

AVERAGING THEOREMS AND AVERAGED EQUATIONS FOR TRANSPORT OF INTERFACE PROPERTIES IN MULTIPHASE SYSTEMS

W. G. GRAY

Department of Civil Engineering, University of Notre Dame, Notre Dame, IN 46556, U.S.A.

S. M. HASSANIZADEH

National Institute of Public Health and Environmental Protection (RIVM), P.O. Box 1,
 3720 BA Bilthoven, The Netherlands

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Abstract—Theorems which relate averages of surface derivatives to spatial derivatives of surface averages are derived. The theorems are then applied to balance equations for surface properties in multiphase systems. Macroscopic point equations complementing the macroscopic equations for bulk phases are obtained which allow for a more complete fundamental description of multiphase transport.

Key Words: multiphase flow, porous media, averaging theory, surface properties, macroscopic equations, transport phenomena, flow physics, interface properties

INTRODUCTION

The theoretical description of multiphase flow at the microscopic level is complicated by the complex geometry of interphase boundaries. One procedure for working around this problem is the use of local volume averaging (Anderson & Jackson 1967; Bachmat 1972; Gray & Lee 1977; Slattery 1967; Whitaker 1967). By this process, classical equations of continuum mechanics valid at the microscopic level are averaged over a representative local volume, indicated as δV , to obtain an average description of phase behavior at each point in space. The effect of this procedure is to represent the multiphase mixture as a collection of overlapping continua. The averaged, or macroscale, equations depend on the void fraction (which does not exist at the microscale) as well as products of deviations from mean values and terms accounting for interphase transport.

The microscopic balance equation for a general property ψ having the (intrapphase) flux i^k , external supply f and production G may be expressed in cartesian coordinates as follows (Brodkey 1967):

$$\frac{\partial \rho \psi}{\partial t} + (\rho \psi v^k)_{,k} - i^k_{,k} - \rho f - G = 0. \quad [1]$$

By averaging this equation over a representative volume composed of a mixture of phases, the following averaged point equation or macroscopic equation for a phase α may be obtained and expressed in cartesian coordinates as (e.g. Hassanizadeh & Gray 1979a):

$$\begin{aligned} \frac{\partial \epsilon^\alpha \langle \rho \rangle^\alpha \bar{\psi}^\alpha}{\partial t} + (\epsilon^\alpha \langle \rho \rangle^\alpha \bar{\psi}^\alpha \bar{v}^{\alpha k})_{,k} - (I^{\alpha k})_{,k} - \epsilon^\alpha \langle \rho \rangle^\alpha \bar{f}^\alpha - \epsilon^\alpha \langle \rho \rangle^\alpha \bar{G}^\alpha \\ = \frac{1}{\delta V} \int_{S_{\alpha\beta}} [\rho^\alpha \psi^\alpha (w^k - v^{\alpha k}) + i^{\alpha k}] n^{\alpha k} dS, \quad [2] \end{aligned}$$

where

- ϵ^α = the volume fraction of phase α ,
- ρ^α = the microscopic density within phase α ,
- $\langle \rho \rangle^\alpha$ = the intrinsic average mass density of the α -phase,
- ψ^α = a microscopic property of the α -phase,

- $\bar{\psi}^\alpha$ = the mass average of ψ^α for the α -phase,
 $v^{\alpha k}$ = the microscopic velocity within the α -phase,
 $S_{\alpha\beta}$ = the interfacial area between the α -phase and all other phases in δV ,
 w^k = the microscopic velocity of the interphase boundary $S_{\alpha\beta}$
 $\bar{v}^{\alpha k}$ = the mass average velocity of the α -phase,
 $i^{\alpha k}$ = the microscopic intraphase flux vector for the α -phase,
 $I^{\alpha k}$ = the macroscopic intraphase flux vector for the α -phase (it includes the average of the product of deviations of ψ^α and $v^{\alpha k}$),
 \bar{f}^α = the mass average of f for the α -phase

and

\bar{G}^α = the mass average of G for the α -phase.

The integral of microscopic quantities over $S_{\alpha\beta}$ accounts for interphase transport and mechanical interactions between the α -phase and all other phases. Throughout this text, superscripts i, j , and k refer to cartesian coordinates. In addition to [2] averaging of microscopic equations must also include the averaging of microscopic jump conditions at interfaces. Previous studies based on volume averaging (e.g. Hassanizadeh & Gray 1979a) have not included intrafacial transport. Thus, the possibility that thermo-mechanical properties may be stored within the interface or transported along the interface has been excluded in the averaging approach. This exclusion places a severe restriction on developing complete theories for multiphase flows at the macroscale. In particular, systems wherein mass accumulates at interfaces or where interfacial tension and energy play an important role, can not be modeled properly. For such systems, although [2] remains valid, equations are needed which account for the *macroscopic* manifestation of microscopic interfacial properties.

In the past, Ishii (1975) has employed a time-averaging approach along with a number of simplifying assumptions to include surface effects in a two-phase flow model. Drew (1971) and Drew & Segel (1971) have included surface momentum effects in their model but did not consider surface mass, energy or entropy contributions. Hassanizadeh (1979) recognized the need to incorporate such momentum, energy and entropy in macroscopic jump conditions at the macroscale. Abriola & Gray (1985) considered massless interfaces and examined the way that surface properties might manifest themselves in volume-averaged phase equations. Perhaps the most complete incorporation of surface effects in macroscopic phase equations is found in Marle (1981, 1982). His work incorporates the properties of interphase surfaces and considers curves where interface surfaces meet (i.e. contact lines). Despite the quality of this work, it is somewhat incomplete in that macroscopic pressure and temperature, variables that should enter the equations only after application of a constitutive theory, appear in the averaged equations. Furthermore, it is assumed *a priori* that thermodynamic relations valid at the microscale are also appropriate for macroscopic quantities, whereas such relations must be obtained as outcomes of the constitutive theory. These shortcomings make incorporation of Marle's equations in a completely general constitutive theory rather difficult. Nevertheless, Marle's work represents the most complete description of multiphase flow at the macroscale available. His contention that macroscopic quantities for interfaces and macroscopic equations involving these quantities must be written and fully exploited in the study of multiphase flows remains true.

