.50), (3.51), (3.75), (3.76) and (3.91)

$$\mathscr{K}(\mathbf{x}, t) = \frac{1}{\Delta}\sum_{i=1}^{N}\left\{\sum_{i_k}\frac{1}{2}m_i\mathbf{v}_i^2(t_{i_k})w(\mathbf{x}_i(t_{i_k}) - \mathbf{x}) - \sum_{i_j}\frac{1}{2}m_i\mathbf{v}_1^2(t_{i_j})w(\mathbf{x}_i(t_{i_j}) - \mathbf{x})\right\}. \tag{3.94}$$

Thus $\mathscr{K}$ represents the spatial density for the net supply of molecular kinetic energy to $\mathscr{S}$ due to migration between $\mathscr{S}$ and all the other systems which constitute $\mathscr{M}$ (see (2.5)). Relation (3.91) is a decomposition of this kinetic energy supply into heat supply $(\mathscr{K}^{\mathrm{in}} - K^{\mathrm{out}})$, macroscopic kinetic energy supply $((\mathscr{G}^{\mathrm{in}} - \mathscr{G}^{\mathrm{out}})\mathbf{v}^2/2)$, and the thermo-mechanical hybrid $(\mathbf{I}^{\mathrm{in}} - \mathbf{I}^{\mathrm{out}}) \cdot \mathbf{v}$.

Remark 17. Energy balance (3.92) delineates the time evolution of energy, and is to be compared with momentum and mass balances (3.45) and (3.12), respectively. The right-hand sides of these evolution equations are the appropriate generalisations of those for time-*independent* systems ($\mathscr{G} = 0$). This can be seen by noting that

$$\rho\dot{f} + \mathscr{G}f = \frac{\partial}{\partial t}\{\rho f\} + \mathrm{div}\{\rho f\mathbf{v}\} \tag{3.95}$$

for any scalar field f. (The relation also holds for any vector field f if $\rho f\mathbf{v}$ is interpreted to be $\rho f \otimes \mathbf{v}$.) Accordingly, if $\mathscr{R}$ is a regular region then

$$\int_{\mathscr{R}} (\rho\dot{f} + \mathscr{G}f) = \frac{\partial}{\partial t}\left\{\int_{\mathscr{R}} \rho f\right\} + \int_{\mathscr{R}} \rho f\mathbf{v} \cdot \mathbf{n}. \tag{3.96}$$

The foregoing observation motivated inclusion of term $\mathscr{G}\beta$ in the differential equation (3.90) defining the *interaction energy density* (per unit mass) β. (For discussion of (3.90) see Murdoch and Soliman, 1999, Remark 10.)

Employing the notation of Remark 13, balance of energy (3.92) may be written as

$$\begin{aligned}
&\mathrm{div}\{\mathbf{T}^{\mathrm{T}}_{\mathscr{S}}\mathbf{v}_{\mathscr{S}} - \mathbf{q}_{\mathscr{S}}\} + r_{\mathscr{S}} + \mathbf{b}_{\mathscr{S}} \cdot \mathbf{v}_{\mathscr{S}} + \sum_{\mathscr{S}' \neq \mathscr{S}} \Big\{\mathrm{q}^{\mathscr{S}'}_{\mathscr{S}} + \mathscr{K}^{\mathscr{S}' \to \mathscr{S}} - \mathscr{K}^{\mathscr{S} \to \mathscr{S}'} \\
&\quad + (\mathbf{f}^{\mathscr{S}'}_{\mathscr{S}} + \mathbf{I}^{\mathscr{S}' \to \mathscr{S}} - \mathbf{I}^{\mathscr{S} \to \mathscr{S}'}) \cdot \mathbf{v}_{\mathscr{S}}\Big\} \\
&\qquad = \rho_{\mathscr{S}}\Big\{\dot{e}_{\mathscr{S}} + \dot{\widehat{\mathbf{v}^2_{\mathscr{S}}}}/2\Big\} + \sum_{\mathscr{S}' \neq \mathscr{S}} \Big\{\mathscr{G}^{\mathscr{S}' \to \mathscr{S}} - \mathscr{G}^{\mathscr{S} \to \mathscr{S}'}\Big\} e_{\mathscr{S}}.
\end{aligned} \tag{3.97}$$

Here $\mathrm{q}^{\mathscr{S}'}_{\mathscr{S}}$ and $(\mathscr{K}^{\mathscr{S}' \to \mathscr{S}} - \mathscr{K}^{\mathscr{S} \to \mathscr{S}'})$ represent conductive heat supply rate densities from $\mathscr{S}'$ into $\mathscr{S}$, associated with the work done by interactions in thermal motion and diffusion of thermal kinetic energy, respectively.

Remark 18. Although the considerations of this section concerned the seven time-dependent material systems associated with two immiscible liquids within a porous body, balances (3.60), (3.61) and (3.97) are general. That is, once material systems of interest in multiphase flows in a porous body are identified, then the derivations here developed give rise to these forms of balance. Recall Remark 1 in respect of liquid–vapour and gaseous phases.

4. Discussion: constitutive considerations

4.1. General remarks

Multiphase flows in porous media give rise to a wide variety of observed behaviour (see, for example, the comprehensive survey in Nitsche and Brenner, 1989). Since full account of molecular behaviour has been taken in the foregoing, the balance relations here derived are relevant to all physical situations in which molecules preserve their integrity. [4] However, in formulating a continuum theory which adequately predicts (and is capable of furnishing quantitative understanding of) specific behaviour, there are two essential steps to be taken.

Step 1. Having identified all molecular species of significance, appropriate material systems must be selected. Once this is done, the forms of the balance relations for each system are those established here, and the fields involved are defined precisely in terms of space–time averages of molecular quantities.

Step 2. In order to obtain a system of (coupled, partial differential) equations which suffices to determine the time evolution of mass density, displacement, and temperature fields for each material system, it is necessary to supplement balance relations with appropriate constitutive assumptions. While balance relations are general in nature (for example, in Section 3 'W' and 'O' could denote *any* pair of immiscible liquids), constitutive relations introduce specific characteristics of system behaviour at length-time scales of interest. Of course, it is these scales which are adopted in defining all fields which appear in the balance relations.

