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BALANCE EQUATIONS AND STRUCTURAL MODELS FOR PHASE INTERFACES

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Abstract—The general balance equations are developed for an interface represented by a dividing surface and for a moving common line represented as an intersection of dividing surfaces. The surface excess variables associated with a dividing surface are expressed both in terms of those variables describing the three-dimensional interfacial region of finite thickness and in terms of those variables describing bulk phases that extend up to the dividing surface.

A structural model for the interface is suggested in which a suspension of solid bodies representing surfactant molecules is distributed about a singular surface separating two adjacent bulk solvent phases. The suspension is required to have the same average behavior as the interfacial region. This is interpreted as meaning that the general jump balance for a continuum dividing surface represented by an interfacial suspension is a local area average. Specific results are derived for two structural models, each in the same simple shear field. One consists of a dilute suspension of neutrally buoyant spheres floating with their centers restricted to the dividing surface. The other is a dilute suspension of chains of neutrally buoyant spheres with the sphere at one end of the chain floating in the dividing surface.

INTRODUCTION

Let us define a phase interface to be that region separating two phases in which the properties or behavior of the material differ from those of the adjoining phases.

There is considerable evidence that density and the concentrations of the various species present are appreciably different in the neighborhood of an interface (Defay *et al.* 1966). As the critical point is approached, density is observed to be a continuous function of position in the direction normal to the interface (Hein 1914; Maass 1938; McIntosh *et al.* 1939; Palmer 1952). This suggests that the phase interface is a three-dimensional region, the thickness of which may be several molecular diameters or more.

Molecular models for the interfacial region are a separate subject which we will not discuss here. It is sufficient to mention that the three-dimensional character of the phase interface is explicitly recognized in statistical mechanical calculations (Ono & Kondo 1960).

There are two continuum models for the phase interface.

The most obvious model is a three-dimensional region of finite thickness. Korteweg (1901) suggested that the stress-deformation behavior in such a region could be described by saying that the stress tensor is a function of the rate of deformation tensor, the gradient of density and the second gradient of density. He used a linear form of this relationship to analyze the stresses in a spherical shell that represented the interface of a static spherical bubble. In the limit as the thickness of the shell was allowed to approach zero, the result took the same form as that obtained by assuming a uniform tension acts in a two-dimensional spherical surface separating the two phases. While Korteweg's approach is appealing, there are inherent difficulties. We have no way of studying experimentally the stress and velocity distributions in the thin interfacial region. His model for interfacial stress-deformation behavior can be tested only by observing the effect of the interfacial region upon the adjoining phases. No dynamic problems have been solved using Korteweg's model for interfacial behavior.

As a model for a phase interface in a body at rest or at equilibrium, Gibbs (1928) proposed a two-dimensional dividing surface that sensibly coincides with the phase interface and separates two homogeneous phases. By a homogeneous phase, he meant one in which all variables, such as mass density and stress, assume uniform values. He suggested that the cumulative effects of the interface upon the adjoining phases be taken into account by the assignment to the dividing surface of an excess mass or energy not accounted for by the adjoining homogeneous phases.

Gibbs' approach may be extended to include dynamic phenomena, if we define a homogeneous phase to be one throughout which each constitutive equation or description of material behavior applies uniformly. As in the static case, the cumulative effects of the interface upon the adjoining phases can be described by associating densities and fluxes with the dividing surface.

If we are to describe how this dividing surface moves as a function of time, we must be able to locate it at some reference time. It is not sufficiently precise to say that the dividing surface is sensibly coincident with the phase interface (Defay *et al.* 1966). Sometimes it is convenient to define the location of the reference dividing surface to be such that either the surface mass density or the surface molar density is everywhere zero. More often the reference dividing surface is chosen to be that for which the mass or molar density of one of the species is zero (Defay *et al.* 1966).

If both a three-dimensional region of finite thickness and a dividing surface can be used as models for a phase interface, then we should be able to express the variables appearing in one model in terms of those appropriate to the other. Buff (1956) and Buff & Saltsburg (1957) assumed a simple expression for the actual stress tensor in the interfacial region at equilibrium and studied surface tension. Slattery (1967*a*) derived a generalized form for balance equations at a dividing surface. The source terms in these balance equations were in turn expressed in terms of two types of variables on either side of the dividing surface: those corresponding to the three-dimensional interfacial region of finite thickness and those describing a bulk phase that extends up to the dividing surface.

Einstein (1956) suggested that a dilute suspension of neutrally buoyant solid spheres has the same average stress-deformation behavior as a dilute solution of a solute, whose molecular weight is large in comparison with that of the solvent. More specifically, the equations of motion for the continuum represented by the suspension are obtained by taking the local volume average of the equations of motion for the individual phases in the suspension (Batchelor 1970; Russel 1976; Jeffrey & Acrivos 1976). This suggests how one might proceed in developing a hydrodynamic or structural model for the interface.

We begin with the general balance equations for an interface represented by a dividing surface and for a moving common line represented as an intersection of dividing surfaces. The jump mass and momentum balances at a dividing surface as well as the mass and momentum balances at a moving common line are developed as specific examples.

The balance equations for an interface visualized as a region of finite thickness must be consistent with those appropriate to a dividing surface. This leads to interpretations for the surface excess variables in terms of those describing the three-dimensional interfacial region of finite thickness and those describing bulk phases that extend up to the dividing surface.

A structural model for the interface is suggested in which a suspension of solid bodies representing surfactant molecules are distributed about a singular surface separating two adjacent bulk solvent phases. This suspension is visualized as having the same average behavior as an interfacial region containing a dilute solution of surfactant whole molecular weight is large in comparison with that of either solvent. The jump mass and momentum balances at the singular surface are developed for this structural model.

The suspension is required to have the same average behavior as the interfacial region. This is interpreted as meaning that the general jump balance for a continuum dividing surface represented by an interfacial suspension is a local area average. The local area averages of the jump mass and momentum balances are developed in detail.

Specific results are derived for two structural models, each in the same simple shear field. One consists of a dilute suspension of neutrally buoyant spheres floating with their centers restricted to the dividing surface. The other is a dilute suspension of chains of neutrally buoyant spheres with the sphere at one end of the chain floating in the dividing surface.

GENERAL BALANCE EQUATIONS WHEN INTERFACE IS REPRESENTED BY A DIVIDING SURFACE

With the assumption that the effect of the interface may be attributed to a dividing surface, the general balance or general conservation law for some quantity associated with a multiphase material body takes the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_R \psi\,\mathrm{d}V + \int_\Sigma \psi\,\mathrm{d}A\right) = -\int_S \boldsymbol{\varphi}\cdot\mathbf{n}\,\mathrm{d}A - \int_C \boldsymbol{\varphi}^{(\sigma)}\cdot\boldsymbol{\mu}\,\mathrm{d}s + \int_R \rho\zeta\,\mathrm{d}V + \int_\Sigma \rho^{(\sigma)}\zeta^{(\sigma)}\,\mathrm{d}A. \qquad [1]$$

Here R denotes the region occupied by the body, S the closed surface bounding the body, Σ the dividing surfaces enclosed by S, C the lines formed by the intersection of Σ with S, t time, ψ the density of the quantity per unit volume within the bulk phases, $\psi^{(\sigma)}$ the density of the quantity per unit area on Σ, $\boldsymbol{\varphi}$ the flux of the quantity (per unit area) through S, $\mathbf{n}$ the unit vector normal and outwardly directed with respect to the closed surface S, $\boldsymbol{\varphi}^{(\sigma)}$ the flux of the quantity (per unit length of line) through C, $\boldsymbol{\mu}$ the unit vector normal to C that is both tangent and outwardly directed with respect to Σ, ρ the mass density within the bulk phases, $\rho^{(\sigma)}$ the mass density (per unit area) on Σ, ζ the rate of production of the quantity per unit mass at each point within the bulk phases, and $\zeta^{(\sigma)}$ the rate of production of the quantity per unit mass at each point on Σ, $\mathrm{d}V$ indicates that a volume integration is to be performed, and $\mathrm{d}A$ that an area integration is to be carried out.

The left side of [1] can be arranged in a more convenient form by means of the transport theorem for a body containing intersecting dividing surfaces (Appendix a)

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_R \psi\,\mathrm{d}V + \int_\Sigma \psi^{(\sigma)}\,\mathrm{d}A\right) = {} & \int_R \left(\frac{\mathrm{d}_{(m)}\psi}{\mathrm{d}t} + \psi\,\operatorname{div}\mathbf{v}\right)\mathrm{d}V \\ & + \int_\Sigma \left\{\frac{\mathrm{d}_{(s)}\psi^{(\sigma)}}{\mathrm{d}t} + \psi^{(\sigma)}\,\operatorname{div}_{(\sigma)}\mathbf{v}^{(\sigma)}[+ [\psi(\mathbf{v}-\mathbf{v}^{(\sigma)})\cdot\boldsymbol{\xi}]\right\}\mathrm{d}A \\ & \int_{C^{(cl)}} (\psi^{(\sigma)}[\mathbf{v}^{(\sigma)} - \mathbf{u}^{(cl)}]\cdot\boldsymbol{\mu})\,\mathrm{d}s \qquad [2]\end{aligned}$$

where

$$\frac{\mathrm{d}_{(m)}\psi}{\mathrm{d}t} \equiv \left(\frac{\partial\psi}{\partial t}\right)_{x^1,x^2,x^3} + \nabla\psi\cdot\mathbf{v} \qquad [3]$$

is the material derivative,

$$\frac{\mathrm{d}_{(s)}\psi^{(\sigma)}}{\mathrm{d}t} \equiv \left(\frac{\partial\psi^{(\sigma)}}{\partial t}\right)_{y^1,y^2} + \nabla_{(\sigma)}\psi^{(\sigma)}\cdot(\mathbf{v}^{(\sigma)} - \mathbf{u}) \qquad [4]$$

