

On the thermodynamics of fluids with nonlocal interactions: a nonlocal view of phase boundaries

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A PHENOMENOLOGICAL theory of equilibrium of one-component fluids is developed under the assumption that the free energy density is a function of temperature, density and functionals of the density. Consistency with previous "gradient" models is demonstrated in that such models obtain from appropriate truncations or approximations of the functional arguments of the free energy density. Conditions for mechanical and thermodynamic equilibrium are obtained. Interpretations of the nonlocal quantities are then derived on the basis of the forms of these equilibrium conditions. It is shown that the results of classical thermodynamics are obtained when due account is taken of the nonlocal nature of the thermodynamic potential functions. Detail structuring of "phase boundaries" and externally imposed boundaries are obtained when the nonlocal interactions are assumed to be of short range. Formulae are also obtained for surface tension and the surface excesses when a Gibbsian construct of ideal homogeneous phases is introduced as a comparison configuration.

Fenomenologiczna teoria równowagi cieczy jednoskładnikowych opracowana została przy założeniu, że gęstość energii swobodnej jest funkcją temperatury, gęstości i funkcjonalów gęstości. Wykazano, że zgodność z poprzednimi modelami "gradientowymi" otrzymuje się przez odpowiednie obcięcie lub aproksymacje funkcjonalnych argumentów gęstości energii swobodnej. Otrzymano warunki równowagi mechanicznej i termodynamicznej. Na ich podstawie przeprowadzono interpretację wielkości nielokalnych. Wykazano, że wyniki klasycznej termodynamiki można otrzymać, jeśli uwzględni się nielokalną naturę termodynamicznych funkcji potencjalnych. Szczegółową konstrukcję "granic faz" oraz brzegów narzuconych z zewnątrz otrzymano przy założeniu, że oddziaływania nielokalne są krótkiego zasięgu. Otrzymano również wzory na napięcie powierzchniowe i na nadmiar powierzchni, gdy jako konfigurację porównawczą wprowadzono Gibbsowską ideę idealnych jednorodnych faz.

Феноменологическая теория равновесия однокомпонентных жидкостей разработана при предположении, что плотность свободной энергии является функцией температуры, плотности и функционалов плотности. Доказано, что совпадение с предыдущими "градиентными" моделями получается путем соответствующих обзоров или аппроксимаций функциональных аргументов плотности свободной энергии. Получены условия механического и термодинамического равновесия. На их основе проведена интерпретация нелокальных величин. Доказано, что результаты классической термодинамики можно получить, если учитывается нелокальная природа термодинамических потенциальных функций. Подробное построение "границ фаз" и границ заданных извне получено при предположении, что нелокальные взаимодействия имеют малый радиус действия. Получены также формулы для поверхностного натяжения и для избытка поверхности, когда в виде сравнительной конфигурации введена идея Гиббса об идеальных однородных фазах.

1. Introduction

ALTHOUGH a multiple phase system is known not to have sharp surfaces of demarcation between its phases, the modeling by GIBBS [1] of a phase boundary as a surface with a sharp discontinuity has proven markedly successful for a large class of problems. However, when questions are posed as to the structure and physical properties of the transition region between two phases, the Gibbsian construct must and does fail because the discontinuity model can provide no information about what is precluded by the model.

Attempts to rectify this intrinsic although often unimportant deficiency of the Gibbsian construct fall into two basic categories. The first of these is based upon the assumption that specific interfacial forces operate within the transition region, such as interfacial stresses of the classical sort [2, 3, 4, 5]. The second class consists of the theories which assume that the energy of a mass element within the interface depends explicitly on the gradient of the density as well as on the mass and the entropy content of the element [6, 7, 8, 9, 10, 11]. Models of this latter class usually result in third and higher order stress tensors.

The Gibbsian and the two alternative classes of formulations contain one basic ingredient in common; they all assume that the energy density (or free energy density or enthalpy density, etc.) at a point interior to the system is determined by the values of the thermodynamic state variables (such as density, temperature, density gradient, etc.) at the same point of the system. Stated another way, the thermodynamic potential functions are functions of the local values of the thermodynamic state variables. The theory presented here takes the other point of view; namely, that the thermodynamic potential functions are determined by the values of the thermodynamic state variables throughout the body. Thus, for instance, the internal energy can depend upon the density throughout the body in such a fashion as to reflect the intermolecular forces which are known to be present in any real fluid, solid or gas. In fact, it will be shown that the "nonlocal" models given here provide a natural formulation in terms of such interparticle forces and lead to identifications of the effects of such forces directly from the conditions for mechanical and thermodynamic equilibrium. A phenomenological formalism is thus provided whereby the structure of a transition region between phases can be modeled directly in terms of the intermolecular potentials which are known to structure such transition regions. Further, for mixtures of several constituents, one or more of which exhibit orientation effects such as long chain polymers, there is little or no change which has to be made in the basic theory or its structure. When the Gibbsian construct is used, one obtains explicit expressions for surface tension, surface excess, etc. directly in terms of the intermolecular or nonlocal properties of the fluid. It is also shown that the Gibbsian construct is meaningful in that the intermolecular forces have a zero resultant for homogeneous states, and hence only come into play when there are departures from homogeneous states such as occur in phase boundary regions or in regions where the fluid or gas has specified solid boundaries.

2. Functions, functionals and free energy

We specifically delimit consideration to the equilibrium behavior of a one-component fluid which is assumed to be both physically and thermodynamically continuous. Inclusion of fluids comprised of many molecular species, some or all of which manifest orientation properties, is readily accomplished once the one-component case has been treated. Note will be made at the point in the argument where modifications have to be made in order to include orientation effects, since the modeling of such effects is less familiar than the corresponding problem of including multiple chemical species.

Classical thermodynamics assumes that a local free energy density (free energy per unit mass) can be defined within *homogeneous* parts of a one-component fluid. When the

fluid is in a state of thermodynamic equilibrium, this free energy density can be written as

$$(2.1) \quad f = f(\theta, \rho),$$

where θ and ρ are the values of the temperature and the mass density at the point in the fluid where f is evaluated. The form of the function $f(\cdot, \cdot)$ then characterizes the chemical component which comprises the fluid.

The primary purpose of this paper is to extend the formulation in terms of a free energy density so as to account for configurations in which the homogeneity assumption is not satisfied. In particular, we wish to account for the presence of nonzero density gradients in equilibrium states, such as occur in the transition region between two phases of a one-component fluid. Further, since nonzero density gradients in an equilibrium state arise as a consequence of intermolecular forces, an extension of a free energy formulation should give rise to a representation of the intermolecular forces in a natural way. Obviously, the formulation must be consistent with thermodynamic principles, reduce to a formulation based upon (2.1) if the density is homogeneous, and lead to the known results for the surface tension on a boundary between two phases *and* on the physical boundary of the fluid as a whole.

We assume a reference configuration for the fluid and refer the "particles" of the fluid to a material coordinate system $\{X^a\}$ of this reference configuration. The mass density $\rho(\mathbf{X})$ and the temperature $\theta(\mathbf{X})$ are assumed to be defined at each particle \mathbf{X} of the fluid in the reference configuration. As is customary, the current configuration of the fluid is referred to spatial coordinates $\{x^i\}$ which are related to the reference coordinates by a one-to-one continuously differentiable transformation

$$(2.2) \quad \mathbf{x} = \mathbf{x}(\mathbf{X}), \quad \mathbf{X} = \mathbf{X}(\mathbf{x}).$$

Further, let B denote the region of E_3 occupied by the fluid in the reference configuration and let b be the region of E_3 occupied by the fluid in the current configuration, B and b being related by the mapping (2.2).

