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THE TWO-PHASE INTERFACE IN A SIMPLE ONE-COMPONENT FLUID

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ABSTRACT

A continuum model of an interface in a one-component fluid is developed in the special case when the fundamental equation of the fluid may be written in the local form

$$F = \hat{F}(\theta, \rho, (\nabla\rho)^2, \nabla^2\rho) .$$

The fluid governed by this equation is shown to behave as a classical fluid when the density is nearly uniform, but has properties associated with interfacial behavior when the local variation of density is large. The material near a two-phase interface in such a fluid is subject to a complex system of multipolar stresses. However, the thermodynamic behavior of the fluid near the interface is governed by the familiar relation

$$\rho F = \mu\rho - P$$

where P may be regarded as a thermodynamic pressure. Gibbs' thermodynamics of surfaces follows naturally for an interface in this fluid when the Gibbs construction is used. The relation of this model to prior continuum and statistical models of the fluid interface is discussed.

1. INTRODUCTION

As has long been realized, the interfaces separating fluid phases in contact are not strict physical discontinuities. They are rather thin transition shells across which material properties and thermodynamic densities vary from the values appropriate to one phase to those appropriate to the other. The properties of the material located within the transition shell are of great interest since these properties determine interfacial behavior.

The finite thickness of the interfacial shell is explicitly recognized in the classical equilibrium thermodynamics of surfaces developed by J. W. Gibbs (1879). Gibbs avoided the difficulty of specifying local behavior within the interfacial shell in a simple formal way. Gibbs defined a geometrical "dividing surface" lying in or near the interface and placed so as to pass through "points which are similarly situated with respect to the condition of the adjacent matter". He imagined that the homogeneous phases to either side of the interface extended up to this dividing surface. He then forced this hypothetical two-dimensional interface to have a thermodynamic content duplicating that of the actual transition shell by attributing "surface excess" quantities of energy ($\epsilon^{(s)}$), entropy ($\eta^{(s)}$), and mass ($m^{(s)}$) to the dividing surface.

Gibbs argued that the increment to surface excess energy due to an infinitesimal change in the states of the adjacent phases together with an infinitesimal variation in the form of the dividing surface will satisfy the inequality (presume a one-component system).

$$\delta \epsilon^{(s)} \geq \theta \delta \eta^{(s)} + \mu \delta m^{(s)} + \sigma \delta S + C \delta \bar{K} \quad (1.1)$$

In this equation S is the area of the element of dividing surface to which $\epsilon^{(S)}$ refers, $\bar{K}$ is its mean curvature, and θ , μ , σ and C are multipliers. The variation is taken from a state of equilibrium. The inequality (1.1) becomes an equality if the varied state is also of equilibrium. Gibbs full thermodynamics of surfaces at equilibrium follows as a consequence of this relation. In particular, the fundamental equation of the surface may be written

$$F^{(S)} = \epsilon^{(S)} - \theta \eta^{(S)} = \mu m^{(S)} + \sigma s \quad (1.2)$$

where $F^{(S)}$ is the surface excess of the Helmholtz free energy.

While the value of Gibbs' thermodynamics of surfaces is well known his approach avoids a number of relevant problems, including the following. (a) The relation between interfacial and bulk properties is left unknown; the properties of the interface cannot be predicted from a knowledge of the properties of the adjacent phases. (b) The parameters θ , μ , σ and C are defined only as multipliers in the variational form (1.1). Using the conditions of thermal and chemical equilibrium Gibbs was able to show the identity of θ and μ with the temperature and chemical potential of the adjacent phases. The "surface tension" σ and the coefficient C are presumably mechanical parameters, but it is not obvious how these parameters relate to the mechanics of the material actually contained within the interfacial shell. (c) It is not at all clear how the thermodynamics of surfaces can be extended to consider non-equilibrium states. The solution of these problems requires a theory of the material within the interfacial shell.

A number of theoretical models have been proposed to treat the interfacial shell. The most general of these are based on the continuum

theory. The most widely used are the mechanical model of the interface suggested by Young (1805) and developed recently by Buff (1951, 1955, 1956) and the thermodynamic model of the continuous interface developed by Van der Waals (Van der Waals 1894; Bakker 1928) and by Cahn and Hilliard (Cahn and Hilliard 1958, 1959; Cahn 1959, 1961, 1962).

The mechanical model used by Young and by Buff provides an interpretation of the surface tension based on a classical continuum mechanics. The approach is implicit in the original work of Young (1805). It is assumed that a classical (second-order tensor) stress may be defined at any point within a two-phase fluid. Within the homogeneous phases the stress reduces to a hydrostatic pressure. Within the interfacial shell the stress is assumed given by

$$\underline{t} = \sigma_N (\underline{e}_3 \underline{e}_3) + \sigma_T (\underline{e}_1 \underline{e}_1 + \underline{e}_2 \underline{e}_2) \quad (1.3)$$

where $\underline{e}_3$ is a unit vector normal to the dividing surface and $\underline{e}_1$ and $\underline{e}_2$ are unit vectors in a plane parallel to the dividing surface. The thermodynamic surface tension (σ) is then identified as the surface excess ($\sigma_T^{(s)}$) of the tangential stress σ_T . When the interface is plane this treatment gives

$$\sigma = \sigma_T^{(s)} = \int_{-\infty}^{\infty} (\sigma_T + P) dx_3 \quad (1.4)$$

where x_3 is the coordinate along the normal vector $\underline{e}_3$, equal to zero at the dividing surface, and P is the pressure of the fluid phases, equal since the interface is plane.

Buff (1955, 1956) employed this mechanical model in studies of curved interfaces in the presence of external force fields. Buff recognized, however, that the identification $\sigma = \sigma_T^{(s)}$ might fail for non-simple

interfaces.