is the surface material derivative,

$$\mathbf{u} \equiv \left(\frac{\partial\mathbf{p}^{(\sigma)}}{\mathrm{d}t}\right)_{y^1,y^2} \qquad [5]$$

is the velocity of a fixed point on the dividing surface,

$$\mathbf{z} = \mathbf{p}^{(\sigma)}(y^1, y^2, t) \qquad [6]$$

is the parametric equation for the moving and deforming dividing surface, x^1, x^2, and x^3 are coordinates denoting position in space, y^1 and y^2 are the surface coordinates denoting position on the dividing surface, $\mathbf{v}$ the velocity vector, $\mathbf{v}^{(\sigma)}$ the surface velocity vector or the time rate of change of position of a material particle on the dividing surface, $C^{(cl)}$ the union of all the common lines or three-phase lines of contact formed by the intersection of dividing surfaces, div the divergence operator, $\mathrm{div}_{(\sigma)}$ the surface divergence operator (Hopke & Slattery 1975), and $\mathrm{d}s$ denotes that a line integration is to be performed. The boldface brackets are used on the dividing surface between phases i and j as a shorthand notation

$$[B\,\boldsymbol{\xi}] \equiv B^{(i)}\boldsymbol{\xi}^{(i)} + B^{(j)}\boldsymbol{\xi}^{(j)} \qquad [7]$$

with the understanding that $B^{(i)}$ is evaluated within phase i in the limit as the dividing surface is approached and $\boldsymbol{\xi}^{(i)}$ is the unit normal to the dividing surface pointing into phase i. Similarly, the boldface parentheses are used on the common line formed by phases i, j, and k as a shorthand notation

$$(B^{(\sigma)}\boldsymbol{\nu}) \equiv B^{(\sigma,ij)}\boldsymbol{\nu}^{(ij)} + B^{(\sigma,ik)}\boldsymbol{\nu}^{(ik)} + B^{(\sigma,jk)}\boldsymbol{\nu}^{(jk)} \qquad [8]$$

where $B^{(\sigma,ij)}$ is evaluated on the dividing surface between phases i and j in the limit as the common line is approached and $\boldsymbol{\nu}^{(ij)}$ is the unit normal to the common line which is tangent to and directed into this dividing surface. The scalar $\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\xi}$ is the speed of displacement of the dividing surface in the direction $\boldsymbol{\xi}$. By $\mathbf{u}^{(cl)}$ we mean the velocity of a fixed point on the common line; $\mathbf{u}^{(cl)}\cdot\boldsymbol{\nu}$ is the speed of displacement of the common line in the direction $\boldsymbol{\nu}$. By means of Green's transformation (Slattery 1972), we can say

$$\int_S \boldsymbol{\varphi}\cdot\mathbf{n}\,\mathrm{d}A = \int_R \mathrm{div}\,\boldsymbol{\varphi}\,\mathrm{d}V + \int_\Sigma [\boldsymbol{\varphi}\cdot\boldsymbol{\xi}]\,\mathrm{d}A. \qquad [9]$$

Green's transformation for a surface (McConnell 1957) permits us to write

$$\int_C \boldsymbol{\varphi}^{(\sigma)}\cdot\boldsymbol{\mu}\,\mathrm{d}s = \int_\Sigma \mathrm{div}_{(\sigma)}\boldsymbol{\varphi}^{(\sigma)}\,\mathrm{d}A + \int_{C^{(cl)}} (\boldsymbol{\varphi}^{(\sigma)}\cdot\boldsymbol{\nu})\,\mathrm{d}s. \qquad [10]$$

With [2], [9], and [10], we can rearrange [1] in the form

$$\int_R \left(\frac{\mathrm{d}_{(m)}\psi}{\mathrm{d}t} + \psi\,\mathrm{div}\,\mathbf{v} + \mathrm{div}\,\boldsymbol{\varphi} - \rho\zeta\right)\mathrm{d}V + \int_\Sigma \left\{\frac{\mathrm{d}_{(s)}\psi^{(\sigma)}}{\mathrm{d}t} + \psi^{(\sigma)}\,\mathrm{div}_{(\sigma)}\mathbf{v}^{(\sigma)} + \mathrm{div}_{(\sigma)}\boldsymbol{\varphi}^{(\sigma)} - \rho^{(\sigma)}\zeta^{(\sigma)}\right.$$
$$\left. + [\psi(\mathbf{v}-\mathbf{v}^{(\sigma)})\cdot\boldsymbol{\xi} + \boldsymbol{\varphi}\cdot\boldsymbol{\xi}]\right\}\mathrm{d}A + \int_{C^{(cl)}} (\psi^{(\sigma)}[\mathbf{v}^{(\sigma)} - \mathbf{u}^{(cl)}]\cdot\boldsymbol{\nu} + \boldsymbol{\varphi}^{(\sigma)}\cdot\boldsymbol{\nu})\,\mathrm{d}s = 0. \qquad [11]$$

Equation [11] applies to any body, no matter how large or small. It implies that at each point within a phase

$$\frac{\mathrm{d}_{(m)}\psi}{\mathrm{d}t} + \psi\,\mathrm{div}\,\mathbf{v} + \mathrm{div}\,\boldsymbol{\varphi} - \rho\zeta = 0 \qquad [12]$$

at each point on a dividing surface

$$\frac{\mathrm{d}_{(s)}\psi^{(\sigma)}}{\mathrm{d}t} + \psi^{(\sigma)}\mathrm{div}_{(\sigma)}\mathbf{v}^{(\sigma)} + \mathrm{div}_{(\sigma)}\boldsymbol{\varphi}^{(\sigma)} - \rho^{(\sigma)}\zeta^{(\sigma)} + [\psi(\mathbf{v}-\mathbf{v}^{(\sigma)})\cdot\boldsymbol{\xi} + \boldsymbol{\varphi}\cdot\boldsymbol{\xi}] = 0 \qquad [13]$$

and at each point on a common line

$$(\psi^{(\sigma)}[\mathbf{v}^{(\sigma)} - \mathbf{u}^{(cl)}]\cdot\boldsymbol{\nu} + \boldsymbol{\varphi}^{(\sigma)}\cdot\boldsymbol{\nu}) = 0. \qquad [14]$$

As a particular example of [1], consider conservation of mass for which

$$\begin{aligned} &\psi \equiv \rho, \qquad \psi^{(\sigma)} \equiv \rho^{(\sigma)}, \\ &\varphi = \varphi^{(\sigma)} \equiv 0, \quad \zeta = \zeta^{(\sigma)} \equiv 0. \end{aligned} \qquad [15]$$

From [12] to [14], we see that conservation of mass implies at each point within a phase the *equation of continuity*

$$\frac{d_{(m)}\rho}{dt} + \rho \operatorname{div} \mathbf{v} = 0 \qquad [16]$$

at each point on a dividing surface the *jump mass balance*

$$\frac{d_{(s)}\rho^{(\sigma)}}{dt} + \rho^{(\sigma)}\operatorname{div}_{(\sigma)}\mathbf{v}^{(\sigma)} + [\rho(\mathbf{v} - \mathbf{v}^{(\sigma)})\cdot\boldsymbol{\xi}] = 0 \qquad [17]$$

and at each point on a common line the *mass balance at a common line*

$$(\rho^{(\sigma)}[\mathbf{v}^{(\sigma)} - \mathbf{u}^{(cl)}]\cdot\boldsymbol{\nu}) = 0. \qquad [18]$$

As another example of [1], consider Euler's first law or Newton's second law for which

$$\begin{aligned} &\psi \equiv \rho\,\mathbf{v}, \qquad \psi^{(\sigma)} \equiv \rho^{(\sigma)}\mathbf{v}^{(\sigma)}, \\ &\varphi \equiv -\mathbf{T}, \quad \varphi^{(\sigma)} \equiv -\mathbf{T}^{(\sigma)}, \\ &\zeta \equiv \mathbf{b}, \quad \zeta^{(\sigma)} \equiv \mathbf{b}^{(\sigma)}, \end{aligned} \qquad [19]$$

where **T** is the stress tensor, $\mathbf{T}^{(\sigma)}$ the surface stress tensor (Hopke & Slattery 1975), **b** the external force per unit mass acting within a phase, and $\mathbf{b}^{(\sigma)}$ the external force per unit mass acting on Σ. From [12] to [14], Euler's first law implies at each point within a phase *Cauchy's first law*

$$\rho\frac{d_{(m)}\mathbf{v}}{dt} - \operatorname{div}\mathbf{T} - \rho\,\mathbf{b} = 0 \qquad [20]$$

at each point on a dividing surface the *jump momentum balance*

$$\rho^{(\sigma)}\frac{d_{(s)}\mathbf{v}^{(\sigma)}}{dt} - \operatorname{div}_{(\sigma)}\mathbf{T}^{(\sigma)} - \rho^{(\sigma)}\mathbf{b}^{(\sigma)} + [\rho(\mathbf{v} - \mathbf{v}^{(\sigma)})(\mathbf{v} - \mathbf{v}^{(\sigma)})\cdot\boldsymbol{\xi} - \mathbf{T}\cdot\boldsymbol{\xi}] = 0 \qquad [21]$$

and at each point on a common line the *momentum balance at a common line*

$$(\rho^{(\sigma)}\mathbf{v}^{(\sigma)}[\mathbf{v}^{(\sigma)} - \mathbf{u}^{(cl)}]\cdot\boldsymbol{\nu} - \mathbf{T}^{(\sigma)}\cdot\boldsymbol{\nu}) = 0. \qquad [22]$$

Common practice requires that, in satisfying [16] through [22], we assume the tangential components of velocity are continuous across the dividing surface,

$$\text{at } \Sigma\text{:} \quad \mathbf{P}\cdot\mathbf{v}^{(\sigma)} = \mathbf{P}\cdot\mathbf{v}. \qquad [23]$$

By **P** we mean the projection tensor that transforms every vector on Σ into its tangential component. The normal component of $\mathbf{v}^{(\sigma)}$ is the speed of displacement of Σ.

