ON A CALCULUS OF DISCONTINUOUS FUNCTIONS USED IN INTERFACIAL FLOW MODELING

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Abstract. A calculus of discontinuous functions employed in recent models of interfacial flow phenomena is examined. It is found that this calculus is not the calculus of distribution theory as the models suppose. Misapplication of the calculus leads to an incorrect formulation of the energy conservation equation, the entropy production rate and the phenomenological laws at the interface. The appropriate calculus is derived from first principles and applied to the interfacial flow model. The resulting phenomenological laws at the interface are more physically reasonable than those given in the existing models.

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1. Introduction. Modeling fluid flow at an interface between two phases has always been difficult due to the discontinuity in fluid properties across the interface, invalidating the continuum hypothesis and prohibiting the use of ordinary calculus. Recent models of interfacial flow near a moving liquid/liquid/solid contact line using a calculus of discontinuous functions have been developed by Shikhmurzaev, [5,6,7] with considerable success. However some aspects of the models are unsatisfactory, and a detailed examination of the calculus employed is required to understand the source of the problem.

One approach to modeling the interface between two fluids is to idealise the interface as a surface with no thickness. Considered in isolation such a surface would again fulfil the criteria of the continuum hypothesis and the usual fluid dynamic balance equations could be applied, using the calculus appropriate to the surface (a 2-dimensional manifold, evolving in time). However in reality the interface cannot be considered in isolation. It interacts with the adjacent bulk phases (3-dimensional manifolds, evolving in time) in which a different calculus is appropriate. What is required, therefore, is a calculus which can be applied to this piecewise continuum model of the system.

Shikhmurzaev, [5] employs such a calculus with reference to Bedeaux *et al.*, [2]. The resulting balance equations for the interface seem reasonable for the most part, however the laws describing transport phenomena across the interface suggest that each bulk phase has an equal influence upon the interface, irrespective of the difference in their fluid properties. In fact Bedeaux *et al.* assert that they are free to choose the tangential component of the surface velocity as they wish and select the average of the tangential velocities of the adjacent bulk phases.

In this paper the nature of the discontinuous calculus introduced by Bedeaux *et al.* and employed in the moving contact line models of Shikhmurzaev is examined. It is found not to be generalised calculus or distribution theory as supposed, however when applied correctly it is the right calculus for the application as it preserves the conservation laws across interfaces. Unfortunately the phenomenological laws in the existing models arise from equations which have been manipulated using the product rule of ordinary calculus. This rule does not take its usual form in the discontinuous calculus in question and consequently the phenomenological laws derived in the existing models are incorrect. The correct forms of the phenomenological laws are derived, and found to be more physically reasonable. Another consequence of the rigorous

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application of the calculus is an additional term in the energy conservation equation arising from the discontinuity in the kinetic energy across interfaces.

2. Calculus employed in the existing models. To illustrate the approach of the existing models we consider two fluids occupying regions R_1 and R_2, separated by an interfacial phase occupying the smooth surface R_{12}. The density at any point is described by

$$\rho = \rho_1\delta_1 + \rho_2\delta_2 + \rho_{12}\delta_{12} \tag{1}$$

where δ_1 and δ_2 are the characteristic (Heavyside) functions of R_1 and R_2 respectively, δ_{12} is the δ-function of the surface R_{12} in the sense of generalised calculus, and ρ_i is smooth in R_i, with continuous extension to the boundary of R_i. Note that the apparent dimensional inconsistency of combining two volume densities with a surface density disappears when it is realised that ρ is to be interpreted as a *generalised function* or *distribution*, [4]. That is, ρ acts upon the test function ϕ via

$$< \rho, \phi >= \int_{R_1} \rho_1\phi dV + \int_{R_2} \rho_2\phi dV + \int_{R_{12}} \rho_{12}\phi dS. \tag{2}$$

Note that if δ_{12} is considered as the characteristic function of the surface R_{12} then ρ has a representation as a piecewise continuous function. This is a modification of the usual representation of regular generalised functions.

