

---

# A Micromechanical Investigation of Interfacial Transport Processes. II. Interfacial Constitutive Equations

Gretchen M. Mavrovouniotis, Howard Brenner, David A. Edwards and Li Ting

*Phil. Trans. R. Soc. Lond. A* 1993 **345**, 209-228

doi: 10.1098/rsta.1993.0128

---

## Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

---

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to:  
<http://rsta.royalsocietypublishing.org/subscriptions>

---

# A micromechanical investigation of interfacial transport processes. II. Interfacial constitutive equations

BY GRETCHEN M. MAVROVOUNIOU†, HOWARD BRENNER,  
DAVID A. EDWARDS AND LI TING‡

*Department of Chemical Engineering, Massachusetts Institute of Technology,  
Cambridge, Massachusetts 02139, U.S.A.*

## Contents

	PAGE
1. Introduction	209
2. Linear momentum transport	213
(a) A constitutive law for the surface-excess pressure tensor	213
(b) Validity of the symmetry condition $T^s \cdot n = 0$	218
(c) Discussion	219
3. Surface-active species transport	220
(a) Diffusion-controlled surfactant transport	221
(b) Validity of the local equilibrium assumption	225
(c) Discussion	226
References	227

Macroscale interfacial constitutive equations, as well as expressions for the phenomenological functions appearing therein, are derived via a rigorous matched asymptotic expansion scheme for transport processes occurring in immiscible fluid–fluid systems possessing moving and deforming interfaces. The usefulness of an asymptotic approach is demonstrated by examining a model in which the three-dimensional microscale fluid continuum is assumed to obey an incompressible, transversely-isotropic, linear, newtonian-type constitutive equation possessing position-dependent phenomenological coefficients which depend strongly upon distance normal to the interface. In such circumstances, the macroscale interfacial stress tensor reduces to the familiar isotropic Boussinesq–Scriven form. Similarly, a two-dimensional, isotropic, macroscale interfacial Fick’s law relation is derived from a comparable, three-dimensional, transversely-isotropic, microscale fickian form for the case of a diffusion-controlled surfactant transport exchange between the bulk phases and the interface.

## 1. Introduction

In part I (previous paper) two distinct approaches, namely macroscale and microscale, were discussed in the context of modelling the physicochemical properties of interfaces between immiscible bulk fluids.

† Present address: Allied-Signal Research and Technology, 50 East Algonquin Road, Des Plaines, Illinois 60017-5016, U.S.A.

‡ Present address: Hampshire Chemical Co., 739 Battleground Road, Deer Park, Texas 77536, U.S.A.

*Phil. Trans. R. Soc. Lond. A* (1993) **345**, 209–228

© 1993 The Royal Society

Printed in Great Britain

209

Upon adopting a macroscale view, the interface is envisioned as a singular two-dimensional surface endowed with distinct interfacial areal (and lineal) material properties, playing roles analogous to comparable volumetric material properties encountered with conventional three-dimensional bulk fluids. Constitutive equations for such a two-dimensional interface have generally been constructed by analogy with their three-dimensional fluid counterparts. For example, Scriven (1960), building upon earlier work by Boussinesq (1913), developed newtonian-like constitutive equations for the interfacial stress tensor by appropriately modifying for two-dimensional, riemannian surfaces the usual three-dimensional, euclidean, newtonian fluid equations for bulk fluids. Moeckel (1975) and Lindsay & Straughan (1979) examined interfacial constitutive equations by similarly extending continuum thermodynamic theory. Subsequently, constitutive equations for a simple surface material (Slattery & Ramamohan 1984) and a transversely isotropic viscoelastic interface (Waxman 1984) were invoked by analogy with their three-dimensional fluid counterparts.

With the more detailed microscale approach adopted in this series of papers, the three-dimensional structure of the interfacial transition region is explicitly recognized. In Part I, a rigorous, matched-asymptotic, small-parameter expansion scheme provided a method for systematically and rationally developing macroscale conservation equations for the singular, two-dimensional macroscale interface from the more exact, continuous microscale equations underlying these macroscale relations. In that theory generic surface-excess areal density fields  $\lambda^s$  and linear flux density fields  $\varphi^s$ , respectively derivable from the microscale forms of the comparable volumetric continuum density field  $\lambda$  and areal flux-density field  $\varphi$  within the interfacial transition region, were assigned to the two-dimensional macroscale interface.

To proceed from the 'exact' microscale description of the pertinent transport phenomena to a formulation of the macroscale interfacial constitutive equations, the respective constitutive forms adopted by the microscale continuum density fields within the interfacial transition region must be hypothesized. One important difference between the interfacial region and the contiguous bulk-fluid regions, and one which must be incorporated into any rational interfacial model, is the strong local inhomogeneity in material-property and/or microscale field densities existing within the transition region (in a direction normal to the interface) created by the existence of short-range intermolecular and physicochemical forces; that is, steep gradients exist perpendicular to the interface. Two distinct theoretical approaches – statistical-mechanical and continuum-mechanical – have previously been used to model the interfacial transition region. In both types, the inhomogeneities are generally incorporated by assuming that, within the interfacial transition region, all microscale continuum fields are locally transversely isotropic with respect to the direction normal to the dividing surface (Eliassen 1963; Kirkwood & Buff 1949; Goodrich 1981), and that the variation in microscale material properties and/or microscale field densities normal to the interface are strongly inhomogeneous. Far from the interface, the microscale fields are assumed to become locally isotropic, with all properties and densities appearing in these field descriptions only varying slowly, if at all.

Equilibrium statistical-mechanical methods (Kirkwood & Buff 1949; Irving & Kirkwood 1950; Buff 1955; Hill 1959; Defay *et al.* 1966; Rowlinson & Widom 1982) have frequently been used to investigate the diffuse interfacial transition region in

equilibrium systems. In many of these schemes, an anisotropic microscale pressure tensor possessing both normal and tangential components is postulated to exist within the interfacial transition region. This stress tensor is then determined from the singlet and pair molecular distribution functions. Far from this interfacial region, the hydrostatic microscale pressure tensor is assumed to possess its standard isotropic form, characterized simply by a single scalar pressure field. Using such microscale models, the macroscale constitutive equation for the surface pressure tensor is shown (Buff 1955) to be characterized by a scalar interfacial tension, itself a surface-excess quantity, in particular a surface-excess *pressure*.

Gradient theory (van der Waals & Kohnstamm 1908; Lovett *et al.* 1972; Evans 1979; Davis & Scriven 1982; Gurtin & Matano 1988) has also been used to model the interfacial transition region. In this scheme, the equilibrium properties of the interface are assumed to be expressible solely in terms of the microscale fluid mass density and its normal gradients proximate to the interfacial region.

In recent years, statistical-mechanical approaches have been used to derive the equations of motion for non-equilibrium dynamical interfacial systems (Ronis *et al.* 1978; Ronis & Oppenheim 1983; Davis 1987; Gurtin 1989).

Macroscale constitutive equations for the momentum transport processes accompanying moving and deforming interfaces have been developed from a continuum-mechanical viewpoint (Eliassen 1963; Slattery 1967*a, b*; Goodrich 1981) by supposing the pertinent microscale fields within the interfacial transition region to be transversely isotropic with respect to the direction normal to the dividing surface, while still retaining the basic linear (albeit anisotropic) constitutive forms analogous to those of three-dimensional bulk fluids (appropriately generalized for non-euclidean spatial domains). In particular, the stress tensor is assumed to possess a transversely isotropic newtonian form.

The micromechanical scheme proposed by Brenner (1979) for equilibrium systems provides a physically based approach to physicochemical modelling of the interfacial transition region and, hence, to ultimately establishing the macroscale constitutive equations governing surface-excess densities and fluxes. In this model, the microscale pressure tensor is assumed to be isotropic. However, within the interfacial transition region, the large pressure gradients existing in equilibrium systems are assumed to be balanced by short-range 'external' forces of an intermolecular origin (resulting from large physicochemical field normal-component gradients, such as molecular number density for single-component vapour-liquid systems, or species number density in the case of adsorbed surfactants), jointly with any other longer-ranged external forces that may be acting on the system. Interfacial tension thus appears as the macroscopic manifestation of short-range intermolecular forces arising from physicochemical inhomogeneities existing within the interfacial transition region. This *isotropic* view of the equilibrium pressure tensor stands in marked contrast to the more conventional statistical-mechanical view (Kirkwood & Buff 1949), in which the intermolecular forces are implicitly incorporated into an *anisotropic* equilibrium pressure tensor. Fundamentally, however, both views arrive at physically indistinguishable macroscale results. (Brenner (1979) compares the two theories in depth.)

The effect of surfactants on the transport properties of interfaces was examined by Deemer & Slattery (1978) through the use of models in which surfactant molecules were considered to be adsorbed, three-dimensional solid particles dispersed throughout the interfacial transition region. They calculated the interfacial tension

and the surface-excess shear viscosity arising in a simple shear field for two specific structural models: one a dilute suspension of neutrally buoyant spheres straddling a relatively flat two-dimensional dividing surface (with the sphere centres restricted to this surface), and the other a dilute suspension of chains of non-interacting, neutrally buoyant spheres, with the sphere at one end of the chain straddling the dividing surface, and with the centres of the remaining spheres composing the chain lying along a normal to the dividing surface.