GENERAL BALANCE EQUATION WHEN INTERFACE IS REPRESENTED BY A THREE-DIMENSIONAL REGION

Let us now assume that the effect of the interface may be attributed to a three-dimensional region of finite thickness.

In figure 1, we see a material body that occupies a region R and consists of two phases. In addition to the dividing surface Σ, we also show two surfaces Σ^+ and Σ^-

(a) that are parallel (Willmore 1959) to Σ,
(b) that move with the speed of displacement of Σ, and
(c) that enclose all of the material in R whose behavior is not described by the constitutive equations appropriate to either of the neighboring phases during the time of observation.

We refer to the region enclosed by Σ^+ and Σ^- as $R^{(I)}$. Notice that $R^{(I)}$ always includes the interfacial region, but at any particular time may include a portion of the neighboring phases as well.

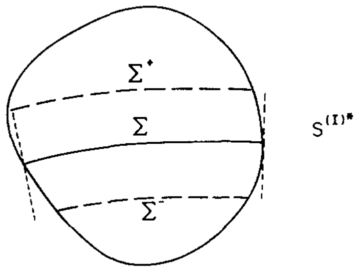

Figure 1. Region R occupied by a material body consisting of two phases. The closed surface S bounds R; $R^{(I)}$ and $S^{(I)}$ are those portions of R and S enclosed by Σ^- and Σ^+; $S^{(I)*}$ is the locus of all the straight lines stretching from Σ^- to Σ^+ that are normal to Σ and that pass through C, the closed curve bounding Σ; $R^{(I)*}$ is bounded by the surfaces Σ^-, Σ^+, and $S^{(I)*}$; λ is measured along the normal to Σ; λ^- and λ^+ are the values of λ at Σ^- and Σ^+ respectively.

Under these circumstances, the general balance or general conservation law for some quantity associated with a multiphase material body takes the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_R \psi^{(I)}\,\mathrm{d}V = -\int_S \boldsymbol{\varphi}^{(I)}\cdot\mathbf{n}\,\mathrm{d}A + \int_R \rho^{(I)}\zeta^{(I)}\,\mathrm{d}V \qquad [24]$$

or

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\{\int_R \psi\,\mathrm{d}V + \int_{R^{(I)}} (\psi^{(I)}-\psi)\,\mathrm{d}V\right\}$$

$$= -\int_S \boldsymbol{\varphi}\cdot\mathbf{n}\,\mathrm{d}A - \int_{S^{(I)}} (\boldsymbol{\varphi}^{(I)}-\boldsymbol{\varphi})\cdot\mathbf{n}\,\mathrm{d}A + \int_R \rho\zeta\,\mathrm{d}V + \int_{R^{(I)}} (\rho^{(I)}\zeta^{(I)}-\rho\zeta)\,\mathrm{d}V \qquad [25]$$

with the understanding that outside the interfacial region

$$\psi^{(I)} = \psi, \qquad \boldsymbol{\varphi}^{(I)} = \boldsymbol{\varphi},$$
$$\rho^{(I)} = \rho, \qquad \zeta^{(I)} = \zeta. \qquad [26]$$

By $S^{(I)}$ we refer to that portion of S bounding $R^{(I)}$.

The surface $S^{(I)*}$ in figure 1 is the locus of all the straight lines stretching from Σ^- to Σ^+ that are normal to Σ and that pass through C, the closed curve bounding Σ. Let us approximate

$$\int_{R^{(I)}} (\psi^{(I)} - \psi)\,\mathrm{d}V \doteq \int_{R^{(I)*}} (\psi^{(I)} - \psi)\,\mathrm{d}V, \quad [27]$$

$$\int_{S^{(I)}} (\varphi^{(I)} - \varphi)\cdot\mathbf{n}\,\mathrm{d}A \doteq \int_{S^{(I)*}} (\varphi^{(I)} - \varphi)\cdot\mathbf{n}\,\mathrm{d}A \quad [28]$$

and

$$\int_{R^{(I)}} (\rho^{(I)}\zeta^{(I)} - \rho\zeta)\,\mathrm{d}V \doteq \int_{R^{(I)*}} (\rho^{(I)}\zeta^{(I)} - \rho\zeta)\,\mathrm{d}V. \quad [29]$$

Here $R^{(I)*}$ is the region bounded by Σ^+, Σ^-, and $S^{(I)*}$. The right side of [28] can be expressed in terms of an integral over C:

$$\int_{S^{(I)*}} (\varphi^{(I)} - \varphi)\cdot\mathbf{n}\,\mathrm{d}A = \int_C \left\{\int_{\lambda^-}^{\lambda^+} (\varphi^{(I)} - \varphi)\,\mathrm{d}\lambda\right\}\cdot\boldsymbol{\mu}\,\mathrm{d}s. \quad [30]$$

By λ, we mean the distance measured along the normal to Σ; λ^+ and λ^- are the values of λ at Σ^+ and Σ^- respectively. For any quantity B (Buff 1956; Slattery 1967*a*)

$$\int_{R^{(I)*}} B\,\mathrm{d}V = \int_\Sigma \int_{\lambda^-}^{\lambda^+} B(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda\,\mathrm{d}A \quad [31]$$

in which κ_1 and κ_2 are the principal curvatures of Σ. Equation [31] permits us to write the R.H.S. of [27] and [29] as integrals over Σ. Using [27]–[31], we can rewrite [25] as

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_R \psi\,\mathrm{d}V + \int_\Sigma \int_{\lambda^-}^{\lambda^+} (\psi^{(I)} - \psi)(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda\,\mathrm{d}A\right) \\ &= -\int_S \varphi\cdot\mathbf{n}\,\mathrm{d}A - \int_C \left\{\int_{\lambda^-}^{\lambda^+} (\varphi^{(I)} - \varphi)\,\mathrm{d}\lambda\right\}\cdot\boldsymbol{\mu}\,\mathrm{d}s \\ &\quad + \int_R \rho\zeta\,\mathrm{d}V + \int_\Sigma \int_{\lambda^-}^{\lambda^+} (\rho^{(I)}\zeta^{(I)} - \rho\zeta)(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda\,\mathrm{d}A. \end{aligned} \quad [32]$$

If we now compare [32] with [1], we can identify

$$\psi^{(\sigma)} \equiv \int_{\lambda^-}^{\lambda^+} (\psi^{(I)} - \psi)(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda, \quad [33]$$

$$\varphi^{(\sigma)} \equiv \left\{\int_{\lambda^-}^{\lambda^+} (\varphi^{(I)} - \varphi)\,\mathrm{d}\lambda\right\}\cdot\mathbf{P} \quad [34]$$

and

$$\rho^{(\sigma)}\zeta^{(\sigma)} \equiv \int_{\lambda^-}^{\lambda^+} (\rho^{(I)}\zeta^{(I)} - \rho\zeta)(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda. \quad [35]$$

When [1] is restricted by [15], it describes conservation of mass and [33] requires

$$\rho^{(\sigma)} \equiv \int_{\lambda^-}^{\lambda^+} (\rho^{(I)} - \rho)(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda. \quad [36]$$

When [1] is restricted by [19], it describes Euler's first law and [33]–[35] require

$$\rho^{(\sigma)}\mathbf{v}^{(\sigma)} = \int_{\lambda^-}^{\lambda^+} (\rho^{(I)}\mathbf{v}^{(I)} - \rho\mathbf{v})(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda, \tag{37}$$

$$\begin{aligned}\mathbf{T}^{(\sigma)} &\equiv \left\{\int_{\lambda^-}^{\lambda^+} (\mathbf{T}^{(I)} - \mathbf{T})\,\mathrm{d}\lambda\right\}\cdot\mathbf{P} \\ &= \mathbf{P}\cdot\left\{\int_{\lambda^-}^{\lambda^+} (\mathbf{T}^{(I)} - \mathbf{T})\,\mathrm{d}\lambda\right\}\cdot\mathbf{P}\end{aligned} \tag{38}$$

and

$$\mathbf{b}^{(\sigma)} \equiv \frac{1}{\rho^{(\sigma)}}\int_{\lambda^-}^{\lambda^+} (\rho^{(I)}\mathbf{b}^{(I)} - \rho\mathbf{b})(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda. \tag{39}$$

Note that $\mathbf{v}^{(\sigma)}$ is not defined by [37]. In view of [23] and the requirement that $\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\xi}$ be the speed of displacement of Σ, $\mathbf{v}^{(\sigma)}$ is specified by the location and motion of Σ. In the second line of [38], we have recognized the symmetry of the surface stress tensor, a result of Euler's second law.

STRUCTURAL MODELS FOR INTERFACE

Our objective here is to study the effect of surfactant upon the behavior of the interface.

We will make the following assumptions concerning the system.

(i) There are only three components present: two mutually insoluble solvents and a surfactant that may be soluble in both.

(ii) The molecular weight of the surfactant is much larger than that of either of the solvents.

A structural or hydrodynamic model for the interface is sketched in figure 2. The interface is a three-dimensional region surrounding a singular surface that separates the two solvent phases. Solid bodies, representing the surfactant molecules, are dispersed in some manner within this region. Some may intercept the singular surface. The interfacial region, modelled in this way, has the same average behavior as an interfacial region containing a solution of surfactant whose molecular weight is large in comparison with that of either solvent.