Now the calculus of generalised functions or distributions is well known, and could be applied to the usual balance equations of fluid mechanics where fluid properties are now expressed as generalised functions. The models proceed along these lines, proposing the calculus:

$$\begin{gathered}
\nabla\delta_1 = -\mathbf{n}_1\delta_{12} \quad \nabla\delta_2 = -\mathbf{n}_2\delta_{12} \quad \nabla\delta_{12} = 0 \\
\frac{\partial\delta_1}{\partial t} = \mathbf{v}\cdot\mathbf{n}_1\delta_{12} \quad \frac{\partial\delta_2}{\partial t} = \mathbf{v}\cdot\mathbf{n}_2\delta_{12} \quad \frac{\partial\delta_{12}}{\partial t} = 0 \\
\frac{d\delta_1}{dt} = 0 \quad \frac{d\delta_2}{dt} = 0 \quad \frac{d\delta_{12}}{dt} = 0
\end{gathered} \tag{3}$$

where $\mathbf{n}_i$ is the unit outward normal of R_i, $\mathbf{v}$ is the fluid velocity, and a limited form of the product rule is assumed to apply —

$$\begin{aligned}
\nabla(\rho_i\delta_i) &= (\nabla\rho_i)\delta_i + \rho_i(\nabla\delta_i) \\
\frac{\partial}{\partial t}(\rho_i\delta_i) &= \frac{\partial\rho_i}{\partial t}\delta_i + \rho_i\frac{\partial\delta_i}{\partial t}
\end{aligned} \tag{4}$$

There are a number of difficulties with this calculus. It is not clear what the spatial derivative should mean for a function ρ_{12} defined only at the surface, nor what the partial time derivative should mean for such a function if the surface is moving. These questions will be resolved. More fundamentally, it is not clear that generalised calculus is the correct calculus to preserve the physical meaning of the balance equations — in fact it is not. Moreover the proposed calculus is *not* generalised calculus. Bedeaux *et al.* state that "*Quantities which are only defined on the surface ... vary along the surface, but not normal to it. The normal derivatives of these quantities are therefore*

zero". This is certainly the case for the calculus which they have adopted, however it is not true of generalised calculus. Applying the definition of differentiation in generalised calculus results in

$$< \nabla\delta_{12}, \phi >= - < \delta_{12}, \nabla\phi >= - \int_{R_{12}} \nabla\phi dS \tag{5}$$

and there is no reason to suppose this is zero for an arbitrary test function ϕ as suggested by the calculus used in the models.

3. Development of the calculus. Since the calculus employed by the existing models is not generalised calculus, but nonetheless appears to be the appropriate calculus for the interfacial flow model when applied correctly, its justification must be sort elsewhere. In fact the calculus is part of the more general theory of de Rham currents, however we give an elementary derivation of the calculus which shows it to be a natural generalisation of the usual definition of differentiation.

Consider a multiphase system in which Phase i occupies a region $R_i \subset \mathbf{R}^3 \times \mathbf{R}$, where R_i is an open submanifold of $\mathbf{R}^3 \times \mathbf{R}$ with piecewise smooth boundary Γ_i. The multiphase system decomposes $\mathbf{R}^3 \times \mathbf{R}$ into a partition of such regions R_i. Within each such region the fluid properties can be described in the usual way — ρ_i, $\mathbf{v}_i$ etc. — where each is a bounded, smoothly varying function. As such they have a continuous extension to Γ_i, which we denote — $\bar{\rho}_i$, $\bar{\mathbf{v}}_i$, and so forth. The fluid properties fall naturally into two categories — those which are expressed as densities, describing extensive properties of the system; and those which are not, describing intensive properties of the system. The (mass) density is the archetypical example of the former, and velocity an example of the latter. It is with densities that we are initially concerned. For such a fluid property f the notation of the existing models is maintained

$$f = \sum_i f_i \delta_i \tag{6}$$

however rather than acting as a generalised function on the space of test functions, f now operates directly on *volume elements* V (simply-connected, non-empty, open subsets of $\mathbf{R}^3$ with piecewise smooth boundary), via

$$f(V,t) = \sum_i (f_i\delta_i)(V,t) \equiv \sum_i \int_{V\cap R_i} f_i(\mathbf{r},t) dR_i(t). \tag{7}$$

For example, the density ρ of the system is a function acting on volume elements, returning the total mass within the volume element at any time. Once again if the δ_i are thought of as characteristic functions of the region R_i then f has a representation as a piecewise continuous function. It would be possible to extend the domain of f to measurable sets, and then f is simply a measure on $\mathbf{R}^3$, evolving in time. However, in order to define the calculus the more restricted class of sets is required.