Brenner & Leal (1977, 1978, 1982) examined the surface diffusion, convection and mass transfer of adsorbed surfactants within and across a two-dimensional, stationary, planar interface. Although they too modelled the surfactant solute molecules as solid, albeit 'bipolar', spheres, the possibility of molecular diffusion of the surfactant was admitted by the inclusion of brownian motion of these spheres. In addition, short-range physicochemical adsorption forces resulting from the inhomogeneous, physicochemically bipolar nature of the brownian sphere surface itself provided a physical mechanism for accumulating the surface-active species at the interface. Use of this model permitted expressions for the adsorption coefficient, surface diffusivity, surface solute velocity and macroscale concentration jump across the interface to be obtained.

In this paper, the asymptotic scheme developed in Part I will be used rationally to derive macroscale interfacial constitutive equations (together with the interfacial phenomenological coefficients appearing therein) from knowledge of the comparable microscale equations, in particular from the (strongly inhomogeneous) phenomenological material functions appearing in these microscale constitutive equations. To illustrate the explicit procedure whereby two-dimensional macroscale interfacial constitutive equations are determined from the corresponding three-dimensional microscale constitutive forms (albeit possessing strongly inhomogeneous phenomenological coefficients), we will herein adopt the usual (Kirkwood & Buff 1949; Eliassen 1963; Goodrich 1981; Brenner & Leal 1982) microscale model for the interfacial region, in which all microscale continuum fields are supposed locally transversely isotropic with respect to the direction normal to the macroscale interface. Additionally, these fields are assumed to possess linear constitutive forms analogous to those of their relatively homogeneous (and isotropic) bulk-phase counterparts. Far from the interface, the microscale fields become locally isotropic.

The particular examples to be considered herein pertain to linear momentum and material species transport. Contrary to the conclusions of Goodrich (1981*b*) for the momentum transport example, the Boussinesq–Scriven interfacial stress tensor (Boussinesq 1913; Scriven 1960) for a material newtonian interfacial fluid 'phase' will be shown to be applicable to systems in which the microscale stress tensor is transversely isotropic. For the species transport example the surface-excess diffusion flux will be found to obey a two-dimensional, isotropic, macroscale Fick's law constitutive relation, possessing a (scalar) surface diffusion coefficient whose general form agrees with the comparable results of Brenner & Leal (1982) for a 'discontinuous' interface.

The microscale  $\rightarrow$  macroscale linear constitutive examples provided in this paper are to be regarded as purely illustrative of the general asymptotic scheme. Alternative three-dimensional microscale constitutive model choices, e.g. non-newtonian models, will of course, lead to other types of macroscale interfacial constitutive behaviour, e.g. non-boussinesquian.

Throughout this paper, the notation and terminology of Part I will be used. When

referring to equations given in Part I, the prefix I- will be inserted before citation of that equation number.

## 2. Linear momentum transport

The interfacial conservation equation for the linear momentum density  $\rho\mathbf{v}$  can frequently be written in the form (I-7.7)

$$\nabla_s \cdot (I_s \cdot P^s) + F^s = \mathbf{n} \cdot [(\bar{\mathbf{v}} - \mathbf{u}) \bar{\rho} \bar{\mathbf{v}} - \bar{\mathbf{P}}], \quad (2.1)$$

with the various symbols defined as in Part I. Equation (2.1) provides the jump boundary condition relating the normal components of the macroscale flux of linear momentum on either side of the interface. To apply this equation to any specific physical system, macroscale constitutive equations for the surface-excess quantities  $F^s$  and  $P^s$  are needed. Such equations can be developed from the generic defining relations (I-4.18) (with  $\lambda = F$ ) and (I-4.36) (with  $\varphi \equiv P$ ) once constitutive models for the microscale quantities  $F$  and  $P$  are supplied. Note that, upon using the generic definition (I-4.36) for a surface-excess flux density, the relation

$$P^s = I_s \cdot P^s \quad (2.2)$$

is found to hold.

### (a) A constitutive law for the surface-excess pressure tensor

A macroscale constitutive equation for the surface-excess pressure tensor  $P^s$  is derived in the following section via use of (I-4.36) upon postulating an assumed form for the microscale pressure tensor  $P$ . For this purpose, attention is restricted to an incompressible, (locally) transversely isotropic fluid continuum satisfying the microscale kinematical constraint (2.13) appropriate to a material interface. The microscale pressure tensor is regarded as being both transversely isotropic and linearly related to the rate of fluid deformation. In these model circumstances it will be shown that the Boussinesq–Scriven interfacial stress tensor (Boussinesq 1913; Scriven 1960) results. Thus, not only does the example illustrate our general microscale asymptotic scheme for deriving macroscale interfacial constitutive relations, but equally it provides a microscale rationale for the most common mode of macroscale interfacial rheological behaviour postulated, as embodied in the classical Boussinesq–Scriven constitutive model.

The three-dimensional microscale stress tensor possesses the usual decomposition

$$P = -pI + T, \quad (2.3)$$

with  $p$  the equilibrium (thermodynamic) pressure and  $T$  the (symmetric) viscous or deviatoric stress tensor. Following Brenner (1979), the microscale equilibrium pressure term  $p$  is assumed to be everywhere isotropic. The microscale anisotropy assumed to exist within the interfacial region is supposed fully attributable to short-range intermolecular forces identified with the microscale external force density vector  $F$ , rather than with the microscale pressure  $p$ .

Upon using (I-4.36), the surface-excess pressure tensor  $P^s$  can be written as

$$P^s = \sigma I_s + T^s, \quad (2.4)$$

wherein the scalar

$$\sigma(\mathbf{x}_s) \sim \epsilon L \int_{\tilde{n}=-\infty}^{+\infty} [\bar{p}(\mathbf{x}_s, 0) - \tilde{p}(\mathbf{x}_s, \tilde{n})] d\tilde{n} \quad (2.5)$$

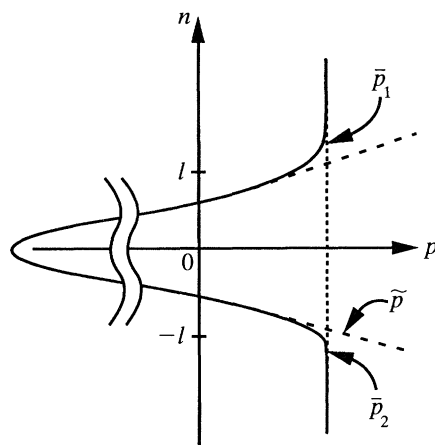


Figure 1. A hypothetical microscale pressure profile is depicted within the interfacial transition region ( $-l \lesssim n \lesssim l$ ) separating bulk-phase fluids 1 and 2. Negative values of the microscale pressure scalar  $p$  within the interfacial region are required in order to satisfy the assumption of a positive interfacial tension  $\sigma$  according to the surface-excess formulation. Classical statistical-thermodynamical theories of interfaces (see, for example, Rowlinson & Widom 1982) predict interfacial tension from microscale data by employing formulas which assume (in addition to a normal stress  $p_N$ ) the existence of a tangential microscale stress  $p_T$ . Statistical-thermodynamic models (see, for example, the review of Ono & Kondo (1960)) have demonstrated that the scalar  $p_T$  achieves large negative values (as depicted above for  $p$ ) within the interfacial transition region, owing to the highly inhomogeneous nature of this region.

provides a surface-excess formulation of the equilibrium interfacial tension in terms of the microscale pressure field  $p(\mathbf{x})$  (see figure 1); similarly, the expression

$$T^s(\mathbf{x}_s) \sim \epsilon L \int_{\tilde{n}=-\infty}^{+\infty} l_s \cdot [\tilde{T}(\mathbf{x}_s, \tilde{n}) - \bar{T}(\mathbf{x}_s, 0)] d\tilde{n} \quad (2.6)$$

formulates the surface-excess viscous stress tensor in terms of the microscale deviatoric stress field  $T(\mathbf{x})$ .

Within the diffuse interfacial region, the existence of short-range, anisotropic, intermolecular forces (attributable to the presence of steep mass density and/or species concentration gradients in a direction normal to the macroscale interface) is assumed to endow the microscale viscous stress tensor  $T$  with local axial symmetry about the local direction of the normal vector  ${}^*\mathbf{n}$ . (Recall from Part I that the asterisk pre-superscript is used to designate field variables at some point on a familial coordinate surface  ${}^*A$  not coinciding with the parent surface,  $A$ ; the latter being identified with the macroscale interface in the limit  $\epsilon \rightarrow 0$ .) In addition,  $T$  is supposed linearly proportional to the rate-of-deformation tensor,

$$\mathbf{e} = \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^\dagger), \quad (2.7)$$

by analogy with comparable three-dimensional bulk fluid hypotheses. Upon further assuming the microscale fluid to be incompressible, namely

$$\nabla \cdot \mathbf{v} = \mathbf{e} : l_s = (\mathbf{e} : {}^*l_s) + (\mathbf{e} : {}^*\mathbf{n}^*\mathbf{n}) = 0, \quad (2.8)$$

the viscous stress tensor can thus be written in the transversely isotropic form (Eliassen 1963; Goodrich 1981 *b*)

$$T = \eta(\mathbf{e} : {}^*l_s) {}^*l_s + 2\mu({}^*l_s \cdot \mathbf{e} \cdot {}^*l_s) + 2\mu'({}^*l_s \cdot \mathbf{e} \cdot {}^*\mathbf{n}^*\mathbf{n} + {}^*\mathbf{n}^*\mathbf{n} \cdot \mathbf{e} \cdot {}^*l_s) - 2\mu''(\mathbf{e} : {}^*l_s) {}^*\mathbf{n}^*\mathbf{n}, \quad (2.9)$$

with the microscale phenomenological viscosity functions  $\eta$ ,  $\mu$ ,  $\mu'$  and  $\mu''$  each functions of  $\mathbf{x}$  in general. (To obtain such a relation from the theory of anisotropic fluids (Stokes 1984), the director inertia must be negligible.) Steep surfactant concentration gradients existing in the interfacial region are postulated to impart a strong functional dependence upon normal distance  $n$  to each of the four phenomenological viscosity coefficients appearing in (2.9). Within the two bulk fluid regions, the effect of the interfacial inhomogeneity upon the constitutive form of  $\mathcal{T}$  is assumed negligible. In particular, the microscale fluid is supposed locally isotropic within these regions; explicitly,

$$\bar{\mu} = \bar{\mu}' = \bar{\mu}'' \quad \text{and} \quad \bar{\eta} = 0. \quad (2.10)$$

Thus, upon formally passing to the outer limit (I-3.11) in (2.9), we obtain  $\bar{\mathcal{T}} = 2\bar{\mu}\bar{\mathbf{e}}$ , which is the usual constitutive equation for an incompressible, isotropic newtonian fluid.