In introducing a molecular perspective, the approach here adopted complements existing continuum modelling of multiphase flows. Such modelling usually involves continuum theories of mixtures, or REV averaging of continuum relations postulated to hold at the scale of pores. When such theories embody a full thermodynamic exposition, constitutive relations may be simplified using the Coleman and Noll method of exploiting the entropy inequality. (See, for example, the mixture-theoretic approach of Bowen, 1982, and average-continuum discussions of Hassanizadeh and Gray, 1980, 1990.) Aspects of flows for which a molecular viewpoint is envisaged as being of particular value are indicated in the final Section 4.4. In the following two sections somewhat simplistic illustrations are given of how *existing* theories may be viewed as consequences of Steps 1 and 2. In future work we hope to exploit the greater insight provided by the molecular approach, particularly the role played by surfactants.

4.2. Flow in a porous solid saturated with a single liquid

In the case of a porous solid body saturated with a single liquid, explicit account of the solid–liquid interface may be obviated by considering that time-dependent material system, $\mathscr{M}_{B^+}$ say, which, at any instant, consists of the fixed set of solid body molecules together with those liquid molecules instantaneously belonging to the solid–liquid interfacial system. Using the notation of

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[4] Molecular ionisation modifies the nature of pairwise interactions (which become long range). This is relevant when treating chemical reactions and solutions which usually involve dissociation of molecules into ions. Such considerations are outwith this work, but can be accommodated within the corpuscular approach adopted here.

the previous sections, 'W' denotes liquid, and 'B' solid, matter. In the absence of 'O' material, the counterparts of relations (2.2) are

$$\mathscr{M}_{\mathrm{B}^+}(\tau) := \mathscr{M}^{\mathrm{B}}_{\mathrm{B}}(\tau) \cup \mathscr{M}^{\mathrm{B}}_{\mathrm{W}}(\tau) \cup \mathscr{M}^{\mathrm{W}}_{\mathrm{B}}(\tau) = \mathscr{M}^{\mathrm{B}}_{\mathrm{B}}(\tau) \cup \mathscr{I}_{\mathrm{BW}}(\tau) \tag{4.1}$$

and

$$\mathscr{M}_{\mathrm{W}}(\tau) := \mathscr{M}^{\mathrm{W}}_{\mathrm{W}}(\tau).$$

Linear momentum balance for $\mathscr{M}_{\mathrm{B}^+}$ is obtained by summing (3.54) and (3.56). This yields

$$\operatorname{div} \mathbf{T}_{\mathrm{B}^+} + \mathbf{f}^{\mathrm{W}}_{\mathrm{B}^+} + \mathbf{b}_{\mathrm{B}^+} = \frac{\partial}{\partial t}\{\rho_{\mathrm{B}^+}\mathbf{v}_{\mathrm{B}^+}\} + \operatorname{div}\,\{\rho_{\mathrm{B}^+}\mathbf{v}_{\mathrm{B}^+} \otimes \mathbf{v}_{\mathrm{B}^+}\}, \tag{4.2}$$

where

$$\rho_{\mathrm{B}^+} := \rho_{\mathrm{B}} + \rho_{\mathrm{BW}}, \quad \mathbf{v}_{\mathrm{B}^+} := \frac{1}{\rho_{\mathrm{B}^+}}(\rho_{\mathrm{B}}\mathbf{v}_{\mathrm{B}} + \rho_{\mathrm{BW}}\mathbf{v}_{\mathrm{BW}}), \tag{4.3}$$

$$\mathbf{T}_{\mathrm{B}^+} := \mathbf{T}_{\mathrm{B}} + \mathbf{T}_{\mathrm{BW}} - \frac{\rho_{\mathrm{B}}\rho_{\mathrm{BW}}}{(\rho_{\mathrm{B}} + \rho_{\mathrm{BW}})}(\mathbf{v}_{\mathrm{BW}} - \mathbf{v}_{\mathrm{B}}) \otimes (\mathbf{v}_{\mathrm{BW}} - \mathbf{v}_{\mathrm{B}}), \tag{4.4}$$

$$\mathbf{f}^{\mathrm{W}}_{\mathrm{B}^+} := \mathbf{f}^{\mathrm{W}}_{\mathrm{BW}} + \mathbf{P}^{\mathrm{W}\to\mathrm{BW}} - \mathbf{P}^{\mathrm{BW}\to\mathrm{W}} \quad \text{and} \quad \mathbf{b}_{\mathrm{B}^+} := \mathbf{b}_{\mathrm{B}} + \mathbf{b}_{\mathrm{BW}}. \tag{4.5}$$

The last term in (4.4) is expected to be small, and $(4.5)_1$ is a consequence of the vanishing of $\mathbf{f}^{\mathrm{BW}}_{\mathrm{B}} + \mathbf{f}^{\mathrm{B}}_{\mathrm{BW}}$ (via satisfaction of Newton's third law by molecular interactions).

Linear momentum balance for $\mathscr{M}_{\mathrm{W}}$ is the relevant version of (3.52), namely

$$\operatorname{div} \mathbf{T}_{\mathrm{W}} + \mathbf{f}^{\mathrm{B}^+}_{\mathrm{W}} + \mathbf{b}_{\mathrm{W}} = \frac{\partial}{\partial t}\{\rho_{\mathrm{W}}\mathbf{v}_{\mathrm{W}}\} + \operatorname{div}\{\rho_{\mathrm{W}}\mathbf{v}_{\mathrm{W}} \otimes \mathbf{v}_{\mathrm{W}}\}, \tag{4.6}$$

where

$$\mathbf{f}^{\mathrm{B}^+}_{\mathrm{W}} := \mathbf{f}^{\mathrm{BW}}_{\mathrm{W}} + \mathbf{P}^{\mathrm{BW}\to\mathrm{W}} - \mathbf{P}^{\mathrm{W}\to\mathrm{BW}} = -\mathbf{f}^{\mathrm{W}}_{\mathrm{B}^+}. \tag{4.7}$$

The effect of the porous body on momentum transport of bulk liquid is thus seen to derive entirely from molecules in the W–B interfacial system.