The essential departure of the treatment of this paper from that of classical thermodynamics is the presence of N functions $q_r(\mathbf{x}, \rho(\mathbf{x}); \mathbf{z}, \rho(\mathbf{z}))$, $r = 1, \dots, N$, which are used in forming the N functionals

$$(2.3) \quad k_r[\rho](\mathbf{x}) = \int_b \rho(\mathbf{z}) q_r(\mathbf{x}, \rho(\mathbf{x}); \mathbf{z}, \rho(\mathbf{z})) dV(\mathbf{z}).$$

We demand that each of these N functionals be unchanged in value for each $\mathbf{x} \in b$ when the current configuration is changed by an arbitrary time-independent rigid body displacement (invariance under time-independent rigid body motions). This gives us the requirement

$$(2.4) \quad q_r(\mathbf{x}, \rho(\mathbf{x}); \mathbf{z}, \rho(\mathbf{z})) = q_r(\rho(\mathbf{x}), \rho(\mathbf{z}), r(\mathbf{x}, \mathbf{z})),$$

where

$$(2.5) \quad r(\mathbf{x}, \mathbf{z})^2 = (\mathbf{z} - \mathbf{x}) \cdot (\mathbf{z} - \mathbf{x}) = r(\mathbf{z}, \mathbf{x})^2.$$

The explicit \mathbf{x} and \mathbf{z} dependence of q_r is therefore isotropic. We shall have cause to place several mild additional restrictions on the functions q_r in the next section.

It is at this point that modifications must be made if the fluid particles exhibit orientation effects. What must be done is to include an orientation field $\mathbf{j}(\mathbf{x})$ associated with each

fluid particle and to replace the functions g_r by functions of the form $h_r(\mathbf{x}, \varrho(\mathbf{x}), \mathbf{j}(\mathbf{x}); \mathbf{z}, \varrho(\mathbf{z}), \mathbf{j}(\mathbf{z}))$. Invariance under time-independent rigid body deformations then gives

$$h_r = g_r(\varrho(\mathbf{x}), \varrho(\mathbf{z}), r(\mathbf{x}, \mathbf{z}), \mathbf{j}(\mathbf{x}) \cdot (\mathbf{x} - \mathbf{z}), \mathbf{j}(\mathbf{z}) \cdot (\mathbf{x} - \mathbf{z}), \mathbf{j}(\mathbf{x}) \cdot \mathbf{j}(\mathbf{z}), \dots),$$

so that we obtain anisotropic explicit dependence on \mathbf{x} and \mathbf{z} .

Next, we assume that the free energy density at any point \mathbf{x} of b can be written in the form

$$(2.6) \quad f = f(\theta, \varrho(\mathbf{x}); k_r[\varrho](\mathbf{x})).$$

The total free energy of the fluid body is then given by the functional of functionals

$$(2.7) \quad F(b) = \int_b \varrho(\mathbf{x}) f(\theta, \varrho(\mathbf{x}); k_r[\varrho](\mathbf{x})) dV(\mathbf{x}).$$

In view of the invariance of the functions g_r , we have that $F(b)$ and $f(\theta, \varrho(\mathbf{x}); k_r[\varrho](\mathbf{x}))$ are invariant under time-independent rigid body deformations.

Although we cannot establish direct interpretations of the functionals $k_r[\varrho](\mathbf{x})$ at this point, there are several observations that can be made with respect to models previously reported in the literature. First, if we expand $\varrho(\mathbf{z}) = \varrho(\mathbf{x} + (\mathbf{z} - \mathbf{x}))$ in a Taylor series in $(\mathbf{z} - \mathbf{x})$, it is evident that (2.3) can be written in the equivalent form

$$k_r[\varrho](\mathbf{x}) = h_r(\mathbf{x}, \varrho(\mathbf{x}), \nabla\varrho(\mathbf{x}) \cdot \nabla\varrho(\mathbf{x}), \nabla^2\varrho(\mathbf{x}), \dots).$$

Second, if the dependence of the functions g_r on $r(\mathbf{x}, \mathbf{z})$ is taken to be sufficiently singular at $r = 0$, we again obtain representations of $k_r[\varrho](\mathbf{x})$ in the above form. A substitution of these representations of $k_r[\varrho](\mathbf{x})$ in (2.6) then gives

$$f = \bar{f}(\theta, \varrho, \nabla\varrho \cdot \nabla\varrho, \nabla^2\varrho, \dots).$$

The theory presented here will thus have those of VAN der WAALS [6], CAHN and HILLIARD [7, 10], and MORRIS [9] as approximations. Although the formulation we use appears more complex than those based directly upon density gradients, we hope to convince the reader of its physical simplicity and its intrinsic advantages. In particular, we will show a direct relation between the functionals $k_r[\varrho](\mathbf{x})$ and the intermolecular forces which are known to be present in real fluids.

Classical Gibbsian thermodynamics is usually formulated in terms of variations of quantities such as total free energy. It is therefore useful to pause at this point and establish the form which the variation of $F(b)$ takes, since we now have to deal with functionals of functionals.

We consider two configurations \mathbf{x} and $\mathbf{x} + \delta\mathbf{x}(\mathbf{x})$ and two corresponding states $\theta(\mathbf{x})$, $\varrho(\mathbf{x})$ and $\theta(\mathbf{x}) + \delta\theta(\mathbf{x})$, $\varrho(\mathbf{x}) + \delta\varrho(\mathbf{x})$, where $\delta\mathbf{x}(\mathbf{x})$, $\delta\theta(\mathbf{x})$ and $\delta\varrho(\mathbf{x})$ are arbitrary C^1 functions defined over b . The first thing we have to note is that

$$(2.8) \quad \delta \int_b h dV(\mathbf{x}) = \int_b \left\{ \delta h + h \frac{\partial \delta x^i}{\partial x^i} \right\} dV(\mathbf{x}),$$

where the summation convention is assumed. This result is easily established by writing $\int_b h dV(\mathbf{x}) = \int_B h |\det(\partial x^i / \partial X^\alpha)| dV(\mathbf{X})$, computing the variation in terms of functions defined over the reference configuration, and then transforming back to an integration over the

current configuration b . The following result is now an immediate consequence of the definition of the operation δ (Fréchet differentiation)

$$(2.9) \quad \delta F(b) = \int_b \left\{ f \delta \varrho(\mathbf{x}) + \varrho f - \frac{\partial \delta x^i(\mathbf{x})}{\partial x^i} + \varrho \frac{\partial f}{\partial \theta} \delta \theta(\mathbf{x}) \right. \\ \left. + \varrho \frac{\partial f}{\partial \varrho(\mathbf{x})} \Big|_{k_R} \delta \varrho(\mathbf{x}) + \varrho \frac{\partial f}{\partial k_R} \delta k_R[\varrho](\mathbf{x}) \right\} dV(\mathbf{x}).$$

Similarly, we have

$$(2.10) \quad \delta k_R[\varrho](\mathbf{x}) = \int_b \left\{ g_R \delta \varrho(\mathbf{z}) + \varrho(\mathbf{z}) g_R - \frac{\partial \delta x^i(\mathbf{z})}{\partial z^i} + \varrho(\mathbf{z}) \frac{\partial g_R}{\partial \varrho(\mathbf{x})} \delta \varrho(\mathbf{x}) \right. \\ \left. + \varrho(\mathbf{z}) \frac{\partial g_R}{\partial \varrho(\mathbf{z})} \delta \varrho(\mathbf{z}) + \varrho(\mathbf{z}) \frac{\partial g_R}{\partial x^i} \Big|_{\varrho} \delta x^i(\mathbf{x}) + \varrho(\mathbf{z}) \frac{\partial g_R}{\partial z^i} \Big|_{\varrho} \delta x^i(\mathbf{z}) \right\} dV(\mathbf{z}).$$