Consistent with our assumption of a material fluid interface, the microscale velocity vector  $\mathbf{v}$  in the following analysis will be taken to be a 'macroscale quantity', in the sense that

$$\left(\frac{1}{U}\right) \frac{\partial \mathbf{v}}{\partial \bar{n}} = O(1) \quad (2.11)$$

everywhere; i.e.  $O(1)$  changes in  $\mathbf{v}$  are assumed to occur only over macroscale distances. Such a supposition implies that  $\mathbf{v}$  is continuous across the interface when viewed from the macroscale, as shown by the following argument: Upon using (I-3.30)–(I-3.34) (with  $^*\mathbf{f} \equiv \mathbf{v}(\mathbf{x}_s, n)$  and  $\mathbf{f} \equiv \mathbf{v}(\mathbf{x}_s, 0)$ ), the respective inner and outer limits of  $\mathbf{v}$  are identical, and are given by the relation

$$\bar{\mathbf{v}}(\mathbf{x}_s, \bar{n}) = \mathbf{v}(\mathbf{x}_s, 0) = \lim_{\bar{n} \rightarrow 0^+} \bar{\mathbf{v}}_1(\mathbf{x}_s, \bar{n}) = \lim_{\bar{n} \rightarrow 0^-} \bar{\mathbf{v}}_2(\mathbf{x}_s, \bar{n}). \quad (2.12)$$

Formally, our assumption of a *material* macroscale interface requires that the normal components of the bulk-phase velocities be both continuous across the interface and equivalent to the normal surface velocity  $\mathbf{n} \cdot \mathbf{u}$ ; thus

$$\mathbf{n} \cdot \lim_{\bar{n} \rightarrow 0^+} \bar{\mathbf{v}}_1(\mathbf{x}_s, \bar{n}) = \mathbf{n} \cdot \lim_{\bar{n} \rightarrow 0^-} \bar{\mathbf{v}}_2(\mathbf{x}_s, \bar{n}) = \mathbf{n} \cdot \mathbf{u} = \mathbf{n} \cdot \mathbf{V}, \quad (2.13)$$

where

$$\mathbf{V}(\mathbf{x}_s) \equiv \mathbf{v}(\mathbf{x}_s, 0) \quad (2.14)$$

is defined to be the material interfacial velocity. (Note that the material interfacial velocity  $\mathbf{V}$  is equivalent to the definition (I-6.19) obtained for phase interfaces.)

Owing to the assumed, relatively homogeneous, transverse physicochemical properties of the interfacial region, macroscale discontinuities can arise only in the normal component of the macroscale flux fields across the interface. Thus, transverse or lateral gradients of the microscale velocity vector  $\mathbf{v}$  within the interfacial region are explicitly assumed to be macroscale in nature. This assures that no discontinuity at  $\bar{n} = 0$  can exist in the tangential components of the macroscale stress tensor; thus,

$$\left(\frac{L}{U}\right) \frac{\partial}{\partial \bar{n}} (^*\nabla_s \mathbf{v}) = O(1). \quad (2.15)$$



Upon using (I-3.30)–(I-3.34) (with  $*\mathbf{f} \equiv * \nabla_s \mathbf{v}(\mathbf{x}_s, n)$  and  $\mathbf{f} \equiv \nabla_s V(\mathbf{x}_s)$ ), we may then write

$$\overline{(*\nabla_s \mathbf{v})} = \nabla_s V = \lim_{\bar{n} \rightarrow 0^+} \overline{(*\nabla_s \mathbf{v})_1} = \lim_{\bar{n} \rightarrow 0^-} \overline{(*\nabla_s \mathbf{v})_2} \quad (2.16)$$

for the respective inner and outer limits of the tangential contribution to the microscale velocity gradient. In contrast with the above condition of continuity, the normal gradient of  $\mathbf{v}$  may appear to be discontinuous across the interface in the asymptotic, macroscale limit.

To establish the constitutive form adopted by the macroscale interfacial viscous stress tensor  $T^s$  from the definition (2.6) together with the microscale constitutive equation (2.9), inner and outer expansions of the various deformational terms appearing in (2.9) must be calculated. Use of (2.16) together with the definition (2.7) of  $\mathbf{e}$  shows that the inner limit of  $\mathbf{e} : *I_s$  can be written in the form

$$\overline{(\mathbf{e} : *I_s)} = \overline{[(\nabla \mathbf{v}) : *I_s]} = \overline{(*\nabla_s \cdot \mathbf{v})} = (\nabla_s \cdot V). \quad (2.17)$$

Similarly, the outer limit of  $\mathbf{e} : *I_s$  is given by the relation

$$\overline{(\mathbf{e} : *I_s)_\alpha} = \overline{(*\nabla_s \cdot \mathbf{v})_\alpha} \quad (\alpha = 1, 2). \quad (2.18)$$

Form the respective interfacial limits  $\bar{n} \rightarrow 0^\pm$  of the above equation, and use (2.16) to obtain

$$\lim_{\bar{n} \rightarrow 0^+} \overline{(\mathbf{e} : *I_s)_1} = \lim_{\bar{n} \rightarrow 0^-} \overline{(\mathbf{e} : *I_s)_2} = (\nabla_s \cdot V). \quad (2.19)$$

The inner and outer limits of the term  $*I_s \cdot \mathbf{e} \cdot *I_s$  can similarly be reduced through use of the product relations (I-3.15) and (I-3.16), jointly with the definition (2.7) of the deformation dyadic  $\mathbf{e}$ , and the limiting relation (2.16); this yields

$$\overline{(*I_s \cdot \mathbf{e} \cdot *I_s)} = \frac{1}{2} [(\nabla_s V) \cdot I_s + I_s \cdot (\nabla_s V)^\dagger] = \lim_{\bar{n} \rightarrow 0^+} \overline{(*I_s \cdot \mathbf{e} \cdot *I_s)_1} = \lim_{\bar{n} \rightarrow 0^-} \overline{(*I_s \cdot \mathbf{e} \cdot *I_s)_2}. \quad (2.20)$$

As shown later in this section, the term appearing in (2.9) involving the quantity  $*I_s \cdot \mathbf{e} \cdot *n *n$  does not contribute to the macroscale constitutive equation for  $T^s$ . Rather than being detoured into a lengthy proof of this assertion at this point, we will anticipate the result and assume that

$$T^s \cdot n = \mathbf{0}, \quad (2.21)$$

postponing a formal proof until §2b.

Given the limiting forms (2.17), (2.19) and (2.20), together with the assertion (2.21), we are now in a position to calculate the constitutive form adopted by the surface-excess viscous stress tensor  $T^s$ . This may be done by substituting the microscale constitutive equation (2.9) for  $T$  into the integral formulation (2.6) of  $T^s$ . Thus, consider the integral arising when the first term appearing in (2.9) is substituted into (2.6). Application of (2.17) and (2.19) to this integral yields

$$\epsilon L \int_{\bar{n}=-\infty}^{+\infty} I_s \cdot \{ \overline{[\eta(\mathbf{e} : *I_s) *I_s]}(\mathbf{x}_s, \bar{n}) - \overline{[\eta(\mathbf{e} : *I_s) *I_s]}(\mathbf{x}_s, 0) \} d\bar{n} = \eta^s (\nabla_s \cdot V) I_s, \quad (2.22)$$

as the contribution of this term to the constitutive equation for  $T^s$ . Here, the interfacial viscosity coefficient  $\eta^s$  is given by the surface-excess relation

$$\eta^s \sim \epsilon L \int_{\bar{n}=-\infty}^{+\infty} [\bar{\eta}(\mathbf{x}_s, \bar{n}) - \bar{\eta}(\mathbf{x}_s, 0)] d\bar{n}. \quad (2.23)$$

Similarly, the integral arising when the second term of (2.9) is substituted into the definition (2.6) can be written in the form

$$\epsilon L \int_{\tilde{n}=-\infty}^{+\infty} I_s \cdot \{ \overbrace{[2\mu(*I_s \cdot \mathbf{e} \cdot *I_s)]} (\mathbf{x}_s, \tilde{n}) - \overbrace{[2\mu(*I_s \cdot \mathbf{e} \cdot *I_s)]} (\mathbf{x}_s, 0) \} d\tilde{n} = 2\mu^s D^s, \quad (2.24)$$

wherein

$$\mu^s \sim \epsilon L \int_{\tilde{n}=-\infty}^{+\infty} [\tilde{\mu}(\mathbf{x}_s, \tilde{n}) - \bar{\mu}(\mathbf{x}_s, 0)] d\tilde{n}, \quad (2.25)$$

is an interfacial viscosity coefficient (explicitly, the interfacial shear viscosity (Scriven 1960) for a newtonian interface; cf. (2.28)), and

$$D^s = \frac{1}{2}[(\nabla_s V) \cdot I_s + I_s \cdot (\nabla_s V)^\dagger] \quad (2.26)$$

is the interfacial rate-of-deformation tensor. Due to the constraint (2.21), none of the other terms in (2.9) contribute to  $T^s$ .