The current paper accomplishes two tasks in progressing toward the complete description of multiphase flows. First, local-volume-averaging theorems for time derivatives and surface gradients of interfacial properties are developed. These theorems are analogous to the theorems for bulk properties in that they relate the averages of derivatives to the derivatives of averages. Additionally, they transform the *surface* derivatives at the microscale to *spatial* derivatives at the macroscale. Second, the theorems are applied to the surface balance equations of mass, momentum, energy and entropy to obtain the macroscopic description of these transport equations. In other words, a general macroscopic equation suitable for multiphase systems where microscopic interfaces attain surface properties is derived. These equations complement volume-averaged equations for bulk phases [2], and they are essential for developing a general constitutive theory. Finally, an appropriate formulation of the second law of thermodynamics for such multiphase systems is obtained.

INTERFACES IN MULTIPHASE SYSTEMS

Bulk phases in a multiphase system are separated by very narrow transition zones which, in a continuum description (yet at the microscale), are treated as two-dimensional interfaces. Depending on the types of processes being studied, one may assume that these interfaces do not store or attain thermodynamic properties, rather they only act as singular surfaces within the phases. For many important processes, however, such an assumption is overly restrictive. For example, in systems where adsorption and desorption play an important role in the dynamics of phases, one must assign mass to the interfaces. Also, in systems composed of immiscible phases, surface tension may be an important force which must be considered in a global balance of momentum even though the interfaces may be considered massless.

Similar to their description in bulk phases, thermodynamic processes at interfaces are in general described by conservation laws of surface mass, momentum, energy and entropy. The general balance equation for a typical thermodynamic property ψ^s of the interface is (Moeckel 1975)

$$\frac{\partial \Gamma \psi^s}{\partial t} + (\Gamma \psi^s w^a)_{,a} - 2\Gamma w^i n^i K_M \psi^s - i^{sa}_{,a} - \Gamma F^s - \Gamma G^s = - \sum_{\alpha=1}^2 [\rho^\alpha \psi^\alpha (w^k - v^{\alpha k}) + i^{\alpha k}] n^{\alpha k}, \quad [3]$$

where

- Γ = the surface density or mass per unit area,
- w^a = the flow velocity within the surface (i.e. $a = 1, 2$),
- K_M = the mean curvature of the surface,
- F^s = the external supply term for the surface,
- G^s = the production term within the surface

and

i^{sa} = the flux within the surface.

The superscripts and subscripts a, b and c are used throughout to indicate surface coordinates and the subscript $,a$ denotes differentiation with respect to surface coordinates. The summation in [3] is over the two phases on each side of the interface. Obviously, constitutive equations are needed for interface and bulk phase properties to complete the description of the interface (e.g. Scriven 1960; Moeckel 1975; Deemer & Slattery 1978). However, often a detailed description of the thermodynamic state of the interface at the microscale is not required for multiphase systems. Rather, the macroscopic (or averaged) manifestation of thermodynamic processes are normally needed. For this purpose, one has to be able to average [3] over the union of interfaces of interest within an averaging volume. In the following, necessary tools are developed and a systematic averaging approach is implemented to achieve this goal.

For locating interfaces within an averaging volume, the distribution function introduced by Gray & Lee (1977) can be used conveniently. Consider figures, 1a and 1b where two possible types of surface areas for a two-phase system are depicted. Define the distribution function $\gamma = 1$ on one side of the surface of interest and $\gamma = 0$ on the other side. The linking of γ with a physical distribution of phases will occur later in the paper in order to prevent confusing the averaging procedure with application of the resulting theorems. Then, it can be shown (Gray & Lee 1977)

$$\gamma_{,i} = -n^i \delta(x^k - x_s^k) \quad [4]$$

and

$$\frac{\partial \gamma}{\partial t} = -w^i \gamma_{,i} = w^i n^i \delta(x^k - x_s^k), \quad [5]$$

where x_s^k is the coordinate of a point on the surface, n^i is the normal to the surface pointing into the side where $\gamma = 0$, w^i is the velocity of the interface and $\delta(x^k - x_s^k)$ is the Dirac function. Note that the interface may be a closed surface, as in figure 1a, or may terminate on the boundary of the averaging volume of interest, as in figure 1b. Although values of γ are indicated in the figure, the selection is arbitrary in that the averaging theorems will be unchanged if γ is replaced by $1 - \gamma$. Because of the properties of a delta function, the integrals containing derivatives of γ can be

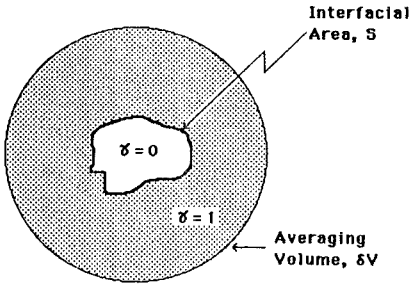


Figure 1a. Interfacial surface area, S , which is closed within an averaging volume δV .

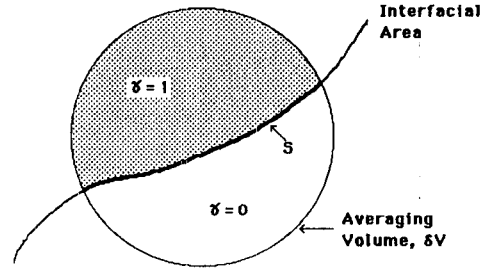


Figure 1b. Interfacial surface area, S , which intersects the boundary of the averaging volume, δV .

rewritten as integrals over surfaces, such as

$$\int_V h \gamma_{,i} dV = - \int_S h n^i dS \tag{6a}$$

and

$$\int_V h \frac{\partial \gamma}{\partial t} dV = \int_S h w^i n^i dS, \tag{6b}$$

where h is an arbitrary function. Replacement of h with $h n^i$ in [6a] yields

$$\int_V h n^i \gamma_{,i} dV = - \int_S h dS. \tag{6c}$$

Thus, the function γ is a mathematical convenience which allows for transferring between surface and volume integrals.