A thermodynamic model of the interface was also well developed before 1900, due principally to the work of Van der Waals and his students. In this model it is assumed that fluid density varies continuously across a two-phase interface in a one-component fluid and that a local Helmholtz free energy density (free energy per unit mass) (f) may be defined at any point within the two-phase fluid. On the presumption that the free energy of a fluid element embedded in a density gradient will be influenced by the gradient, f is assumed given by the expansion

$$f = f(\theta, \rho) + K_1(\theta, \rho) (\nabla \rho)^2 + K_2(\theta, \rho) (\nabla^2 \rho) + \dots \quad (1.5)$$

In the expansion the temperature θ , density ρ , and density gradients $\nabla \rho$ and $\nabla^2 \rho$ are evaluated at the point of which f refers. If the expansion for f is truncated at the terms shown in equation (1.6), the density is assumed to vary only along the normal to the dividing surface, and the surface tension (σ) is identified with the surface excess of the thermodynamic density

$$\Omega = f - \mu, \quad (1.6)$$

the surface tension of a plane interface is

$$\sigma = \int_{-\infty}^{\infty} K(\theta, \rho) (d\rho/dx_3)^2 dx_3 \quad (1.7)$$

This model was independently constructed and developed by Cahn and Hilliard, and is referred to as the Van der Waals-Cahn-Hilliard (VCH) model in the following.

It is by no means obvious that the Young-Buff and VCH models of the continuous interface are compatible with one another. Recent results in theoretical mechanics (Green and Rivlin, 1964) argue strongly that a

fluid whose local free energy depends explicitly on gradients of the density will behave as a multipolar continuum; such a fluid can be in mechanical equilibrium in the presence of density gradients only if it is acted on by "multipolar" stresses of tensor order greater than two (e.g., the third order stress with components t_{kmp}) in addition to a classical second-order stress. Hence a continuous interface in a fluid of the VCH type may be subject to stresses other than the simple classical stress apparently assumed by Young and by Buff. On the other hand, both the Young-Buff and the VCH models have been obtained from molecular treatments of the interface in simple fluids.

Molecular models have been applied to the interface in a one-component fluid having pairwise particle interactions. In early work Kirkwood and Buff (1949) and Buff (1955) obtained an expression for the surface tension of a simple fluid interface in the absence of external fields. They found a statistical expression for the tangential stress σ_T appearing in the Young-Buff continuum model. Stillinger and Buff (1962) later studied the statistical mechanics of a simple fluid in the presence of external forces. They demonstrated the existence of a statistical parameter $\hat{p}$ which functions as a local pressure within regions of the fluid where the gradients of density are appreciable. They then derived an expression for the surface tension of a simple fluid which identifies σ as the negative of the surface excess of this local "pressure" $\hat{p}$. Stillinger and Buff further showed that if the free energy of the simple fluid is written as an integral over the volume and if the kernel of this integral is regarded as the local free energy f , then f may be expanded in local gradients of the mass density ρ . The lead terms in this expansion are

formally identical to the corresponding terms of the VCH expansion (equation 1.5). These results have been confirmed through an alternate derivation by Lebowitz and Percus (1963).

The results of these molecular treatments indicate that the Young-Buff and VCH continuum models are at least not wholly incompatible. These results also suggest the possibility of a more fundamental continuum model which is based on, or leads to a continuum parameter analogous to the statistical pressure $\hat{p}$.

Recently one of us, Morris (1972), has reexamined the fluid interface from the point of view of the continuum theory. That study resulted in a rather general model of the fluid interface which includes the VCH model as a special case. It was shown that while, in agreement with the modern continuum theory, the material within the interfacial shell supports a system of multipolar stresses, the interface as a whole behaves with the mechanical simplicity implied by Gibb's variational form. Moreover, the surface tension σ is associated with the surface excess of a generalized pressure P which appears to be the continuum analogue of the statistical parameter $\hat{p}$. In the present paper we develop that model for fluid interfaces of the general type considered by Van der Waals and by Cahn and Hilliard, and emphasize points of contact with the molecular theory of simple fluids and with the alternate continuum model used by Young and by Buff.

2. FORMULATION OF A FUNDAMENTAL EQUATION

We specifically consider the equilibrium behavior of a one-component fluid. The fluid is assumed both physically and thermodynamically continuous.

In classical thermodynamics it is assumed that a local free energy density may be defined within homogeneous parts of such a fluid. When the fluid is in thermodynamic equilibrium this free energy is given by a "fundamental equation"

$$f = \hat{f}(\theta, \rho) \quad (2.1)$$

where f is free energy per unit mass and θ and ρ are the values of temperature and density at the point to which f refers. The functional form of $\hat{f}$ is specific to the chemical component composing the fluid.

Extrapolating this result, we presume that local free energy density may also be defined within parts of the fluid where density gradients exist at equilibrium, for example, within the interfacial shell, and that this free energy is given by a fundamental equation which generalizes equation 2.1. To be consistent with the known thermodynamics of fluids this fundamental equation must lead to material behavior compatible with the laws of thermodynamics, must predict a non-zero interfacial tension, and must naturally reduce to the classical form, equation 2.1, when the fluid density is uniform. A plausible fundamental equation which satisfies these constraints may be constructed in the following way.

Assume a configuration of the fluid, which may consist of two homogeneous phases separated by an interface. Let a system of material coordinates $\{X^\alpha\}$ be laid down over this reference configuration. Then the elements of continuum "particles" of the fluid may be named by their positions X in this coordinate net, and retain this name through all continuous deformations of the fluid. We concentrate on an arbitrary particle X_0 in the interior of the fluid and make three physical assumptions.

(1) The mass density $\rho(\underline{x})$ and the temperature θ are defined for all particles $\underline{x}$ in the fluid. $\rho(\underline{x})$ is a scalar field continuous and differentiable to whatever order is required. θ is assumed constant (it may be shown (Morris, 1972) that θ must be constant at equilibrium).

(2) The temperature θ and the scalar field $\rho(\underline{x})$ determine the thermodynamic state of the fluid; in particular, they determine the free energy density of the element $\underline{x}_0$ of the fluid. Hence there exists a scalar-valued functional $\hat{F}$ such that

$$f(\underline{x}_0) = \hat{F} \{ \theta, \rho(\underline{x}) \} \quad (2.2)$$

Equation 2.2 is the fundamental equation of the fluid. It is assumed continuous in the parameter θ and the function $\rho(\underline{x})$ to whatever order is required.