However, (2.4) and (2.5) give

$$\frac{\partial g_R}{\partial x_i} \Big|_{\varrho} = \frac{1}{r} \frac{\partial g_R}{\partial r} (x_i - z_i), \quad \frac{\partial g_R}{\partial z^i} \Big|_{\varrho} = \frac{1}{r} \frac{\partial g_R}{\partial r} (z_i - x_i)$$

and

$$\varrho(\mathbf{z}) g_R - \frac{\partial \delta x^i(\mathbf{z})}{\partial z^i} = \frac{\partial}{\partial z^i} (\varrho(\mathbf{z}) g_R \delta x^i(\mathbf{z})) - \delta x^i(\mathbf{z}) \frac{\partial}{\partial z^i} (\varrho(\mathbf{z}) g_R).$$

Upon substitution of these results into (2.10), we obtain

$$(2.11) \quad \delta k_R[\varrho](\mathbf{x}) = \int_b \left\{ g_R \delta \varrho(\mathbf{z}) + \varrho(\mathbf{z}) g_R - \frac{\partial \delta x^i(\mathbf{z})}{\partial z^i} + \varrho(\mathbf{z}) \frac{\partial g_R}{\partial \varrho(\mathbf{x})} \delta \varrho(\mathbf{x}) \right. \\ \left. + \varrho(\mathbf{z}) \frac{\partial g_R}{\partial \varrho(\mathbf{z})} \delta \varrho(\mathbf{z}) + \frac{\varrho(\mathbf{z})}{r(\mathbf{x}, \mathbf{z})} \frac{\partial g_R}{\partial r} ((\mathbf{x} - \mathbf{z}) \cdot \delta \mathbf{x}(\mathbf{x}) + (\mathbf{z} - \mathbf{x}) \cdot \delta \mathbf{x}(\mathbf{z})) \right\} dV(\mathbf{z}).$$

We now set

$$(2.12) \quad \left(\frac{\partial f}{\partial k_R} \right)^* = \frac{\partial f(\theta, \varrho(\mathbf{z}); k_R[\varrho](\mathbf{z}))}{\partial k_R[\varrho](\mathbf{z})},$$

$$(2.13) \quad g_R^* = g_R(\varrho(\mathbf{z}), \varrho(\mathbf{x}), r(\mathbf{x}, \mathbf{z})),$$

so that g^* comes from replacing \mathbf{z} by \mathbf{x} and \mathbf{x} by \mathbf{z} in the functions g . When (2.11) is substituted into (2.9) and the order of integrations in the resulting double integrals is interchanged, we obtain

$$(2.14) \quad \delta F(b) = \int_b \varrho(\mathbf{x}) \left\{ f + \int_b \varrho(\mathbf{z}) \left(\frac{\partial f}{\partial k_R} \right)^* g_R^* dV(\mathbf{z}) \right\} \frac{\partial \delta x^i(\mathbf{x})}{\partial x^i} dV(\mathbf{x}) \\ + \int_b \varrho(\mathbf{x}) \frac{\partial f}{\partial \theta} \delta \theta(\mathbf{x}) dV(\mathbf{x}) + \int_b \varrho(\mathbf{x}) \frac{\partial f}{\partial x_i} \delta x^i(\mathbf{x}) dV(\mathbf{x}) \\ + \int_b \left\{ f + \int_b \varrho(\mathbf{z}) \left(\frac{\partial f}{\partial k_R} \right)^* g_R^* dV(\mathbf{z}) + \varrho(\mathbf{x}) \frac{\partial f}{\partial \varrho} \right\} \delta \varrho(\mathbf{x}) dV(\mathbf{x}),$$

where

$$(2.15) \quad \frac{\delta f}{\delta x^i} = \int_b \frac{\varrho(\mathbf{z})}{r(\mathbf{x}, \mathbf{z})} \left\{ \frac{\partial f}{\partial k_r} \frac{\partial g_r}{\partial r} + \left(\frac{\partial f}{\partial k_r} \right)^* \frac{\partial g_r^*}{\partial r} \right\} (x^i - z^i) dV(\mathbf{z}),$$

$$(2.16) \quad \frac{\delta f}{\delta \varrho} - \frac{\partial f}{\partial \varrho(\mathbf{x})} \Big|_{k_r} + \int_b \varrho(\mathbf{z}) \left\{ \frac{\partial f}{\partial k_r} \frac{\partial g_r}{\partial \varrho(\mathbf{x})} + \left(\frac{\partial f}{\partial k_r} \right)^* \frac{\partial g_r^*}{\partial \varrho(\mathbf{x})} \right\} dV(\mathbf{z}).$$

We note that (2.15) gives

$$\begin{aligned} \int_b \varrho(\mathbf{x}) \frac{\delta f}{\delta x^i} dV(\mathbf{x}) &= \int_b \int_b \frac{\varrho(\mathbf{x})\varrho(\mathbf{z})}{r(\mathbf{x}, \mathbf{z})} \left\{ \frac{\partial f}{\partial k_r} \frac{\partial g_r}{\partial r} + \left(\frac{\partial f}{\partial k_r} \right)^* \frac{\partial g_r^*}{\partial r} \right\} (x^i - z^i) dV(\mathbf{z}) dV(\mathbf{x}) \\ &= \int_b \int_b \frac{\varrho(\mathbf{x})\varrho(\mathbf{z})}{r(\mathbf{x}, \mathbf{z})} \frac{\partial f}{\partial k_r} \frac{\partial g_r}{\partial r} \{ (x^i - z^i) + (z^i - x^i) \} dV(\mathbf{z}) dV(\mathbf{x}), \end{aligned}$$

upon interchange of the orders of integration in the term involving "starred" quantities. We thus have the identity

$$(2.17) \quad \int_b \varrho(\mathbf{x}) \frac{\delta f}{\delta x^i} dV(\mathbf{x}) \equiv 0.$$

This result will be fundamental in establishing a physical interpretation of $\delta f/\delta x^i$ in the next section.

There is one further notational convenience which we shall need in later sections. Define the quantity f^* by the relation

$$(2.18) \quad f^* = \int_b \varrho(\mathbf{z}) \left(\frac{\partial f}{\partial k_r} \right)^* g_r^* dV(\mathbf{z}).$$

It is then easily seen that

$$(2.19) \quad \frac{\partial f}{\partial \theta} = \frac{\partial}{\partial \theta(\mathbf{x})} (f + f^*),$$

$$(2.20) \quad \frac{\delta f}{\delta x^i} = \frac{\partial}{\partial x^i} (f + f^*) \Big|_{\varrho(\mathbf{x})},$$

$$(2.21) \quad \frac{\delta f}{\delta \varrho} = \frac{\partial}{\partial \varrho(\mathbf{x})} (f + f^*),$$

while (2.14) becomes

$$\begin{aligned} (2.22) \quad \delta F(b) &= \oint_b \varrho(\mathbf{x}) (f + f^*) \frac{\partial \delta x^i(\mathbf{x})}{\partial x^i} dV(\mathbf{x}) \\ &\quad + \int_b \varrho(\mathbf{x}) \left\{ \frac{\partial (f + f^*)}{\partial \theta(\mathbf{x})} \delta \theta(\mathbf{x}) + \frac{\partial (f + f^*)}{\partial x^i} \Big|_{\varrho(\mathbf{x})} \delta x^i(\mathbf{x}) \right\} dV(\mathbf{x}) \\ &\quad + \int_b \left\{ f + f^* + \varrho \frac{\partial (f + f^*)}{\partial \varrho(\mathbf{x})} \right\} \delta \varrho(\mathbf{x}) dV(\mathbf{x}). \end{aligned}$$

It thus follows that if we replace f by $f+f^*$, then we can use the standard formulae from the calculus of variations provided we compute all partial derivatives with respect to functions of \mathbf{x} alone; that is, we hold all \mathbf{z} -dependence fixed during the integration process. The function $f+f^*$ thus acts as an effective free energy per unit mass and accounts for the functional dependence of the function f . Quantities like $f+f^*$ have been obtained previously [12, 13] in the study of the thermodynamics of systems in which the energy density is a function of functionals. The term "protopotential" has been used to signify quantities like $f+f^*$, since (2.19)–(2.21) show that it is $f+f^*$ which acts as a potential-like function rather than just f as is the case in the classical analysis. We note that the results obtained above can also be derived directly within the discipline of the nonlocal calculus of variations [14].