In systems with three or more phases, other types of interface surfaces may be encountered. In figure 2, some possible types are depicted. In such cases, one may be interested in the macroscopic effect of processes occurring at the interfaces between phases, say, I and II (portion S_p in figure 2). Then it is necessary to transfer between a surface integration carried out over S_p and one carried out over the whole of S . For this purpose a surface distribution function $\overset{\circ}{\gamma}$ is defined such that

$$\overset{\circ}{\gamma}(u^a, t) = 1 \quad \text{on } S_p \tag{7a}$$

and

$$\overset{\circ}{\gamma}(u^a, t) = 0 \quad \text{otherwise,} \tag{7b}$$

where u^a is the surface coordinate of a point on S . Similarly to the manipulations with γ , the following relations hold for $\overset{\circ}{\gamma}$.

$$\overset{\circ}{\gamma}_{,a} = - v_a \delta(u^a - u_c^a)$$

and

$$\frac{\partial \overset{\circ}{\gamma}}{\partial t} = - U^a \overset{\circ}{\gamma}_{,a} = U^a v_a \delta(u^a - u_c^a),$$

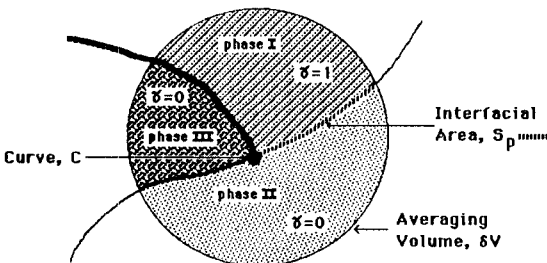


Figure 2a. Interfacial surface area, S_p , which separates phase I from phase II and has bounding curve C .

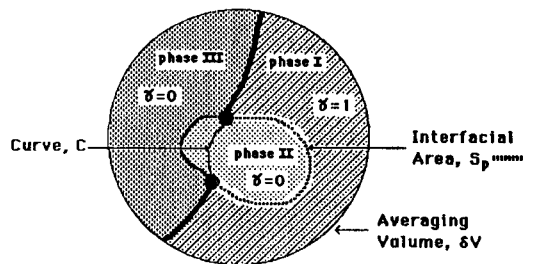


Figure 2b. Interfacial surface area, S_p , which separates phase I from phase II, terminates within δV along curve C , and intersects the boundary of δV .

where v_a is a surface unit vector tangent to the interface and normal to the edge of S_p at the intersection curve C (figure 2), U^a is the surface velocity of curve C , u_c^a is the surface coordinate of points on curve C and $\delta(u^a - u_c^a)$ is the Dirac function in terms of surface coordinates. Furthermore, this function has the properties that

$$\int_S f^a \hat{\gamma}^a dS = \int_{S_p} f^a dS \quad [8a]$$

and

$$\int_S f^a \hat{\gamma}_{,a}^a dS = - \int_C f^a v_a dC = - \int_C f^i v^i dC, \quad [8b]$$

where f^i and v^i are spatial representations of f^a and v_a , respectively (see further below).

BACKGROUND RELATIONSHIPS

In order to develop averaging theorems for interfacial properties, it is necessary to be able to transfer between surface and spatial coordinates. The manipulations needed may be found in Moeckel (1975), Aris (1962) or any other standard source of information on vectors and tensors. For convenience, a few of the most useful required relationships are summarized here.

If x^i is a rectangular cartesian coordinate of a point, then a moving surface $S(t)$ has the representation

$$S(t): x^i = x^i(u^a, t), \quad i = \overline{1, 3} \quad \text{and} \quad a = \overline{1, 2}, \quad [9]$$

where u^a are surface parameters and t is time. (Recall that throughout this paper, the subscripts/superscripts i, j and k will refer to the cartesian coordinates, while superscripts/subscripts a, b and c will denote surface parameters.) The mapping given in [9] is taken to be smooth so that the tangent vectors to the surface S are $x_{,a}^i$ and are defined at all points on the surface; the comma indicates covariant differentiation. At every point on the surface S , a unit normal vector $n^i = n^i(u^a, t)$ exists for which

$$n^i n^i = 1 \quad [10]$$

and

$$x_{,a}^i n^i = 0. \quad [11]$$

The metric tensor (first fundamental form) for the surface is given by

$$g_{ab} = x_{,a}^i x_{,b}^i \quad [12]$$

and has the inverse g^{ab} given by

$$g_{ac} g^{cb} = \delta_a^b, \quad [13]$$

where δ_a^b is the Kronecker delta. The parameterization is made such that

$$\frac{\partial x^i}{\partial t} = w^j n^j n^i \quad [14]$$

where w^j is the velocity of surface S and $w^j n^j$ is its normal component. Additionally, the second fundamental form for the surface b_{ab} is defined by

$$b_{ab} = x_{,ab}^i n^i \quad [15]$$

and has the following properties:

$$x_{,ab}^i = b_{ab} n^i, \quad [16]$$

$$b_a^c = g^{cb} b_{ba}, \quad [17]$$

$$b_a^a = 2 K_M \quad [18]$$

and

$$n^i_{,a} = -b^c_a x^i_{,c}, \quad [19]$$

where K_M is the mean curvature. An additional identity which will prove convenient in subsequent manipulations is (Aris 1962)

$$\delta^{ij} = n^i n^j + g^{ab} x^i_{,a} x^j_{,b}. \quad [20]$$

A general spatial vector, f^k , which has a component normal to a surface (as well as tangential components) may be expressed in terms of its surface components (the surface vector, f^a) and its normal component as

$$f^k = f^a x^k_{,a} + f^j n^j n^k. \quad [21]$$

A surface vector, F^a , has no components normal to the surface. Nevertheless, it may be expressed in terms of a spatial vector, F^k , (where $F^k n^k = 0$) as

$$F^k = F^a x^k_{,a}. \quad [22]$$

Multiplication of [21] by $x^k_{,b} g^{ab}$ yields

$$f^a = f^k x^k_{,c} g^{ca}. \quad [23]$$

Differentiation of f^a with respect to surface coordinates may be performed to obtain the equation

$$f^a_{,a} = f^k_{,i} x^i_{,a} x^k_{,c} g^{ca} + f^k x^k_{,ac} g^{ca} + f^k x^k_{,c} g^{ca}_{,a} \quad [24]$$

in which the last term is zero because $g^{ca}_{,a} = 0$. On the r.h.s. of [24], substitute [20] into the first term and [16] into the second term such that

$$f^a_{,a} = f^k_{,i} (\delta^{ik} - n^i n^k) + f^k n^k b_{ac} g^{ca}. \quad [25]$$

Then from [17] and [18], $b_{ac} g^{ca} = b^a_a = 2K_M$. Thus,

$$f^a_{,a} = f^k_{,k} - n^i n^k f^k_{,i} + 2K_M n^k f^k. \quad [26]$$

Note that if f^k is a unit normal vector n^k in [26], the following identity is obtained:

$$n^i_{,i} = -2K_M. \quad [27]$$

Therefore [26] may also be written as

$$f^a_{,a} = f^k_{,k} - n^k (f^k n^i)_{,i}. \quad [28]$$

These last two equalities are particularly useful in deriving averaged conservation equations for surfaces.