If the only external body forces are due to gravity then body force densities $\mathbf{b}_{\mathrm{B}^+}$ and $\mathbf{b}_{\mathrm{W}}$ are readily identified as $\rho_{\mathrm{B}^+}\mathbf{g}$ and $\rho_{\mathrm{W}}\mathbf{g}$, respectively, where $\mathbf{g}$ denotes gravitational acceleration.

At this point it is necessary to postulate constitutive relations for $\mathbf{T}_{\mathrm{B}^+}$, $\mathbf{f}^{\mathrm{B}^+}_{\mathrm{W}}$ $(= -\mathbf{f}^{\mathrm{W}}_{\mathrm{B}^+})$, and $\mathbf{T}_{\mathrm{W}}$. To this end insight may be gained by adopting a viewpoint appropriate to length scales large compared with the molecular perspective, yet small enough for pore features to be evident. At such scales a continuum approach is possible for both fluid phases and the porous body. Of course, in this approach fields associated with fluid phases are only defined in the pore space, and porous body fields make sense only in the region occupied by the body at the scale chosen. [5] (This is in contrast to REV-scale fields which appear in the balance relations derived in Section 3. For example, ρ_S, ρ_{W} and ρ_{O} may all be positive at a given point $\mathbf{x}$: this would be the case were *S*, W

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[5] It is to be noted that the boundary of the porous body (and hence the pore space therein) depends upon the precise scale adopted. See Murdoch, 1995.

and O molecules to be found within that REV centred at $\mathbf{x}$ – in particular, were a common line to be found within this REV.)

The remaining part of this subsection is devoted to the case of saturation of pore space by an incompressible Newtonian fluid undergoing steady creeping flow through a rigid porous body, since a number of precise observations can be made. In such context the relevant form of (4.6) may be compared with the relation obtained by spatial averaging of Navier–Stokes flow within pore space at the REV scale. To this end, and consistent with the foregoing weighting function approach, the (REV scale) average $\langle f \rangle$ of any field f which appears in the Navier–Stokes equation is defined by

$$\langle f \rangle(\mathbf{x}) := \int_{\mathscr{E}} f(\mathbf{y}) w(\mathbf{y} - \mathbf{x})\, \mathrm{d}\mathbf{y}. \tag{4.8}$$

Integration is taken over all Euclidean space $\mathscr{E}$, w denotes the (REV scale) weighting function introduced in (2.9), and f is taken to be zero at points unoccupied by fluid.

The relevant form of the Navier–Stokes equation is

$$-\nabla P + \frac{\mu}{\rho^{\mathrm{i}}_{\mathrm{W}}} \Delta \mathbf{p} + \rho^{\mathrm{i}}_{\mathrm{W}} \mathbf{g} = \mathbf{0}, \tag{4.9}$$

where P denotes pressure, μ viscosity, $\rho^{\mathrm{i}}_{\mathrm{W}}$ density (constant) and $\mathbf{p}$ denotes momentum density. If relation (4.9) is evaluated at point $\mathbf{y}$, each term is multiplied by $w(\mathbf{y} - \mathbf{x})$, and integration is effected over $\mathscr{E}$, then use of the non-slip condition on pore walls and the divergence theorem (see Murdoch and Soliman, 1999, Section 5(a)) yield

$$-\nabla\{\langle P \rangle\} + \frac{\mu}{\rho^{\mathrm{i}}_{\mathrm{W}}} \Delta\{\langle \mathbf{p} \rangle\} + \hat{\mathbf{f}}_{\mathrm{W}} + \mu \tilde{\mathbf{f}}_{\mathrm{W}} + \rho^{\mathrm{i}}_{\mathrm{W}} \nu \mathbf{g} = \mathbf{0}. \tag{4.10}$$

Here ν denotes porosity and (suppressing time dependence),

$$\begin{aligned} \hat{\mathbf{f}}_{\mathrm{W}}(\mathbf{x}) &:= \int_{\Sigma} -P(\mathbf{y}) \mathbf{n}(\mathbf{y}) w(\mathbf{y} - \mathbf{x})\, \mathrm{d}A\mathbf{y}, \\ \tilde{\mathbf{f}}_{\mathrm{W}}(\mathbf{x}) &:= \frac{1}{\rho^{\mathrm{i}}_{\mathrm{W}}} \int_{\Sigma} ((\nabla \mathbf{p})(\mathbf{y})) \mathbf{n}(\mathbf{y}) w(\mathbf{y} - \mathbf{x})\, \mathrm{d}A\mathbf{y}, \end{aligned} \tag{4.11}$$

where Σ denotes all pore boundaries and $\mathbf{n}$ is that unit normal field on Σ directed into the porous body. The factor w in the integrand results in contributions only from pore boundaries within that REV centred at $\mathbf{x}$ (see Remark 4). Comparison of (4.10) with the form of (4.6) appropriate to steady creeping flow yields the identifications

$$\begin{aligned} &\operatorname{div} \mathbf{T}_{\mathrm{W}} + \mathbf{f}^{\mathrm{B}^+}_{\mathrm{W}} \leftrightarrow -\nabla\{\langle P \rangle\} + \frac{\mu}{\rho^{\mathrm{i}}_{\mathrm{W}}} \Delta\{\langle \mathbf{p} \rangle\} + \hat{\mathbf{f}}_{\mathrm{W}} + \mu \tilde{\mathbf{f}}_{\mathrm{W}}, \\ &\mathbf{b}_{\mathrm{W}} \leftrightarrow \rho^{\mathrm{i}}_{\mathrm{W}} \nu \mathbf{g}. \end{aligned} \tag{4.12}$$

Here symbol ‘↔’ is employed as shorthand for ‘is to be identified with’.