Equation 2.2 is adopted by assumption in the present treatment. However, Stillinger and Buff (1962) have shown that an equation of this form results from the molecular model in the specific case of a fluid whose molecules interact in pairs.

(3) The relation 2.2 is assumed to reflect the limited range of atomic interaction. Thus the free energy density $f(\underline{x}_0)$ is influenced only by the density of elements $\underline{x}$ within a small neighborhood $N(\underline{x}_0)$ of $\underline{x}_0$. This assumption may also be given a quantitative meaning in statistical theories of simple fluids, as Lebowitz and Percus (1961) have shown.

Assumption (1) has the consequence that the density $\rho(\underline{x})$ of a particle $\underline{x}$ in $N(\underline{x}_0)$ may be expanded in a Taylor series about $\underline{x}_0$ to give

$$\rho(\underline{x}) = \rho(\underline{x}_0) + \nabla \rho \cdot (\underline{x} - \underline{x}_0) + 1/2 \nabla \nabla \rho : (\underline{x} - \underline{x}_0) (\underline{x} - \underline{x}_0) + \dots \quad (2.3)$$

If this result is substituted in equation 2.2 the functional $\hat{F}$ may be

rewritten as a scalar-valued tensor function of θ , $\rho(X_0)$ and the gradients of ρ at X_0 :

$$f(X_0) = \hat{f}(\theta, \rho, \nabla\rho, \nabla\nabla\rho, \dots) \quad (2.4)$$

The assumed continuity of $\hat{F}$ in its arguments θ and $\rho(X)$ implies continuity of $\hat{f}$ in θ , ρ , and the gradients of ρ .

When the density does not vary sharply near X_0 we may use the assumed small size of $N(X_0)$ to argue that the series 2.3 may be truncated after the low order terms. f then depends explicitly only on the first few gradients of the density. However, it is known empirically that very rapid density variations may occur near a two-phase fluid interfaces, since the region influenced by the interface may be only a few atom diameters in thickness. An early termination of the series 2.3 is questionable in this case. In the interest of mathematical simplicity, however, we here assume that only the first two gradients of ρ need explicitly appear in the fundamental equation. The influence of higher order gradients is considered elsewhere (Morris, 1972).

The fundamental equation of the fluid may now be written

$$F = \hat{f}(\theta, \rho, \nabla\rho, \nabla\nabla\rho). \quad (2.5)$$

The explicit retention of the first two gradients of ρ in this equation is not arbitrary. As we shall see below there are plausible cases in which the correction to f due to the second gradient $\nabla\nabla\rho$ is of the same order as that due to the first gradient; hence the second gradient cannot be ignored if the first is included. If both gradients are neglected $\hat{f}$ is reduced to $\hat{f}(\theta, \rho)$, the fundamental equation of a classical fluid. We shall show in the following that the fundamental equation $\hat{f}(\theta, \rho)$

leads to the empirically unacceptable result that the surface tension of a plane fluid interface is zero.

The form of the function $\hat{f}$ is constrained by the requirement that it lead to fluid behavior consistent with the presumed isotropic symmetry of the fluid. If the fluid is isotropic then the value of the free energy density near any interior point must be insensitive to the orientation of the gradients $\nabla\rho$ and $\nabla\nabla\rho$ with respect to fixed material coordinates. This constraint has the consequence that $\hat{f}$ can depend explicitly only on scalar invariants of the tensor variables $\nabla\rho$, $\nabla\nabla\rho$, and their products. The independent invariants are: the inner product of the vector $\nabla\rho$, $(\nabla\rho)^2$; the three invariants of the second order tensor $\nabla\nabla\rho$: $\text{tr}(\nabla\nabla\rho) = \nabla^2\rho$, $\text{tr}(\nabla\nabla\rho)^2$, and $\text{tr}(\nabla\nabla\rho)^3$; and the scalar product $\nabla\rho \cdot \nabla\nabla\rho \cdot \nabla\rho$. In the interest of mathematical simplicity we shall assume the function $\hat{f}$ is dominated by terms in $(\nabla\rho)^2$ and $\nabla^2\rho$ and ignore its dependence on the higher order invariants. With this simplification the fundamental equation takes the final form

$$f(X_0) = \hat{f}(\theta, \rho, (\nabla\rho)^2, \nabla^2\rho) \quad (2.6)$$

In the discussion leading to equation 2.6 the fluid was referred to material coordinates $\{X^\alpha\}$ and the gradients were computed with respect to these coordinates. However, the function $\hat{f}$ in the equation 2.6 is a scalar function depending only on tensor invariants. The function $\hat{f}$ has the same form whether the fluid is referred to material coordinates $\{X^\alpha\}$ or to coordinates $\{x^k\}$ fixed in space. In particular, the fluid may be described by a system of cartesian coordinates fixed in space. In the following cartesian coordinates will be assumed unless otherwise stated and tensor components will be written in cartesian tensor notation when

convenient.

Since x_0 is an arbitrary point in the fluid the fundamental equation 2.7 is assumed to govern every part of the fluid, including homogeneous phases. One may easily show that this assumption is compatible with the classical thermodynamics of homogeneous fluids. More specifically the fundamental equation 2.6 reduces to the VCH form (equation 1.6) and finally to the fundamental equation of a homogeneous fluid (equation 2.1) as the density becomes more nearly uniform. A simple demonstration in the case of a unidirectional density variation has been suggested by Cahn and Hilliard (1971). In the context of this model the argument is as follows.