For the purpose of defining the calculus it suffices to consider a single region R with boundary Γ_R (possibly empty). As a smooth submanifold, R has its own differential operator, D_R. Let $f_R : R \to \mathbf{R}$ be smooth and bounded on R and $\bar{f}_R : \Gamma_R \to \mathbf{R}$ be the continuous extension of f_R to the boundary. The calculus of $f = f_R\delta_R$ must be related to the calculus of f_R as a function on R. Letting R_t be the cross-section of R at time t, then for a volume element V at time t we have

$$f(V,t) = \int_{V\cap R_t} f_R dR_t. \tag{8}$$

The derivative of f at (V,t) in the direction $(\mathbf{u},s)$ can be defined in the obvious way

$$\lim_{h\to 0}\frac{f(V+h\mathbf{u},t+hs)-f(V,t)}{h}. \tag{9}$$

However f has a convenient representation as a piecewise continuous function, and it is desirable to find the equivalent representation for its derivative. Once again the idea is natural, the derivative at a point is found by taking the limit as the set V shrinks conformally. Thus we define the differential operator D acting on $f = f_R\delta_R$ at the point $(\mathbf{r},t)$ in the direction $(\mathbf{u},s)$ by

$$(\mathbf{u},s)\cdot(Df)(\mathbf{r},t) = \lim_{\epsilon\to 0}\frac{1}{|V_\epsilon\cap\overline{R}_t|}\lim_{h\to 0}\frac{f(V_\epsilon+h\mathbf{u},t+hs)-f(V_\epsilon,t)}{h} \tag{10}$$

where $V_\epsilon = \mathbf{r}+\epsilon B$ for some fluid element B containing the origin; and the notation $|V_\epsilon\cap\overline{R}_t|$ is used to denote

$$\int_{V_\epsilon\cap R_t} dR_t + \int_{V_\epsilon\cap\Gamma_{R_t}} d\Gamma_{R_t}. \tag{11}$$

This definition is converted into a usable calculus through Stokes' Theorem. Consider the set $\cup_{\lambda\in[0,h]}(V_\epsilon+\lambda\mathbf{u},t+\lambda s)\cap\overline{R}$. This set is bounded by

$$\begin{aligned} S_1 &= (V_\epsilon+h\mathbf{u},t+hs)\cap R \\ S_2 &= (V_\epsilon,t)\cap R \\ S_3 &= !(\Gamma_{V_\epsilon}+\lambda\mathbf{u},t+\lambda s)\cap\overline{R} \quad \text{for } \lambda\in[0,h]. \end{aligned} \tag{12}$$

The integrals over S_1 and S_2 appear in the definition, and can be related to the differential operator on R through Stokes' Theorem. We arrive at

$$(Df)(\mathbf{r},t) = \lim_{\epsilon\to 0}\frac{1}{|V_\epsilon\cap\overline{R}_t|}\left(\int_{V_\epsilon\cap R_t} D_R f_R dR_t - \int_{V_\epsilon\cap\Gamma_{R_t}} \bar{f}_R\cdot(\mathbf{n}_R,-\mathbf{v}_{\Gamma_R}\cdot\mathbf{n}_R)d\Gamma_{R_t}\right) \tag{13}$$

where $\mathbf{n}_R$ is the unit outward normal to Γ_{R_t} and $\mathbf{v}_{\Gamma_R}$ is the velocity of the boundary of R. There are now three cases to consider.

Case 1: $\mathbf{r}\in R_t$ — In this case, for sufficiently small epsilon, $V_\epsilon\cap\Gamma_{R_t}$ is empty, and so $Df = (D_R f_R)\delta_R$.

Case 2: $\mathbf{r}\notin\overline{R}_t$ — Then for sufficiently small ϵ the domains of both integrals are empty, and $Df = 0$.