3. Conditions for mechanical equilibrium

The current configuration b is assumed to be in a state of mechanical equilibrium at constant temperature and under the action of an *externally* imposed body force field $\mathbf{B}(\mathbf{x})$ and applied tractions $\mathbf{T}(\mathbf{x})|_{\partial b}$ on the boundary, ∂b , of b per unit of surface area of ∂b . The outward directed normal to ∂b is denoted by $\mathbf{n}(\mathbf{x})$.

The simplest way of realizing the conditions imposed by the assumed mechanical equilibrium is to use the variational approach of Gibbs. Thus, let $\delta\mathbf{x}(\mathbf{x})$ and $\delta\rho(\mathbf{x})$ be variations of the spatial configuration and the density of the fluid, and set $\delta\theta(\mathbf{x}) = 0$ in accordance with the assumption of constant temperature. Since mass is conserved in each part of a fluid body during any deformation, while the mass of any part p of b is given by

$$M(p) = \int_p \rho(\mathbf{x}) dV(\mathbf{x}),$$

we obtain the condition

$$(3.1) \quad \delta\rho(\mathbf{x}) = -\rho(\mathbf{x})\nabla \cdot \delta\mathbf{x}(\mathbf{x});$$

that is,

$$\delta M(p) = \int_b \{ \delta\rho(\mathbf{x}) + \rho(\mathbf{x})\nabla \cdot \delta\mathbf{x}(\mathbf{x}) \} dV(\mathbf{x}).$$

All variations are thus a consequence of the variation $\delta\mathbf{x}(\mathbf{x})$ of the configuration of the fluid. The "virtual work" performed on the body by the externally applied forces (body forces and surface tractions) as a consequence of the variation $\delta\mathbf{x}(\mathbf{x})$ is given by

$$(3.2) \quad \delta W(b) = \int_b \mathbf{B}(\mathbf{x}) \cdot \delta\mathbf{x}(\mathbf{x}) dV(\mathbf{x}) + \int_{\partial b} \mathbf{T}(\mathbf{x}) \cdot \delta\mathbf{x}(\mathbf{x}) dS(\mathbf{x}).$$

The standard Gibbsian definition of mechanical equilibrium then takes the following form. *The configuration b with mass density $\rho(\mathbf{x})$ is in mechanical equilibrium at constant temperature θ if, and only if,*

$$(3.3) \quad \delta F(b) \geq \delta W(b)$$

holds for all variations $\delta\mathbf{x}(\mathbf{x})$ which conserve mass.

When the conditions (3.1) and $\delta\theta(\mathbf{x}) = 0$ are substituted into (2.14), we obtain

$$(3.4) \quad \delta F(b) = \int_b \varrho(\mathbf{x}) \left\{ \frac{\delta f}{\delta x^i} \delta x^i(\mathbf{x}) - \varrho(\mathbf{x}) \frac{\delta f}{\delta \varrho} \frac{\partial \delta x^i(\mathbf{x})}{\partial x^i} \right\} dV(\mathbf{x}) \\ = \int_b \left\{ \varrho \frac{\delta f}{\delta x^i} + \frac{\partial}{\partial x^i} \left(\varrho(\mathbf{x})^2 \frac{\delta f}{\delta \varrho} \right) \right\} \delta x^i(\mathbf{x}) dV(\mathbf{x}) - \int_{\partial b} \varrho(\mathbf{x})^2 \frac{\delta f}{\delta \varrho} \delta x^i(\mathbf{x}) n_i(\mathbf{x}) dS(\mathbf{x}).$$

Accordingly, (3.2) through (3.4) demand that

$$(3.5) \quad \int_b \left\{ \varrho \frac{\delta f}{\delta x^i} + \frac{\partial}{\partial x^i} \left(\varrho(\mathbf{x})^2 \frac{\delta f}{\delta \varrho} \right) \right\} \delta x^i(\mathbf{x}) dV(\mathbf{x}) \\ - \int_{\partial b} \varrho(\mathbf{x})^2 \frac{\delta f}{\delta \varrho} \delta x^i(\mathbf{x}) n_i(\mathbf{x}) dS(\mathbf{x}) \geq \int_b B_i \delta x^i dV(\mathbf{x}) + \int_{\partial b} T_i(x) \delta x^i(\mathbf{x}) dS(\mathbf{x})$$

hold for all C^1 functions $\delta \mathbf{x}(\mathbf{x})$ of b . A subset of such functions consists of all C^1 which vanish on the boundary of b . The fundamental lemma of the calculus of variations then shows that a necessary condition for satisfaction of the requirement (3.5) is that

$$(3.6) \quad \varrho \frac{\delta f}{\delta x^i} + \frac{\partial}{\partial x^i} \left(\varrho(\mathbf{x})^2 \frac{\delta f}{\delta \varrho} \right) = B_i$$

hold at all points interior to b . Putting this result back into (3.5), we are left with

$$\int_{\partial b} \varrho(\mathbf{x})^2 \frac{\delta f}{\delta \varrho} \delta x^i(\mathbf{x}) n_i dS(\mathbf{x}) \geq \int_{\partial b} T_i(\mathbf{x}) \delta x^i(\mathbf{x}) dS(\mathbf{x}).$$

The fundamental lemma of the calculus of variations applied to C^1 functions $\delta \mathbf{x}(\mathbf{x})$ over the two-dimensional space ∂b then gives the necessary conditions

$$(3.7) \quad T_i(\mathbf{x}) \Big|_{\partial b} = - \left\{ \varrho(\mathbf{x})^2 \frac{\delta f}{\delta \varrho} \right\} \Big|_{\partial b} n_i.$$

Since these conditions are obviously sufficient for satisfaction of (3.5), (3.6) and (3.7) are the conditions for the mechanical equilibrium of a fluid body b at constant temperature θ .

The body force $\mathbf{B}(\mathbf{x})$ and the surface traction $\mathbf{T}(\mathbf{x})|_{\partial b}$ are already identified. The boundary conditions (3.7) and the standard definition of thermodynamic pressure P in terms of the variational derivative of the internal energy density give

$$(3.8) \quad P = \varrho(\mathbf{x})^2 \frac{\delta f}{\delta \varrho}.$$

We can thus restate the conditions for mechanical equilibrium in the equivalent form

$$(3.9) \quad \mathbf{B}(\mathbf{x}) - \nabla P = \varrho \frac{\delta f}{\delta \mathbf{x}},$$

$$(3.10) \quad \mathbf{T}(\mathbf{x})|_{\partial b} = -P(\mathbf{x})|_{\partial b} \mathbf{n}.$$

Further, if we introduce a stress tensor $\{t_{ij}\}$ by the standard static relation

$$(3.11) \quad t_{ij} = -P\delta_{ij},$$

(3.9) can be written in the equivalent form

$$(3.12) \quad B_i(\mathbf{x}) - \rho \frac{\delta f}{\delta x^i} + \frac{\partial t_{ij}}{\partial x^j} = 0.$$

This shows that

$$(3.13) \quad m_i = - \frac{\delta f}{\delta x^i}$$

may be interpreted as an *internally generated* body force field per unit mass. Accordingly, (2.2) shows that $(f+f^*)$ is a protopotential for this body force field [12]. This interpretation is further substantiated, since the total resultant of this internal body force field is given by

$$- \int_b \rho(\mathbf{x}) \frac{\delta f}{\delta x^i} dV(\mathbf{x})$$

and hence vanishes for every configuration b and every mass density function $\rho(\mathbf{x})$ by (2.17); further, for the classical case where $f = f(\theta, \rho(\mathbf{x}))$, $m_i = 0$. The simplest explanation of such an internally generated body force field is provided by the intermolecular forces which are ignored in the classic treatment. Thus, although we cannot make an unequivocal identification of m_i with the intermolecular forces, such an identification is not inconsistent with the formulation presented here.