The above results combine to yield the purely macroscale expression

$$T^s = \eta^s (\nabla_s \cdot V) I_s + 2\mu^s D^s \quad (2.27)$$

as the operational form of the interfacial constitutive equation for  $T^s$ . Substitution of the above relation into (2.4) furnishes the interfacial constitutive equation for the total stress tensor, namely

$$P^s = \sigma I_s + 2\mu^s (D^s - \frac{1}{2} I_s : D^s) + \kappa^s I_s : D^s, \quad (2.28)$$

where  $\mu^s$  is the interfacial shear viscosity, and

$$\kappa^s \stackrel{\text{def}}{=} \eta^s + \mu^s \quad (2.29)$$

is the interfacial dilatational viscosity.

The macroscale expression (2.28) for the interfacial pressure tensor  $P^s$  reproduces identically the Boussinesq (1913) and Scriven (1960) interfacial stress tensor, previously proposed on a purely phenomenological, continuum-mechanical basis by analogy with conventional three-dimensional newtonian fluids (albeit modified to reflect the generally non-euclidean nature of the curved, two-dimensional, interfacial domain). Using our asymptotic approach, we have been able to furnish a rational derivation of this macroscale interfacial equation from the corresponding microscale constitutive form. Equation (2.28) has been obtained strictly only for material interfaces, and then only for circumstances in which the three-dimensional microscale fluid in proximity to the interfacial region possesses the linear, transversely-isotropic form (2.9). An important condition upon the validity of (2.28) is contained in (2.21). As demonstrated in subsequent paragraphs, this condition (indeed, as is clearly true for the kinematical conditions (2.16)–(2.20)) is appropriate only in the asymptotic limit as  $\epsilon \rightarrow 0$ . We make this  $\epsilon \rightarrow 0$  remark explicit because other microscale  $\rightarrow$  macroscale interfacial theories (see, for example, Eliassen 1963) claim to be *exact*, rather than *asymptotic*, whence the validity of the relation  $T^s \cdot \mathbf{n} = \mathbf{0}$  remains an open question in their theories. In turn, the answer to this question impacts upon the question of whether or not the interfacial stress tensor  $T^s$  (or  $P^s$ ) is *symmetric*, and this is an important issue in connection with the moment-of-momentum equation for interfaces, as discussed in Part I.

In general, the microscale viscosity fields  $\mu(\mathbf{x}) \equiv \mu(\mathbf{x}_s, \mathbf{n})$  and  $\eta(\mathbf{x}) \equiv \eta(\mathbf{x}_s, \mathbf{n})$  required in the respective evaluation of  $\mu^s$  and  $\eta^s$  via (2.23) and (2.25) may possess

a steep gradient in the neighbourhood of the interface when ‘adsorbed’ surfactants are present; that is, since the three-dimensional, microscale mass density  $\rho_A(\mathbf{x})$  of the surfactant species A, say, varies steeply within the interfacial region (with  $\partial\rho_A/\partial n = 0$  in the neighbourhood of  $n = 0$ ), the same is supposed true of the viscosities. This fact implicitly assumes a local functional dependence of both  $\mu$  and  $\eta$  upon  $\rho_A$  (with both  $d\mu/d\rho_A$  and  $d\eta/d\rho_A > 0$ ), in the manner of, say, the analogue of the Einstein equation (Einstein 1905, 1956; see also Adler *et al.* 1990) for the viscosity of suspensions, with the surfactant molecules playing the role of suspended particles in that theory. Thus, the monolayer coverage achieved by adsorbed surfactants at the interface can be expected to yield very large three-dimensional viscosities within the diffuse interfacial region proximate to  $n = 0$  (such as depicted in curve B of Part I, figure 5). The existence of such large microscale viscosities thus accounts for the concomitant existence of sensible (Wasan *et al.* 1971; Jiang *et al.* 1983; Ting *et al.* 1985) interfacial viscosities  $\mu^s$  and  $\kappa^s$ .

If the microscale pressure tensor  $\mathbf{P}$  is everywhere locally isotropic, then  $\mu = \mu' = \mu''$  and  $\eta = 0$  in (2.9). In such circumstances, the interfacial shear and dilatational viscosities appearing in (2.28) can be shown to be identical, namely  $\mu^s = \kappa^s$ , and to be given explicitly in terms of the prescribed microscale viscosity data  $\mu(\mathbf{x}_s, n)$  as

$$\mu^s(\mathbf{x}_s) \equiv \kappa^s(\mathbf{x}_s) \sim \epsilon L \int_{\tilde{n}=-\infty}^{+\infty} [\tilde{\mu}(\mathbf{x}_s, \tilde{n}) - \bar{\mu}(\mathbf{x}_s, 0)] d\tilde{n}. \quad (2.30)$$

This equality of interfacial viscosities may be viewed as providing indirect theoretical confirmation of the experimentally observed fact (Ting *et al.* 1984) that measured values of  $\mu^s$  and  $\kappa^s$  are of similar orders of magnitude at a gas–liquid interface.

(b) *Validity of the symmetry condition  $T^s \cdot \mathbf{n} = \mathbf{0}$*

In the preceding analysis, we asserted that the term  $*I_s \cdot \mathbf{e} \cdot * \mathbf{n} \cdot \mathbf{n}$  in (2.9) does not contribute to the macroscale constitutive equation for  $T^s$  (owing to the restriction (2.21)). This is demonstrated in the following to be a consequence of the microscale linear momentum equation

$$\rho \left[ \frac{\delta \mathbf{v}}{\delta t} + (\mathbf{v} - * \mathbf{u}) \cdot \nabla \mathbf{v} \right] = \mathbf{F} + \nabla \cdot \mathbf{P}. \quad (2.31)$$

(Note that it is convenient here to use the surface-fixed derivative  $\delta/\delta t$  defined in Part I.)

Within the interfacial transition region, the tangential component of (2.31) can, with the use of (2.3), be written in the form

$$\begin{aligned} \frac{1}{\epsilon L} \left[ * \mathbf{n} \cdot \frac{\partial \mathbf{T}}{\partial \tilde{n}} + \rho(\mathbf{v} - * \mathbf{u}) \cdot * \mathbf{n} \frac{\partial \mathbf{v}}{\partial \tilde{n}} \right] \cdot * I_s = * \nabla_s p - \mathbf{F} \cdot * I_s \\ + \left[ \rho \frac{\delta \mathbf{v}}{\delta t} + \rho(\mathbf{v} - * \mathbf{u}) \cdot * \nabla_s \mathbf{v} - * \nabla_s \cdot \mathbf{T} \right] \cdot * I_s. \end{aligned} \quad (2.32)$$

Upon supposing that all terms appearing on the right-hand side of the above are  $O(1)$ , this equation furnishes the scaling

$$* \mathbf{n} \cdot \frac{\partial \mathbf{T}}{\partial \tilde{n}} \cdot * I_s + \rho(\mathbf{v} - * \mathbf{u}) \cdot * \mathbf{n} \frac{\partial \mathbf{v}}{\partial \tilde{n}} \cdot * I_s = O(\epsilon). \quad (2.33)$$

Application of the order-of-magnitude relations (I-6.7) and (2.11) gives

$$\frac{\partial}{\partial \bar{n}} (*\mathbf{n} \cdot \mathcal{T} \cdot *I_s) = O(\epsilon) \quad (2.34)$$

as the appropriate scaling of the linear momentum equation within the interfacial transition region. Since  $\mathcal{T}$  is symmetric, the identity

$$*\mathbf{n} \cdot \mathcal{T} \cdot *I_s = *I_s \cdot \mathcal{T} \cdot *\mathbf{n} \quad (2.35)$$

is applicable. Upon using (I-3.30)–(I-3.34), the above two relations combine to yield

$$[*I_s \cdot \mathcal{T} \cdot *\mathbf{n} * \mathbf{n}] = \lim_{\bar{n} \rightarrow 0^+} \overline{[*I_s \cdot \mathcal{T} \cdot *\mathbf{n} * \mathbf{n}]_1} = \lim_{\bar{n} \rightarrow 0^-} \overline{[*I_s \cdot \mathcal{T} \cdot *\mathbf{n} * \mathbf{n}]_2}. \quad (2.36)$$

Since the inner and outer limits in the latter are seen to be identical, the term  $*I_s \cdot \mathcal{T} \cdot *\mathbf{n} * \mathbf{n}$  will not contribute to the surface-excess stress tensor  $\mathcal{T}^s$  upon inserting the corresponding term appearing in (2.9) into (2.6). Hence,  $\mathcal{T}^s \cdot \mathbf{n} = \mathbf{0}$ , as asserted in (2.21). QED

### (c) Discussion

The macroscale jump boundary condition (2.1), together with the interfacial constitutive equation (2.28) for  $\mathcal{P}^s$  and the assumed continuity of the tangential component of the macroscale velocity across the interface, completely defines the macroscale system in the absence of surface-excess external forces.