Case 3: $\mathbf{r}\in\Gamma_{R_t}$ — It is important at this point that the set B is fixed, so that V_ϵ shrinks conformally to $\mathbf{r}$. Because of this $|V_\epsilon\cap\overline{R}_t|\to|V_\epsilon\cap\Gamma_{R_t}|$, and likewise the second integral dominates the first. Therefore $Df = -\bar{f}_R(\mathbf{n}_R,-\mathbf{v}_{\Gamma_R}\cdot\mathbf{n}_R)\delta_{\Gamma_R}$. This result may be expressed as

$$D(f_R\delta_R) = (D_R f_R)\delta_R + \bar{f}_R D\delta_R. \tag{14}$$

It is important to note that some of the operations of standard calculus no longer take the same form in this calculus of discontinous functions. In particular the product rule changes, and the failure to appreciation this leads the existing models astray. One

difficulty is that the calculus has so far only been defined for extensive fluid properties, however if we make the natural definition for intensive fluid properties a usable form of the product rule emerges. Thus if $f = \sum f_i \delta_i$ is an extensive property, and $g = \sum g_i$ is an intensive property, then the derivatives of f and g are defined by

$$\begin{aligned} Df &= \sum (D_i f_i)\delta_i + \bar{f}_i D\delta_i \\ Dg &= \sum D_i g_i. \end{aligned} \tag{15}$$

It follows simply that the product rule in this calculus takes the form

$$D(fg) = fDg + gDf + \sum \bar{f}_i(\bar{g}_i - g_{\Gamma_i})D\delta_i \tag{16}$$

which collapses to the usual product rule if and only if g is continuous.

For applications in fluid mechanics it would be helpful to extract the derivatives which are familiar from the conservation equations — the spatial derivative, the temporal derivative and derivative following the motion. The spatial and temporal derivatives come directly as the directional derivatives in the directions $(\mathbf{u}, 0)$ and $(\mathbf{0}, 1)$ respectively; thus

$$(\mathbf{u}, s) \cdot Df = \mathbf{u} \cdot \nabla f + s\frac{\partial f}{\partial t}. \tag{17}$$

The derivative following the motion is the rate of change as seen by an observer who is traveling with the velocity of the flow; that is,

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \tag{18}$$

just as it is in standard calculus.

It is instructive to consider the physical interpretation of the partial time derivative. Note that

$$\frac{\partial f}{\partial t} = (\mathbf{0}, 1) \cdot Df = (\mathbf{v}_R^{\perp} + \mathbf{v}_{\Gamma_R}, 1) \cdot Df \tag{19}$$

where $\mathbf{v}_R^{\perp}$ is the component of the velocity of R which is perpendicular to R. That is, $\mathbf{v}_R^{\perp} + \mathbf{v}_{\Gamma_R}$ is the evolution velocity of the manifold R and its boundary Γ_R. Therefore the partial time derivative is the *derivative following the motion of the manifold.* This is distinct from the derivative following the motion of the fluid, which includes motion tangent to the manifold as well as normal to it. Of course within a bulk phase all directions are tangent to the manifold, and none are normal, so the partial time derivative is the rate of change as we remain motionless.

4. Piecewise continuum form of the balance equations. For completeness we state the form of all the balance equations, although the mass and momentum balances do not differ from those given by Shikhmurzaev, [5].

Mass conservation (equation of continuity)
The usual continuum model for mass conservation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \tag{20}$$

extends to the piecewise continuum model

$$\sum_i \left(\frac{\partial_i \rho_i}{\partial t} + \nabla_i \cdot (\rho_i \mathbf{v}_i) - \bar{\rho}_i (\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i}) \cdot \mathbf{n}_i \delta_{\Gamma_i} \right) = 0. \tag{21}$$

Momentum conservation (force balance)
The usual momentum balance

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v}\mathbf{v}) - \rho \mathbf{F} - \nabla \cdot \sigma = 0 \tag{22}$$

becomes

$$\sum_i \left(\frac{\partial_i}{\partial t}(\rho_i \mathbf{v}_i) + \nabla_i \cdot (\rho_i \mathbf{v}_i \mathbf{v}_i) - \rho_i \mathbf{F}_i - \nabla_i \cdot \sigma_i \right) \delta_i - \sum_i \left(\bar{\rho}_i \bar{\mathbf{v}}_i (\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i}) \cdot \mathbf{n}_i + \bar{\sigma}_i \cdot \mathbf{n}_i \right) \delta_{\Gamma_i} = 0 \tag{23}$$

where $\mathbf{F}$ is the body force and σ the stress tensor.