It is worth considering a simple explicit model at this point in order to see that the results obtained are physically plausible. Let $h(r(\mathbf{x}, \mathbf{z})) r(\mathbf{x}, \mathbf{z})^{-1} (\mathbf{z} - \mathbf{x})$ denote the force that is exerted on a molecule at \mathbf{x} by a molecule at \mathbf{z} . If N denotes the number of molecules per unit mass, then $N\rho(\mathbf{z}) h(r(\mathbf{x}, \mathbf{z})) r(\mathbf{x}, \mathbf{z})^{-1} (\mathbf{z} - \mathbf{x}) dV(\mathbf{z})$ is the force on a molecule at \mathbf{x} due to all molecules in a volume element $dV(\mathbf{z})$. The force per unit volume at \mathbf{x} due to all molecules is accordingly given by

$$\begin{aligned} \rho(\mathbf{x}) \int_b \rho(\mathbf{z}) \frac{N^2 h(r(\mathbf{x}, \mathbf{z}))}{r(\mathbf{x}, \mathbf{z})} (\mathbf{z} - \mathbf{x}) dV(\mathbf{z}) \\ = -\rho(\mathbf{x}) \nabla_x \int_b \rho(\mathbf{z}) g(r(\mathbf{x}, \mathbf{z})) dV(\mathbf{z}) = -\rho(\mathbf{x}) \frac{\delta}{\delta \mathbf{x}} \int_b \rho g dV(\mathbf{z}), \end{aligned}$$

where

$$g(r(\mathbf{x}, \mathbf{z})) = N^2 \int h(r(\mathbf{x}, \mathbf{z})) dr.$$

Thus, if we take

$$(3.14) \quad f = f_0(\theta, \rho) + \frac{1}{2} \int_b \rho(\mathbf{z}) g(r(\mathbf{x}, \mathbf{z})) dV(\mathbf{z}),$$

then

$$\begin{aligned} (3.15) \quad -\rho \frac{\delta f}{\delta x^i} = \rho m_i = -\rho \frac{\partial}{\partial x^i} \int_b \rho(\mathbf{z}) g(r(\mathbf{x}, \mathbf{z})) dV(\mathbf{z}) \\ = \rho(\mathbf{x}) \int_b \rho(\mathbf{z}) \frac{N^2 h(r(\mathbf{x}, \mathbf{z}))}{r(\mathbf{x}, \mathbf{z})} (\mathbf{z} - \mathbf{x}) dV(\mathbf{z}). \end{aligned}$$

This gives the identification

$$(3.16) \quad g_1(\varrho(\mathbf{x}), \varrho(\mathbf{z}), r(\mathbf{x}, \mathbf{z})) = g(r(\mathbf{x}, \mathbf{z})),$$

when (2.3) and (2.6) are used. Further, this model gives

$$(3.17) \quad P = \varrho^2 \frac{\delta f}{\delta \varrho} = \varrho^2 \frac{\partial f_0}{\partial \varrho},$$

which is in complete agreement with the classical theory if $f_0(\theta, \varrho)$ is identified with the classic free energy density. The formalism we have constructed above thus provides a consistent treatment of this simplistic model of intermolecular forces. Particular note should be made of the "gradient property" exhibited by (3.15). This property will be shown to be of great importance below.

The macroscopic phenomenological formulation of intermolecular interactions presented here has a further aspect which is most easily illustrated in the simplistic model considered above. For motions in a neighborhood of an equilibrium state, the governing equations are conservation of mass,

$$(3.18) \quad \dot{\varrho} + \varrho \nabla \cdot \mathbf{v} = 0,$$

and balance of linear momentum,

$$(3.19) \quad \dot{\mathbf{v}} = \frac{1}{\varrho} \left(-\nabla P - \frac{\delta f}{\delta \mathbf{x}} + \mathbf{B} \right).$$

When (3.14) and (3.17) are used, the linear momentum equation becomes

$$(3.20) \quad \dot{\mathbf{v}} = -\frac{1}{\varrho} \nabla \left(\varrho^2 \frac{\partial f_0}{\partial \varrho} \right) + \frac{1}{\varrho} \mathbf{B} + \int_b \varrho(\mathbf{z}) \frac{N^2 h(r(\mathbf{x}, \mathbf{z}))}{r(\mathbf{x}, \mathbf{z})} (\mathbf{z} - \mathbf{x}) dV(\mathbf{z}).$$

Since the nonlocal term is a linear operator on the density, standard techniques of the acoustic approximation and Fourier transform methods may be employed. Comparison of the results so obtained with experimental phonon dispersion relations can then be used as in reference [16] to infer the function $h(r(\mathbf{x}, \mathbf{z}))$. Intermolecular forces determined in this manner lead to computations of surface tension and surface excess by use of the results which are given in Sec. 6. A specific method is thus provided for correlating phonon dispersion experiments for quasi-homogeneous single phases with effects present in regions of demarcation between distinct phases.

4. Integrability and equations of state

If we use a subscript h to designate quantities referred to homogeneous states, then classic theory gives

$$(4.1) \quad P_h = \varrho_h^2 \frac{\partial f_h}{\partial \varrho_h}, \quad \mathbf{B}_h = -\varrho_h \nabla \phi,$$

where ϕ is the body force (gravitational) potential, and

$$(4.2) \quad \nabla P_h = -\varrho_h \nabla \phi.$$

The integrability conditions of (4.2) give us

$$(4.3) \quad \mathbf{0} = \nabla \times \nabla P_h = -\nabla \varrho_h \times \nabla \phi$$

and hence there exists a function α such that

$$(4.4) \quad \alpha \nabla \varrho_h = \nabla \phi.$$

The integrability conditions of (4.4) in turn imply $\alpha = \alpha(\varrho)$ and hence (4.2) and (4.4) become

$$(4.5) \quad \nabla P_h = -\nabla \int \varrho_h \alpha(\varrho_h) d\varrho_h, \quad \nabla \int \alpha(\varrho_h) d\varrho_h = \nabla \phi.$$

Integration then gives

$$(4.6) \quad \begin{aligned} P_h &= -\int \varrho_h \alpha(\varrho_h) d\varrho_h + \text{constant}, \\ \int \alpha(\varrho_h) d\varrho_h &= \phi + \text{constant}. \end{aligned}$$

Further, since θ is constant, the function α can depend on θ as can the integration constants in (4.6). This proves the existence of a local equation of state; i.e., the pressure at a point \mathbf{x} is a function of the density at the same point \mathbf{x} .

For the theory given here, (4.2) is replaced by (see (3.9))

$$(4.7) \quad \nabla P = \varrho(\mathbf{b} + \mathbf{m}),$$

where we have written

$$(4.8) \quad \mathbf{B} = \varrho \mathbf{b}, \quad \mathbf{m} = -\frac{\delta f}{\delta \mathbf{x}}.$$

Since mechanical equilibrium demands that (4.7) be satisfied, its integrability conditions must likewise be satisfied. We therefore must have

$$\mathbf{0} = \nabla \times \nabla P = \nabla \varrho \times (\mathbf{b} + \mathbf{m}) + \varrho \nabla \times (\mathbf{b} + \mathbf{m}).$$

Equations (2.5) and (4.8) show that \mathbf{m} is determined by the manner in which f depends on the functionals $k_r[\varrho](\mathbf{x})$ and on the functions g_r . Accordingly, these dependences must be such as to satisfy the integrability conditions

$$(4.9) \quad \varrho \nabla \times (\mathbf{b} + \mathbf{m}) + \nabla \varrho \times (\mathbf{b} + \mathbf{m}) = \mathbf{0}.$$

An integration of (4.7) now gives

$$(4.10) \quad P(\mathbf{x}) = P(\mathbf{x}_0) + \int_{\mathbf{x}_0}^{\mathbf{x}} \varrho(\mathbf{b} + \mathbf{m}) \cdot d\mathbf{x},$$

where \mathbf{x}_0 is a given point in the fluid body b and the integral is a line integral along any path in b connecting \mathbf{x}_0 and \mathbf{x} . This shows that the pressure is a functional rather than just a function of the density; that is, the pressure at \mathbf{x} depends upon the density at points other than \mathbf{x} .