For a system that is at equilibrium,  $\mathcal{T}^s = \mathbf{0}$ , whence (2.1) becomes

$$\nabla_s \sigma + 2H\sigma \mathbf{n} = \mathbf{n}[\bar{p}]. \quad (2.37)$$

This vector expression can be separated into its normal and tangential components, respectively yielding

$$[\bar{p}] = 2H\sigma, \quad \text{and} \quad \nabla_s \sigma = \mathbf{0}. \quad (2.38a, b)$$

Equation (2.38a) is, of course, the familiar Laplace equation for an equilibrium system (in the absence of surface-excess forces).

Although we have assumed that the microscale fluid obeys the incompressibility relation  $\nabla \cdot \mathbf{v} = 0$ , the comparable quantity  $\nabla_s \cdot \mathbf{V}$  for the macroscale interface is generally non-zero. Thus, the dynamic interfacial tension, namely

$$\sigma_{\text{dynamic}} = \frac{1}{2}I_s : \mathcal{P}^s = \sigma + \kappa^s \nabla_s \cdot \mathbf{V}, \quad (2.39)$$

is generally not equivalent to the equilibrium interfacial tension  $\sigma$ . This is particularly important since, in contrast to the usual (compressible) three-dimensional bulk fluid equations, in which  $\kappa$  is often small (Bird *et al.* 1960, p. 79), the value of the interfacial dilatational viscosity  $\kappa^s$  is often comparable to that of the interfacial shear viscosity. Indeed,  $\kappa^s \equiv \mu^s$  for an isotropic fluid (cf. (2.30)).

The usefulness of our asymptotic approach is demonstrated by comparing the macroscale interfacial constitutive equations rigorously derived herein with the constitutive equations obtained by Eliassen (1963) and Goodrich (1981*b*) using alternative microscale theories.

In contrast with the approach of Eliassen (1963), our asymptotic scheme provides a rational method for identifying the *sensible* terms which appear in the interfacial transport equations.

Goodrich (1981*b*) used a Taylor series approximation approach to obtain a constitutive equation for  $\mathcal{T}^s$  from the microscale form (2.9). However, his resulting constitutive equation contained two additional terms, respectively multiplied by

what in our terminology would be  $\mu^s$  and  $\mu''^s$ . Our rigorous asymptotic approach shows *inter alia* that the two extra terms and concomitant phenomenological coefficients, which Goodrich (1981*b*) claims must be added to the Boussinesq–Scriven equation (2.28) for it to be complete, are not rationally derivable from a transversely-isotropic microscale fluid model.

This discrepancy arises due to two main causes: (i) an oversight in Goodrich's Taylor series expansion given in his second equation on p. 351 leads him to write  $(\mathbf{V}_s \cdot \mathbf{P}^\dagger)$  in place of  $[\mathbf{V}_s \cdot (I_s \cdot \mathbf{P}^\dagger)]$  in his equation (25); (ii) Goodrich failed to account for the constraint (2.21). (Goodrich's  $\mathbf{P}^\dagger$  is equal to our  $\mathbf{P}$ .)

Yet another apparent oversight arises in Goodrich's reduction of the term involving  $*I_s \cdot \mathbf{e} \cdot *n \cdot n$ . In particular, consider the integral

$$\int_1^2 \mathbf{v} \left( \frac{\partial \mu'}{\partial \tilde{n}} \right) d\tilde{n} \quad (2.40)$$

appearing in his equation (69). (Goodrich (1981*b*) has actually multiplied through by  $(\mathbf{V}_s \cdot \cdot)$  and thus uses  $\Theta$  rather than  $\mathbf{v}$  in his analysis. (He assumes the viscosity coefficients are independent of  $\mathbf{x}_s$ .) In addition, his  $\mu''$  is our  $\mu'$ .) Substitution of the relation

$$\mathbf{v}(\mathbf{x}_s, n) = \mathbf{V}(\mathbf{x}_s) + \tilde{n}O(\epsilon), \quad (2.41)$$

which can be obtained from (I-3.33) given that (2.11) holds, into (2.38), followed by subsequent integration yields the expression

$$\int_1^2 \mathbf{v} \left( \frac{\partial \mu'}{\partial \tilde{n}} \right) d\tilde{n} = \mathbf{V}[\mu']_1^2 + O(\epsilon) \int_1^2 \left( \frac{\partial \mu'}{\partial \tilde{n}} \right) \tilde{n} d\tilde{n}. \quad (2.42)$$

Although the final term in this equation appears on cursory examination to be negligible (i.e. of  $O(\epsilon)$ ), it is actually of  $O(1)$ ; for, when  $\mu'$  attains large values, namely of  $O(\epsilon^{-1})$ , within the interfacial transition region (as is necessary for the appearance of measurable interfacial viscosities according to our theory),  $\partial \mu' / \partial \tilde{n}$  will also be of  $O(\epsilon^{-1})$ . Goodrich's neglected this term in his analysis, inappropriately in our view.

### 3. Surface-active species transport

The interfacial conservation equation (I-7.17) for the areal mass density  $\rho_i^s$  of some material species  $i$  can be written as

$$\frac{\delta_s \rho_i^s}{\delta t} + (\mathbf{v} - \mathbf{u}) \cdot \nabla_s \rho_i^s + \{\nabla_s \cdot [\mathbf{v}_s(\mathbf{x}_s, 0) + \mathbf{nn} \cdot \mathbf{u}]\} \rho_i^s + \nabla_s \cdot (I_s \cdot \mathbf{j}_i^s) - R_i^s + \mathbf{n} \cdot [(\bar{\mathbf{v}} - \mathbf{u}) \bar{\rho}_i + \bar{\mathbf{j}}_i] = 0, \quad (3.1)$$

with the various symbols appearing herein defined as in Part I. This equation supplies the general 'jump' boundary condition relating the respective normal components  $\mathbf{n} \cdot \bar{\mathbf{j}}_{i\alpha}$  ( $\alpha = 1, 2$ ) of the macroscale species flux vector  $\bar{\mathbf{j}}_{i\alpha}$  on either side of the non-material fluid interface. In obtaining the above expression, the tangential component,  $\mathbf{v}_s$ , of the microscale velocity vector has been assumed to be a macroscale quantity (see equation (I-6.14)). Adsorbed surface-active substances will exhibit sensible values for  $\rho_i^s$  since they generally possess a relatively large volumetric number density within the interfacial transition region as compared with the bulk-fluid regions.

To apply (3.1) to any specific physical system, macroscale constitutive equations for  $R_i^s$  and  $\mathbf{j}_i^s$  are needed. Such equations can be developed from the defining relations (I-4.18) and (I-4.36) once microscale constitutive models for the comparable three-dimensional quantities  $R_i$  and  $\mathbf{j}_i$  are adopted. In addition, appropriate equilibrium isotherms relating bulk and surface-excess surfactant densities at each interfacial point  $\mathbf{x}_s$  are required. (These concomitantly jointly provide the corresponding bulk-phase partitioning relation, as in (3.16).)

In the following analysis a macroscale constitutive equation for  $\mathbf{j}_A^s$  is derived for an inert, non-reactive surfactant species A. The precursor microscale constitutive equation for  $\mathbf{j}_A$  will be assumed to possess a transversely isotropic (cf. (3.4)) Fick's law form for the ordinary diffusion contribution. In addition, a short-range conservative, microscale physicochemical 'adsorption' force is imagined to act upon the surfactant in proximity to the interface, tending to attract the surfactant to the interfacial region. Ultimately, we derive an isotropic, macroscale, interfacial Fick's law constitutive relation governing interfacial diffusion of the surfactant, together with a microscale interpretation of the (scalar) surface diffusion coefficient  $D^s$  appearing therein in terms of a quadrature of the normal-position-dependent microscale diffusivities and microscale potential energy function (cf. (3.22)).

Our analysis will focus upon the case of diffusion-controlled surfactant transport. Thus, local microscale equilibrium is assumed to exist in the vicinity of the interface, leading eventually to the deduction of a linear, macroscale, equilibrium, adsorption isotherm of the Henry's-law type (cf. (3.14)), together with a microscale interpretation of the Henry's law coefficient  $K_{Aa}$  (cf. (3.15)) appearing therein.

#### (a) *Diffusion-controlled surfactant transport*

Consider the transport of a non-reactive ( $R_A = 0$ ) surfactant species A whose microscale transport is governed by the constitutive equations given in the following three paragraphs.

The microscale constitutive equation for the 'non-convective' flux of A, namely the flux relative to the mass-average velocity  $\mathbf{v}$ , is assumed to be given by the expression†

$$\mathbf{j}_A = \mathbf{M} \cdot \mathbf{F} \rho_A - D \cdot \nabla \rho_A \quad (3.2)$$

at all points  $\mathbf{x}$  of the microfluid, including the interfacial transition region. In this equation, the first term represents the 'convective' contribution to the flux arising from the physicochemical adsorption force  $\mathbf{F}$ , whereas the second term represents the diffusive, Fick's law contribution. The diffusion dyadic  $D$  appearing therein is assumed to be related to the mobility dyadic  $\mathbf{M}$  of the surfactant species through the Stokes–Einstein relation

$$D = kTM, \quad (3.3)$$

where  $k$  is the Boltzmann constant and  $T$  the absolute temperature.