Let the density field near a point x_0 in the fluid be given by an equation of the form

$$\rho(x) = \rho(x_0) + A\hat{g}(\beta \cdot (x - x_0)) \quad , \quad (2.7)$$

where the function g and its derivatives are well behaved near zero and $\hat{g}$ increases from zero to one as $\beta \cdot (x - x_0)$ increases from zero to some large number. Then a density variation near x_0 may be "turned on" by increasing the magnitude (β) of β at fixed A , and may be turned off by letting β approach zero. When β is small one may form a Taylor expansion for f about a state of uniform density. The result is

$$f = \hat{f}(\theta, \rho) + (\partial \hat{f} / \partial (\nabla \rho)^2)_0 (\nabla \rho)^2 + (\partial \hat{f} / \partial \nabla^2 \rho)_0 \nabla^2 \rho + O(\beta^4), \quad (2.8)$$

reproducing the VCH formula to within terms of order β^4 . As β approaches zero the same expansion yields

$$f = \hat{f}(\theta, \rho) + O(\beta^2) \quad , \quad (2.9)$$

Hence the fundamental equation 2.6 reduces to the fundamental equation of

the classical homogeneous fluid to within terms of second order in the small parameter β when the density is nearly uniform. Note that both the term in $\nabla^2 \rho$ and the term in $(\nabla \rho)^2$ have order β^2 when β is small.

3. THE MECHANICS OF THE INTERFACE AT EQUILIBRIUM

An element of fluid governed by equation 2.6 is assumed to be at mechanical equilibrium under the action of a body force $\mathbf{b}$, due to gravity or other externally imposed scalar fields, and a system of stresses which account for the interaction of the element with other parts of the fluid. The body force $\mathbf{b}$ is assumed given by

$$\mathbf{b} = -\rho \nabla \phi, \quad (3.1)$$

where $\phi(\mathbf{x})$ is the potential energy per unit mass of the fluid at position $\mathbf{x}$ in the external field. In keeping with the results of earlier work a proper representation of the interaction between elements of the inhomogeneous fluid may require the use of "multipolar" stresses having tensor order greater than two, in addition to the classical second-order stress (t_{km}).

The multipolar stresses do work in an inhomogeneous deformation of the fluid. Specifically, if the material elements contained in a part B of the fluid are given displacements δx_k , where δx_k may vary from particle to particle over B, the mechanical work done on the body is

$$W = \int_B \mathbf{b}_k \delta x_k dv + \int_S (t_{km_1} \delta x_k + \dots + t_{km_1 \dots m_n} \delta x_k, m_2 \dots m_n) n_{m_1} dS \quad (3.2)$$

where the $t_{km_1 m_2}, \dots, t_{km_1 \dots m_n}$ are multipolar stresses of tensor order up to n , S is the surface of B , and $\mathbf{n}$ is the normal vector to this surface. (Here, as in the following, partial differentiation with respect to cartesian spatial coordinates is denoted by a comma and the summation

convention holds for repeated indices).

If the part B of the fluid is in an unconstrained mechanical equilibrium then the change in its total free energy during an arbitrary deformation at constant temperature cannot be less than the mechanical work done by the forces and stresses applied to it. Hence the formal condition of mechanical equilibrium is

$$\delta \left\{ \int_B \rho f \, dv \right\} = \int_B \rho \delta f \, dv \geq W \quad (3.3)$$

The variation in free energy written in equation III.3 is due to a change in the configuration of the material particles of the fluid. We wish to refer this variation to a fixed cartesian spatial frame. Using the fundamental equation (2.6) of the fluid,

$$\rho \delta f = \rho f_{\rho} \delta \rho + \rho f^{(1)}_{\rho,k} \delta(\rho_{,k}) + \rho f^{(2)}_{\rho,kk} \delta(\rho_{,kk}) \quad (3.4)$$

where

$$\begin{aligned} f_{\rho} &= \partial \hat{f} / \partial \rho \\ f^{(1)}_{\rho,k} &= 2 \partial \hat{f} / \partial (\nabla \rho)^2 \\ f^{(2)}_{\rho,kk} &= \partial \hat{f} / \partial (\nabla^2 \rho) \end{aligned} \quad (3.5)$$

and the variation is taken at constant temperature. Using the principal of mass conservation,

$$\delta \rho = -\rho \delta x_{k,k}, \quad (3.6)$$

and the tensor identities

$$\begin{aligned} \delta(\rho_{,k}) &= (\delta \rho)_{,k} - \rho_{,m} \delta x_{m,k} \\ \delta(\nabla^2 \rho) &= \delta_{km} \delta(\rho_{,km}) = \delta_{km} \{ [\delta(\rho_{,k})]_{,m} - \rho_{,kp} \delta x_{p,m} \}, \end{aligned} \quad (3.7)$$

where δ_{km} is the Kronecker delta, equation 3.4 may be written in the form

$$\rho \delta f = \tau_{km} \delta x_{k,m} + \tau_{kmp} \delta x_{k,mp} + \tau_{kmpq} \delta x_{k,mpq}, \quad (3.8)$$

where

$$\begin{aligned} \tau_{kmpq} &= -\rho^2 f^{(2)} \delta_{km} \delta_{pq} \\ \tau_{kmp} &= -\delta_{km} \{2\rho f^{(2)} \rho_{,p} + \rho^2 f^{(1)} \rho_{,p}\} - \rho f^{(2)} \rho_{,k} \delta_{mp} \\ \tau_{km} &= -\delta_{km} \{\rho^2 f_{\rho} + \rho f^{(1)} (\nabla \rho)^2 + \rho f^{(2)} \nabla^2 \rho\} \\ &\quad - \rho f^{(1)} \rho_{,k} \rho_{,m} - 2\rho f^{(2)} \rho_{,km}. \end{aligned} \quad (3.9)$$

If equation (3.8) is substituted into the integral on the left hand side of (3.3), and the result is compared with equation (3.2), one obtains the condition

$$\begin{aligned} \int_B \{ &-(b_k + t_{km,m}) \delta x_k + (\tau_{km} - t_{km} - t_{kmp,p}) \delta x_{k,m} \} \\ &+ (\tau_{kmp} - t_{kmp} - t_{kmpq,q}) \delta x_{k,mp} \\ &+ (\tau_{kmpq} - t_{kmpq} - t_{kmpqr,r}) \delta x_{k,mpq} \\ &- \dots - (t_{km_1 \dots m_n}) \delta x_{k,m_1 \dots m_n} dv \geq 0 \end{aligned} \quad (3.10)$$