Several interesting conclusions can be drawn from the above analysis for the classic fluid. We first observe that the results obtained from the equilibrium condition (4.7) do not depend on the assumption of a free energy density function. If we set $\mathbf{m} = \mathbf{0}$, we obtain the following results. *An equilibrium state of a classic fluid at constant temperature can*

exist in the presence of a body force field \mathbf{b} per unit mass if, and only if, $\rho \nabla \times \mathbf{b} + \nabla \rho \times \mathbf{b} = \mathbf{0}$.

If this condition is satisfied, then $P = \int_{x_0}^x \rho \mathbf{b} \cdot d\mathbf{x} + \text{constant}$. If the body force field is conservative, then the existence of an equilibrium state at constant temperature implies the existence of a function $h(\theta, \rho)$ such that $P = h(\theta, \rho)$. This in turn implies the existence of a function $f_0(\theta, \rho)$ such that $\partial f_0(\theta, \rho) / \partial \rho = \rho^{-2} h(\theta, \rho) = P \rho^{-2}$, and hence there exists a free energy density function for the fluid.

It is customary to have a conservative body force field \mathbf{b} per unit mass, while the simple example constructed at the end of the last section gave a conservative field \mathbf{m} . We therefore confine our attention in the remainder of this section to the conservative case

$$(4.11) \quad \mathbf{b} + \mathbf{m} = \nabla \psi, \quad \nabla \times (\mathbf{b} + \mathbf{m}) = \mathbf{0},$$

so that

$$(4.12) \quad \mathbf{m} = \nabla \psi - \mathbf{b}.$$

Under these conditions, (4.9) reduces to

$$(4.13) \quad \alpha(\rho) \nabla \rho = \nabla \psi = \mathbf{b} + \mathbf{m}$$

and hence (4.7) gives

$$(4.14) \quad \nabla P = \rho \alpha(\rho) \nabla \rho.$$

Integrations of (4.13) and (4.14) give us

$$(4.15) \quad P = \int \rho \alpha(\rho) d\rho + \text{constant},$$

$$(4.16) \quad \psi = \int \alpha(\rho) d\rho + \text{constant},$$

where the last equations is equivalent to

$$(4.17) \quad \mathbf{b} + \mathbf{m} = \nabla \int \alpha(\rho) d\rho.$$

The conservative case (4.11) thus leads to the existence of a local equation of state (4.15). Accordingly, there exists a function $f_0(\theta, \rho)$ such that

$$(4.18) \quad P = \rho^2 \left. \frac{\partial f_0}{\partial \rho} \right|_{\theta} = \int \rho \alpha(\rho) d\rho + \text{constant}.$$

When (3.8) is combined with (4.18), we obtain

$$(4.19) \quad \frac{\delta f}{\delta \rho} = \frac{\partial f_0(\theta, \rho)}{\partial \rho}.$$

We thus conclude that the nonlocal pressure-density relation (3.8) is equivalent to a local pressure density relation (4.18) in the conservative case. Finally, we note that for a conservative body force field \mathbf{b} per unit mass, the conservative case can only be obtained when

$$(4.20) \quad \nabla \times \mathbf{m} = \mathbf{0}.$$

5. Conditions for thermodynamic equilibrium

Classically, a body is said to be in a state of thermodynamic equilibrium if, and only if, it is in a state of mechanical equilibrium and the total energy of the body is a minimum relative to all competing states with the same total entropy. Thus, let η denote the entropy density of the fluid, let e denote the total internal energy density of the fluid, and let ϕ denote the potential energy field of the external forces per unit mass. We then have

$$(5.1) \quad e = f + \theta\eta + \phi.$$

Mechanical equilibrium being the absence of all accelerations and the conservation of mass, we must have

$$(5.2) \quad M(b) = \int_b \rho dV(\mathbf{x}),$$

while a simple transformation of coordinates to the center of mass allows us to dispense with the kinetic energy terms. The total energy is thus given by

$$(5.3) \quad E(b) = \int_b \rho(f + \phi + \theta\eta) dV(\mathbf{x}).$$

Finally, since mechanical equilibrium fixes the configuration, $\delta\mathbf{x}(\mathbf{x}) = \mathbf{0}$. Accordingly, a fluid is in a state of thermodynamic equilibrium if, and only if,

$$(5.4) \quad \delta E(b) \geq 0$$

holds for all variations $\delta\theta(\mathbf{x})$, $\delta\eta(\mathbf{x})$, $\delta\rho(\mathbf{x})$ ($\delta\mathbf{x}(\mathbf{x}) = 0$) for which the total mass $M(b)$ and the total entropy

$$(5.5) \quad S(b) = \int_b \rho\eta dV(\mathbf{x})$$

are invariant in value.

The first thing we do is to convert the above variational problem with constraints into a free variational problem by introducing Lagrange multipliers α and β . The condition for thermodynamic equilibrium thus becomes

$$(5.6) \quad \delta \int_b \rho(f + \phi + (\theta - \alpha)\eta - \beta) dV(\mathbf{x}) \geq 0$$

shall hold for all variations $\delta\theta(\mathbf{x})$, $\delta\eta(\mathbf{x})$ and $\delta\rho(\mathbf{x})$ with $\delta\mathbf{x}(\mathbf{x}) = \mathbf{0}$. When (2.22) is used to eliminate $\delta F(b) = \delta \int_b \rho f dV(\mathbf{x})$ from (5.6) with $\delta\mathbf{x}(\mathbf{x}) = 0$, we are left with

$$(5.7) \quad \int_b \left\{ \left(f + f^* + \phi + (\theta - \alpha)\eta + \rho \frac{\partial(f + f^*)}{\partial\rho(\mathbf{x})} - \beta \right) \delta\rho(\mathbf{x}) \right. \\ \left. + (\theta - \alpha) \delta\eta(\mathbf{x}) + \rho \left(\eta + \frac{\partial(f + f^*)}{\partial\theta} \right) \delta\theta \right\} dV(\mathbf{x}) \geq 0.$$

We thus obtain the conditions

$$(5.8) \quad \theta = \alpha = \text{constant},$$

$$(5.9) \quad \eta = -\frac{\partial(f+f^*)}{\partial\theta},$$

$$(5.10) \quad f+f^* + \phi + \varrho \frac{\partial(f+f^*)}{\partial\varrho(\mathbf{x})} = \beta = \text{constant}$$

for thermodynamic equilibrium. Since mechanical equilibrium is assumed, we also have

$$(5.11) \quad P = \varrho^2 \frac{\delta f}{\delta\varrho} = \varrho^2 \frac{\partial(f+f^*)}{\partial\varrho(\mathbf{x})}$$

and hence (5.10) assumes the form

$$(5.12) \quad f+f^* = \beta - \phi - \frac{P}{\varrho}.$$

We have seen that $f+f^*$ plays the role of a thermodynamic potential in the theory presented here, in contrast to the classic theory in which f is the basic thermodynamic potential. If we follow classic thermodynamics with the symbol “ d ” replaced by δ , or if we use the definition of the intrinsic chemical potential used by HART [15] and by CAHN and HILLIARD [10], then

$$(5.13) \quad \int_b \mu \delta\varrho(\mathbf{x}) dV(\mathbf{x}) \equiv \int_b \left. \frac{\delta(f\varrho)}{\delta\varrho(\mathbf{x})} \right|_{\theta, \mathbf{x}} \delta\varrho(\mathbf{x}) dV(\mathbf{x}).$$