SPATIAL AVERAGING THEOREM FOR SURFACE VECTOR

The quantity to be averaged is the surface derivative of a surface vector denoted as $f^a_{,a}$. The averaging is to be done over a surface S which is within an averaging volume, δV , as pictured in figure 1. From [28] the integral of $f^a_{,a}$ can be expressed as

$$\frac{1}{\delta V} \int_S f^a_{,a} dS = \frac{1}{\delta V} \int_S f^k_{,k} dS - \frac{1}{\delta V} \int_S n^k (f^k n^i)_{,i} dS. \quad [29]$$

The goal here is to relate the integral of the surface derivative to the spatial derivative of a surface integral for an averaging volume which is of constant size and orientation but which is located at every point in space. Although δV does not vary with space, the amount of interface within δV and the values of the integrands will depend on the location of the averaging volume. Therefore interchanging the order of integration and differentiation is non-trivial. It will be understood here

ing the integrals on the r.h.s. to integrals over the averaging volume making use of

$$[30] \quad \int^S f_a^v dS = \int^S f_k^x n_k dS - \int^S n_k (f_k n_i)_i dS.$$

s substitution has the effect of changing the limits of integration from being temporally varying to limits which are constant with the variation being accounted for by γ . The used to reorder the differentiation in [31] to obtain

$$[31] \quad \int^S f_a^v dS = - \int^{\delta V} f_k^x (n_i \gamma_j)_i dV + \int^{\delta V} n_k (f_k n_i)_i (n_i \gamma_j)_j dV.$$

Under the last integral in [32]. The quantity $(n_i \gamma_j)_i$ can be rearranged to

$$[33] \quad (n_i \gamma_j)_i = n_i^x \gamma_j^i + n_i \gamma_j^x.$$

th, one can replace γ_j^i and obtain

$$[34] \quad (n_i \gamma_j)_i = - n_i^x \gamma_j^i \delta(x^i - x^j) + n_i \gamma_j^x.$$

on the r.h.s. of this equation is zero because $n_i^x \gamma_j^i = 0$. Therefore, the last expression es the equality

$$[35] \quad \int^{\delta V} (f_k - n_k f_i n_i) (n_i \gamma_j)_i dV = \int^{\delta V} (f_k - n_k f_i n_i) n_i \gamma_j^x dV.$$

[4] to obtain

$$[36] \quad \gamma_j^x = (\gamma^x)_j = - n_k \delta_j^k - n_k \delta_j^k.$$

ing back into the r.h.s. of [35] leaves

$$[37] \quad - n_k f_i n_i (n_i \gamma_j)_i dV = - \int^{\delta V} (f_k - n_k f_i n_i) n_i \delta_j^k + n_k \delta_j^k dV.$$

ms on the r.h.s. of [37] yields

$$[38] \quad (f_k - n_k f_i n_i) n_i \delta_j^k + n_k \delta_j^k = f_k n_i n_j \delta_j^k.$$

$$[39] \quad \int^{\delta V} (f_k - n_k f_i n_i) (n_i \gamma_j)_i dV = - \int^{\delta V} f_k n_i n_j \delta_j^k dV.$$

$n_i \delta_j^k = - \gamma_j^k$, the r.h.s. of [39] can be returned to [32], which becomes

$$[40] \quad \int^S f_a^v dS = - \int^{\delta V} (f_k n_i \gamma_j)_i dV + \int^{\delta V} n_k (f_k n_i)_i (n_i \gamma_j)_j dV + \int^{\delta V} f_k n_k \gamma_j^j dV.$$

imits of integration on the r.h.s. are independent of time and space, the order of and integration of the complete integrand in [40] can be interchanged to obtain

$$- \left(\int^{\delta V} f_k n_i \gamma_j^j dV \right)^k + \left(\int^{\delta V} n_k (f_k n_i)_i (n_i \gamma_j)_j dV \right)^k.$$

terms, when converted back to surface integrals using [6a], can be seen to cancel. The

first two integrals on the right may also be converted to surface integrals using [6a] to obtain the relation

$$\int_S f^a_{,a} dS = \left(\int_S f^k dS \right)_{,k} - \left(\int_S n^k f^k n^i dS \right)_{,i}. \quad [42]$$

Thus, interchanging the order of differentiation and integration in this averaging process for surfaces results in quantities which are completely in terms of spatial coordinates.

Equation [42] applies to surfaces which are closed or which intersect the boundary of the constant averaging volume. However, in multiphase flow modeling, surfaces will exist which intersect other surfaces and undergo abrupt changes in properties (e.g. S_p in figure 2). Thus, surfaces may themselves be considered as multiphase (two-dimensional) regions which undergo abrupt changes of properties on curves (i.e. across contact lines). To treat these discontinuities, it is necessary to obtain the equivalent form of [42] for specific portions of the interface. For this purpose the distribution function $\dot{\gamma}$ will be employed.