If χ_{W} denotes the characteristic function of pore space $\mathscr{P}$ (so $\chi_{\mathrm{W}}(\mathbf{x}) = 1$ if $\mathbf{x} \in \mathscr{P}$, $\chi_{\mathrm{W}}(\mathbf{x}) = 0$ if $\mathbf{x} \notin \mathscr{P}$), then (*op. cit.* (2.25))

$$\nu = \langle \chi_{\mathrm{W}} \rangle \quad \text{and} \quad \nabla \nu = -\int_{\Sigma} \mathbf{n} w\, \mathrm{d}A. \tag{4.13}$$

If the pore pressure is constant, P_0 say, then from $(4.11)_1$ and (4.13)

$$\hat{\mathbf{f}}_{\mathrm{W}} = P_0 \nabla v = \bar{P} \nabla v, \tag{4.14}$$

where

$$\bar{P} := v^{-1} \langle P \rangle \tag{4.15}$$

denotes the intrinsic average pressure. For more general situations, relation (4.14) motivates writing $(4.11)_1$ as

$$\hat{\mathbf{f}}_{\mathrm{W}}(\mathbf{x}) = \bar{P}(\mathbf{x}) \nabla v(\mathbf{x}) + \mathbf{F}_{\mathrm{W}}(\mathbf{x}), \tag{4.16}$$

where

$$\mathbf{F}_{\mathrm{W}}(\mathbf{x}) := -\int_{\Sigma} (P(\mathbf{y}) - \bar{P}(\mathbf{x})) \mathbf{n}(\mathbf{y}) w(\mathbf{y} - \mathbf{x}) \, \mathrm{d}A_{\mathbf{y}}. \tag{4.17}$$

Incompressibility implies

$$\operatorname{div} \mathbf{p} = 0 \tag{4.18}$$

and hence (non-trivially: see argument in *op. cit.* between (3.13) and (3.15))

$$\operatorname{div}\{\langle \mathbf{p} \rangle\} = 0. \tag{4.19}$$

In view of (4.15), (4.16) and (4.19), identification $(4.12)_1$ is compatible with identifications

$$\begin{aligned} \mathbf{T}_{\mathrm{W}} &\leftrightarrow -\bar{P} v \mathbf{1} + \frac{\mu}{\rho^{\mathrm{i}}_{\mathrm{W}}} \left\{ \nabla\{\langle \mathbf{p} \rangle\} + (\nabla\{\langle \mathbf{p} \rangle\})^{\mathrm{T}} \right\}, \\ \mathbf{f}^{\mathrm{B}^+}_{\mathrm{W}} &\leftrightarrow \bar{P} \nabla v + \mathbf{F}_{\mathrm{W}} + \mu \tilde{\mathbf{f}}_{\mathrm{W}}, \end{aligned} \tag{4.20}$$

upon noting

$$\operatorname{div}\left\{ (\nabla\{\langle \mathbf{p} \rangle\})^{\mathrm{T}} \right\} = \nabla\{\operatorname{div}\langle \mathbf{p} \rangle\} = \mathbf{0}. \tag{4.21}$$

In terms of the natural identifications

$$\begin{aligned} \rho_{\mathrm{W}} &\leftrightarrow \langle \rho \rangle = \langle \rho^{\mathrm{i}}_{\mathrm{W}} \chi_{\mathrm{W}} \rangle = \rho^{\mathrm{i}}_{\mathrm{W}} v, \\ \rho_{\mathrm{W}} \mathbf{v}_{\mathrm{W}} &\leftrightarrow \langle \mathbf{p} \rangle, \end{aligned} \tag{4.22}$$

$$\frac{1}{\rho^{\mathrm{i}}_{\mathrm{W}}} \langle \mathbf{p} \rangle \leftrightarrow v \mathbf{v}_{\mathrm{W}} =: \mathbf{Q}, \tag{4.23}$$

where $\mathbf{Q}$ is the *volumetric flux vector*. Identification (4.20) thus may be written as

$$\mathbf{T}_{\mathrm{W}} \leftrightarrow -\bar{P} v \mathbf{1} + \mu\{\nabla \mathbf{Q} + (\nabla \mathbf{Q})^{\mathrm{T}}\}. \tag{4.24}$$

The remaining term $\tilde{\mathbf{f}}_{\mathrm{W}}$ in (4.10) introduces the concept of permeability. If the porous body is isotropic, the assumption that the resistive force density represented by $\mu \tilde{\mathbf{f}}_{\mathrm{W}}$ depends linearly upon relative velocity yields

$$\tilde{\mathbf{f}}_{\mathrm{W}} = -\frac{1}{k} (\mathbf{v}_{\mathrm{W}} - \mathbf{v}_{\mathrm{B}}) \tag{4.25}$$

for some constant $k > 0$. Eq. (4.10) may now be written, using (4.16), (4.23) and (4.25), as

$$-\nu\nabla\bar{P} + \mu\Delta\mathbf{Q} + \mathbf{F}_{\mathrm{W}} - \frac{\mu}{k}(\mathbf{v}_{\mathrm{W}} - \mathbf{v}_{\mathrm{B}}) + \rho^{\mathrm{i}}_{\mathrm{W}}\nu\mathbf{g} = \mathbf{0}. \tag{4.26}$$

Remark 19. It is possible to obtain an explicit expression for $\mathbf{F}_{\mathrm{W}}$ in a stationary body in the absence of flow. In such case the pore space pressure is hydrostatic: that is,

$$P(\mathbf{y}) = P_0 - \rho^{\mathrm{i}}_{\mathrm{W}}g(\mathbf{y} - \mathbf{x}_0)\cdot\mathbf{e}_3, \tag{4.27}$$

with $P_0 := P(\mathbf{x}_0)$, where $\mathbf{x}_0$ is some fixed point in pore space and $\mathbf{e}_3$ is a unit vector directed vertically up. Then for any point $\mathbf{x}$ (not necessarily in pore space),

$$\begin{aligned}\langle P\rangle(\mathbf{x}) &:= \int_{\text{pore space}} P(\mathbf{y})w(\mathbf{y}-\mathbf{x})\,\mathrm{d}\mathbf{y} = \int_{\text{pore space}} \{P_0 - \rho^{\mathrm{i}}_{\mathrm{W}}g(\mathbf{y}-\mathbf{x}_0)\cdot\mathbf{e}_3\}w(\mathbf{y}-\mathbf{x})\,\mathrm{d}\mathbf{y} \\ &= P_0\nu(\mathbf{x}) - \rho^{\mathrm{i}}_{\mathrm{W}}g\Big((\bar{\mathbf{x}}(\mathbf{x}) - \mathbf{x}_0)\cdot\mathbf{e}_3\Big)\nu(\mathbf{x}),\end{aligned} \tag{4.28}$$

where $\bar{\mathbf{x}}(\mathbf{x})$ denotes the centroid of the pore space which lies within that REV with centroid at $\mathbf{x}$. (Here w denotes the weighting function associated with REVs: see Remark 4.)