However, $\int_b \left. \frac{\delta(f\varrho)}{\delta\varrho(\mathbf{x})} \right|_{\theta, \mathbf{x}} \delta\varrho(\mathbf{x}) dV(\mathbf{x})$ is given by (2.22) upon setting $\delta\theta = 0$, $\delta\mathbf{x}(\mathbf{x}) = 0$, and hence

$$(5.14) \quad \int_b \mu \delta\varrho(\mathbf{x}) dV(\mathbf{x}) = \int_b \left(f+f^* + \varrho \frac{\partial(f+f^*)}{\partial\varrho(\mathbf{x})} \right) \delta\varrho(\mathbf{x}) dV(\mathbf{x}).$$

Since this equality is to hold for all C^1 functions $\delta\varrho(\mathbf{x})$, we obtain the following expression for the intrinsic chemical potential:

$$(5.15) \quad \mu = f+f^* + \varrho \frac{\partial(f+f^*)}{\partial\varrho(\mathbf{x})} = f+f^* + \frac{P}{\varrho}.$$

Thus, (5.12) can be written in the classic Gibbsian form

$$(5.16) \quad f+f^* = \mu - \frac{P}{\varrho}$$

and the equilibrium condition (5.15) becomes

$$(5.17) \quad \mu + \phi = \beta = \text{constant}.$$

It is thus seen that we obtain all of the classic results although f and hence f^* and μ are now functions of functionals of the state variables.

6. The fundamental equation for a phase boundary and a physical boundary

Up to this point, the functions $g_r(\varrho(\mathbf{x}), \varrho(\mathbf{z}), r(\mathbf{x}, \mathbf{z}))$ have been quite general. We now specialize these functions in order to realize the requirement that intermolecular forces are short range forces. Section 3 showed that $-\varrho(\mathbf{x}) \delta f / \delta \mathbf{x}$ was the force per unit volume that acted upon the fluid element because of the arguments $k_r[\varrho](\mathbf{x})$ and we have

$$(6.1) \quad \varrho(\mathbf{x}) \frac{\delta f}{\delta \mathbf{x}} = \int_b \varrho(\mathbf{x}) \varrho(\mathbf{z}) \left\{ \frac{\partial f}{\partial k_r} \frac{\partial g_r}{\partial r} + \left(\frac{\partial f}{\partial k_r} \right)^* \frac{\partial g_r^*}{\partial r} \right\} \frac{\mathbf{x} - \mathbf{z}}{r(\mathbf{x}, \mathbf{z})} dV(\mathbf{z})$$

$$= \int_b \varrho(\mathbf{x}) \varrho(\mathbf{z}) \left\{ \frac{\partial g_r(\varrho(\mathbf{x}), \varrho(\mathbf{z}), r)}{\partial r} \frac{\partial}{\partial k_r} f(\varrho(\mathbf{x}), \theta, k_r[\varrho](\mathbf{x})) \right.$$

$$\left. + \frac{\partial g_r(\varrho(\mathbf{z}), \varrho(\mathbf{x}), r)}{\partial r} \frac{\partial}{\partial k_r} f(\varrho(\mathbf{z}), \theta, k_r[\varrho](\mathbf{z})) \right\} \frac{\mathbf{x} - \mathbf{z}}{r(\mathbf{x}, \mathbf{z})} dV(\mathbf{z})$$

and

$$(6.2) \quad \int_b \varrho(\mathbf{x}) \frac{\delta f}{\delta \mathbf{x}} dV(\mathbf{z}) \equiv 0.$$

We now assume that

$$(6.3) \quad \frac{\partial}{\partial r} g_r(\varrho(\mathbf{x}), \varrho(\mathbf{z}), r) = 0 \quad \text{for } r > L,$$

where L is a given length that is characteristic of the molecular composition of the fluid. If $s(\mathbf{x}, L)$ denotes the ball with center at \mathbf{x} and radius L , then (6.1) can be written as

$$(6.4) \quad \varrho(\mathbf{x}) \frac{\delta f}{\delta \mathbf{x}} = \int_{s(\mathbf{x}, L) \cap b} \varrho(\mathbf{x}) \varrho(\mathbf{z}) \left\{ \frac{\partial f}{\partial k_r} \frac{\partial g_r}{\partial r} + \left(\frac{\partial f}{\partial k_r} \right)^* \frac{\partial g_r^*}{\partial r} \right\} \frac{\mathbf{x} - \mathbf{z}}{r(\mathbf{x}, \mathbf{z})} dV(\mathbf{z}).$$

Further, for L sufficiently small, it is to be expected that

$$k_r[\varrho](\mathbf{x}) = \int_b \varrho(\mathbf{z}) g_r(\varrho(\mathbf{x}), \varrho(\mathbf{z}), r(\mathbf{x}, \mathbf{z})) dV(\mathbf{z})$$

should admit of expansions in powers of $\nabla \varrho(\mathbf{x})$ which can be terminated after only a few terms with a small error. We would then be led back to previous theories based upon $f = f(\theta, \varrho(x), \nabla \varrho \cdot \nabla \varrho(x), \nabla^2 \varrho(x), \dots)$. In other words, it is the short range of the intermolecular forces in real materials which validates theories based upon the approximation $f = f(\theta, \varrho, \nabla \varrho \cdot \nabla \varrho, \nabla^2 \varrho)$. Such approximations and their attendant complications are unnecessary if we allow for functional arguments $k_r[\varrho](x)$ in f .

It now follows that for *constant density*

$$(6.5) \quad \left(\varrho(\mathbf{x}) \frac{\delta f}{\delta \mathbf{x}} \right) \Big|_{\varrho = \text{constant}} = 0$$

at every point \mathbf{x} within the body b which is a distance L away from any point on the boundary of b . We then have the classical results for constant density at all points of the body a distance L away from boundary points.

Gibbs' thermodynamics of internal phase boundary surfaces may now be obtained from our previous results. We consider a part p of the fluid which contains a section of a phase boundary between two phases. We also consider the fluid as modeled by two homogeneous phases α and β with a phase boundary S . Under these conditions, it is convenient to take the piece p of the fluid to be comprised of a curvilinear cylinder, so that the coordinate lines x^3 form orthogonal trajectories of a family of surfaces, one of which is the phase boundary surface S , and for convenience we choose $x^3 = 0$ to specify the surface S . The coordinates x^1 and x^2 are then surface coordinates in the phase boundary S . Since the range of molecular forces is small, we can also assume that the piece p is bounded by the surfaces $x^3 = -h_1$ and $x^3 = h_2$, where h_1 and h_2 are positive numbers significantly greater in value than L . The element of volume in these coordinates is then given by [9]

$$(6.6) \quad dV(\mathbf{x}) = \nu dx^3 dS,$$

where

$$(6.7) \quad \nu = 1 - Kx^3 + K'(x^3)^2,$$

K = mean curvature of S , K' = Gaussian curvature of S , and dS denotes the element of differential surface area. Let $\rho_i^{\alpha\beta}$, $P^{\alpha\beta}$ and $f_0^{\alpha\beta}$ denote the density, pressure and free energy of the corresponding homogeneous phases α and β . Since $f_0^{\alpha\beta}$ contains no functionals as arguments, we have $f_0^{\alpha\beta*} = 0$. The surface excess $F^{(s)}$ (p) of the thermodynamic protopotential $f+f^*$ for a part p of the body can accordingly be written

$$(6.8) \quad F^{(s)}(p) = \int_p \rho(f+f^*)dV(\mathbf{x}) - \int_p \rho_i^{\alpha\beta}(f^{\alpha\beta} + f^{\alpha\beta*})dV(\mathbf{x}).$$