If the fluid is to be in an unconstrained mechanical equilibrium the inequality 3.10 must hold for arbitrary deformations and arbitrary choices of the material element B. It is therefore necessary that the coefficient of each component of the displacement vector vanish uniformly along with the coefficient of each independently variable component of each displacement gradient tensor. The components of the displacement gradient tensors are independently variable unless they are identical by symmetry. Since the order of differentiations of δx_k is immaterial, two components $\delta x_{k,m_1 \dots m_n}$ and $\delta x_{l,r_1 \dots r_n}$ are identical if k and l are

the same and if the sequence of indices $(r_1 \dots r_n)$ is a permutation of the sequence $(m_1, \dots, m_n)$. Recognizing this symmetry, we are led to the following necessary conditions for mechanical equilibrium:

$$\begin{aligned} t_{k(m_1 \dots m_j)} &= 0 & (j > 3) \\ t_{k(mpq)} &= \tau_{k(mpq)} \\ t_{k(mp)} + t_{k(mp)q,q} &= \tau_{k(mp)} & (3.11) \\ t_{km} + t_{kmp,p} &= \tau_{km} \\ t_{km,m} + b_k &= 0 \end{aligned}$$

where the symbol $A_{k(m_1 \dots m_j)}$ represents the sum of all tensor components related through a permutation of the indices enclosed in brackets.

The last of equations 3.11 is the classical form of Cauchy's First Law. This equation remains valid within material subject to a system of multipolar stresses. It may be derived as a consequence of the requirement that the free energy of the fluid at equilibrium be invariant to rigid-body displacements (Green and Rivlin, 1964). The free energy of the fluid must also be invariant to rigid-body rotations. This condition is automatically satisfied since the tensor τ_{km} (equation 3.9) is symmetric.

Equations 3.11, taken together with equations 3.9, show that inhomogeneous parts of the fluid we are considering will be subject to a complex system of stresses, including multipolar stresses of tensor order three and four. Equations 3.11, 3.9 and 3.8 determine the work done by this system of stresses in an arbitrary deformation of the fluid. However, equations 3.11 are not sufficient to determine the stresses themselves uniquely, since only certain symmetric sums of the multipolar

stress components appear in these equations. Equations 3.11 may determine a unique stress system if they are supplemented by suitable boundary conditions; this question is under investigation. For the purposes of this paper, however, it does not matter what specific system of stresses is assumed so long as that system is consistent with the conditions of mechanical equilibrium. We therefore assume the simplest consistent system of stresses. This system is obtained by removing the parentheses in equation (3.11) to give the equalities:

$$\begin{aligned} t_{km_1 \dots m_j} &= 0 & (j > 3) \\ t_{kmpq} &= \tau_{kmpq} \\ t_{kmp} + t_{kmpq,q} &= \tau_{kmp} \end{aligned} \quad (3.11a)$$

plus the last two of equations 3.11. The solution of these equations gives the stress system:

$$\begin{aligned} t_{kmpq} &= -\rho^2 f^{(2)} \delta_{km} \delta_{pq} \\ t_{kmp} &= -\delta_{km} [\rho^2 f^{(1)} \rho_{,p} - \rho^2 f^{(2)}]_{,p} - \rho f^{(2)} \rho_{,k} \delta_{mp} \\ t_{km} &= -\delta_{km} \{ \rho^2 f \rho - \rho \nabla \cdot [\rho f^{(1)} \nabla \rho] + \rho \nabla^2 [\rho f^{(2)}] \} \\ &\quad - \rho f^{(1)} \rho_{,k} \rho_{,m} - \rho f^{(2)} \rho_{,km} + \rho_{,k} (\rho f^{(2)})_{,m} \end{aligned} \quad (3.12)$$

In parts of the fluid in which the density is uniform the second order stress tensor reduces to

$$t_{km} = -P \delta_{km} \quad (3.13)$$

where P is a hydrostatic pressure given by the classical formula

$$P = \rho^2 f \quad (3.14)$$

The third order stress t_{kmp} vanishes when the density is uniform. The fourth-order stress t_{kmpq} does not vanish within homogeneous fluid, but the arguments of the preceeding section may be used to show that the work done by this stress in an infinitesimal variation from a state of nearly uniform density is at most a second order correction to the classical work done by the hydrostatic pressure.

When the fluid element considered is taken from a region of a rapidly varying density, as from within an interfacial shell, the third order stress may be large and the fourth order stress may also have an appreciable effect. These stresses do no work in simple dilation or compression of the fluid, but rather influence deformations which alter the local variation of fluid density. These are the mechanical forces which maintain density gradients in the fluid at equilibrium.

4. THE CONDITION OF CHEMICAL EQUILIBRIUM

The results of the previous section argue that a complex system of local stresses will be operative within a continuous two-phase interface in even a rather simple one-component fluid. Despite this mechanical complexity, the free energy density at any point in the fluid may be written in the familiar form

$$f = - P/\rho + \mu , \quad (4.1)$$

where P is a thermodynamic pressure and μ an intrinsic chemical potential. We show this through a straight-forward application of the condition of chemical equilibrium used by Gibbs.

Consider an element of the fluid which may contain a portion of the interfacial shell. Let the internal state of this element be infinitesimally altered while its temperature and total mass remain constant and its

boundaries remain fixed in space. If the fluid is in thermodynamic equilibrium its total energy cannot be decreased through such a variation. Mathematically we may write

$$\delta \left\{ \int_V \rho (f + \phi) dv \right\} - \mu^* \delta \left\{ \int_V \rho dv \right\} \geq 0 \quad (4.2)$$

where μ^* is a Lagrangian multiplier, and ϕ is potential energy per unit mass.