Within the interfacial transition region, the existence of short-range, anisotropic, intermolecular forces (attributable to the presence of steep mass density and/or

† This equation results from a dilute solution approximation for the usual species mass flux constitutive equation of a relatively constant density binary fluid mixture composed of respective solvent species and surfactant species (A). In addition, the microscale equations of this section are similar to those developed by Brenner & Leal (1982) using a micromechanical model, in which the surfactant molecules are considered to be solid, brownian spheres of radii much larger than the 'thickness'  $l$  of the interfacial transition region.

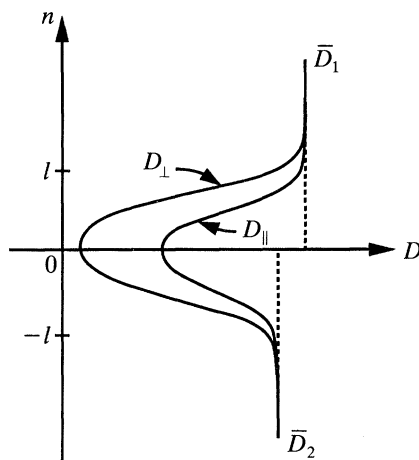


Figure 2. Variation in the normal ( $D_{\perp}$ ) and tangential ( $D_{\parallel}$ ) microscale diffusivity coefficients with respect to the normal distance  $n$  from the parent coordinate surface. This qualitative sketch displays the diffusivity minima expected to occur within the interfacial transition region,  $-l \lesssim n \lesssim l$ . Both diffusivity coefficients attain identical bulk-fluid values  $\bar{D}_1$  and  $\bar{D}_2$  at sufficiently large distances,  $n \gg l$  and  $n \ll -l$ , respectively, from the interface.

species concentration gradients in the direction normal to the macroscale interface) is assumed to endow the microscale fluid with axial symmetry about the normal vector  $\mathbf{n}$ . Thus,  $D$  is assumed to possess the transversely isotropic form

$$D(\mathbf{x}_s, n) = \ast I_s D_{\parallel}(\mathbf{x}_s, n) + \ast \mathbf{n} \ast \mathbf{n} D_{\perp}(\mathbf{x}_s, n). \quad (3.4)$$

In general,  $D_{\perp}$  and  $D_{\parallel}$ , which respectively represent the diffusivity coefficients in the normal and tangential directions, are expected to attain (positive) minimum values within the interfacial transition region due to the strong forces existing therein (figure 2). Far from the interfacial region, in the bulk-phase regions where the diffusion is assumed isotropic, both diffusivity components necessarily attain the same values, namely

$$\lim_{|\bar{n}| \rightarrow \infty} D_{\parallel}(\mathbf{x}_s, \bar{n}) = \lim_{|\bar{n}| \rightarrow \infty} D_{\perp}(\mathbf{x}_s, \bar{n}) = \bar{D}, \quad (3.5)$$

where

$$\bar{D} = \begin{cases} \bar{D}_1 & \text{for } \bar{n} > 0, \\ \bar{D}_2 & \text{for } \bar{n} < 0. \end{cases} \quad (3.6)$$

Thus, far from the interface the microscale (and macroscale) diffusivity dyadic attains the isotropic value

$$\bar{D} = I\bar{D}, \quad (3.7)$$

wherein  $\bar{D}_1$  and  $\bar{D}_2$  are macroscale phenomenological functions.

The physicochemical adsorption force  $\mathbf{F}$  acting upon the surfactant species A in proximity to the interface is assumed to be conservative, and hence expressible as

$$\mathbf{F} = -kT\nabla E \quad (3.8)$$

in terms of the dimensionless physicochemical potential energy function  $E(\mathbf{x}_s, n)$ . The main features of this force are that: (i) it is non-zero only in the interfacial transition region  $n = O(\epsilon)$  (and hence is ‘short-range’ compared with any of the more conventional ‘long-range’ external forces, whose length scale is such that they are

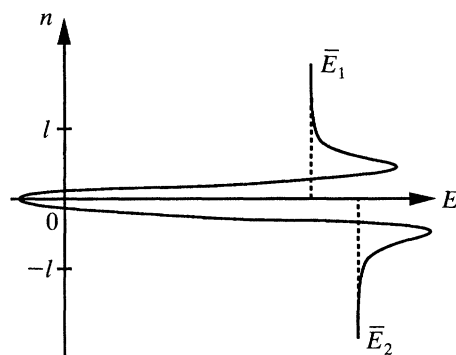


Figure 3. Variation in the (dimensionless) adsorption potential  $E$  with respect to the normal distance  $n$  from the parent coordinate surface. This qualitative sketch displays the deep potential well existing within the interfacial transition region,  $-l \lesssim n \lesssim l$ , as well as the possible energy barriers on either side of this region.

sensible in the domain  $n = O(1)$ ); (ii) it is an attractive force, tending to cause surfactant molecules to accumulate in the vicinity of the macroscale interface,  $\bar{n} = 0$ . Accordingly,  $E$  necessarily possesses a deep potential well within the interfacial transition region (figure 3). This well accounts for the strong adsorption of the surfactant at the interface and, consequently, the existence of an experimentally observable (i.e. non-vanishing) value for the surface-excess areal density  $\rho_A^s$ . Far from the interface, the adsorptive force vanishes. Thus, the potential energy function  $E$  possesses the macroscale asymptotic form

$$\bar{E} = \begin{cases} \bar{E}_1 & \text{for } \bar{n} > 0, \\ \bar{E}_2 & \text{for } \bar{n} < 0, \end{cases} \quad (3.9)$$

where  $\bar{E}_1$  and  $\bar{E}_2$  are constants, independent of  $\mathbf{x}_s$  and  $n$ .

We will suppose in what follows that within the interfacial transition region, and to terms of lowest-order in  $\epsilon$ , the microscale species mass fraction  $\tilde{\rho}_A$  can be written as the Boltzmann distribution (justification for which is provided later in this section)

$$\tilde{\rho}_A = C(\mathbf{x}_s) \exp[-\tilde{E}(\mathbf{x}_s, \tilde{n})], \quad (3.10)$$

where the normalization coefficient  $C(\mathbf{x}_s)$  is independent of  $n$ . The above expression is equivalent to assuming that the surfactant rapidly attains local thermodynamic equilibrium in the normal direction. This circumstance corresponds to the case of 'diffusion-controlled' surfactant transport, wherein surfactant molecules overcome energy barriers to adsorption at a rate that appreciably exceeds the rate of molecular diffusion towards the interface. It will also be assumed in what follows that  $E$  possesses a relatively weak dependence upon  $\mathbf{x}_s$  in comparison to  $C$ ; explicitly, we suppose that

$$C|\nabla_s E|/|\nabla_s C| \ll 1. \quad (3.11)$$

Use of the matching conditions (I-3.18), together with the outer limiting form (3.9) for  $E$ , yields

$$\lim_{\bar{n} \rightarrow 0^+} \overline{(\rho_A)_1}(\mathbf{x}_s, \bar{n}) = C(\mathbf{x}_s) \exp(-\bar{E}_1), \quad (3.12a)$$

$$\lim_{\bar{n} \rightarrow 0^-} \overline{(\rho_A)_2}(\mathbf{x}_s, \bar{n}) = C(\mathbf{x}_s) \exp(-\bar{E}_2). \quad (3.12b)$$



(Here, the relations  $\exp(a) = \overline{\exp(\tilde{a})}$  and  $\overline{\exp(a)} = \exp(\bar{a})$  have been used. Assuming that the limits  $\bar{a}$  and  $\tilde{a}$  exist, the validity of these relations can easily be proven. In particular, define  $\alpha_1 = \ln[1 + \alpha|\exp(\tilde{a})|^{-1}]$ . Then  $\alpha_1 > 0$  when  $\alpha > 0$ . Now, if  $\tilde{a}$  exists, then there must exist a positive function  $\delta > 0$ , say, such that  $|a(\epsilon) - \tilde{a}| < \alpha_1$  for all  $0 < \epsilon < \delta$ . Thus,  $|\exp[a(\epsilon)] - \exp(\tilde{a})| < \alpha$  for all  $0 < \epsilon < \delta$ , which proves the validity of the first relation. This same proof holds for the second relation as well.) The surface-excess surfactant species mass fraction  $\rho_A^s$  can now be determined. Substitution of the limiting forms (3.10) and (3.12) into the generic definition (I-4.18) (with  $\lambda \equiv \rho_A$ ) yields

$$\rho_A^s(\mathbf{x}_s) \sim \epsilon LC(\mathbf{x}_s) \int_{\tilde{n}=-\infty}^{+\infty} \{\exp[-\tilde{E}(\mathbf{x}_s, \tilde{n})] - \exp(-\bar{E})\} d\tilde{n}. \quad (3.13)$$

Comparison with (3.12) thereby provides the linear, Henry's law, constitutive adsorption isotherm

$$\bar{\rho}_{A\alpha} = K_{A\alpha} \rho_A^s \quad (\alpha = 1, 2), \quad (3.14)$$

in which

$$K_{A\alpha} \stackrel{\text{def}}{=} \exp(-\bar{E}_\alpha) / \epsilon L \int_{\tilde{n}=-\infty}^{+\infty} [\exp(-\tilde{E}) - \exp(-\bar{E})] d\tilde{n} \quad (3.15)$$

is the linear (equilibrium) adsorption coefficient based upon the  $\alpha$ -phase. Furthermore, upon division of (3.12a) by (3.12b), we obtain the bulk-phase linear partition constitutive relation

$$\bar{\rho}_{A1}(0+) = K \bar{\rho}_{A2}(0-), \quad (3.16)$$

with

$$K \stackrel{\text{def}}{=} \exp(\bar{E}_2 - \bar{E}_1) \quad (3.17)$$

the bulk-phase partition coefficient.