Conservation of energy
Letting e be the total energy per unit volume and u be the internal energy per unit volume, then [3]

$$e = \rho \left(\frac{1}{2} \mathbf{v}.\mathbf{v} + \psi \right) + u. \tag{24}$$

That is, total energy comprises kinetic, potential and internal energy. Conservation of energy requires that

$$\frac{\partial e}{\partial t} + \nabla \cdot \mathbf{J}_e = 0 \tag{25}$$

where $\mathbf{J}_e$ is the total energy flux. This energy flux can be decomposed into mechanical work, a convection term and a heat flux, [3] — thus

$$\mathbf{J}_e = -\sigma \cdot \mathbf{v} + e\mathbf{v} + \mathbf{J}_q. \tag{26}$$

The energy conservation equation then becomes

$$\left(\frac{\partial (\frac{1}{2}\rho \mathbf{v} \cdot \mathbf{v})}{\partial t} + \nabla \cdot ((\frac{1}{2}\rho \mathbf{v} \cdot \mathbf{v})\mathbf{v}) \right) + \left(\frac{\partial (\rho \psi)}{\partial t} + \nabla \cdot (\rho \psi \mathbf{v}) \right) +$$

$$\left(\frac{\partial u}{\partial t} + \nabla \cdot (u\mathbf{v}) \right) - \nabla \cdot (\sigma \cdot \mathbf{v}) + \nabla \cdot \mathbf{J}_q = 0. \tag{27}$$

Under normal circumstances the body forces are due to gravity, so that $\mathbf{F} = -\nabla \psi$, where ψ is smooth and independent of time. Because ψ is continuous the product rule takes its usual form, and

$$\frac{\partial (\rho \psi)}{\partial t} + \nabla \cdot (\rho \psi \mathbf{v}) = \psi \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right) + \rho \frac{\partial \psi}{\partial t} + \rho \mathbf{v} \cdot \nabla \psi = -\rho \mathbf{F} \cdot \mathbf{v} \tag{28}$$

using continuity and the fact that ψ is independent of time. Using the momentum balance equation (22), the energy balance now takes the form

$$\left(\frac{\partial u}{\partial t} + \nabla \cdot (u\mathbf{v})\right) + \left((\nabla \cdot \sigma) \cdot \mathbf{v} - \nabla \cdot (\sigma \cdot \mathbf{v})\right) + \nabla \cdot \mathbf{J}_q +$$

$$\left(\frac{\partial}{\partial t}\left(\frac{1}{2}\rho\mathbf{v} \cdot \mathbf{v}\right) + \nabla \cdot \left(\frac{1}{2}\rho\mathbf{v} \cdot \mathbf{v}\right)\mathbf{v}\right) - \mathbf{v} \cdot \left(\frac{\partial}{\partial t}(\rho\mathbf{v}) + \nabla \cdot (\rho\mathbf{v}\mathbf{v})\right) = 0. \tag{29}$$

The final two terms cancel in standard calculus (modulo the continuity equation) and so are ignored in the existing models, but this is not the case in our piecewise continuum calculus. Using the generalised product rule

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho\mathbf{v} \cdot \mathbf{v}\right) - \mathbf{v}\frac{\partial}{\partial t}(\rho\mathbf{v}) = -\frac{1}{2}\mathbf{v}\frac{\partial}{\partial t}(\rho\mathbf{v}) + \frac{1}{2}\rho\mathbf{v}\frac{\partial \mathbf{v}}{\partial t} + \sum \frac{1}{2}\bar{\rho}_i\bar{\mathbf{v}}_i(\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i})\frac{\partial \delta_i}{\partial t}. \tag{30}$$

Again employing this rule we find

$$\rho\frac{\partial \mathbf{v}}{\partial t} = \frac{\partial}{\partial t}(\rho\mathbf{v}) - \mathbf{v}\frac{\partial \rho}{\partial t} - \sum \bar{\rho}_i(\mathbf{v}_i - \mathbf{v}_{\Gamma_i})\frac{\partial \delta_i}{\partial t}. \tag{31}$$