Since the field ϕ is fixed in space, the inequality 4.2 may be rewritten:

$$\int_V \{ \rho \delta f + (f - \mu^* + \phi) \delta \rho \} dv \geq 0, \quad (4.3)$$

where the symbols δf and $\delta \rho$ indicate variations of the spatial fields $f(\mathbf{x})$ and $\rho(\mathbf{x})$. With this understanding

$$\begin{aligned} \int_V (\rho \delta f) dv &= \int_V \{ \rho f_{\rho} \delta \rho + \rho f^{(1)} \nabla_{\rho} \cdot \delta (\nabla_{\rho}) + \rho f^{(2)} \delta (\nabla_{\rho}^2) \} dv \\ &= \int_V \{ \rho f_{\rho} \delta \rho + \rho f^{(1)} \nabla_{\rho} \cdot \nabla (\delta \rho) + \rho f^{(2)} \nabla^2 (\delta \rho) \} dv \end{aligned} \quad (4.4)$$

Using partial integration with the condition that δx_k , and hence $\delta \rho$ vanishes over the boundary of the volume v , equation 4.4 can be brought into the form

$$\int_V \{ \rho \delta f \} dv = \int_V [\rho f_{\rho} - \nabla \cdot (\rho f^{(1)} \nabla_{\rho}) + \nabla^2 (\rho f^{(2)})] \delta \rho dv \quad (4.5)$$

If we define a scalar field P by the equation

$$P = \rho^2 f_{\rho} - \rho \nabla \cdot (\rho f^{(1)} \nabla_{\rho}) + \rho \nabla^2 (\rho f^{(2)}) \quad (4.6)$$

the inequality 4.3 becomes

$$\int_V [f + P/\rho - \mu^* + \phi] \delta \rho dv \geq 0 \quad (4.7)$$

This inequality is satisfied for arbitrary choices of v and $\delta \rho$ only if

$$\mu^* = f + P/\rho + \phi, \quad (4.8)$$

where μ^* is a constant. If we set

$$\mu = \mu^* - \phi \quad (4.9)$$

equation 4.10 becomes

$$f = \mu - P/\rho, \quad (4.10)$$

the form (4.1) of the fundamental equation we wished to derive.

The parameter P defined in equation 4.8 is equal to the hydrostatic pressure of the fluid ($\rho^2 f_\rho$) when the density is locally constant, and takes the place of the pressure in the fundamental equation (4.1) when the density is non-uniform. Hence the parameter P can be consistently taken as the "thermodynamic pressure" at any point in the fluid. The parameter μ defined in equation 4.9 is identical to Gibbs' "intrinsic chemical potential" when the density is locally constant, and may be consistently regarded as the intrinsic chemical potential at any material point in the fluid. A comparison of these results with the statistical thermodynamics of non-uniform simple fluids developed by Stillinger and Buff (1962) and by Lebowitz and Percus (1963) suggests the parameters μ and P are the continuum analogous of the parameters μ and $\hat{p}$ appearing in the statistical treatment.

The quantity μ^* , equal to the sum of the intrinsic chemical potential and the potential due to externally imposed fields, is constant at every point of the fluid at equilibrium. This conclusion slightly generalizes the classical result of Gibbs on the equilibrium of fluid phases in the presence of gravity. Equations 4.1 and 4.8 derived here for fluid governed by the fundamental equation $\hat{f}(\theta, \rho, (\nabla \rho)^2, \nabla^2 \rho)$, remain valid when density gradients of arbitrarily higher order are explicitly retained

in the fundamental equation. Retention of these gradients changes only the specific relation giving the thermodynamic pressure P (equation 4.9).

Finally, we note that the intrinsic potential μ may be written as the variational derivative

$$\mu = (\delta (\rho f) / \delta \rho)_\theta \quad (4.10)$$

the variation of the free energy per unit volume with respect to density at constant temperature. This variational form of Gibbs definition of the intrinsic chemical potential has been previously used by Hart (1963) and by Cahn and Hilliard (1971).

5. THE FUNDAMENTAL EQUATION OF THE SURFACE

Gibbs thermodynamics of surfaces at equilibrium may be obtained from the results of the previous section by applying Gibbs construction to the continuous interface. Consider an element of the fluid at equilibrium containing a section of the interface and portions of the homogeneous phases (α and β) to either side of it. Imagine a dividing surface sensibly parallel to the interface, and let the fluid element be such as can be generated by moving normal to the surface. The fluid element is referred to a set of spatial coordinates (x^1, x^2, x^3) such that the coordinates x^1 and x^2 are orthogonal and tangential to the dividing surface, and the coordinate x^3 is everywhere normal to the dividing surface (these coordinates are cartesian only when the surface is plane). The fluid element is bounded by upper and lower surfaces $x^3 = (h_0, -h_1)$, where h_0 and h_1 are large enough that these surfaces lie wholly within homogeneous phase, and is bounded laterally by surfaces over which x_1 and x_2 are constant.

Let the coordinate x^3 be positive on the α side of the interface. In the Gibbs construction the phase α is then imagined to extend homogeneously up to the dividing surfaces from the positive side, and the phase β is imagined to extend homogeneously to the dividing surface from the negative side.

Using equation 4.8 the total free energy contained within this fluid element is

$$\int_V \rho f \, dv = \mu^* \int_V \rho \, dv - \int_V (\rho \phi) \, dv - \int_V P \, dv \quad (5.1)$$

The differential volume dv in the coordinate system to which this fluid element is referred may be written (Morris, 1972)

$$dv = v \, dx^3 \, dS \quad (5.2)$$

In this equation dS is the differential area of the dividing surface and

$$v = 1 - \bar{K} x^3 + K (x^3)^2, \quad (5.3)$$

where $\bar{K}$ is the mean curvature of the dividing surface, and K is its Gaussian curvature. Hence

$$\int \rho f \, dv = \int_S dS \left\{ \int_{-h_1}^{h_0} \rho f \, v \, dx^3 \right\}, \quad (5.4)$$

and the integrals on the right hand side of equation 5.1 may be rewritten in similar form.