Let S_p be the portion of surface S where $\dot{\gamma} = 1$. Therefore,

$$\int_{S_p} f^a_{,a} dS = \int_S f^a_{,a} \dot{\gamma} dS. \quad [43]$$

Application of the chain rule provides

$$\int_{S_p} f^a_{,a} dS = \int_S (f^a \dot{\gamma})_{,a} dS - \int_S f^a \dot{\gamma}_{,a} dS. \quad [44]$$

Now application of [42] to the first integral on the r.h.s. and of [8b] to the last integral yields

$$\int_{S_p} f^a_{,a} dS = \left(\int_S f^k \dot{\gamma} dS \right)_{,k} - \left(\int_S n^k f^k n^i \dot{\gamma} dS \right)_{,i} + \int_C f^a v_a dC. \quad [45]$$

Elimination of $\dot{\gamma}$ from this equation using [8a] gives the final form of the theorem:

$$\int_{S_p} f^a_{,a} dS = \left(\int_{S_p} f^k dS \right)_{,k} - \left(\int_{S_p} n^k f^k n^i dS \right)_{,i} + \int_C f^i v^i dC. \quad [46]$$

TIME-AVERAGING THEOREM FOR SURFACE QUANTITIES

The balance equations for surface quantities typically contain a partial derivative with respect to time. This partial derivative is one where the surface parameters rather than the spatial coordinates are held constant. The total derivatives of a surface quantity f may be given in two equivalent forms:

$$\dot{f} = \frac{\partial f}{\partial t} \Big|_{x^k} + w^i f_{,i} = \frac{\partial f}{\partial t} \Big|_{u^a} + w^a f_{,a}. \quad [47a]$$

Thus,

$$\frac{\partial f}{\partial t} \Big|_{u^a} = \frac{\partial f}{\partial t} \Big|_{x^k} + w^i f_{,i} - w^a f_{,a}, \quad [47b]$$

where w^i is the velocity of the interface and w^a includes only its tangential components; they are related by [23]. For simplicity of notation, the explicit conditions under which the partial time derivative is evaluated will be omitted when the chance for confusion is small. Thus, for a point surface equation or for $\partial/\partial t$ in the integrand of a surface integral, $|_{u^a}$ will be understood. However when $\partial/\partial t$ appears in the integrand of a volume integral or as operating on an integral, $|_{x^k}$ is understood.

With w^a transformed to a spatial vector by [23] and because $f_{,a} = f_{,i} x^i_{,a}$, the last term in [47b] becomes

$$w^a f_{,a} = w^k f_{,i} g^{ia} x^k_{,c} x^i_{,a}. \quad [48]$$

Substitution of [20] then yields

$$w^a f_{,a} = w^i f_{,i} - w^k f_{,i} n^i n^k. \quad [49]$$

This expression allows [47b] to be written as

$$\left. \frac{\partial f}{\partial t} \right|_{u^a} = \left. \frac{\partial f}{\partial t} \right|_{x^k} + w^k f_{,i} n^i n^k. \quad [50]$$

Integration of [50] will be performed over a surface S contained in a time- and space-independent averaging volume V . The surface S is itself time and space dependent and its location within V is given using the spatial distribution function γ :

$$\int_S \frac{\partial f}{\partial t} dS = \int_S \left. \frac{\partial f}{\partial t} \right|_{x^k} dS + \int_S w^k f_{,i} n^i n^k dS. \quad [51]$$

Application of [6c] to the first term on the r.h.s. of [51] yields

$$\int_S \left. \frac{\partial f}{\partial t} \right|_{x^k} dS = - \int_{\delta V} \frac{\partial f}{\partial t} (n^i \gamma_{,i}) dV, \quad [52]$$

Which can be expanded out to the form

$$\int_S \left. \frac{\partial f}{\partial t} \right|_{x^k} dS = - \int_{\delta V} \frac{\partial}{\partial t} (f n^i \gamma_{,i}) dV + \int_{\delta V} f \frac{\partial (n^i \gamma_{,i})}{\partial t} dV. \quad [53]$$

Because the integration volume is independent of time, the order of differentiation and integration may be reversed in the first term on the r.h.s. of [53]. After this operation, [6c] may be invoked to convert the first volume integral to a surface integral. Then, substitution back into [51] leads to

$$\int_S \frac{\partial f}{\partial t} dS = \frac{\partial}{\partial t} \int_S f dS + \int_{\delta V} f \frac{\partial (n^i \gamma_{,i})}{\partial t} dV + \int_S w^k f_{,i} n^i n^k dS. \quad [54]$$

The second integral on the r.h.s. must be worked on further to complete the derivation of the time-averaging theorem.

Expand the volume integral in [54] to obtain

$$\int_{\delta V} f \frac{\partial (n^i \gamma_{,i})}{\partial t} dV = \int_{\delta V} f n^i \left(\frac{\partial \gamma}{\partial t} \right)_{,i} dV + \int_{\delta V} f \frac{\partial n^i}{\partial t} \gamma_{,i} dV. \quad [55]$$

Replace $\partial \gamma / \partial t$ in the first term on the r.h.s. with $-w^k \gamma_{,k}$, as given in [5], and convert the last term to a surface integral using [6a]. These steps lead to

$$\int_{\delta V} f \frac{\partial (n^i \gamma_{,i})}{\partial t} dV = - \int_{\delta V} f n^i (w^k \gamma_{,k})_{,i} dV - \int_S f n^i \frac{\partial n^i}{\partial t} dS. \quad [56]$$

The last term in this equation is zero and the first term on the r.h.s. may be rearranged to obtain

$$\int_{\delta V} f \frac{\partial (n^i \gamma_{,i})}{\partial t} dV = - \int_{\delta V} (f n^i w^k \gamma_{,k})_{,i} dV + \int_{\delta V} (f n^i)_{,i} w^k \gamma_{,k} dV. \quad [57]$$

Now interchanging the order of differentiation and integration in the first term on the r.h.s. (allowable because δV is spatially invariant) and conversion of both the volume integrals on the r.h.s. to surface integrals leaves

$$\int_{\delta V} f \frac{\partial (n^i \gamma_{,i})}{\partial t} dV = \left(\int_S n^i f w^k n^k dS \right)_{,i} - \int_S (f n^i)_{,i} w^k n^k dS. \quad [58]$$

Finally, substitution of [58] into [54] and rearrangement of terms provide the averaging theorem for a surface S identifiable using the spatial distribution function γ ,

$$\int_S \frac{\partial f}{\partial t} dS = \frac{\partial}{\partial t} \int_S f dS + \left(\int_S n^i f w^k n^k dS \right)_{,i} - \int_S f n^i_{,i} w^k n^k dS, \quad [59]$$

or with $n^i_{,i}$ related to the mean curvature by [27],

$$\int_S \frac{\partial f}{\partial t} dS = \frac{\partial}{\partial t} \int_S f dS + \left(\int_S n^i f w^k n^k dS \right)_{,i} + \int_S 2f K_M w^k n^k dS. \quad [60]$$