Substituting into the above gives

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho\mathbf{v} \cdot \mathbf{v}\right) - \mathbf{v}\frac{\partial}{\partial t}(\rho\mathbf{v}) = -\frac{1}{2}\mathbf{v}^2\frac{\partial \rho}{\partial t} + \sum \frac{1}{2}\bar{\rho}_i(\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i})^2\frac{\partial \delta_i}{\partial t}. \tag{32}$$

A similar calculation results in

$$\nabla \cdot \left(\left(\frac{1}{2}\rho\mathbf{v}^2\right)\mathbf{v}\right) - \mathbf{v} \cdot \nabla \cdot (\rho\mathbf{v}\mathbf{v}) = -\frac{1}{2}\mathbf{v}^2\nabla \cdot (\rho\mathbf{v}) + \sum \frac{1}{2}\bar{\rho}_i\bar{\mathbf{v}}_i(\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i})^2\nabla\delta_i. \tag{33}$$

It can then be seen that the contribution from these terms is

$$\sum_i -\frac{1}{2}\bar{\rho}_i(\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i})^2(\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i}) \cdot \mathbf{n}_i\delta_{\Gamma_i} \tag{34}$$

which is zero if and only if the normal components of the velocities are continuous across the boundary.

Entropy balance

Letting s be the entropy per unit volume and $\mathbf{J}_s$ be the non-convective entropy flux [de Groot and Mazur], the entropy product rate $\tilde{\sigma}$ is given by

$$\tilde{\sigma} = \frac{\partial s}{\partial t} + \nabla \cdot (s\mathbf{v} + \mathbf{J}_s) \tag{35}$$

or

$$\sum_i \tilde{\sigma}_i\delta_i = \sum_i \left(\frac{\partial_i s_i}{\partial t} + \nabla_i \cdot (s_i\mathbf{v}_i + (\mathbf{J}_s)_i)\right)\delta_i - \left((\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i}) - (\bar{\mathbf{J}}_s)_i\right) \cdot \mathbf{n}_i\delta_{\Gamma_i}. \tag{36}$$

Equation of state (Gibbs' relation)

$$u = Ts + \mu\rho - p_e \tag{37}$$

where T is temperature, μ is chemical potential and p_e the thermodynamic (equilibrium) pressure.

5. Phenomenological laws at an interface. The basic postulate of non-equilibrium thermodynamics is that a state of local equilibrium exists as we follow the flow. As pointed out by de Groot and Mazur, "*The hypothesis of local equilibrium can, from a macroscopic point of view, only be justified by virtue of the validity of the conclusions derived from it*". The local equilibrium assumption seems as likely to be valid in a piecewise continuum setting as it is in a continuum model. If we apply this to the Gibbs' relation, noting $\mathbf{J}_s = \mathbf{J}_q/T$, and further simplify under the assumption of isothermal conditions, the entropy production rate becomes

$$\begin{aligned} T\tilde{\sigma} = & \Big(\nabla\cdot(\sigma\cdot\mathbf{v}) - \mathbf{v}\cdot\nabla\cdot\sigma\Big) + \Big(\nabla\cdot(p_e\mathbf{v}) - \mathbf{v}\cdot\nabla p_e\Big) + \\ & \mu\Big(\nabla\cdot(\rho\mathbf{v}) - \mathbf{v}\cdot\nabla\rho\Big) - \Big(\nabla\cdot(\mu\rho\mathbf{v}) - \mathbf{v}\cdot\nabla\mu\rho\Big) + \\ & \sum_i \frac{1}{2}\bar{\rho}_i(\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i})^2(\bar{\mathbf{v}}_i - \mathbf{v}_{\Gamma_i})\cdot\mathbf{n}_i\delta_{\Gamma_i}. \end{aligned} \tag{38}$$