When (5.16) and (5.17) are substituted into this expression and we note that the same external body force acts on the actual fluid and on the ideal phases α and β , we obtain

$$(6.9) \quad \begin{aligned} F^{(s)}(p) &= \int_p (\beta - \phi)(\rho - \rho^{\alpha\beta})dV(\mathbf{x}) + \int_p (P^{\alpha\beta} - P)dV(\mathbf{x}) \\ &= \int_p (\beta - \phi)(\rho - \rho^{\alpha\beta})dV(\mathbf{x}) + \int dS \int_{-h_1}^{h_2} (P^{\alpha\beta} - P)\nu dx^3. \end{aligned}$$

Now, if p cuts out a sufficiently small piece of surface ΔS , (6.9) gives

$$(6.10) \quad \begin{aligned} F^{(s)}(p) &= \int_{\Delta S} f^{(s)}dS \approx f^{(s)}\Delta S \\ &= (\beta - \phi)|_S m^{(s)} + \sigma \Delta S, \end{aligned}$$

where

$$(6.11) \quad m^{(s)} = \int_p (\rho - \rho^{\alpha\beta})dV(\mathbf{x})$$

is the surface excess of mass and

$$(6.12) \quad \sigma = \int_{-h_1}^{h_2} (P^{\alpha\beta} - P)\nu dx^3$$

is the surface tension. When (5.17) is used, we thus obtain the classical result

$$(6.13) \quad f^{(s)} = \mu|_S m^{(s)} / \Delta S + \sigma.$$

We can now use the results obtained in the previous section on mechanical equilibrium to evaluate the surface tension. With $\mathbf{b} = -\nabla\phi$, (4.7) gives

$$(6.14) \quad \nabla P = -\rho \nabla\phi + \rho \mathbf{m},$$

where

$$(6.15) \quad \mathbf{m} = -\frac{\delta f}{\delta \mathbf{x}} = -\left. \frac{\partial(f+f^*)}{\partial \mathbf{x}} \right|_{\rho}.$$

On the other hand, if Γ denotes the surface excess of mass per unit area of the idealized phase boundary surface, we have

$$(6.16) \quad \nabla P^{\alpha\beta} = -(\rho^{\alpha\beta} + \Gamma \delta(x_3 = 0)) \nabla\phi.$$

Combining (6.14) and (6.15) gives us

$$(6.17) \quad \nabla(P^{\alpha\beta} - P) = \{\rho - \rho^{\alpha\beta} - \Gamma \delta(x^3 = 0)\} \nabla\phi - \rho \mathbf{m},$$

and hence

$$(6.18) \quad (P^{\alpha\beta} - P)(x^3) = \int_{-h_1}^{x^3} \{\rho - \rho^{\alpha\beta} - \Gamma \delta(x^3 = 0)\} \frac{\partial\phi}{\partial x^{3'}} dx^{3'} - \int_{-h_1}^{x^3} \rho m_3 dx^{3'},$$

since $P^{\alpha\beta}(-h_1) = P(-h_1)$. When this is substituted into (6.12), we see that

$$(6.19) \quad \sigma = -\int_{h_1}^{h_2} \int_{-h_1}^{x^3} \rho m_3 dx^{3'} \nu dx^3 + \int_{-h_1}^{h_2} \int_{-h_1}^{x^3} \{\rho - \rho^{\alpha\beta} - \Gamma \delta(x^3 = 0)\} \frac{\partial\phi}{\partial x^{3'}} dx^{3'} \nu dx^3.$$

Since the last term can be made to vanish by properly positioning the phase boundary surface, we finally have

$$(6.20) \quad \sigma = \int_{h_1}^{h_2} \int_{-h_1}^{x^3} \rho \left. \frac{\partial(f+f^*)}{\partial x^{3'}} \right|_{\rho} (x^3) dx^{3'} \nu dx^3.$$

Also, upon noting that $\rho^\alpha(x^3 = h_1) = \rho(x^3 = h_1)$, $\rho^\beta(x^3 = h_2) = \rho(x^3 = h_2)$, we obtain

$$dS \int_{-h_1}^0 \rho^\alpha \nu dx^3 + dS \int_0^{h_2} \rho^\beta \nu dx^3 + \Gamma dS = dS \int_{-h_1}^{h_2} \rho \nu dx^3,$$

so that

$$(6.21) \quad \Gamma = \int_{-h_1}^{h_2} \rho \nu dx^3 - \int_{h_1}^0 \rho^\alpha \nu dx^3 - \int_0^{h_2} \rho^\beta \nu dx^3 = m^{(s)} / \Delta S.$$

Hence

$$(6.22) \quad m^{(s)} = \Delta S \int_{-h_1}^{h_2} \rho \nu dx^3 - \Delta S \left\{ \int_{-h_1}^0 \rho^\alpha \nu dx^3 + \int_0^{h_2} \rho^\beta \nu dx^3 \right\}.$$

We now come to the question of the physical boundary ∂b of the fluid body b . We have already seen that the intermolecular force field $\mathbf{m}(\mathbf{x})$ vanishes for homogeneous states only if \mathbf{x} is further than the characteristic distance L from ∂b . Accordingly, we may pursue the same analysis as above with respect to the boundary ∂b . In this instance, however, since we have included intermolecular forces in the fluid, we should also include the effects of the intermolecular forces which arise from molecules of the material which constitutes the material boundary of the fluid body. We therefore write

$$(6.23) \quad \mathbf{b} = -\nabla\phi - \nabla\psi,$$

where ϕ is the usual potential for the external field, while ψ is the potential for the intermolecular forces which are applied to the fluid from molecules outside of the body. On the other hand, if we replace the fluid by an idealized homogeneous phase α , then the only body force on the phase α is given by $-\nabla\phi$. This gives us the same results as obtained above, where the integrals now extend from $x^3 = 0$ to $x^3 = h_2$. In particular, we have

$$(6.24) \quad \sigma = \int_0^{h_2} (P^\alpha - P) \nu dx^3,$$

$$(6.25) \quad m^{(s)} = \int_{p \wedge b} (\varrho - \varrho^\alpha) dV(\mathbf{x}).$$

However,

$$(6.26) \quad \nabla P = -\varrho(\nabla\phi + \nabla\psi) + \varrho\mathbf{m},$$

$$(6.27) \quad \nabla P^\alpha = -\varrho^\alpha \nabla\phi - \Gamma \delta(x_3 = 0) \nabla\phi,$$

so that

$$\nabla(P^\alpha - P) = (\varrho - \varrho^\alpha - \Gamma \delta(x_3 = 0)) \nabla\phi + \varrho(\nabla\psi - \mathbf{m}).$$

Since $P^\alpha(x^3 = h_2) = P(x^3 = h_2)$, we then obtain

$$P^\alpha - P = \int_0^{x^3} (\varrho - \varrho^\alpha - \Gamma \delta(x_3 = 0)) \frac{\partial\phi}{\partial x^3} dx^{3'} + \int_0^{x^3} \varrho \left(\frac{\partial\psi}{\partial x^{3'}} - m_3 \right) dx^{3'}$$

and hence

$$(6.28) \quad \sigma = \int_0^{h_1} \int_0^{h_1} \varrho \left(\frac{\partial(f+f^*)}{\partial x^{3'}} \Big|_e - \frac{\partial\psi}{\partial x^{3'}} \right) \nu dx^{3'} dx^3,$$

$$(6.29) \quad \Gamma = \int_0^{h_2} \varrho \nu dx^3 - \int_0^{h_2} \varrho^\alpha \nu dx^3 = m^{(s)} / \Delta S.$$

The theory presented here thus provides for the known surface effects of fluids in the presence of physical boundaries not comprised of the fluid.

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