Once again if attention is confined to specific portions of S , then [60] should be manipulated further. Recall that S_p is the portion of S of interest such that

$$\int_{S_p} \frac{\partial f}{\partial t} dS = \int_S \frac{\partial f}{\partial t} \dot{\gamma} dS. \quad [61]$$

Application of the chain rule and use of the fact that

$$\frac{\partial \dot{\gamma}}{\partial t} + U^a \dot{\gamma}_{,a} = 0, \quad [62]$$

where U^a is the velocity of the boundary of S_p , leads to

$$\int_{S_p} \frac{\partial f}{\partial t} \dot{\gamma} dS = \int_S \frac{\partial}{\partial t} (f \dot{\gamma}) dS - \int_S f \frac{\partial \dot{\gamma}}{\partial t} dS = \int_S \frac{\partial}{\partial t} (f \dot{\gamma}) dS + \int_S f U^a \dot{\gamma}_{,a} dS \quad [63]$$

so that [61] may be written as

$$\int_{S_p} \frac{\partial f}{\partial t} dS = \int_S \frac{\partial}{\partial t} (f \dot{\gamma}) dS + \int_S f U^a \dot{\gamma}_{,a} dS. \quad [64]$$

Then applications of [60] and [42] to the r.h.s. yield

$$\int_{S_p} \frac{\partial f}{\partial t} dS = \frac{\partial}{\partial t} \int_S f \dot{\gamma} dS + \left(\int_S n^i f w^k n^k \dot{\gamma} dS \right)_{,i} + \int_S 2f K_M w^k n^k \dot{\gamma} dS - \int_C f U^a v_a dC \quad [65]$$

or

$$\int_{S_p} \frac{\partial f}{\partial t} dS = \frac{\partial}{\partial t} \int_{S_p} f dS + \left(\int_{S_p} n^i f w^k n^k dS \right)_{,i} + \int_{S_p} 2f K_M w^k n^k dS - \int_C f U^i v^i dC. \quad [66]$$

Recall that by the notation convention adopted, $\partial/\partial t$ on the l.h.s. of [66] is evaluated with u^a held constant (i.e. $\partial/\partial t|_{u^a}$) while $\partial/\partial t$ on the r.h.s. is evaluated with spatial coordinates held constant (i.e. $\partial/\partial t|_{x^i}$). The theorem presented as [66] allows the time derivative of a surface property to be converted to derivatives at the macroscale.

TRANSPORT THEOREM

The time- and space-averaging theorems for surface quantities, [66] and [46] respectively, are of interest by themselves. However when averaging the surface conservation equation [3], both averaging theorems are needed. The combination of the first three terms, T , in [3] is

$$T = \frac{\partial \Gamma \psi^s}{\partial t} \Big|_{u^a} + (\Gamma \psi^s w^a)_{,a} - 2w^i n^i K_M \Gamma \psi^s. \quad [67]$$

In this equation, w^a is the velocity of the flow in the surface tangent to the surface. If this group of terms is integrated over a surface S_p and averaging theorems [46] and [66] are applied,

$$\begin{aligned} \int_{S_p} \left[\frac{\partial \Gamma \psi^s}{\partial t} + (\Gamma \psi^s w^a)_{,a} - 2w^i n^i K_M \Gamma \psi^s \right] dS \\ = \frac{\partial}{\partial t} \int_{S_p} \Gamma \psi^s dS + \left(\int_{S_p} \Gamma \psi^s w^i dS \right)_{,i} + \int_C \Gamma \psi^s (w^i - U^i) v^i dC. \end{aligned} \quad [68]$$

This is the transport theorem for surface properties within a constant averaging volume when observed at the macroscale.

CONSIDERATIONS FOR SURFACE AVERAGING

The development of the averaging theorems has made use of both a phase distribution function γ and a surface distribution function $\dot{\gamma}$. These functions can be used to locate all interfacial surfaces and parts of surfaces within an averaging volume. In a three-phase system composed of α -, β - and δ -phases, the interfacial surface S is composed of three interfacial types— $S_{\alpha\beta}$, $S_{\alpha\delta}$ and $S_{\beta\delta}$, where

the subscripts denote the phases on each side of the interface. In a four-phase system, six different interface types exist. Using the transport theorem [68], macroscale balance equations can be developed for each of these surface types. Alternatively, one can sum over all the surface types and obtain a balance equation for all the surfaces within an averaging volume. In the following section, the averaging is performed over only one surface type in the averaging volume to demonstrate the application of the theorem presented.

BALANCE EQUATIONS

To obtain the appropriate macroscopic balance law for the averaged effect of thermodynamic processes which take place at interfaces, [3] needs to be averaged over interfaces of interest within an averaging volume. Integration of [3] over the union of interfacial areas between two phases of interest within the averaging volume for a multiphase system, application of transport theorem [68] and application of spatial averaging theorem [46] to the flux term yields

$$\begin{aligned} \frac{\partial}{\partial t} \int_{S_p} \Gamma \psi^s \, dS + \left(\int_{S_p} \Gamma \psi^s w^k \, dS \right)_{,k} - \left(\int_{S_p} i^{sk} \, dS \right)_{,k} + \left(\int_{S_p} n^k i^{sk} n^i \, dS \right)_{,i} - \int_{S_p} \Gamma F^s \, dS - \int_{S_p} \Gamma G^s \, dS \\ = \sum_{\alpha=1}^2 \left\{ \int_{S_p} [\rho^\alpha \psi^\alpha (v^{\alpha k} - w^k) - i^{\alpha k}] n^{\alpha k} \, dS \right\} + \int_C [\Gamma \psi^s (U^k - w^k) + i^{sk}] v^k \, dC. \end{aligned} \quad [69]$$