The general balance [25] may be extended to include this structural model for the interface:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left\{\int_R \psi\,\mathrm{d}V + \int_{R^{(I)}} (\psi^{(I)} - \psi)\,\mathrm{d}V + \int_{\Sigma^{(l)}} \psi_0^{(\sigma)}\,\mathrm{d}A\right\} &= -\int_S \boldsymbol{\varphi}\cdot\mathbf{n}\,\mathrm{d}A - \int_{S^{(I)}} (\boldsymbol{\varphi}^{(I)} - \boldsymbol{\varphi})\cdot\mathbf{n}\,\mathrm{d}A \\ &\quad - \int_{C^{(l)}} \boldsymbol{\varphi}_0^{(\sigma)}\cdot\boldsymbol{\mu}\,\mathrm{d}s + \int_R \rho\zeta\,\mathrm{d}V + \int_{R^{(I)}} (\rho^{(I)}\zeta^{(I)} - \rho\zeta)\,\mathrm{d}V + \int_{\Sigma^{(l)}} \rho_0^{(\sigma)}\zeta_0^{(\sigma)}\,\mathrm{d}A.\end{aligned} \tag{40}$$

Here $\Sigma^{(l)}$ is the liquid–liquid singular surface, $C^{(l)}$ are the lines formed by the intersection of $\Sigma^{(l)}$ with S, $\psi_0^{(\sigma)}$ is the density of the quantity per unit area on $\Sigma^{(l)}$, $\boldsymbol{\varphi}_0^{(\sigma)}$ is the flux of the quantity (per unit length of line) through $C^{(l)}$, $\rho_0^{(\sigma)}$ the mass density (per unit area) on $\Sigma^{(l)}$, and $\zeta_0^{(\sigma)}$ the rate of production of the quantity per unit mass at each point on $\Sigma^{(l)}$. We can think of $\psi_0^{(\sigma)}$, $\boldsymbol{\varphi}_0^{(\sigma)}$, $\rho_0^{(\sigma)}$, and $\zeta_0^{(\sigma)}$ as being the values of $\psi^{(\sigma)}$, $\boldsymbol{\varphi}^{(\sigma)}$, $\rho^{(\sigma)}$, and $\zeta^{(\sigma)}$ appropriate to a clean interface. Let the dividing surface Σ be a simply connected extension of $\Sigma^{(l)}$. Using an argument essentially the same as that outlined in the previous section, we conclude that on $\Sigma^{(l)}$

$$\psi^{(\sigma,l)} \equiv \psi_0^{(\sigma)} + \int_{\lambda^-}^{\lambda^+} (\psi^{(I)} - \psi)(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda, \tag{41}$$

$$\boldsymbol{\varphi}^{(\sigma,l)} \equiv \boldsymbol{\varphi}_0^{(\sigma)} + \left\{\int_{\lambda^-}^{\lambda^+} (\boldsymbol{\varphi}^{(I)} - \boldsymbol{\varphi})\,\mathrm{d}\lambda\right\}\cdot\mathbf{P} \tag{42}$$

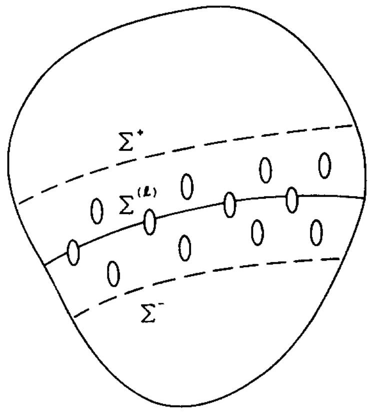

Figure 2. Region R occupied by a material body consisting of two phases. The interface is a three-dimensional region surrounding a singular surface $\Sigma^{(l)}$ that separates the two solvent phases. Rigid bodies, representing the surfactant molecules, are dispersed in some manner within this region. The lines formed by the intersection of $\Sigma^{(l)}$ with S are denoted by $C^{(l)}$; the dividing surface Σ is a simple connected extension of $\Sigma^{(l)}$.

and

$$\rho^{(\sigma,l)}\zeta^{(\sigma,l)} \equiv \rho_0^{(\sigma)}\zeta_0^{(\sigma)} + \int_{\lambda^-}^{\lambda^+} (\rho^{(I)}\zeta^{(I)} - \rho\zeta)(1-\kappa_1\lambda)(1-\kappa_2\lambda)\,\mathrm{d}\lambda. \qquad [43]$$

In contrast, on $\Sigma^{(s)} \equiv \Sigma - \Sigma^{(l)}$, that portion of Σ passing through the rigid bodies, $\psi^{(\sigma,s)}$, $\varphi^{(\sigma,s)}$, and $\rho^{(\sigma,s)}\zeta^{(\sigma,s)}$ are given by [33]–[35]. In using [33]–[35] in this context or [41]–[43], keep in mind that $\psi^{(I)}$, $\varphi^{(I)}$, and $\rho^{(I)}\zeta^{(I)}$ are now discontinuous functions taking different forms in the fluid and solid phases.

LOCAL AREA AVERAGES

In introducing the structural model, we proposed that a suspension of rigid bodies distributed about a singular surface has the same *average* behavior as an interfacial region. All quantities such as mass, momentum, and stress are continuously distributed over a continuum dividing surface. Equations [33]–[35] and [41]–[43] do not have this feature. It must be an average of [33] and [41], of [34] and [42], of [35] and [43] with which we are to be concerned.

The problem is similar to that encountered with a structural or hydrodynamic model for a bulk solution, in which rigid bodies, representing large solute molecules, are dispersed in a solvent. The equations of motion for the continuum represented by the suspension are obtained by taking the local volume average of the equations of motion for the individual phases in the suspension (Batchelor 1970; Russel 1976; Jeffrey & Acrivos 1976). This suggests that the general jump balance for the continuum dividing surface represented by an interfacial suspension is a local area average of the jump balance for the individual phases intercepted by Σ in figure 2.

Let us make an additional assumption concerning the system.

(iii) The characteristic length of a rigid body representing a surfactant molecule is everywhere very small compared with the radius of curvature of the dividing surface. At each point on the dividing surface, the surface may be considered flat over a region that is large compared with the region over which averages are to be defined.

Let us center upon each point on Σ in figure 2 a circle $\mathscr{C}$. The diameter of the circle should not be so small that $\mathscr{C}$ encloses only a portion of $\Sigma^{(l)}$ or only a portion of $\Sigma^{(s)}$ at any point on Σ. On the other hand, the diameter of $\mathscr{C}$ must be sufficiently small that the region over which Σ is locally flat is large compared with the region enclosed by $\mathscr{C}$.

Let us define $\mathscr{S}$ to be the region enclosed by $\mathscr{C}$ at each point on Σ; $\mathscr{A}$ is the area of $\mathscr{S}$. We will denote by $\mathscr{C}^{(i)}$ the closed curve (or curves) bounding all of $\Sigma^{(i)}$ contained within $\mathscr{C}$; $\mathscr{S}^{(i)}$ is the region bounded by $\mathscr{C}^{(i)}$; $\mathscr{A}^{(i)}$ is the area of $\mathscr{S}^{(i)}$.

Assume that $B^{(i)}$ is some scalar, vector, or tensor associated with $\Sigma^{(i)}$. We can speak of the *local area average* for $\Sigma^{(i)}$ of $B^{(i)}$

$$\bar{B}^{(i)} \equiv \frac{1}{\mathscr{A}} \int_{\mathscr{S}^{(i)}} B^{(i)} \, \mathrm{d}A \qquad [44]$$

as well as the *intrinsic area average* for $\Sigma^{(i)}$ of $B^{(i)}$

$$\langle B \rangle^{(i)} \equiv \frac{1}{\mathscr{A}^{(i)}} \int_{\mathscr{S}^{(i)}} B^{(i)} \, \mathrm{d}A. \qquad [45]$$

We will also require the *total local area average* of B,

$$\langle B \rangle \equiv \bar{B}^{(l)} + \bar{B}^{(s)}. \qquad [46]$$

In view of assumption (iii), we can develop a proof directly analogous to that used for the theorem for the local volume average of a gradient (Slattery 1967*b*; Slattery 1972) to determine that

$$\overline{\nabla_{(\sigma)} B^{(i)}} = \nabla_{(\sigma)} \bar{B}^{(i)} - \frac{1}{\mathscr{A}} \int_{\mathscr{C}^{(i)} - \mathscr{C}_e^{(i)}} B^{(i)} \boldsymbol{\nu}^{(i)} \, \mathrm{d}s \qquad [47]$$

where

$$\mathscr{C}_e^{(i)} \equiv \mathscr{C} \cap \mathscr{C}^{(i)} \qquad [48]$$

denotes that portion of $\mathscr{C}$ which coincides with $\mathscr{C}^{(i)}$. We can refer to [47] as the theorem for the *local area average of a surface gradient.* The theorem for the *local area average of a surface divergence*

$$\overline{\mathrm{div}_{(\sigma)} \mathbf{B}^{(i)}} = \mathrm{div}_{(\sigma)} \bar{\mathbf{B}}^{(i)} - \frac{1}{\mathscr{A}} \int_{\mathscr{C}^{(i)} - \mathscr{C}_e^{(i)}} \mathbf{B}^{(i)} \cdot \boldsymbol{\nu}^{(i)} \, \mathrm{d}s \qquad [49]$$

follows immediately.

The next two sections illustrate how these ideas can be used.

LOCAL AREA AVERAGE OF THE JUMP MASS BALANCE FROM A STRUCTURAL MODEL

In developing the local area average of the jump mass balance, we will assume:

(iv) The solid bodies are neutrally buoyant.

(v) The intersection of Σ with a solid body does not change relative to the body as a function of time.