Accordingly, from (4.15),

$$\bar{P}(\mathbf{x}) = P_0 - \rho^{\mathrm{i}}_{\mathrm{W}}g(\bar{\mathbf{x}}(\mathbf{x}) - \mathbf{x}_0)\cdot\mathbf{e}_3. \tag{4.29}$$

It follows that

$$\nabla\bar{P} = -\rho^{\mathrm{i}}_{\mathrm{W}}g\ \nabla\bar{x}_3, \tag{4.30}$$

where $\bar{x}_3(\mathbf{x})$ denotes the height of $\bar{\mathbf{x}}(\mathbf{x})$ above some fixed horizontal plane. Writing

$$h(\mathbf{x}) := \bar{x}_3(\mathbf{x}) - x_3 \tag{4.31}$$

(so that $h(\mathbf{x})$ is the height of the centroid of the *pore space* within an REV centred at $\mathbf{x}$ above the centroid of this REV, namely $\mathbf{x}$),

$$\nabla\bar{P} = -\rho^{\mathrm{i}}_{\mathrm{W}}g(\nabla h + \mathbf{e}_3). \tag{4.32}$$

From (4.26) and (4.32), noting $\mathbf{Q} = \mathbf{v}_{\mathrm{W}} = \mathbf{v}_{\mathrm{S}} = \mathbf{0}$,

$$\mathbf{F}_{\mathrm{W}} = -\rho^{\mathrm{i}}_{\mathrm{W}}\nu g\nabla h. \tag{4.33}$$

Thus $\mathbf{F}_{\mathrm{W}}$ vanishes if $\nabla h = \mathbf{0}$. In particular this holds when the centroid of pore space within an REV coincides with the REV centroid. More generally $\mathbf{F}_{\mathrm{W}}$ is negligible if, within any REV, the spatial pressure fluctuation $P(\mathbf{y}) - \bar{P}(\mathbf{x})$ is not spatially correlated with pore boundary orientation, as follows immediately from (4.17). Were a flow to yield

$$\mathbf{F}_{\mathrm{W}}(\mathbf{x}) = -\int_{\Sigma} \boldsymbol{\alpha}(\mathbf{x})\cdot(\mathbf{y}-\mathbf{x})\mathbf{n}(\mathbf{y})w(\mathbf{y}-\mathbf{x})\,\mathrm{d}A_{\mathrm{y}} \tag{4.34}$$

for some vector $\boldsymbol{\alpha}(\mathbf{x})$ (a much weaker assumption than requiring $P(\mathbf{y}) - \bar{P}(\mathbf{x})$ to equal $\boldsymbol{\alpha}(\mathbf{x})\cdot(\mathbf{y}-\mathbf{x})$ *pointwise*), then, since it may be shown that

$$\int_{\Sigma}(\mathbf{y}-\mathbf{x})\otimes\mathbf{n}(\mathbf{y})w(\mathbf{y}-\mathbf{x})\,\mathrm{d}A_{\mathrm{y}} = \nabla\nabla\nu, \tag{4.35}$$

we should have, using the symmetry of the linear transformation field $\nabla\nabla\nu$,

$$\mathbf{F}_W = (\nabla\nabla\nu)\boldsymbol{\alpha}. \tag{4.36}$$

While the above comments do not *prove* $\mathbf{F}_W$ is negligible they do suggest it is linked with highly inhomogeneous porosity. Further, as far as we are aware, there does not appear to be experimental evidence for holding on to this term: its neglect in (4.26) yields the Brinkman equation and thence, provided $\Delta\mathbf{Q}$ is negligible, the Darcy-type relation

$$-\nu\nabla\bar{P} + \rho_W^i \nu \mathbf{g} = \frac{\mu}{k}\mathbf{v}_W \tag{4.37}$$

in an inertial frame in which the porous body is stationary.

Remark 20. For anisotropic bodies (4.25) takes the form

$$\tilde{\mathbf{f}}_W = -\mathbf{K}^{-1}(\mathbf{v}_W - \mathbf{v}_B), \tag{4.38}$$

where $\mathbf{K}$ denotes the permeability tensor. The counterpart of (4.37) (in which $\mathbf{K} = k\mathbf{1}$) is accordingly

$$-\nu\nabla\bar{P} + \rho_W^i \nu \mathbf{g} = \mu\mathbf{K}^{-1}\mathbf{v}_W. \tag{4.39}$$

Both (4.37) and (4.39) correspond to a simplified version of $(4.20)_1$, namely

$$\mathbf{T}_W \leftrightarrow -\nu\bar{P}\mathbf{1}. \tag{4.40}$$

In view of the foregoing it would appear to be unnecessary, at least for steady creeping flows in porous bodies saturated with incompressible liquid, to go into the greater complexity of taking *explicit* account of the BW interfacial system, since the Brinkman equation and its Darcy-type simplification seem to be adequate in practice.

Remark 21. The definition of permeability tensor varies in the literature. That resulting in (4.39) was employed in Hassanizadeh and Gray (1980). Whitaker (1986a) wrote (4.39) as

$$-\nabla\bar{P} + \rho_W^i \mathbf{g} = \mu\hat{\mathbf{K}}^{-1}\mathbf{Q} \tag{4.41}$$

(cf. *op. cit.*, Eq. (3.38) in the case of constant porosity) while Murdoch and Soliman (1999) wrote (4.38) as

$$\tilde{\mathbf{f}}_W = -\nu\tilde{\mathbf{K}}^{-1}(\mathbf{v}_W - \mathbf{v}_B). \tag{4.42}$$

Clearly these permeability tensors are related by

$$\nu^{-1}\hat{\mathbf{K}} = \tilde{\mathbf{K}} = \nu\mathbf{K}. \tag{4.43}$$

Remark 22. Based upon thermodynamic considerations Hassanizadeh and Gray (1980) has argued that more generally

$$\mathbf{T}_W \leftrightarrow -\nu\{\bar{P} - \lambda\,\mathrm{div}\,\mathbf{v}_W\}\mathbf{1} + \nu\mu\{\nabla\mathbf{v}_W + (\nabla\mathbf{v}_W)^{\mathrm{T}}\}. \tag{4.44}$$

This coincides with (4.24) when porosity is constant and the liquid incompressible.