Because the surface flux i^{sa} is tangent to the surface, $i^{sk} = i^{sa} x_a^k$ from [22]. Thus, the fourth term in [69] drops out. This equation may now be written conveniently as a point equation, in terms of surface-averaged properties after dividing the equation by the averaging volume, as

$$\begin{aligned} \frac{\partial}{\partial t} (\langle \Gamma \rangle^s \bar{\psi}^s a_{sp}) + (\langle \Gamma \rangle^s \bar{w}^k \bar{\psi}^s a_{sp})_{,k} - (I^{sk} a_{sp})_{,k} - \langle \Gamma \rangle^s \bar{F}^s a_{sp} - \langle \Gamma \rangle^s \bar{G}^s a_{sp} \\ = - \sum_{\alpha=1}^2 \left\{ \frac{1}{\delta V} \int_{S_p} [\rho^\alpha \psi^\alpha (w^k - v^{\alpha k}) - i^{\alpha k}] n^{\alpha k} \, dS \right\} + \frac{1}{\delta V} \int_C [\Gamma \psi^s (U^k - w^k) + i^{sk}] v^k \, dC, \end{aligned} \quad [70]$$

where

$$\delta V = \int_{\delta V} dV \quad [71]$$

is the averaging volume. The surface average mass density is

$$\langle \Gamma \rangle^s = \frac{\int_{S_p} \Gamma \, dS}{\int_{S_p} dS}. \quad [72]$$

The surface mass average of ψ^s , w^k , F and G is defined by

$$\bar{f}^s = \frac{\int_{S_p} \Gamma f \, dS}{\int_{S_p} \Gamma \, dS}. \quad [73]$$

The surface average flux vector is

$$I^{sk} = \frac{\int_{S_p} [i^{sk} - \Gamma \bar{\psi}^s \bar{w}^{sk}] \, dS}{\int_{S_p} dS}, \quad [74]$$

Table 1. Quantities for specific forms of the general microscopic balance equation [69] and the macroscopic balance equation [70]

	ψ^s	i^{sk}	F^s	G^s	ψ^α	$i^{\alpha k}$
Mass	1	0	0	0	1	0
Chemical species	ω^s	j^{sk}	0	r	ω^α	$j^{\alpha k}$
Momentum	w^j	t^{sjk}	g^j	0	v^{sj}	t^{sjk}
Energy	$E^s + \frac{1}{2}w^2$	$t^{sjk}w^j + q^{sk}$	$g^jw^j + h^s$	0	$E^\alpha + \frac{1}{2}v^{\alpha 2}$	$t^{sjk}v^{sj} + q^{\alpha k}$
Entropy	η^s	φ^{sk}	b^s	A^s	η^α	$\varphi^{\alpha k}$

where

$$\tilde{f}^s = f - \bar{f}^s. \quad [75]$$

The specific interfacial area for surface S_p is

$$a_{sp} = \frac{1}{\delta V} \int_{S_p} dS. \quad [76]$$

Table 1 provides the terms which are substituted into [3] to give the conservation equations for interface transport at the microscopic scale. Based on this table and the general macroscopic conservation equation [69], equations of balance for various thermomechanical properties are obtained as follows:

mass balance,

$$\frac{\partial}{\partial t} (\langle \Gamma \rangle^s a_{sp}) + (\langle \Gamma \rangle^s \bar{w}^{sk} a_{sp})_{,k} = \sum_{\alpha=1}^2 \left[\frac{1}{\delta V} \int_{S_p} \rho^\alpha (v^{\alpha k} - w^k) n^{\alpha k} dS \right] + \frac{1}{\delta V} \int_C \Gamma (U^k - w^k) v^k dC; \quad [77]$$

chemical species balance,

$$\begin{aligned} & \frac{\partial}{\partial t} (\langle \Gamma \rangle^s \bar{\omega}^s a_{sp}) + (\langle \Gamma \rangle^s \bar{w}^{sk} \bar{\omega}^s a_{sp})_{,k} - (J^{sk} a_{sp})_{,k} - \langle \Gamma \rangle^s \bar{r}^s a_{sp} \\ &= \sum_{\alpha=1}^2 \left\{ \frac{1}{\delta V} \int_{S_p} [\rho^\alpha \omega^\alpha (v^{\alpha k} - w^k) - j^{\alpha k}] n^{\alpha k} dS \right\} + \frac{1}{\delta V} \int_C [\Gamma \omega^\alpha (U^k - w^k) + j^{\alpha k}] v^k dC; \quad [78] \end{aligned}$$

momentum balance,

$$\begin{aligned} & \frac{\partial}{\partial t} (\langle \Gamma \rangle^s \bar{w}^{sj} a_{sp}) + (\langle \Gamma \rangle^s \bar{w}^{sj} \bar{w}^{sk} a_{sp})_{,k} - (T^{sjk} a_{sp})_{,k} - \langle \Gamma \rangle^s \bar{g}^{sk} a_{sp} \\ &= \sum_{\alpha=1}^2 \left\{ \frac{1}{\delta V} \int_{S_p} [\rho^\alpha v^{sj} (v^{\alpha k} - w^k) - t^{sjk}] n^{\alpha k} dS \right\} + \frac{1}{\delta V} \int_C [\Gamma w^j (U^a - w^a) + t^{sja}] v_a dC; \quad [79] \end{aligned}$$

energy balance,

$$\begin{aligned} & \frac{\partial}{\partial t} [\langle \Gamma \rangle^s (\bar{\mathcal{E}}^s + \frac{1}{2} \bar{w}^{s2}) a_{sp}] + [\langle \Gamma \rangle^s (\bar{\mathcal{E}}^s + \frac{1}{2} \bar{w}^{s2}) \bar{w}^{sk} a_{sp}]_{,k} \\ & \quad - [(T^{sjk} \bar{w}^{sj} + \mathcal{Q}^{sk}) a_{sp}]_{,k} - \langle \Gamma \rangle^s (\bar{g}^{sk} \bar{w}^{sk} + h^s) a_{sp} \\ &= \sum_{\alpha=1}^2 \left\{ \frac{1}{\delta V} \int_{S_p} [\rho^\alpha (E^\alpha + \frac{1}{2} v^{\alpha 2}) (v^{\alpha k} - w^k) - t^{sjk} v^{sj} - q^{\alpha k}] n^{\alpha k} dS \right\} \\ & \quad + \frac{1}{\delta V} \int_C [\Gamma (E^s + \frac{1}{2} w^2) (U^k - w^k) + t^{sjk} w^j + q^{sk}] v^k dC, \quad [80] \end{aligned}$$