(vi) The surface mass density $\rho_0^{(\sigma)}$ appropriate to a clean interface is a constant, independent of position and time on $\Sigma^{(l)}$.

(vii) There is no mass transfer between the interface and either of the adjoining bulk phases.

In view of assumption (iv), the surface mass density can be computed on $\Sigma^{(l)}$ from [41] as

$$\rho^{(\sigma,l)} = \rho_0^{(\sigma)} + \int_{\lambda^-}^{\lambda^+} (\rho^{(l)} - \rho) \, \mathrm{d}\lambda = \rho_0^{(\sigma)} \qquad [50]$$

and on $\Sigma^{(s)}$ from [33] as

$$\rho^{(\sigma,s)} = \int_{\lambda^-}^{\lambda^+} (\rho^{(l)} - \rho) \, \mathrm{d}\lambda = 0. \qquad [51]$$

As a result, the total local area average of the surface mass density is

$$\langle\rho^{(\sigma)}\rangle = \overline{\rho^{(\sigma)}}^{(l)} = (1-x)\rho_0{}^{(\sigma)} \qquad [52]$$

in which x is introduced as the fraction of Σ occupied by the solid.

Using [50] and recognizing assumption (vi) and (vii), we find that on $\Sigma^{(l)}$ the jump mass balance [17] reduces to

$$\mathrm{div}_{(\sigma)}\,\mathbf{v}^{(\sigma,l)} = 0. \qquad [53]$$

Employing [51] and assumption (vii), we see that the jump mass balance [17] is identically satisfied on $\Sigma^{(s)}$.

Because of assumption (v), area is preserved on $\Sigma^{(s)}$. Defining

$$\psi = \psi^{(\sigma,s)} \equiv 1, \quad \varphi = \varphi^{(\sigma,s)} \equiv 0, \quad \zeta = \zeta^{(\sigma,s)} \equiv 0 \qquad [54]$$

and remembering assumption (vii), we observe that [13] requires on $\Sigma^{(s)}$

$$\mathrm{div}_{(\sigma)}\mathbf{v}^{(\sigma,s)} = 0. \qquad [55]$$

The theorem for the local area average of a surface divergence [49] requires

$$\overline{\mathrm{div}_{(\sigma)}\mathbf{v}^{(\sigma)}}^{(i)} = \mathrm{div}_{(\sigma)}{}^{\overline{(\sigma)}(i)} - \frac{1}{\mathscr{A}}\int_{\mathscr{C}^{(ls)}} \mathbf{v}^{(\sigma,i)}\,.\,\boldsymbol{\nu}^{(i)}\,\mathrm{d}s = 0 \qquad [56]$$

where $\mathscr{C}^{(ls)}$ are the curves formed by the intersections of the rigid bodies and Σ within $\mathscr{S}$. We will require $\mathbf{v}^{(\sigma)}$ to be a continuous function of position

$$\text{at } \mathscr{C}^{(ls)}: \quad \mathbf{v}^{(\sigma,l)} = \mathbf{v}^{(\sigma,s)}. \qquad [57]$$

We conclude from [53], [55], and [56] that

$$\mathrm{div}_{(\sigma)}\langle\mathbf{v}^{(\sigma)}\rangle = 0 \qquad [58]$$

which we can refer to as the total local area average of the jump mass balance for the structural model.

LOCAL AREA AVERAGE OF THE JUMP MOMENTUM BALANCE FROM A STRUCTURAL MODEL

Let us make these further assumptions.

(viii) The surface stress tensor $\mathbf{T}_0^{(\sigma)}$ appropriate to a clean interface is proportional to a constant surface tension γ_0, independent of position and time on $\Sigma^{(l)}$:

$$\mathbf{T}_0^{(\sigma)} = \gamma_0\mathbf{P}. \qquad [59]$$

The surface viscosity is taken to be zero for a clean interface.

(ix) Inertial effects can be neglected in the interface.

(x) The same external force (gravity) acts upon both the interface and the bulk phases. It can be expressed in terms of potential energy per unit mass φ:

$$\mathbf{b}^{(\sigma)} = \mathbf{b} = -\nabla\varphi. \qquad [60]$$

We will refer to a region in which the velocity distribution is disturbed by the presence of a body as the *disturbance neighborhood* of the body. If there are no bodies present, we will speak of the *undisturbed velocity* distribution.

(xi) The suspension is sufficiently dilute that the disturbance neighborhoods associated with any two bodies do not overlap.

With assumption (viii), the surface stress tensor can be calculated on $\Sigma^{(I)}$ from [42] as

$$\mathbf{T}^{(\sigma,I)} = \gamma_0\mathbf{P} + \mathbf{P}\cdot\int_{\lambda^-}^{\lambda^+} (\mathbf{T}^{(I)} - \mathbf{T})\,\mathrm{d}\lambda\cdot\mathbf{P} \qquad [61]$$

and on $\Sigma^{(s)}$ from [34] as

$$\mathbf{T}^{(\sigma,s)} = \mathbf{P}\cdot\int_{\lambda^-}^{\lambda^+} (\mathbf{T}^{(I)} - \mathbf{T})\,\mathrm{d}\lambda\cdot\mathbf{P}. \qquad [62]$$

We have recognized here that Euler's second law implies that the surface stress tensor is symmetric. The total local area average of the surface stress tensor is consequently

$$\langle\mathbf{T}^{(\sigma)}\rangle = (1-x)\gamma_0\,\mathbf{P} + \mathbf{P}\cdot\frac{1}{\mathscr{A}}\int_{\mathscr{S}}\left\{\int_{\lambda^-}^{\lambda^+} (\mathbf{T}^{(I)} - \mathbf{T})\,\mathrm{d}\lambda\right\}\mathrm{d}A\cdot\mathbf{P} \qquad [63]$$

where

$$\int_{\mathscr{S}}\left\{\int_{\lambda^-}^{\lambda^+} (\mathbf{T}^{(I)} - \mathbf{T})\,\mathrm{d}\lambda\right\}\mathrm{d}A = \sum\nolimits_{\text{bodies}}\int_{R_{\text{disturb}}} (\mathbf{T}^{(I)} - \mathbf{T})\,\mathrm{d}V. \qquad [64]$$

Here R_{disturb} is that region surrounding and including a single body in which $\mathbf{T}^{(I)}$ is not equal to the undisturbed stress distribution $\mathbf{T}$.

Russel (1976) has observed that

$$\operatorname{div}[\mathbf{z}(\mathbf{T} - \rho\varphi\mathbf{I})] = \mathbf{T} - \rho\varphi\mathbf{I} + \mathbf{z}\operatorname{div}(\mathbf{T} - \rho\varphi\mathbf{I}) = \mathbf{T} - \rho\varphi\mathbf{I} \qquad [65]$$

in which we have noted that Cauchy's first law[20] takes the form

$$\operatorname{div}(\mathbf{T} - \rho\varphi\,\mathbf{I}) = 0 \qquad [66]$$

for assumptions (ix) and (x). Equation [65] permits us to say that in the region R_{body} occupied by the body

$$\begin{aligned}\int_{R_{\text{body}}} (\mathbf{T}^{(I,s)} - \mathbf{T})\,\mathrm{d}V &= \int_{R_{\text{body}}} \{\operatorname{div}[\mathbf{z}(\mathbf{T}^{(I,s)} - \rho^{(I,s)}\varphi\,\mathbf{I})] + \rho^{(I,s)}\varphi\,\mathbf{I} - \operatorname{div}[\mathbf{z}(\mathbf{T} - \rho\varphi\,\mathbf{I})] - \rho\varphi\,\mathbf{I}\}\,\mathrm{d}V \\ &= \int_{R_{\text{body}}} \{\operatorname{div}[\mathbf{z}(\mathbf{T}^{(I,s)} - \mathbf{T})] - \mathbf{z}(\rho - \rho^{(I,s)})\mathbf{b}\}\,\mathrm{d}V = \int_{R_{\text{body}}} \operatorname{div}[\mathbf{z}(\mathbf{T}^{(I,s)} - \mathbf{T})]\,\mathrm{d}V \\ &= \int_{S_{\text{body}}} \mathbf{z}(\mathbf{T}^{(I,s)} - \mathbf{T})\cdot\mathbf{n}\,\mathrm{d}A = \int_{S_{\text{body}}} \mathbf{z}(\mathbf{T}^{(I,s)} - \mathbf{T})\cdot\mathbf{n}\,\mathrm{d}A \qquad [67]\end{aligned}$$

in which we have introduced S_{body} as the closed bounding surface of the body. In the third line of this argument, we have reasoned

$$\int_{R_{\text{body}}} \{\operatorname{div}[\mathbf{z}(\rho - \rho^{(I,s)})\,\varphi\,\mathbf{I}] + (\rho^{(I,s)} - \rho)\varphi\,\mathbf{I}\}\,\mathrm{d}V = \int_{R_{\text{body}}} -\mathbf{z}(\rho - \rho^{(I,s)})\,\mathbf{b}\,\mathrm{d}V. \qquad [68]$$

This is zero for neutrally buoyant bodies either floating wholly within one phase or straddling Σ so long as the density distribution within the solid is such that locally $\rho^{(I,s)} = \rho$. For bodies of uniform density straddling Σ, we neglect its effect with respect to the first term on the right in the second line. In the fourth line, we have used Green's transformation (Slattery 1972) and the jump momentum balance[21] for the clean interface. In the fifth line, we have again employed the jump momentum balance[21], this time at the fluid–solid interface.