4.3. Flows involving two immiscible liquid phases which together saturate a porous solid

Consider the flow of two immiscible liquids (materials ‘O’ and ‘W’) through a body which they jointly saturate. As in the previous section, it is possible to avoid *explicit* account of *all* interfacial systems. This is accomplished by defining

$$\mathscr{M}_{\mathrm{W}^-}(\tau) := \mathscr{M}_{\mathrm{W}} - (\mathscr{I}_{\mathrm{BW}} \cup \mathscr{T}_{\mathrm{WOB}}) \cap \mathscr{M}_{\mathrm{W}}, \tag{4.45}$$

$$\mathscr{M}_{\mathrm{O}^-}(\tau) := \mathscr{M}_{\mathrm{O}} - (\mathscr{I}_{\mathrm{BO}} \cup \mathscr{T}_{\mathrm{WOB}}) \cap \mathscr{M}_{\mathrm{O}}, \tag{4.46}$$

and

$$\mathscr{M}_{\mathrm{B}^{++}}(\tau) := \mathscr{M}_{\mathrm{B}} \cup \mathscr{I}_{\mathrm{BW}} \cup \mathscr{I}_{\mathrm{BO}} \cup \mathscr{T}_{\mathrm{WOB}}. \tag{4.47}$$

Thus, at any instant τ, $\mathscr{M}_{\mathrm{W}^-}(\tau)$ consists of all W molecules except those which are in the W–B interfacial, or W–O–B common line, systems. In particular, this system includes all those W molecules in the W–O interfacial system. System $\mathscr{M}_{\mathrm{O}^-}(\tau)$ is similarly defined, and $\mathscr{M}_{\mathrm{B}^{++}}(\tau)$ consists of all B molecules together with all W and O molecules which at instant τ lie in an interface including B molecules or in the W–O–B common line system.

Linear momentum balances for the three systems take the forms given by (3.59), namely

$$\operatorname{div}\mathbf{T}_{\mathrm{W}^-} + \mathbf{F}_{\mathrm{W}^-}^{\mathrm{O}^-} + \mathbf{F}_{\mathrm{W}^-}^{\mathrm{B}^{++}} + \mathbf{b}_{\mathrm{W}^-} = \frac{\partial}{\partial t}\{\rho_{\mathrm{W}^-}\mathbf{v}_{\mathrm{W}^-}\} + \operatorname{div}\{\rho_{\mathrm{W}^-}\mathbf{v}_{\mathrm{W}^-} \otimes \mathbf{v}_{\mathrm{W}^-}\}, \tag{4.48}$$

$$\operatorname{div}\mathbf{T}_{\mathrm{O}^-} + \mathbf{F}_{\mathrm{O}^-}^{\mathrm{W}^-} + \mathbf{F}_{\mathrm{O}^-}^{\mathrm{B}^{++}} + \mathbf{b}_{\mathrm{O}^-} = \frac{\partial}{\partial t}\{\rho_{\mathrm{O}^-}\mathbf{v}_{\mathrm{O}^-}\} + \operatorname{div}\{\rho_{\mathrm{O}^-}\mathbf{v}_{\mathrm{O}^-} \otimes \mathbf{v}_{\mathrm{O}^-}\} \tag{4.49}$$

and

$$\operatorname{div}\mathbf{T}_{\mathrm{B}^{++}} + \mathbf{F}_{\mathrm{B}^{++}}^{\mathrm{W}^-} + \mathbf{F}_{\mathrm{B}^{++}}^{\mathrm{O}^-} + \mathbf{b}_{\mathrm{B}^{++}} = \frac{\partial}{\partial t}\{\rho_{\mathrm{B}^{++}}\mathbf{v}_{\mathrm{B}^{++}}\} + \operatorname{div}\{\rho_{\mathrm{B}^{++}}\mathbf{v}_{\mathrm{B}^{++}} \otimes \mathbf{v}_{\mathrm{B}^{++}}\}. \tag{4.50}$$

Here, noting there is no molecular exchange between $\mathscr{M}_{\mathrm{W}^-}$ and $\mathscr{M}_{\mathrm{O}^-}$,

$$\mathbf{F}_{\mathrm{W}^-}^{\mathrm{O}^-} := \mathbf{f}_{\mathrm{W}^-}^{\mathrm{O}^-} \quad \text{and} \quad \mathbf{F}_{\mathrm{W}^-}^{\mathrm{B}^{++}} := \mathbf{f}_{\mathrm{W}^-}^{\mathrm{B}^{++}} + \mathbf{P}^{\mathrm{B}^{++}\to\mathrm{W}^-} - \mathbf{P}^{\mathrm{W}^-\to\mathrm{B}^{++}}. \tag{4.51}$$

Similarly,

$$\mathbf{F}_{\mathrm{O}^-}^{\mathrm{W}^-} := \mathbf{f}_{\mathrm{O}^-}^{\mathrm{W}^-} \; (= -\mathbf{F}_{\mathrm{W}^-}^{\mathrm{O}^-}) \quad \text{and} \quad \mathbf{F}_{\mathrm{O}^-}^{\mathrm{B}^{++}} := \mathbf{f}_{\mathrm{O}^-}^{\mathrm{B}^{++}} + \mathbf{P}^{\mathrm{B}^{++}\to\mathrm{O}^-} - \mathbf{P}^{\mathrm{O}^-\to\mathrm{B}^{++}}. \tag{4.52}$$