$$\bar{\mathcal{E}}^s = \bar{E}^s + \frac{1}{2} \bar{w}^{s2}, \quad [81a]$$

$$\mathcal{Q}^{sk} = Q^{sk} + \langle t^{sjk} \bar{w}^{sj} \rangle^s \quad [81b]$$

and

$$h^s = \bar{h}^s + \langle \bar{w}^{sk} \bar{g}^{sk} \rangle^s; \quad [81c]$$

and

entropy balance,

$$\begin{aligned} \frac{\partial}{\partial t} (\langle \Gamma \rangle^s \bar{\eta}^s a_{sp}) + (\langle \Gamma \rangle^s \bar{w}^{sk} \bar{\eta}^s a_{sp})_k - (\Phi^{sk} a_{sp})_k - \langle \Gamma \rangle^s \bar{b}^s a_{sp} - \langle \Gamma \rangle^s \bar{A}^s a_{sp} \\ = \sum_{\alpha=1}^2 \left\{ \frac{1}{\delta V} \int_{S_p} [\rho^\alpha \eta^\alpha (v^{\alpha k} - w^k) - \varphi^{\alpha k}] n^{\alpha k} dS \right\} + \frac{1}{\delta V} \int_C [\Gamma \eta^s (U^k - w^k) + \varphi^{sk}] v^k dC. \end{aligned} \quad [82]$$

The averaged equations above are conservation principles for interfacial properties which complement the averaged equations obtained for bulk phases (cf. Hassanizadeh & Gray 1979a,b) using the well-known volume-averaging theorems (Slattery 1967; Whitaker 1967; Gray & Lee 1977). These are similar to equations obtained by Marle (1982). However, balance laws for energy and entropy obtained here are more general. Heretofore, averaging theory has been applied without considering the properties of an interface. If one assumes that the contact line C of three or more interfaces does not attain thermodynamic properties, the following jump condition at points along C holds:

$$\sum_I^M [\Gamma \psi^s (U^k - w^k) + i^{sk}] v^k = 0, \quad [83]$$

where the summation sign indicates that the terms must be evaluated as the contact line C is approached from within the M interfaces and then summed up. Summation of [70] over all interface types in an averaging volume, acknowledging restriction [83], yields

$$\begin{aligned} \sum_{S_p} \left[\frac{\partial}{\partial t} (\langle \Gamma \rangle^s \bar{\psi}^s a_{sp}) + (\langle \Gamma \rangle^s \bar{w}^{sk} \bar{\psi}^s a_{sp})_k - (i^{sk} a_{sp})_k - \langle \Gamma \rangle^s \bar{F}^s a_{sp} - \langle \Gamma \rangle^s \bar{G}^s a_{sp} \right] \\ = \sum_{S_p} \sum_{\alpha=1}^2 \frac{1}{\delta V} \int_{S_p} [\rho^\alpha \psi^\alpha (v^{\alpha k} - w^k) - i^{\alpha k}] n^{\alpha k} dS. \end{aligned} \quad [84]$$

This equation is a general relation which accounts for a jump in bulk properties across interfaces. The l.h.s. [84] accounts for the contribution of interface phenomena to macroscopic processes.

The new macroscopic balance equations cannot be solved independently of the bulk phase equations. However, they complete the description of global conservation principles for a system consisting of bulk phases and interfaces. These equations will also be important in deriving constitutive relations for averaged phase quantities such as stress and heat flux. For example, capillarity is due to interfacial stress and this effect cannot be properly captured in a constitutive theory which does not account for surface properties. Additionally, although the utility and application of surface balance equations at the microscale are greatly hindered by a lack of knowledge of surface properties, the macroscopic balance equations require only a knowledge of how the interfaces affect bulk phases on the average. This information may be more readily obtainable at the macroscale (e.g. relative permeability curves for multiphase porous media flow account for average surface tension effects) and, in any event, is crucial for a complete understanding of the flow. The equations derived here provide a rigorous framework for development and interpretation of experiments and computational models of multiphase phenomena.

SECOND LAW OF THERMODYNAMICS

To complete the development of macroscopic laws for multiphase systems an appropriate statement of the second law is required. According to the second law, the net rate of production of entropy of the whole system must be non-negative. Denote the rate of production of entropy of each phase by $\epsilon^\alpha \langle \rho^\alpha \rangle^\alpha \bar{A}^\alpha$ (see Hassanizadeh & Gray 1979b), then the second law for an N -phase system may be stated as

$$\sum_{\alpha=1}^N \epsilon^\alpha \langle \rho^\alpha \rangle^\alpha \bar{A}^\alpha + \sum_{S_p} \langle \Gamma \rangle^s \bar{A}^s a_{sp} \geq 0. \quad [85]$$

This inequality, with the second summation included, plays an important role in restricting the general form of constitutive equations to be developed for multiphase systems. Without inclusion of the surface entropy equation [82] in this expression, erroneous results are obtained for multiphase constitutive theory.

CONCLUSION

The averaging theorems developed in this paper, [46], [66] and [68], are new contributions to the fundamental tools for obtaining conservation laws applicable to multiphase systems. The new theorems average surface derivatives of interfacial properties over the surface within an averaging volume to obtain derivatives in space of the averaged properties. Thus, an averaging procedure for surface equations is obtained which is analogous to the standard averaging procedures for bulk phase equations. The theorems are applied to a general form of a conservation equation for a surface and then equations of conservation of mass, chemical species, momentum, energy and entropy for interfaces are obtained. These equations together with macroscopic conservation equations for bulk phases provide a complete set of balance laws for multiphase systems. The averaged equations obtained contain source terms due to the adjacent phases. These sources are seen to be of exactly the same form as the interphase transport terms which appear in macroscopic balance equations for bulk phases. If surface properties are neglected, the averaged equations reduce to restrictions on interphase transport terms typically obtained in earlier phase-averaging attempts. This observation confirms the utility of the averaging procedure to obtain averaged surface equations which will result in a more complete description of multiphase systems and also enable a more sophisticated constitutive theory to be implemented. Application of the averaged equations to specific systems is a topic for further study.

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