Concentrating attention on the surface entropy rate production we find

$$\begin{aligned} T\tilde{\sigma}_{12} = & \Big(\sigma_{12} + p_{e12}\mathbf{I}\Big) : \nabla\mathbf{v}_{12} - \\ & \mathbf{n}_1\cdot(\bar{\sigma}_1 + \bar{p}_{e1}\mathbf{I})\cdot(\bar{\mathbf{v}}_1 - \mathbf{v}_{12}) - \mathbf{n}_2\cdot(\bar{\sigma}_2 + \bar{p}_{e2}\mathbf{I})\cdot(\bar{\mathbf{v}}_2 - \mathbf{v}_{12}) + \\ & \bar{\rho}_1(\bar{\mu}_1 - \mu_{12})(\bar{\mathbf{v}}_1 - \mathbf{v}_{12})\cdot\mathbf{n}_1 + \frac{1}{2}\bar{\rho}_1(\bar{\mathbf{v}}_1 - \mathbf{v}_{12})^2(\bar{\mathbf{v}}_1 - \mathbf{v}_{12})\cdot\mathbf{n}_1 + \\ & \bar{\rho}_2(\bar{\mu}_2 - \mu_{12})(\bar{\mathbf{v}}_2 - \mathbf{v}_{12})\cdot\mathbf{n}_2 + \frac{1}{2}\bar{\rho}_2(\bar{\mathbf{v}}_2 - \mathbf{v}_{12})^2(\bar{\mathbf{v}}_2 - \mathbf{v}_{12})\cdot\mathbf{n}_2. \end{aligned} \tag{39}$$

Proceeding in the usual fashion, [3,8] we derive the linear phenomenological laws for the interface. Under the assumption of isotropic fluid phases entropy production contributions of different tensorial orders cannot couple, and in any case we are going to ignore any cross-coefficients between tensors of the same order since they are likely to be small in comparison with the principle effects, [5].

The first driving force to be considered is the velocity gradient within the interface. An order two tensor splits into a scalar trace, an antisymmetric and a trace-free symmetric part. The antisymmetric part is zero because the stress tensor is symmetric. Therefore

$$\sigma_{12} = (\eta_{v12}\nabla\cdot\mathbf{v}_{12} - p_{e12})(\mathbf{I}-\mathbf{nn}) + 2\eta_{12}(\mathbf{I}-\mathbf{nn})((\nabla\mathbf{v})^{sym} - \frac{1}{3}(\nabla\cdot\mathbf{v}_{12})\mathbf{I})(\mathbf{I}-\mathbf{nn}) \tag{40}$$

where η_{v12} and η_{12} are the surface 'bulk' and shear viscosities respectively.

The other driving force is the velocity discontinuity across the interface. This splits into normal and tangential components. From the tangential components we get

$$
\begin{aligned}
-\mathbf{n}_1 \cdot (\bar{\sigma}_1 + \bar{p}_{e1}\mathbf{I})(\mathbf{I} - \mathbf{nn}) &= \beta_1(\mathbf{I} - \mathbf{nn})(\bar{\mathbf{v}}_1 - \mathbf{v}_{12}) \\
-\mathbf{n}_2 \cdot (\bar{\sigma}_2 + \bar{p}_{e2}\mathbf{I})(\mathbf{I} - \mathbf{nn}) &= \beta_2(\mathbf{I} - \mathbf{nn})(\bar{\mathbf{v}}_2 - \mathbf{v}_{12})
\end{aligned}
\tag{41}
$$

where β_1 and β_2 are frictional coefficients between the interface and the respective bulk phases.

The normal components of the velocity discontinuity across the interface appear in several terms. Thus

$$
\begin{aligned}
(\bar{\mathbf{v}}_1 - \mathbf{v}_{12}) \cdot \mathbf{n}_1 &= k_1\Big(- \mathbf{n}_1 \cdot (\bar{\sigma}_1 + \bar{p}_{e1}\mathbf{I}) \cdot \mathbf{n}_1 + \bar{\rho}_1(\bar{\mu}_1 - \mu_{12}) + \tfrac{1}{2}\bar{\rho}_1(\bar{\mathbf{v}}_1 - \mathbf{v}_{12})^2\Big) \\
(\bar{\mathbf{v}}_2 - \mathbf{v}_{12}) \cdot \mathbf{n}_2 &= k_2\Big(- \mathbf{n}_2 \cdot (\bar{\sigma}_2 + \bar{p}_{e2}\mathbf{I}) \cdot \mathbf{n}_2 + \bar{\rho}_2(\bar{\mu}_2 - \mu_{12}) + \tfrac{1}{2}\bar{\rho}_2(\bar{\mathbf{v}}_2 - \mathbf{v}_{12})^2\Big)
\end{aligned}
\tag{42}
$$

where k_1 and k_2 are mass transfer coefficients between the surface and the respective bulk phases. Note the driving force for mass transfer has three components — mechanical, chemical and kinetic.