The molecular exchange contributions to $(4.51)_2$ derive from migration of ‘W’ molecules between W^- and B^{++}, and similarly for ‘O’ molecules in $(4.52)_2$, between $\mathscr{M}_{\mathrm{O}^-}$ and $\mathscr{M}_{\mathrm{B}^{++}}$. Force density $\mathbf{F}_{\mathrm{W}^-}^{\mathrm{O}^-}$ represents the effect of bulk and W–O interfacial ‘O’ molecules on bulk and W–O interfacial ‘W’ molecules (and similarly for $\mathbf{F}_{\mathrm{O}^-}^{\mathrm{W}^-} = -\mathbf{F}_{\mathrm{W}^-}^{\mathrm{O}^-}$), while $\mathbf{F}_{\mathrm{W}^-}^{\mathrm{B}^{++}}$ ($\mathbf{F}_{\mathrm{O}^-}^{\mathrm{B}^{++}}$) denotes the effective force density which expresses the resistance to the flow of W^- (O^-) material due to the porous body boundary and the interfaces and common line systems located at this boundary. Of course, in (4.50),

$$\mathbf{F}_{\mathrm{B}^{++}}^{\mathrm{W}^-} = -\mathbf{F}_{\mathrm{W}^-}^{\mathrm{B}^{++}} \quad \text{and} \quad \mathbf{F}_{\mathrm{B}^{++}}^{\mathrm{O}^-} = -\mathbf{F}_{\mathrm{O}^-}^{\mathrm{B}^{++}}. \tag{4.53}$$

If v_{W} and v_{O} denote the volume fractions occupied by the two liquids then saturation implies that the porosity

$$v = v_{\mathrm{W}} + v_{\mathrm{O}}. \tag{4.54}$$

Body force densities $\mathbf{b}_{\mathrm{W}}$ and $\mathbf{b}_{\mathrm{O}}$ are readily identified as

$$\mathbf{b}_{\mathrm{W}} = \rho^{\mathrm{i}}_{\mathrm{W}} v_{\mathrm{W}} \mathbf{g} \quad \text{and} \quad \mathbf{b}_{\mathrm{O}} = \rho^{\mathrm{i}}_{\mathrm{O}} v_{\mathrm{O}} \mathbf{g}, \tag{4.55}$$

where $\rho^{\mathrm{i}}_{\mathrm{W}}$ and $\rho^{\mathrm{i}}_{\mathrm{O}}$ denote the intrinsic mass densities of liquids ‘W’ and ‘O’.

Whitaker (1986b) argued that the “equations of motion” for two-phase fluid flow (through a stationary body in an inertial frame) should take the form (*op. cit.*, Eqs. (1.1) and (1.2))

$$\langle \mathbf{v}_\beta \rangle = -\frac{\hat{\mathbf{K}}_\beta}{\mu_\beta}\{\nabla \bar{P}_\beta - \rho_\beta \mathbf{g}\} + \hat{\mathbf{K}}_{\beta\gamma}\langle \mathbf{v}_\gamma \rangle \tag{4.56}$$

and

$$\langle \mathbf{v}_\gamma \rangle = -\frac{\hat{\mathbf{K}}_\gamma}{\mu_\gamma}\{\nabla \bar{P}_\gamma - \rho_\gamma \mathbf{g}\} + \hat{\mathbf{K}}_{\gamma\beta}\langle \mathbf{v}_\beta \rangle. \tag{4.57}$$

Here β and γ label the two fluid phases, $\mathbf{v}_\beta$ and $\mathbf{v}_\gamma$ (ρ_β and ρ_γ) the corresponding velocities (mass densities) at sub-pore scale, μ_β and μ_γ the viscosities, and $\hat{\mathbf{K}}_\gamma$ and $\hat{\mathbf{K}}_\beta$ the permeability tensors (see Remark 22). Tensors $\hat{\mathbf{K}}_{\beta\gamma}$ and $\hat{\mathbf{K}}_{\gamma\beta}$ represent the “viscous drag that exists between the β-phase and γ-phase”. In the event that the fluids are incompressible liquids, which together saturate the porous solid, then Eqs. (4.56) and (4.57) correspond to relations (4.49) and (4.50) in the case of steady, creeping flow, where

$$\mathbf{T}_{\mathrm{W}^-} := -v_{\mathrm{W}} \bar{P}_{\mathrm{W}} \mathbf{1} \tag{4.58}$$

and

$$\mathbf{F}^{\mathrm{B}^{++}}_{\mathrm{W}^-} + \mathbf{F}^{\mathrm{O}^-}_{\mathrm{W}^-} := \bar{P}_{\mathrm{W}} \nabla v_{\mathrm{W}} - \mu_{\mathrm{W}} v_{\mathrm{W}} \hat{\mathbf{K}}^{-1}_{\mathrm{W}} \mathbf{Q}_{\mathrm{W}} + \mu_{\mathrm{W}} v_{\mathrm{W}} \hat{\mathbf{K}}^{-1}_{\mathrm{W}} \hat{\mathbf{K}}_{\mathrm{WO}} \mathbf{Q}_{\mathrm{O}}, \tag{4.59}$$

together with

$$\mathbf{T}_{\mathrm{O}^-} := -v_{\mathrm{O}} \bar{P}_{\mathrm{O}} \mathbf{1} \tag{4.60}$$

and

$$\mathbf{F}^{\mathrm{B}^{++}}_{\mathrm{O}^-} + \mathbf{F}^{\mathrm{W}^-}_{\mathrm{O}^-} := \bar{P}_{\mathrm{O}} \nabla v_{\mathrm{O}} - \mu_{\mathrm{O}} v_{\mathrm{O}} \hat{\mathbf{K}}^{-1}_{\mathrm{O}} \mathbf{Q}_{\mathrm{O}} + \mu_{\mathrm{O}} v_{\mathrm{O}} \hat{\mathbf{K}}^{-1}_{\mathrm{O}} \hat{\mathbf{K}}_{\mathrm{WO}} \mathbf{Q}_{\mathrm{W}}. \tag{4.61}$$

Of course, we have here taken phases ‘β’ and ‘γ’ to be liquids ‘W’ and ‘O’, v_{W} and v_{O} denote the volume occupation fractions (see (4.54)), and $\mathbf{Q}_{\mathrm{O}}$ and $\mathbf{Q}_{\mathrm{W}}$ represent the appropriate volumetric flux vectors.