The appropriate form of the interfacial constitutive equation for the surface-excess mass flux  $\mathbf{j}_A^s$  can be established via (I-4.36) from the preceding microscale model of the surfactant system as follows. Substitute (3.8) into (3.2), thereby obtaining

$$\mathbf{j}_A = -\mathbf{D} \cdot (\rho_A \nabla E + \nabla \rho_A). \quad (3.18)$$

Form the inner limit (I-3.7) of the above equation, and simplify the resulting expression using the product identity (I-3.16), together with the Boltzmann relation (3.10) and the inequality (3.11), to obtain

$$\tilde{\mathbf{j}}_A = -\tilde{\mathbf{D}} \cdot (\nabla C) \exp(-\tilde{E}). \quad (3.19)$$

Similarly, application of the outer limiting operations (I-3.11), subsequent simplification of the resulting expressions using (I-3.15) and (3.12), and eventual formation of the limits  $\bar{n} \rightarrow 0 \pm$  produces the relations

$$\lim_{\bar{n} \rightarrow 0+} \overline{(\mathbf{j}_A)_1} = - \left( \lim_{\bar{n} \rightarrow 0+} \bar{\mathbf{D}}_1 \right) \cdot (\nabla C) \exp(-\bar{E}_1), \quad (3.20a)$$

$$\lim_{\bar{n} \rightarrow 0-} \overline{(\mathbf{j}_A)_2} = - \left( \lim_{\bar{n} \rightarrow 0-} \bar{\mathbf{D}}_2 \right) \cdot (\nabla C) \exp(-\bar{E}_2). \quad (3.20b)$$

Substitute the limiting forms (3.19) and (3.20) into the integral microscale formulation (I-4.36) (with  $\boldsymbol{\varphi} \equiv \mathbf{j}_A$ ), and subsequently simplify the resulting expression using the order-of-magnitude scaling relation (3.11). This yields the interfacial fickian diffusion formula

$$\mathbf{j}_A^s = -D^s \nabla_s \rho_A^s, \quad (3.21)$$

as the appropriate constitutive equation for the surface-excess diffusive mass flux vector for the surfactant species A. In this equation, the scalar

$$D^s(\mathbf{x}_s) = \frac{\int_{\tilde{n}=-\infty}^{+\infty} \{\tilde{D}_{\parallel}(\mathbf{x}_s, \tilde{n}) \exp[-\tilde{E}(\mathbf{x}_s, \tilde{n})] - \bar{D}(\mathbf{x}_s, 0) \exp(-\bar{E})\} d\tilde{n}}{\int_{\tilde{n}=-\infty}^{+\infty} \{\exp[-\tilde{E}(\mathbf{x}_s, \tilde{n})] - \exp(-\bar{E})\} d\tilde{n}} \quad (3.22)$$

is the interfacial diffusion coefficient.

Substitute the constitutive relation (3.21) for  $\mathbf{j}_A^s$  into the interfacial conservation equation (3.1) to obtain

$$\frac{\delta_s \rho_A^s}{\delta t} + (\mathbf{v} - \mathbf{u}) \cdot \nabla_s \rho_A^s + \{\nabla_s \cdot [\mathbf{v}_s(\mathbf{x}_s, 0) + \mathbf{n}\mathbf{n} \cdot \mathbf{u}]\} \rho_A^s - \nabla_s \cdot (D^s \nabla_s \rho_A^s) + \mathbf{n} \cdot [(\bar{\mathbf{v}} - \mathbf{u}) \bar{\rho}_A - \bar{D} \nabla \bar{\rho}_A] = 0. \quad (3.23)$$

This expression supplies one of the two jump boundary conditions imposed upon the bulk-species flux across the macroscale interface. All of the surface-excess quantities appearing in (3.23) are now completely defined.

(b) *Validity of the local equilibrium assumption*

The microscale surfactant transport conservation equation (cf. the generic equation (I-5.5)) may be expressed in terms of the surface-fixed coordinate system of Part I as

$$\frac{\delta \rho_A}{\delta t} + (\mathbf{v} - \mathbf{u}) \cdot \nabla \rho_A + (\nabla \cdot \mathbf{v}) \rho_A + \nabla \cdot \mathbf{j}_A = 0. \quad (3.24)$$

Separation of the gradient operator into its normal and tangential components yields

$$\frac{1}{\epsilon L} \left[ (\mathbf{v} - \mathbf{u}) \cdot \mathbf{n} \frac{\partial \rho_A}{\partial \tilde{n}} + \mathbf{n} \cdot \left( \frac{\partial \mathbf{v}}{\partial \tilde{n}} \right) \rho_A + \mathbf{n} \cdot \frac{\partial \mathbf{j}_A}{\partial \tilde{n}} \right] + \left[ \frac{d\rho_A}{dt} + (\mathbf{v} - \mathbf{u}) \cdot \nabla_s \rho_A + (\nabla_s \cdot \mathbf{v}) \rho_A + \nabla_s \cdot \mathbf{j}_A \right] = 0. \quad (3.25)$$

Upon assuming that all terms appearing in the second bracket are of  $O(1)$ , and subsequently applying the scaling relations (I-6.7) for  $\mathbf{u}$  and  $\mathbf{n}$ , the above expression becomes

$$\frac{\partial}{\partial \tilde{n}} [(\mathbf{v} - \mathbf{u}) \cdot \mathbf{n} \rho_A + \mathbf{n} \cdot \mathbf{j}_A] = O(\epsilon). \quad (3.26)$$

Substitution of (3.4) and (3.18) into (3.26) thus yields the expression

$$-\frac{D_{\perp}}{\epsilon L} \left( \frac{\partial \rho_A}{\partial \tilde{n}} + \rho_A \frac{\partial E}{\partial \tilde{n}} \right) + \rho_A (\mathbf{v} - \mathbf{u}) \cdot \mathbf{n} = f(\mathbf{x}_s), \quad (3.27)$$

valid within the interfacial transition region. Here, the scalar function  $f(\mathbf{x}_s)$ , which represents the lowest-order contribution to the normal mass flux of species A across the interface, is independent of  $n$ . If A is the only species being transported across the interface, this function will be given by the expression

$$f = \rho(\mathbf{v} - \mathbf{u}) \cdot \mathbf{n} \quad (3.28)$$

within the interfacial region. (Recall that the mass conservation relation (I-6.9) assures that  $f$  is independent of  $n$ .) Examination of the lowest-order terms appearing in (3.27) yields the expression

$$\left(\frac{\partial \rho_A}{\partial \tilde{n}} + \rho_A \frac{\partial E}{\partial \tilde{n}}\right) = O(\epsilon), \quad (3.29)$$

valid within the interfacial region,  $n = O(\epsilon)$ . Since,  $\rho_A = \tilde{\rho}_A + O(\epsilon)$  in this ‘inner’ region, upon integration (3.29) confirms the Boltzmann form (3.10) for  $\tilde{\rho}_A$  used in deriving the interfacial Fick’s law relation (3.21).

### (c) Discussion

The utility of a rational method (such as our asymptotic scheme) for deriving macroscale interfacial constitutive relations from the underlying microscale equations may be explicitly illustrated by examining alternate constitutive forms suggested in the literature for the surface-excess mass flux  $\mathbf{j}_A^s$ . In particular, upon applying macroscale ‘rational’ continuum-mechanical arguments to interfacial systems, Slattery (1980, 1990) proposed the expression

$$\mathbf{j}_A^s = -\rho^s D^s \nabla_s \omega_A^s \quad (3.30)$$

as a possible constitutive relation for the interfacial species mass flux. Equation (3.30) is obviously inappropriate; for, if the density is invariant across the interfacial region (and hence  $\rho^s = 0$ ), the constitutive equation (3.30) predicts that  $\mathbf{j}_A^s \equiv \mathbf{0}$ . In contrast, the prediction of our theory is that

$$\mathbf{j}_A^s = -\rho D^s \nabla_s \omega_A^s \quad (3.31)$$

for a homogeneous density system. (Here, we have supposed  $\omega_A^s$  to be defined by (I-4.18) (with  $\lambda \equiv \omega_A$ ), despite the fact that  $\omega_A = \rho_A/\rho$  is not a volumetric density.)

A major factor in the breakdown of analogies between volumetric and surface-excess densities,  $\rho_i$  and  $\rho_i^s$ , respectively, is that whereas the three-dimensional mass fractions  $w_i = \rho_i/\rho$  exist, the comparable mass fractions  $w_i^s = \rho_i^s/\rho^s$  may not exist (cf. (I-7.3)) and, even if they did, they would not be identical with the quantity  $\omega_i^s$  defined above. The difficulty with Slattery’s (1980, 1990) approach to interfacial transport processes via his pursuit of analogies with comparable three-dimensional transport phenomena stems from his failure to clearly distinguish between surface and surface-excess densities.