6. Comparison with existing models. The entropy production equation used by Shikhmurzaev, [5] is significantly different from that found above, and consequently the phenomenological laws across the interface take a different form. The exception is the law describing the surface stress tensor which agrees with that given by Shikhmurzaev, [5] since it does not involve discontinuous phenomena across phases. Of the other laws, consider firstly the frictional law describing tangential momentum transport across the interface. Shikhmurzaev arrives at

$$
-\frac{1}{2}\mathbf{n} \cdot (\bar{\sigma}_1 + \bar{\sigma}_2) \cdot (\mathbf{I} - \mathbf{nn}) = \beta(\mathbf{I} - \mathbf{nn}) \cdot (\bar{\mathbf{v}}_1 - \bar{\mathbf{v}}_2). \tag{43}
$$

That is, the friction is proportional to the velocity difference between the two bulk phases, and does not depend at all upon the velocity of the intervening surface phase. This is unreasonable since the two bulk phases are not in contact with each other, but can only interact indirectly via the interposing surface phase. The pair of frictional laws given in § 5 above, in which a frictional force exists between each bulk phase and the interface — proportional to the velocity difference between them — is far more realistic.

It is also claimed that the interfacial velocity is defined by

$$
(\mathbf{I} - \mathbf{nn}) \cdot \mathbf{v}_{12} = \frac{1}{2}(\mathbf{I} - \mathbf{nn}) \cdot (\bar{\mathbf{v}}_1 + \bar{\mathbf{v}}_2) - \alpha\nabla \cdot \sigma_{12}. \tag{44}
$$

Here we see the notion that in the absence of a pressure gradient in the surface, the (tangential) surface velocity must be the average of the (tangential) velocities in the adjacent bulk phases. This too is unreasonable. If one phase is a gas, and the other a liquid, it suggests that they equally influence the velocity of the surface. In any case how can such a phenomenological law define the surface velocity without reference to the continuity equation or the momentum/force balance?

Finally the existing model follows the example of Bedeaux *et al.*, [2] in neglecting kinetic energy at the surface because "*there is no surface mass density*". This is despite the fact that the surface mass is considered significant in the continuity and

momentum equations. As a consequence the existing model completely misses the kinetic energy component to the driving force for mass transfer across the interface. Now it may well be the case that the kinetic terms are negligible in comparison with the other terms in most scenarios; however this is not obvious *a priori*, and they must at least be considered before being discounted.

7. Conclusion. In recent models of interfacial flow phenomena [5,6,7] the interfaces are treated as surfaces of zero thickness, and fluid properties then have a representation as piecewise continuous functions. The calculus employed in these models did not correspond to that of distribution theory as suggested, but was related to the calculus of de Rham currents. An elementary derivation of the calculus was given which demonstrates that it is a natural generalisation of the usual definition of the derivative, and that it is the appropriate calculus for the application. However the product rule of standard calculus does not take its usual form in this setting, and its use in the existing models introduced some errors. A new form of the energy balance equation was derived, including extra kinetic terms only present in a discontinuous model. The resulting entropy production equation and phenomenological laws at the interface took new forms, which were found to be more physically reasonable than those of the existing models.

REFERENCES

[1] Batchelor G. K., *Introduction to Fluid Dynamics*, Cambridge University Press. 1967

[2] Bedeaux D., Albano A. M. and Mazur P., Boundary conditions and non-equilibrium thermodynamics, *Physica* **A82**, 1976, 438-462.

[3] de Groot S. R. and Mazur P., *Non-equilibrium thermodynamics*, North-Holland, 1961.

[4] Gel'fand I. M. and Shilov G. E., *Generalized functions, Vol 1*, Academic Press, 1964.

[5] Shikhmurzaev Y. D., The moving contact line on a smooth solid surface, *Int. J. Multiphase Flow* **19**, 1993, 589-610.

[6] Shikhmurzaev Y. D., Mathematical modeling of wetting hydrodynamics, *Fluid Dynamics Research*, **13**, 1994 45-64.

[7] Shikhmurzaev Y. D., Moving contact lines in liquid/liquid/solid systems, *J. Fluid Mech.*, **334**, 1997 211-249.

[8] Woods L. C., *The thermodynamics of fluid systems*, Clarendon Press, 1975.