4.4. Concluding remarks

Remark 23. The molecular viewpoint here adopted enables clear physical identifications and interpretations to be made in respect of all terms which appear in balances of mass, linear momentum, and energy. Attention has been drawn to the differing possibilities in selecting relevant material systems. For example, in Section 4.3 it was suggested that, in the case of two immiscible liquids saturating a porous body, liquid molecules near the solid be grouped together with solid molecules: the alternatives would have been either to treat these as liquid–solid interfacial or common line matter, or not to distinguish them from other liquid molecules of the same type. Each of the three foregoing possible selections of material systems yield the same *forms* of balance relations for those systems which include bulk liquid and solid phases. However, the terms involved have different interpretations in each case. Here it is made clear how a given choice mandates self-consistent physical interpretations of these terms, and accordingly aids formulation of constitutive relations. Further, contributions to momentum and energy transport associated with molecular diffusion are not immediately evident from a continuum perspective, [6] nor are those contributions which originate in mass transfer between distinct material systems. The corpuscular approach has previously rendered transparent the interpretation of partial stresses in mixture theory (Morro and Murdoch, 1986) which had been incorrectly given by Truesdell and Toupin (1960), and Bowen (1976), and shown to lead to a paradox by Gurtin et al. (1973).

Remark 24. Flows in porous bodies are sensitive to surfactant material which, although present in only small amounts, significantly changes interfacial tensions. The extensive literature on surfactant science includes much work that adopts a molecular (or ionic) perspective. Thus a corpuscular approach of the kind here outlined helps to bridge the gap between highly detailed knowledge concerning the microscopic behaviour associated with surfactants and the macroscopic consequences of this behaviour. In this respect surfactants may be considered to constitute distinct material systems, or to form (for example) subsets of interfacial, or common line, systems.

Remark 25. In deriving balance relations no assumptions have been made concerning the spatial distributions of material systems. Thus these relations are valid for *all* such distributions. In particular, they apply to flows of two immiscible liquids in which there is any amount of pore-scale ‘fingering’, or any distribution of ‘pockets’ of one liquid left behind when much of this liquid has been displaced by the other liquid. The extent of such mixing is revealed by the relevant densities, ρ_{O} and ρ_{W}, say. Regions

$$\begin{aligned}\mathscr{R}_{\mathrm{W}}(t) &:= \{\mathbf{x} : \rho_{\mathrm{W}}(\mathbf{x},t) > 0\},\\ \mathscr{R}_{\mathrm{O}}(t) &:= \{\mathbf{x} : \rho_{\mathrm{O}}(\mathbf{x},t) > 0\}\end{aligned} \tag{4.62}$$

are those considered to be ‘occupied’ (at REV scale) by liquid ‘W’ and ‘O’, respectively, at time t. Region

$$\mathscr{R}_M(t) := \mathscr{R}_{\mathrm{W}}(t) \cap \mathscr{R}_{\mathrm{O}}(t) \tag{4.63}$$

is that in which (at the REV averaging scale) *both* liquids are to be found. If $\mathscr{R}_M(t)$ is locally ‘thin’ in one direction then it may be modelled as an (REV-scale) W–O interfacial surface, $\mathscr{I}_M(t)$. Although this is not a situation which usually persists in time ($R_M(t)$ will in general thicken as time evolves), if liquid ‘O’ is being displaced by liquid ‘W’ then the boundary $\partial R_M(t)$ of $R_M(t)$ will in general contain two disjoint components, $\partial R_M^{\mathrm{W}}(t)$ and $\partial R_M^{\mathrm{O}}(t)$, which separate $R_M(t)$ from the regions in which, respectively, $\rho_{\mathrm{W}}(\cdot,t)$ and $\rho_{\mathrm{O}}(\cdot,t)$ vanish. Said differently, $\partial R_M^{\mathrm{O}}(t)$ ($\partial R_M^{\mathrm{W}}(t)$) is the boundary at time t between the region (at REV scale) jointly occupied by ‘O’ and ‘W’ and the region occupied only by ‘W’ (‘O’). Roughly speaking, the ‘thickness’ of $\mathscr{R}_M(t)$ is the ‘separation’ of surfaces $\partial R_M^{\mathrm{O}}(t)$ and $\partial R_M^{\mathrm{W}}(t)$. From the definitions of $\mathscr{R}_{\mathrm{W}}$, $\mathscr{R}_{\mathrm{O}}$, ρ_{W} and ρ_{O}, the minimum thickness

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[6] For example, while any stress tensor in continuum mechanics is regarded as a single entity, the corpuscular viewpoint clearly reveals this tensor to consist of distinct contributions from both molecular interactions and diffusion.

of $\mathscr{R}_M(t)$ is the scale of the REV averaging employed. Analysis of behaviour near $\partial\mathscr{R}_M^{\mathrm{O}}(t)$ or $\partial\mathscr{R}_M^{\mathrm{W}}(t)$ may be helped by considering moment of mass balances (see Murdoch and Bedeaux, 1994, Section 5: specifically Eq. (5.17) and Remark 3). Moment of mass balance for a material system $\mathscr{S}$ delineates the time evolution of the displacement $\mathbf{d}_{\mathscr{S}}$ from an REV centroid (geometric centre) of the mass centre of $\mathscr{S}$ material within the REV. While $\mathbf{d}_{\mathscr{S}}$ is small ($0 < |\mathbf{d}_{\mathscr{S}}| < \varepsilon$, where ε is the REV scale), as a boundary such as $\partial R_M^{\mathrm{O}}(t)$ is crossed $|\mathbf{d}_{\mathscr{S}}|$ changes by an amount of order ε over a distance of 2ε. Thus the spatial gradient $\nabla\mathbf{d}_{\mathscr{S}}$ becomes significant. In such considerations of inhomogeneity within REVs, via REV-scale molecular averaging, it is also instructive to consider the corresponding (tensor-valued) moment of momentum balance (also discussed in *op. cit.* Section 5). This remark has been included to draw further attention to the utility of corpuscular considerations (which serve to establish balances of moments of mass and momentum with precise physical interpretations of all fields involved), here indicating its role in describing the evolution of the boundary which represents the limit of penetration/displacement of one liquid by another.

Remark 26. The averaging procedure here presented avoids the introduction of excess quantities for interfaces and common lines. Excess quantities are not defined unambiguously: their values depend on the choice of surfaces which model interfacial locations.

Acknowledgements

This work was supported under the Joint Study Programme of the British Council and NWO (Netherlands). The authors are grateful for a referee's helpful comments.

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