The surface excess free energy within the fluid element is defined as the total free energy less that contained in the imaginary phases α and β . Define a function $f^{\alpha\beta}$, which has the value f^α for all points located in the imaginary phase α ($x^3 > 0$) and the value f^β within the imaginary phase β ($x^3 < 0$). Let functions $\rho^{\alpha\beta}$ and $P^{\alpha\beta}$ be defined in the same way. Then the surface excess free energy, $F^{(s)}$, may be written

$$\begin{aligned}
 F(s) &= \int_S \left\{ \int_{-h_1}^{h_0} (\rho f - \rho^{\alpha\beta} f^{\alpha\beta}) v dx^3 \right\} dS \\
 &= \mu^* \int (\rho - \rho^{\alpha\beta}) dx^3 dS - \int \phi (\rho - \rho^{\alpha\beta}) v dx^3 dS \\
 &\quad - \int (P - P^{\alpha\beta}) v dx^3 dS
 \end{aligned} \tag{5.5}$$

If the interface is thin enough for the potential ϕ to be taken constant across it, and the lateral dimension of the dividing surface within this fluid element is small enough for the curvatures $\bar{K}$ and K to be assumed constant over it, equation (5.5) may be written

$$F(s) = \mu_m(s) + \sigma S \tag{5.6}$$

where

$$\mu = \mu^* - \phi$$

$$m(s) = \int_V (\rho - \rho^{\alpha\beta}) v dx^3 dS \tag{5.7}$$

$$\sigma = - \int_{-h_1}^{h_0} (P^{\alpha\beta} - P) v dx^3 \tag{5.8}$$

Equation 5.6 is identical to Gibbs fundamental equation for a one-component interface, equation 1.2, with μ the intrinsic chemical potential, $m(s)$ the surface excess mass, and σ the surface tension.

According to equation 5.8 the surface tension σ is simply the negative of the surface excess (per unit area of dividing surface) of the thermodynamic pressure P , irrespective of the complex interfacial stress system, and independent of how the density may actually vary through the interface at equilibrium. Equation 5.8 holds for rather arbitrary choices of the dividing surface. It is not strictly necessary that the dividing surface "pass through points which are similarly situated with respect

to the condition of the adjacent matter", as Gibbs prescribed.

Equation 5.8 is formally identical to the expression for the surface tension of a simple fluid derived from statistical thermodynamics by Stillinger and Buff (1962), if the thermodynamic pressure P is identified with their statistical parameter $\hat{p}$.

If the expression for the second order stress t_{km} (the last of equations 3.12) is compared with the equation 4.8 defining the thermodynamic pressure P , one finds that

$$t_{km} = -P\delta_{km} - \rho f^{(1)} \rho_{,k} \rho_{,m} - \rho f^{(2)} \rho_{,km} + \rho_{,k} (\rho f^{(2)})_{,m} \quad (5.9)$$

Hence P is the spherical part of the second order stress within the transition shell. It should be apparent from the form of equation 5.9, however, that in the most general case one cannot identify σ with the surface excess of the second order stress.

6. THE SURFACE TENSION OF A PLANE INTERFACE

To establish contact with the Young-Buff and Van der Waals-Cahn-Hilliard equations for the surface tension consider the case in which the surface is plane and the variation of density through the interfacial shell is unidirectional. If the dividing surface is chosen as a surface of constant density,

$$\rho = \rho(x^3), \quad (6.1)$$

where x^3 is the coordinate normal to the dividing surface. A discussion of the physical conditions leading to equation 6.1 is beyond the scope of this paper, but if external fields are present it is clearly necessary that the potential ϕ either be nearly constant over the interfacial shell or vary only in the direction of x^3 .

When equation 6.1 holds the components of the second order stress t_{km} within the interface are

$$\begin{aligned} t_{11} &= t_{22} = -P \\ t_{33} &= -P - \rho f^{(1)} (\rho_{,3})^2 - \rho f^{(2)} \rho_{,33} + \rho_{,3} (\rho f^{(2)})_{,3} \\ t_{12} &= t_{21} = t_{13} = t_{31} = t_{23} = t_{32} = 0 \end{aligned} \quad (6.2)$$

Hence the second order stress within the interface may be written in the Young-Buff form (equation 1.3)

$$\sigma = \sigma_T (e_1 e_1 + e_2 e_2) + \sigma_N (e_3 e_3) \quad (6.3)$$

where σ_T is the negative of the thermodynamic pressure P and the normal stress σ_N is equal to t_{33} . Using the definition (equation 5.8) of the surface tension one obtains

$$\sigma = \int_{-\infty}^{\infty} (\sigma_T + P^{\alpha\beta}) dx^3, \quad (6.4)$$

the Young-Buff equation for the surface tension of a plane interface.

The Van der Waals-Cahn-Hilliard equation for the surface tension follows under the additional assumption that the partial derivative $f^{(2)}$ may be considered a function of θ and ρ only.

Using Cauchy's First Law (equation 3.11), the definition of the body force b (equation 3.2) and using the customary symbol Γ for the surface excess mass per unit area, we obtain an equation for the field $P^{\alpha\beta}$:

$$P^{\alpha\beta}(x^3) = -t_{33}(x^3) + \int_{-h_0}^{x^3} [\rho - \rho^{\alpha\beta} - \Gamma \delta(o)] \partial \phi / \partial x^{3'} dx^{3'}, \quad (6.5)$$

where δ is the Dirac delta function. Using the relation,

$$\int_{-h_0}^{h_1} \{P - P^{\alpha\beta}\} dx^3 = \int_{-h_0}^{h_1} [P + t_{33}] dx^3 - \int_{-h_0}^{h_1} \int_{-h_0}^{x^3} [\rho - \rho^{\alpha\beta} - \Gamma \delta(o)] \partial \phi / \partial x^{3'} dx^{3'} dx^3, \quad (6.6)$$

the second integral on the right hand side of equation 6.6 is equal to

$$\int_{-h_0}^{h_1} x^3 [\rho - \rho^{\alpha\beta} - \Gamma\delta(o)] (\partial\phi/\partial x^3) dx^3 \quad (6.7)$$