Equation [67] permits us to write

$$\int_{R_{\text{disturb}}} (\mathbf{T}^{(I)} - \mathbf{T})\,\mathrm{d}V = \int_{S_{\text{body}}} \mathbf{z}(\mathbf{T}^{(I,l)} - \mathbf{T})\cdot\mathbf{n}\,\mathrm{d}A + \int_{R_{\text{disturb}}-R_{\text{body}}} (\mathbf{T}^{(I,l)} - \mathbf{T})\,\mathrm{d}V \qquad [69]$$

where $R_{\text{disturb}} - R_{\text{body}}$ is that portion of the disturbance region occupied by the liquid phases. This together with [63] and [64] gives

$$\langle\mathbf{T}^{(\sigma)}\rangle = (1-x)\,\gamma_0\,\mathbf{P} + \frac{1}{\mathscr{A}}\sum\nolimits_{\text{bodies}} \mathbf{P}\cdot\left\{\int_{S_{\text{body}}} \mathbf{z}(\mathbf{T}^{(I,l)} - \mathbf{T})\cdot\mathbf{n}\,\mathrm{d}A + \int_{R_{\text{disturb}}-R_{\text{body}}} (\mathbf{T}^{(I,l)} - \mathbf{T})\,\mathrm{d}V\right\}\cdot\mathbf{P}. \qquad [70]$$

With assumptions (ix) and (x), the jump momentum balance [21] reduces to

$$\mathrm{div}_{(\sigma)}\,\mathbf{T}^{(\sigma)} + \rho^{(\sigma)}\mathbf{b} + [\mathbf{T}\cdot\boldsymbol{\xi}] = 0. \qquad [71]$$

The local area average of this for $\Sigma^{(i)}$ takes the form

$$\overline{\mathrm{div}_{(\sigma)}\mathbf{T}^{(\sigma)}}^{(i)} + \overline{\rho^{(\sigma)}\mathbf{b}}^{(i)} + \overline{[\mathbf{T}\cdot\boldsymbol{\xi}]}^{(i)} = \mathrm{div}_{(\sigma)}\overline{\mathbf{T}^{(\sigma)}}^{(i)} - \frac{1}{\mathscr{A}}\int_{\mathscr{C}^{(ls)}} \mathbf{T}^{(\sigma,i)}\cdot\boldsymbol{\nu}^{(i)}\,\mathrm{d}s + \overline{\rho^{(\sigma)}}^{(i)}\mathbf{b} + [\bar{\mathbf{T}}^{(i)}\cdot\boldsymbol{\xi}] \qquad [72]$$

in which [49] has been employed. We will require the surface stress vector to be a continuous function of position

$$\text{at } \mathscr{C}^{(ls)}\text{:}\quad \mathbf{T}^{(\sigma,l)}\cdot\boldsymbol{\nu}^{(l)} = \mathbf{T}^{(\sigma,s)}\cdot\boldsymbol{\nu}^{(s)} \qquad [73]$$

and we will assume $\mathscr{S}$ to be sufficiently small that

$$\text{at } \Sigma\text{:}\quad \langle\mathbf{T}\rangle \doteq \mathbf{T}. \qquad [74]$$

With [52], this gives

$$\mathrm{div}_{(\sigma)}\langle\mathbf{T}^{(\sigma)}\rangle + (1-x)\,\rho_0^{(\sigma)}\,\mathbf{b} + [\mathbf{T}\cdot\boldsymbol{\xi}] = 0. \qquad [75]$$

We will refer to this together with [70] as the total local area average of the jump momentum balance for the structural model.

A SIMPLE STRUCTURAL MODEL

In order to obtain more specific results that we might compare with experimental observations, we must describe in more detail the structure of the interface and the flow field to which it is subjected. Let us attribute to the interface a simple structure.

(xii) The bodies used to represent surfactant molecules in the interfacial region are rigid spheres whose centers lie upon Σ as shown in figure 3.

Let us assume that the flow field to which the interface is subjected is also simple.

(xiii) In the flow field undisturbed by the presence of spheres, shear occurs only in planes parallel to Σ.

(xiv) The undisturbed velocity distribution is a linear function of position (homogeneous) with the disturbance neighborhood of any sphere.

(xv) Both bulk liquid phases can be described as incompressible Newtonian fluids.

Up to this point we have not explicitly stated the frame of reference in terms of which we were working. The forms of all the prior equations are independent of the frame of reference.

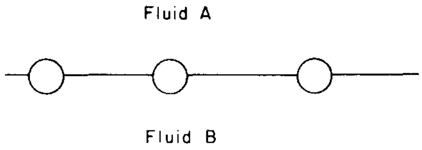

Figure 3. Structural model for the interfacial region in which the surfactant molecules are represented as rigid spheres whose centers lie on the dividing surface.

In considering the stress distribution within an individual sphere, it will be convenient to work in terms of a frame of reference that is centered upon the sphere and that translates with the sphere. For the moment, we will not specify how this frame of reference rotates with respect to the sphere.

All vectors and tensors in the remainder of this section refer to this translating and rotating frame of reference, unless explicitly noted otherwise.

Let the subscript (0) indicate a quantity evaluated at the instantaneous center of the sphere. At any instant of time, let us expand the undisturbed velocity distribution $\mathbf{v}$ on either side of Σ in a Taylor series with respect to the center of the sphere $\mathbf{z}_{(0)} = 0$ (Brenner 1958; Happel & Brenner 1973)

$$\mathbf{v} = \mathbf{v}_{(0)} + \mathbf{D}_{(0)} \cdot \mathbf{z} + \mathbf{W}_{(0)} \cdot \mathbf{z} + \dots. \tag{76}$$

Here we have introduced the rate of deformation tensor

$$\mathbf{D} \equiv \tfrac{1}{2}[\nabla \mathbf{v} + (\nabla \mathbf{v})^T] \tag{77}$$

and the vorticity tensor

$$\mathbf{W} \equiv \tfrac{1}{2}[\nabla \mathbf{v} - (\nabla \mathbf{v})^T]. \tag{78}$$

The higher order terms in [76] may be neglected in view of assumption (xiv).

Let us choose the frame of reference to rotate in such a way that

$$\mathbf{W}_{(0)} = 0. \tag{79}$$

In view of this, [76] requires that in the rotating and translating frome of reference on either side of Σ

$$\mathbf{v} = \mathbf{v}_{(0)} + \mathbf{D}_{(0)} \cdot \mathbf{z} + \dots. \tag{80}$$

With respect to a rectangular cartesian coordinate system (z_1, z_2, z_3) such that Σ lies in the plane $z_3 = 0$, assumption (xiii) requires that $\mathbf{D}_{(0)}$ have only one nonzero component:

$$D_{(0)12} \neq 0, D_{(0)11} = D_{(0)22} = D_{(0)33} = D_{(0)13} = D_{(0)23} = 0. \tag{81}$$

With this restriction, [80] satisfies the jump momentum balance [21] and the requirement that velocity be continuous at Σ. Equation [80] describes the undisturbed velocity distribution everywhere in R_{disturb}, on both sides of Σ.

Assumption (*xi*) and [80] suggest

$$\text{as} \quad r \to \infty: \quad \mathbf{v}^{(I,I)} \to \mathbf{v}_{(0)} + \mathbf{D}_{(0)} \cdot \mathbf{z}. \tag{82}$$

In the rotating and translating frame of reference, the sphere, whose radius is a, is seen to rotate as a solid body with an angular velocity $\boldsymbol{\Omega}$,

$$\text{at} \quad r = a: \quad \mathbf{v}^{(I,l)} = \boldsymbol{\Omega}\Lambda\mathbf{z}. \tag{83}$$

Here Λ indicates that a vector cross product is to be performed. The velocity distribution must be continuous

$$\text{at} \quad \Sigma: \quad \mathbf{v}^{(I,l)} \text{ is continuous} \tag{84}$$

and it must satisfy the jump momentum balance [21]

$$\text{at} \quad \Sigma: \quad [\mathbf{T}^{(I,l)}\cdot\boldsymbol{\xi}] = 0. \tag{85}$$

With inertial effects neglected, a momentum balance states that the sum of the forces imposed upon the sphere by the fluid and by the external force (gravity) must be zero in the rotating and translating frame of reference,

$$\int_{S_{\text{sphere}}} \mathbf{T}^{(I,l)}\cdot\mathbf{n}\,\mathrm{d}A + \int_{R_{\text{sphere}}} \rho^{(I,l)}\,\mathbf{b}\,\mathrm{d}V = 0. \tag{86}$$

A moment of momentum balance similarly requires that the sum of the torques imposed upon the sphere by the fluid and by the external force must also be zero in this frame of reference:

$$\int_{S_{\text{sphere}}} \mathbf{z}\,\Lambda\,(\mathbf{T}^{(I,l)}\cdot\mathbf{n})\,\mathrm{d}A + \int_{R_{\text{sphere}}} \mathbf{z}\,\Lambda\,\rho^{(I,s)}\,\mathbf{b}\,\mathrm{d}V = 0. \tag{87}$$

Lamb's (1945) solution of the equation of continuity [16] and Cauchy's first law [20] for the creeping flow of an incompressible Newtonian fluid was employed in the manner suggested by Happel & Brenner (1973). The velocity and pressure distributions in the disturbance neighborhood of a single sphere consistent with boundary conditions [82]–[84], [86] and [87] take the form

$$\mathbf{v}^{(I,l)} = (1 - r^{*-5})(\mathbf{D}_{(0)}\cdot\mathbf{z}) + \frac{5}{2}\frac{1}{a^2}(r^{*-7} - r^{*-5})(\mathbf{z}\cdot\mathbf{D}_{(0)}\cdot\mathbf{z})\,\mathbf{z}, \tag{88}$$

$$p^{(I,l)} - p_0 + \rho^{(I,l)}\varphi = -5\mu^{(I,l)}\,D_{(0)12}\,r^{*-3}\sin^2\theta'\sin 2\varphi' \tag{89}$$

where

$$r^* \equiv \frac{r}{a}. \tag{90}$$

Here θ' is the spherical coordinate measured from the z_3 axis; φ' is the spherical coordinate measured from the z_1 axis in the $z_1 - z_2$ plane. In arriving at this form of solution, we find that the center of the sphere moves with the local undisturbed velocity and that the angular velocity of the sphere relative to this frame of reference is zero.