Our theory can easily be modified to include systems for which the length scales characterizing changes in  $D$  and  $E$  (in the normal direction) are distinctly different, yet are still of microscale dimensions. In particular, define  $l_D$  and  $l_E$  to be the respective characteristic normal distances over which variations in the surfactant diffusion coefficient and potential energy function occur. For these distances satisfying the inequality  $|n|/l_D \gg 1$ , the effect of the interface on  $D$  may thus be regarded as negligible, whereas for distances  $|n|/l_E \gg 1$  the adsorptive forces may be assumed to vanish. Since both  $l_D$  and  $l_E$  are each assumed to be of microscale dimensions, the relations  $l_D/l \leq O(1)$  and  $l_E/l \leq O(1)$  will both hold. Thus, the bulk-fluid forms (3.7) and (3.9), and consequently the resulting constitutive relation (3.21) and adsorption isotherm (3.14) (together with the definitions (3.13), (3.22) and (3.15)), remain applicable in the altered circumstances of this paragraph.

The quantitative choice of microscale parameter  $l$  appearing in our asymptotic

theory will depend upon the relative magnitudes of the two length scales  $l_D$  and  $l_E$ . In particular,  $l$  necessarily corresponds to the *largest microscale dimension* of the system. Three separate order-of-magnitude relations between the two parameters  $l_D$  and  $l_E$  are possible: (i)  $l_D/l_E \equiv O(1)$ ; (ii)  $l_D/l_E \ll O(1)$ ; and (iii)  $l_D/l_E \gg O(1)$ . Although the results given here are applicable to all three situations, a further perturbation expansion (Brenner & Leal 1982) about the additional small parameter can be used to simplify the equations for cases (ii) and (iii).

G. M. M. and H. B. are grateful to the U.S. Army Research Office and the Office of Basic Energy Sciences of the Department of Energy for their support of this work. D. A. E. and L. T. acknowledge the active encouragement and support of Professor Darsh T. Wasan of the Illinois Institute of Technology through his grant from the Department of Energy.

## References

- Adler, P. M., Nadim, A. & Brenner, H. 1990 Rheological models of suspensions. *Adv. Chem. Engng* **15**, 1–72.
- Bird, R. B., Stewart, W. E. & Lightfoot, E. N. 1960 *Transport phenomena*. Wiley.
- Boussinesq, J. 1913 Sur l'existence d'une viscosité superficielle, dans la mince couche de transition séparant un liquide d'un autre fluide contigu. *C. r. hebd. seanc. Acad. Sci., Paris* **156**, 983–989.
- Brenner, H. 1979 A micromechanical derivation of the differential equations of interfacial statics. *J. Colloid Interface Sci.* **68**, 422–439.
- Brenner, H. & Leal, L. G. 1977 A model of surface diffusion on solids. *J. Colloid Interface Sci.* **62**, 238–258.
- Brenner, H. & Leal, L. G. 1978*a* A micromechanical derivation of Fick's law for interfacial diffusion of surfactant molecules. *J. Colloid Interface Sci.* **65**, 191–209.
- Brenner, H. & Leal, L. G. 1978*b* Interfacial resistance to interphase mass transfer in quiescent two-phase systems. *A.I.Ch.E. JI* **24**, 246–254.
- Brenner, H. & Leal, L. G. 1982 Conservation and constitutive equations for adsorbed species undergoing surface diffusion and convection at a fluid-fluid interface. *J. Colloid Interface Sci.* **88**, 136–184.
- Buff, F. P. 1955 Spherical interface. II. Molecular theory. *J. chem. Phys.* **23**, 419–427.
- Davis, H. T. 1987 Kinetic theory of flow in strongly inhomogeneous fluids. *Chem. Engng Commun.* **58**, 413–430.
- Davis, H. T. & Scriven, L. E. 1982 Stress and structure in fluid interfaces. *Adv. Chem. Phys.* **49**, 357–454.
- Deemer, A. R. & Slattery, J. C. 1978 Balance equations and structural models for phase interfaces. *Int. J. Multiphase Flow* **4**, 171–192.
- Defay, R., Prigogine, I., Bellemans, A. & Everett, D. H. 1966 *Surface tension and adsorption*. Longmans.
- Einstein, A. 1905 Die von der molekularkinetischen Theorie der warme geforderte bewegung von in ruhenden flussigkeiten suspendierker teilchen. *Ann. Phys.* **17**, 549–560.
- Einstein, A. 1956 *Investigations on the theory of the Brownian movement*, p. 54. Dover.
- Eliassen, J. D. 1963 Interfacial mechanics. Ph.D. dissertation. University of Minnesota, Minneapolis, Minnesota, U.S.A.
- Evans, R. 1979 The nature of the liquid-vapor interface and other topics in the statistical mechanics of non-uniform, classical fluids. *Adv. Phys.* **28**, 143–200.
- Goodrich, F. C. 1981*a* Surface viscosity as a capillary excess transport property. In *The modern theory of capillarity* (ed. F. C. Goodrich & A. I. Rusanov). Akademie-Verlag.
- Goodrich, F. C. 1981*b* The theory of capillary excess viscosities. *Proc. R. Soc. Lond. A* **374**, 341–370.
- Gurtin, M. E. 1989 On a nonequilibrium thermodynamics of capillarity and phase. *Q. appl. Math.* **47**, 129–145.

- Gurtin, M. E. & Matano, H. 1988 On the structure of equilibrium phase transitions within the gradient theory of fluids. *Q. appl. Math.* **46**, 301–317.
- Hill, T. L. 1959 Exact definition of quasi-thermodynamic point functions in statistical mechanics. *J. chem. Phys.* **30**, 1521–1523.
- Irving, J. H. & Kirkwood, J. G. 1950 The statistical mechanical theory of transport processes: IV. The equations of hydrodynamics. *J. chem. Phys.* **18**, 817–829.
- Jiang, T.-S., Chen, J.-D. & Slattery, J. C. 1983 Nonlinear interfacial stress-deformation behavior measured with several interfacial viscometers. *J. Colloid Interface Sci.* **96**, 7–19.
- Kirkwood, J. G. & Buff, F. P. 1949 The statistical mechanical theory of surface tension. *J. chem. Phys.* **17**, 338–343.
- Lindsay, K. A. & Straughan, B. 1979 A thermodynamic viscous interface theory and associated stability problems. *Arch. ration. Mech. Analysis* **71**, 307–326.
- Lovett, R., DeHaven, P. W., Viecelli, J. J. & Buff, F. P. 1972 Generalized van der Waals theories for surface tension and interfacial width. *J. chem. Phys.* **58**, 1880–1885.
- Moeckel, G. P. 1975 Thermodynamics of an interface. *Arch. ration. Mech. Analysis* **57**, 255–280.
- Ono, S. & Kondo, S. 1960 Molecular theory of surface tension in liquids. *Handbuch Physik* **10**, 134–280.
- Ronis, D. & Oppenheim, I. 1983 On the derivation of dynamical equations for a system with an interface. II. The gas–liquid interface. *Physica A* **117**, 317–354.
- Ronis, D., Bedeaux, D. & Oppenheim, I. 1978 On the derivation of dynamical equations for a system with an interface. I. General theory. *Physica A* **90**, 487–506.
- Rowlinson, J. S. & Widom, B. 1982 *Molecular theory of capillarity*. Clarendon Press.
- Scriven, L. E. 1960 Dynamics of a fluid interface. Equation of motion for Newtonian surface fluids. *Chem. Engng Sci.* **12**, 98–108.
- Slattery, J. C. 1967*a* General balance equation for a phase interface. *I.E.C. Fundam.* **6**, 108–115.
- Slattery, J. C. 1967*b* Correction. General balance equations for a phase interface. *I.E.C. Fundam.* **7**, 672.
- Slattery, J. C. 1980 Interfacial transport phenomena. *Chem. Engng Commun.* **4**, 149–166.
- Slattery, J. C. 1990 *Interfacial transport phenomena*, pp. 679, 690, 824. Springer-Verlag.
- Slattery, J. C. & Ramamohan, T. R. 1984 A simple surface material. *Chem. Engng Commun.* **26**, 193–218.
- Stokes, V. K. 1984 *Theory of fluids with microstructure*. Springer-Verlag.
- Ting, L., Wasan, D. T., Miyano, K. & Xu, S. Q. 1984 Longitudinal surface waves for the study of dynamic properties of surfactant systems. II. Air–solution interface. *J. Colloid Interface Sci.* **102**, 248–259.
- Ting, L., Wasan, D. T. & Miyano, K. 1985 Longitudinal surface waves for the study of dynamic properties of surfactant systems. III. Liquid–liquid interface. *J. Colloid Interface Sci.* **107**, 345–354.
- van der Waals, J. D. & Kohnstamm, P. 1908 *Lehrbuch der thermodynamik*, vol. I. Mass and van Suchtelen.
- Wasan, D. T., Gupta, L. & Vora, M. K. 1971 Interfacial shear viscosity and fluid–fluid interfaces. *A.I.Ch.E. JI* **17**, 1287–1295.
- Waxman, A. M. 1984 Dynamics of a couple-stress fluid membrane. *Stud. appl. Math.* **70**, 63–86.

*Received 15 October 1991; revised 23 December 1992; accepted 26 February 1993*