This term is negligible if the interfacial shell is very thin or if ϕ is nearly constant over that portion of the interfacial shell where ρ differs significantly from $\rho^{\alpha\beta}$. In any case this term may be made to vanish by properly positioning the dividing surface. Then

$$\begin{aligned} \sigma &= \int_{-h_1}^{h_0} (t_{33} + P) dx^3 \\ &= \int_{-h_1}^{h_0} [\rho f^{(1)} (\rho_{,3})^2 + \rho f^{(2)} \rho_{,33} - \rho_{,3} (\rho f^{(2)})_{,3}] dx^3 \end{aligned} \quad (6.8)$$

where the second form of the equation is found with the help of equation 6.2. A partial integration of the first term on the right hand side of equation 6.8 gives

$$\sigma = \int_{-h_1}^{h_0} \{ [\rho f^{(1)} - 2 \frac{\partial}{\partial \rho} (\rho f^{(2)})] (\rho_{,3})^2 \} dx^3 + [\rho f^{(2)} \rho_{,3}] \int_{-h_1}^{h_0} \quad (6.6)$$

The second term on the right hand side of equation 6.9 may be neglected since the points h_0 and $-h_1$ fall well outside the transition shell. Hence

$$\sigma = \int_{-\infty}^{\infty} K' (\rho_{,3})^2 dx^3 \quad (6.10)$$

with

$$K' = [\rho f^{(1)} - 2 \frac{\partial}{\partial \rho} (\rho f^{(2)})] \quad (6.11)$$

Equation 6.10 is formally identical to the Van der Waals-Cahn-Hilliard form 1.7 (compare equation 2.9 of Cahn and Hilliard, 1958). The derivation of this equation restricts it, also, to plane interfaces.

An incidental result of equation 6.10 is that the surface tension of a plane fluid interface will vanish if the partial derivatives $f^{(1)}$ and $f^{(2)}$ vanish uniformly within the interfacial shell. Thus σ will vanish unless the local free energy density within the fluid depends explicitly on gradients of ρ . Since the surface tension of a typical real fluid does not vanish when the fluid interface is plane and perpendicular to the external force field, the fluid within the interface cannot be assumed governed by a fundamental equation of the classical type $\hat{f}(\theta, \rho)$.

7. CONCLUSION

The principal result of this investigation is the construction of a general continuum model of the fluid interface at equilibrium, developed in the special case when the fundamental equation of the fluid may be written in the local form

$$f = \hat{f}(\theta, \rho, (\nabla\rho)^2, \nabla\rho^2) \quad .$$

The fluid governed by this equation is shown to behave as a classical fluid when the density is nearly uniform, but to have the properties associated with the behavior of fluid interfaces when the local variation of density is large. A classical fluid, on the other hand, will not show interfacial behavior.

The material near a two-phase interface in such a fluid is acted on by a complex system of multipolar stresses, which may be regarded as the mechanical forces which maintain the density variation across the interface. However, the thermodynamic behavior of the fluid near the interface is governed by the familiar equation

$$p_f = \mu p - P.$$

The thermodynamic pressure P may be defined within inhomogeneous parts of the fluid. It is the continuum analogue of the scalar parameter $\hat{p}$ appearing in molecular treatments of inhomogeneous simple fluids. The thermodynamic simplicity of the fluid within the interface has the consequence that Gibbs fundamental equation for surfaces

$$F(s) = \mu m^{(s)} + \sigma S$$

is obeyed. The surface tension σ appearing in this equation is the negative of the surface excess of the thermodynamic pressure P .

When the interface is plane, the density variation through the interface is unidirectional, and the dividing surface is placed so that

$$\rho = \rho(x^3)$$

The second order stress within the interface may be written in the Young-Buff form

$$g = \sigma_T (e_1 e_1 + e_2 e_2) + \sigma_N (e_3 e_3)$$

where the "tangential stress" σ_T is the negative of the thermodynamic pressure P . Then the Young-Buff equation, which identifies σ with the surface excess of σ_T , applies. The Van der Waals-Cahn-Hilliard expression for the surface tension is also valid under these conditions.

In the present paper we have not specifically considered fluids governed by more general forms of the fundamental equation. One may show, however, that the conclusions stated above continue to hold when density gradients of arbitrary order are specifically included in the fundamental equation, with the reservation that VCH equation for the surface tension no longer applies. Parts of this demonstration have been published

elsewhere (Morris, 1972).

The model of the continuous interface considered here may be extended to treat continuous solid interfaces and continuous interfaces in multi-component material. Some initial results are given elsewhere (Morris, 1971). Similarly, a model of this type may be used as a starting point for a non-equilibrium theory of the interface. This extension is now being studied.

REFERENCES

- Bakker, G., 1928, Handbuch der Experimental Physik, Bd. 6, Akademische Verlagsgesellschaft, Leipzig.
- Buff, F. P., 1951, J. Chem. Phys., 19, 1591; 1955, 23, 419; 1956, 25, 146.
- Cahn, J. W., and Hilliard, J. E., 1958, J. Chem. Phys., 28, 258; 1959 31, 688.
- Cahn, J. W., 1959, J. Chem. Phys., 30, 1121; 1961, Acta Met., 9, 795; 1962, 10, 179.
- Gibbs, J. W., 1878, Trans. Conn. Acad., 3, 343, included in Scientific Papers, Vol. I: Thermodynamics, Dover, New York (1961).
- Green, A. E. and Rivlin, R. S., 1964, Arch. Rational Mech. Anal., 16 325; 17, 113.
- Hart, E. W., 1963, J. Chem. Phys., 39, 3075
- Kirkwood, J. G., and Buff, F. P., 1949, J. Chem. Phys., 17, 338.
- Lebowitz, J. L. and Percus, J. K., 1963, J. Math. Phys., 4, 116; 1961, Phys. Rev., 122, 1675.
- Morris, J. W., Jr., 1972, J. Chem. Phys. (in press); 1971, Phil. Mag., 23, 1041.
- Stillinger, F. H., Jr., and Buff, F. P., 1962, J. Chem. Phys., 17, 338.
- Van der Waals, J. D., 1894, Z. Physik Chem., 13, 657.
- Young, T., 1805, Phil. Trans. Roy. Soc. (London), 95, 65; discussed by R. Defay, I. Prigogine and A. Bellmans, Surface Tension and Absorption, J. Wiley, New York, (1966).

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