The z_1 and z_2 (tangential) components of [85] are satisfied identically by [88]. The z_3 (normal) component of [85] requires

$$\text{at} \quad \Sigma: \; -p^{(I,l)} + \mu^{(I,l)} D_{33}{}^{(I,l)} \text{ is continuous.} \tag{91}$$

From [88],

$$\text{at}\,\Sigma: \quad D_{33}^{(I,l)} = \frac{5}{a^2}(r^{*-7} - r^{*-5}). \tag{92}$$

Let us define potential energy such that

$$\text{at } \Sigma: \quad \varphi = 0. \tag{93}$$

So long as

$$\frac{\mu^{(I,I)} D_{(0)12}}{p_0} \ll 1 \tag{94}$$

[89], [92], and [93] imply that

$$\text{at } \Sigma: \; -p^{(I,I)} + \mu^{(I,I)} D_{33}^{(I,I)} = -p_0 \tag{95}$$

which satisfies [91]. For $\mu^{(I,I)} = 10^{-2}$ dyne s/cm^2 (water) and $p_0 = 10^6$ dynes/cm^2 (approximately atmospheric pressure), [94] requires $D_{(0)12} \ll 10^8\ \mathrm{s}^{-1}$. This is well within the bounds of most experiments.

With the restriction [94], we can use [88] to compute

$$\int_{S_{\text{sphere}}} \mathbf{z}(\mathbf{T}^{(I,I)} - \mathbf{T}) \cdot \mathbf{n}\, \mathrm{d}A + \int_{R_{\text{disturb}} - R_{\text{sphere}}} (\mathbf{T}^{(I,I)} - \mathbf{T})\, \mathrm{d}V = 2\pi a^3 (\mu^{(A)} + \mu^{(B)})\, \mathbf{D}_{(0)}. \tag{96}$$

with the understanding that S_{sphere} is the surface of the sphere and R_{sphere} is the region occupied by the sphere. The viscosities of the two adjoining phases are $\mu^{(A)}$ and $\mu^{(B)}$. This together with [70] yields the desired expression for the total local area average of the surface stress tensor

$$\langle \mathbf{T}^{(\sigma)} \rangle = (1 - x)\gamma_0 \mathbf{P} + 2\,\epsilon \langle \mathbf{D}^{(\sigma)} \rangle \tag{97}$$

where we have identified as the surface shear viscosity (Scriven 1960; Slattery 1964)

$$\epsilon \equiv x\, a\, (\mu^{(A)} + \mu^{(B)}). \tag{98}$$

In reaching this result, we have said that locally the fraction of Σ occupied by the solid

$$x = \frac{1}{\mathcal{A}} \sum_{\text{bodies}} (\pi a^2) \tag{99}$$

and that

$$\langle \mathbf{D}^{(\sigma)} \rangle \doteq \mathbf{D}_{(0)}. \tag{100}$$

This last is prompted by [23].

For the simple structural model of the interface shown in figure 3 and restricted by assumptions (i) through (xv), the total local area average of the jump mass balance is given by [58]. The total local area average of the jump momentum balance is described by [75], [97] and [98]. The sphere radius a should be interpreted as the hydrodynamic radius of the surfactant molecule in the interface.

ANOTHER SIMPLE STRUCTURE MODEL

The discussion given in the last section can be extended to another simple structural model for the interface in which assumptions (xii) and (xiv) are replaced by

(xvi) The bodies used to represent surfactant molecules in the interfacial region are flexible chains of n rigid spheres. The chain begins with a sphere centered upon Σ and it extends into phase A as shown in figure 4. The distance between the spheres is arbitrary but sufficiently large that the disturbance neighborhoods of the individual spheres do not overlap.

(xvii) At some point in time, the chain assumes a configuration such that the centers of the spheres lie upon a straight line perpendicular to Σ.

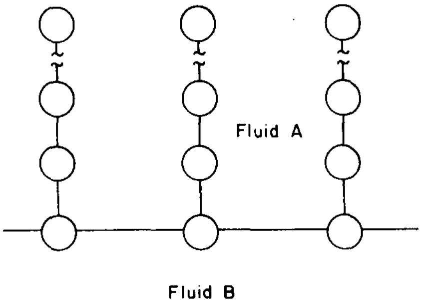

Figure 4. Structural model for the interfacial region in which the surfactant molecules are represented as flexible chains of n rigid spheres. The distance between the spheres is arbitrary but sufficiently large that the disturbance neighborhoods of the individual spheres do not overlap.

(xviii) The undisturbed velocity distribution is a linear function of position (homogeneous) within the union of the disturbance neighborhoods of the elements of the chain.

The velocity and pressure distributions within the disturbance neighborhood of the sphere centered upon Σ are again given by [88] and [89] with the restriction [94]. The velocity and pressure distributions within the disturbance neighborhoods of a sphere lying wholly within phase A are described by equations analogous to [88] and [89] written with respect to a frame of reference in which the sphere is stationary.

Given assumption (xvii), how does the configuration of the chain change with time? Let us view the chain in the rotating and translating frame of reference appropriate to the first sphere, which is centered upon Σ. From [80], [81] and assumption (xviii), we see that the undisturbed velocity at the center of each sphere is the same. Since the center of a sphere moves with the local undisturbed velocity, a chain whose spheres are aligned along a straight line perpendicular to Σ will maintain this configuration.

In the frame of reference chosen to rotate in such a manner that [79] is satisfied, assumption (xviii) requires the vorticity tensor to be zero everywhere within an individual disturbance neighborhood. This implies that the angular velocity of each sphere measured with respect to this frame of reference is zero. The spheres in the chain do not rotate relative to one another.

Reasoning as we did in the previous section, we conclude that the total local area average of the surface stress tensor is again given by [97], where we now identify as the surface shear viscosity

$$\epsilon = xa\,[(2n-1)\,\mu^{(A)} + \mu^{(B)}]. \qquad [101]$$

For the simple structural model of the interface shown in figure 4 and restricted by assumptions (i) through (xi), (xiii), and (xv) through (xviii), the total local area average of the jump momentum balance is given by [75], [97] and [101]. The sphere radius a in this model should be interpreted as the hydrodynamic radius of one of the chain units in the surfactant molecule.

DISCUSSION

For very dilute solutions of surfactant in the interface, the interfacial tension predicted by [97] decreases with increasing surfactant concentration in agreement with common observations.

Equations [98] and [101] predict surface viscosities that are less than the limit of sensitivity of any surface viscometer currently in use. This is also consistent with observations. Wasan *et al.* (1971) and Wei & Slattery (1976) studied a "clean" water–air interface with a deep channel surface viscometer and found that the surface shear viscosity was zero within the accuracy of their measurements. Gupta & Wasan (1974) and Poskanzer & Goodrich (1975) found that the surface shear viscosities were less than the sensitivities of their techniques for dilute solutions of non-interacting surfactants.

Cooper & Mann (1973) estimate on the basis of a kinetic theory calculation that, when the surface available per molecule is greater than 10^3 Å^2, the surface shear viscosity is of the order 10^{-12} (dyne s/cm). Equation [98] gives on the order of 10^{-10} (dyne s/cm) when $a = 10$ Å and the surface available per molecule is 10^3 Å^2. Given some uncertainty regarding the basis for comparison, these two estimates are in good agreement.

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APPENDIX A

TRANSPORT THEOREM FOR A BODY CONTAINING INTERSECTING DIVIDING SURFACES

A moving and deforming dividing surface Σ is the locus of a point whose position is a function of two parameters y^1, y^2 and time t:

$$\mathbf{z} = \mathbf{p}^{(\sigma)}(y^1, y^2, t). \qquad [A1]$$

There exists a many-to-one mapping of a portion of a multiphase body on to Σ,

$$y^\alpha = x^\alpha(\zeta^{(\sigma)}, t). \qquad [A2]$$

We visualize that at any given time there may be many material particles occupying a point on Σ. The set of all material particles at any point on Σ is denoted by $\zeta^{(\sigma)}$ and will be referred to as a surface particle. Consequently, [A2] and

$$\zeta^{(\sigma)} = X^{-1}(y^1, y^2, t) \qquad [A3]$$

may also be thought of as a one-to-one mapping of the set of surface particles on to Σ. These relationships tell us how the surface particles move from point to point on the surface independently of how the surface itself is moving.

The concept of a surface particle is abstract. We have no way of following the surface particles in a dividing surface. We are able to observe only spatial descriptions of a dividing surface. For example, at some reference time t_κ the dividing surface takes the form

$$\mathbf{z}_\kappa = \boldsymbol{\kappa}^{(\sigma)}(y_\kappa^{\ 1}, y_\kappa^{\ 2}) \equiv \mathbf{p}^{(\sigma)}(y_\kappa^{\ 1}, y_\kappa^{\ 2}, t_\kappa) \qquad [A4]$$

which we can call the reference dividing surface. This suggests that we identify surface particles by their location in this reference dividing surface:

$$y_\kappa^A = K^A(\zeta^{(\sigma)}) \equiv X^\alpha(\zeta^{(\sigma)}, t_\kappa), \tag{A5}$$

$$\zeta^{(\sigma)} = K^{-1}(y_\kappa^1, y_\kappa^2) \equiv X^{-1}(y_\kappa^1, y_\kappa^2, t_\kappa). \tag{A6}$$

Equations [A4] and [A5] together describe the reference configuration of the surface particles.

We can use [A2] and [A6] to describe the intrinsic deformation from the reference configuration:

$$y^\alpha = X_K{}^\alpha(y_\kappa^1, y_\kappa^2, t) \equiv X^\alpha(K^{-1}(y_\kappa^1, y_\kappa^2), t). \tag{A7}$$

Let us consider the operation

$$\frac{d}{dt}\int_\Sigma \psi^{(\sigma)}\, dA.$$

Here $\psi^{(\sigma)}$ is any scalar-, vector-, or tensor-valued function of time and position on the dividing surface. The indicated integration is to be performed over the dividing surface in its current configuration Σ. We should expect that Σ, or the limits on this integration, is a function of time.

Generally, the dividing surface will not be composed of a fixed set of material particles; there will be mass transfer between the dividing surface and the two adjoining phases. For the moment, let us confine our attention to a dividing surface composed of a fixed set of surface particles. Either the dividing surface is closed or no surface particles cross the closed curve C bounding Σ. In this case, we can express the integration over the dividing surface in terms of its fixed reference configuration

$$\int_\Sigma \psi^{(\sigma)}\, dA = \int_{\Sigma_\kappa} \psi^{(\sigma)} J^{(\sigma)}\, dA \tag{A8}$$

where

$$J^{(\sigma)} \equiv \frac{\sqrt{a}}{\sqrt{a_\kappa}}\left| \det\left(\frac{\partial X_K{}^\alpha}{\partial y_\kappa{}^A}\right)\right|. \tag{A9}$$

Here a is the determinant whose elements are the covariant components of the metric tensor (McConnell 1957) for the surface in its current configuration; a_κ is the determinant of the covariant components of the metric tensor for the surface in its reference configuration. The advantage is that the integration limits on the right side of [A8] are independent of time:

$$\begin{aligned}\frac{d}{dt}\int_\Sigma \psi^{(\sigma)}\, dA &= \frac{d}{dt}\int_{\Sigma_\kappa} \psi^{(\sigma)} J^{(\sigma)}\, dA = \int_{\Sigma_\kappa}\left(\frac{d_{(s)}\psi^{(\sigma)}}{dt} J^{(\sigma)} + \psi^{(\sigma)}\frac{d_{(s)}J^{(\sigma)}}{dt}\right) dA \\ &= \int_\Sigma \left(\frac{d_{(s)}\psi^{(\sigma)}}{dt} + \frac{\psi^{(\sigma)}}{J^{(\sigma)}}\frac{d_{(s)}J^{(\sigma)}}{dt}\right) dA.\end{aligned} \tag{A10}$$

In the second line of [A10] we have used the surface derivative, because at this point we are thinking of $\psi^{(\sigma)}$ and $J^{(\sigma)}$ as explicit functions of time and position in the reference configuration of the surface. One can prove (for the proof of an analogous result in the context of the transport theorem for a single-phase body, see Slattery (1972))

$$\frac{1}{J^{(\sigma)}}\frac{d_{(s)}J^{(\sigma)}}{dt} = \operatorname{div}_{(\sigma)} \mathbf{v}^{(\sigma)}. \tag{A11}$$

We conclude as a result

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma}\psi^{(\sigma)}\,\mathrm{d}A=\int_{\Sigma}\left(\frac{\mathrm{d}_{(s)}\psi^{(\sigma)}}{\mathrm{d}t}+\psi^{(\sigma)}\,\mathrm{div}_{(\sigma)}\,\mathbf{v}^{(\sigma)}\right)\mathrm{d}A \qquad [A12]$$

or

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma}\psi^{(\sigma)}\,\mathrm{d}A&=\int_{\Sigma}\left[\frac{\partial\psi^{(\sigma)}}{\partial t}-\nabla_{(\sigma)}\psi^{(\sigma)}\cdot\mathbf{u}+\mathrm{div}_{(\sigma)}\,(\psi^{(\sigma)}\mathbf{v}^{(\sigma)})\right]\mathrm{d}A\\&=\int_{\Sigma}\left(\frac{\partial\psi^{(\sigma)}}{\partial t}-\nabla_{(\sigma)}\psi^{(\sigma)}\cdot u-2H\,\psi^{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\xi}\right)\mathrm{d}A+\int_{C}\psi^{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\mu}\,\mathrm{d}s \qquad [A13]\end{aligned}$$

which are alternative forms of the *surface transport theorem*. In arriving at the second line of [A13], we have used the surface divergence theorem (McConnell 1957) and

$$\mathrm{div}_{(\sigma)}\,\boldsymbol{\xi}=-2H \qquad [A14]$$

in which H is the mean curvature (McConnell 1957) of the surface.

In deriving the surface transport theorem, we have followed that portion of a dividing surface associated with a set of surface particles. Now let us follow as a function of time a surface system in the dividing surface that does not contain a fixed set of surface particles. The dividing surface adjoining a moving common line is an example. A rolling motion in one of the phases (Dussan & Davis 1974) may force surface particles to cross the common line. Equations [A13] and [A14] do not apply to such a surface system. On the other hand, there is nothing to prevent us from associating a set of fictitious surface system particles with this system. It is not necessary to fully define these surface system particles. Let $\boldsymbol{\mu}$ be the unit tangent vector that is normal to the curve $C_{(\mathrm{sys})}$ bounding the surface system and that is outwardly directed with respect to the system. Let $\mathbf{v}_{(\mathrm{sys})}.\ \boldsymbol{\mu}$ be the component of the velocity of $C_{(\mathrm{sys})}$ in the direction $\boldsymbol{\mu}$. We will require only that at $C_{(\mathrm{sys})}$ the $\boldsymbol{\mu}$ component of the velocity of the surface system particles be equal to $\mathbf{v}_{(\mathrm{sys})}\cdot\boldsymbol{\mu}$. If in the derivation of [A13] we replace the set of surface particles with this set of surface system particles, the result is

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma_{(\mathrm{sys})}}\psi^{(\sigma)}\,\mathrm{d}A=\int_{\Sigma_{(\mathrm{sys})}}\left(\frac{\partial\psi^{(\sigma)}}{\partial t}-\nabla_{(\sigma)}\psi^{(\sigma)}\cdot\mathbf{u}-2H\psi^{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\xi}\right)\mathrm{d}A+\int_{C_{(\mathrm{sys})}}\psi^{(\sigma)}\,\mathbf{v}_{(\mathrm{sys})}\cdot\boldsymbol{\mu}\,\mathrm{d}s. \qquad [A15]$$

We can refer to this as the *generalized surface transport theorem*.

Now let us consider a multiphase body with two or more dividing surfaces intersecting in one or more moving common lines. The generalized surface transport theorem is applicable to each dividing surface. When it is applied to the sum of the dividing surfaces, we find

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma}\psi^{(\sigma)}\,\mathrm{d}A=\int_{\Sigma}\left(\frac{\partial\psi^{(\sigma)}}{\partial t}-\nabla_{(\sigma)}\psi^{(\sigma)}\cdot\mathbf{u}-2H\psi^{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\xi}\right)\mathrm{d}A+\int_{C}\psi^{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\mu}\,\mathrm{d}s\\+\int_{C^{(cl)}}(\psi^{(\sigma)}\boldsymbol{\nu})\cdot\mathbf{u}^{(cl)}\,\mathrm{d}s. \qquad [A16]\end{aligned}$$

The surface divergence theorem (McConnell 1957) and [A14] require

$$\int_{C}\psi^{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\mu}\,\mathrm{d}s-\int_{\Sigma}2H\,\psi^{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\xi}\,\mathrm{d}A=\int_{C^{(cl)}}(\psi^{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\boldsymbol{\nu})\,\mathrm{d}s+\int_{\Sigma}\mathrm{div}_{(\sigma)}(\psi^{(\sigma)}\mathbf{v}^{(\sigma)})\,\mathrm{d}A. \qquad [A17]$$

This together with

$$\frac{\partial\psi^{(\sigma)}}{\partial t}-\nabla_{(\sigma)}\psi^{(\sigma)}\cdot\mathbf{u}+\mathrm{div}_{(\sigma)}\,(\psi^{(\sigma)}\mathbf{v}^{(\sigma)})=\frac{\mathrm{d}_{(s)}\psi^{(\sigma)}}{\mathrm{d}t}+\psi^{(\sigma)}\,\mathrm{div}_{(\sigma)}\mathbf{v}^{(\sigma)} \qquad [A18]$$

permit us to rewrite [A16] as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma}\psi^{(\sigma)}\,\mathrm{d}A=\int_{\Sigma}\left(\frac{\mathrm{d}_{(s)}\psi^{(\sigma)}}{\mathrm{d}t}+\psi^{(\sigma)}\,\mathrm{div}_{(\sigma)}\,\mathbf{v}^{(\sigma)}\right)\mathrm{d}A+\int_{C^{(cl)}}(\psi^{(\sigma)}\,[\mathbf{v}^{(\sigma)}-\mathbf{u}^{(cl)}]\cdot\boldsymbol{\nu})\cdot\,\mathrm{d}s. \qquad [A19]$$

The transport theorem for a region containing a singular surface (Slattery 1972) tells us

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{R}\psi^{(\sigma)}\,\mathrm{d}A=\int_{R}\left(\frac{\mathrm{d}_{(m)}\psi}{\mathrm{d}t}+\psi\,\mathrm{div}\,\mathbf{v}\right)\mathrm{d}V+\int_{\Sigma}[\psi(\mathbf{v}-\mathbf{v}^{(\sigma)})\cdot\boldsymbol{\xi}]\,\mathrm{d}A. \qquad [A20]$$

The sum of [A19] and [A20] yields [2], the *transport theorem for a body containing intersecting dividing surfaces.*