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ABSTRACT

We utilize a modern continuum mechanics framework to reconsider an old problem for fluid interfaces, also addressed by Maxwell and van der Waals. We prove that their results need not be valid necessarily. This conclusion is arrived at as a consequence of questioning the existence of thermodynamic potentials and the validity of usual thermodynamic relations within unstable (spinodal) regions. One central result is that Maxwell's equal area rule needs not be valid and certain statistical models are shown to be internally inconsistent. Precise conditions for the validity of Maxwell's rule and the variational theory of van der Waals are established in terms of the coefficients defining the interfacial stress. Finally, a generalized continuum thermodynamics framework is developed which provides an alternative derivation of van der Waals variational theory and properly extends it to dynamic situations. However, other possibilities exist which allow a thermodynamics of fluid interfaces not necessarily restricted by the conditions of Maxwell and van der Waals. The results of the paper could be viewed as a convincing argument to utilize this framework (with the necessary modifications) to interpret more complex phenomena of phase transformations.

1. INTRODUCTION

The purpose of this presentation is to indicate that there are situations where use of standard variational thermodynamics may lead to restrictive results. This is illustrated by confining attention to the simplest problem of phase transformations: an equilibrium liquid-vapor transition. Standard approaches to this problem by Gibbs, Maxwell and van der Waals and later by Cahn-Hilliard and Davis-Scriven have assumed the existence of usual thermodynamic functions and validity of thermodynamic relations within the spinodal (unstable region of the p - ρ diagrams). This practice has led, among other things, to a rather questionable derivation of Maxwell's rule. Moreover, it has produced expressions for the interfacial stress which could probably be of limiting validity. To overcome these difficulties an alternative framework is proposed. This proposal is delivered in two parts.

In the first part of the paper we dispense with thermodynamics and consider the liquid-vapor interface within a mechanical framework only. The interface is viewed as a continuum supporting a stress tensor whose constitutive form (expressed in terms of a gradient approximation) is restricted to obey Cauchy's differential equations of equilibrium. This gives rise to an overdetermined system of differential equations which in one dimension yields a non-linear second-order differential equation which can be integrated to give an analytic expression for the interfacial density profile. Existence conditions for this analytic solution are established. These relations are essentially the condition of mechanical equilibrium (equality of pressures in the gas and liquid phases) and a modification of Maxwell's rule by a

weighting factor defined by the constitutive nature of the interfacial layer. Conditions for the validity of Maxwell's rule and van der Waals variational thermodynamic theory within the mechanical theory of interfaces are established. In view of these conditions it is shown that certain statistical models for the interfacial stress are internally inconsistent.

In the second part of the paper we construct a continuum thermodynamics of fluid interfaces. It is shown that such thermodynamics is possible only when the usual law of balance of internal energy is modified to include, an extra term, associated with surface effects. Various thermodynamic models for fluid interfaces are obtained depending on the form of this extra term. When the extra energy is delivered by a divergence, it follows that a dynamic generalization of van der Waals variational thermodynamic theory is derived. As a result, both Maxwell's rule and a very special form of the interfacial stress (the vanishing of a stress coefficient) are obtained. A slight generalization of the form of the extra energy produces a second thermodynamic model where the above restriction is removed but Maxwell's rule and van der Waals variational conditions for the interfacial stress cannot be escaped. Finally, a non-trivial generalization of the extra energy yields a thermodynamic model which implies neither Maxwell's rule nor van der Waals variational conditions. Thus, an underlying thermodynamics of the mechanical theory outlined in the first part is now available.

The concluding section of the paper contains a brief discussion concerning the extension of the method to describe a rather general program of phase transformations.

2. REVIEW

2.1 Gibbs Thermodynamics and Maxwell's Rule

If the interface in a liquid-vapor transition is assumed to be sharp, i.e. the density profile consists of two straight segments ρ_1 (density of vapor) and ρ_2 (density of liquid) with a discontinuity at the interface, the following conditions are assumed to hold within Gibbs framework of macroscopic phenomenological thermodynamics

$$p(\rho_1) = p(\rho_2) = \bar{p} , \quad (2.1)$$

$$\mu(\rho_1) = \mu(\rho_2) = \bar{\mu} . \quad (2.2)$$

The first relation is the condition of mechanical equilibrium (equality of pressures of the two bulk phases) and the second relation is the condition of chemical or thermodynamic equilibrium (equality of chemical potentials of the two bulk phases). Conditions (2.1) and (2.2) together with the usual thermodynamic relations

$$\mu = f' , \quad p = \rho\mu - f , \quad (2.3)$$

where f denotes free energy (per unit volume) and f' its derivative with respect to ρ , yield

$$\int_{\rho_1}^{\rho_2} (p - \bar{p}) \frac{d\rho}{\rho} = 0 , \quad (2.4)$$

a celebrated relation, first noted by Maxwell in 1875. Maxwell's rule (2.4) is offered as a means to determine the characteristic transition numbers \bar{p} , ρ_1 , ρ_2 from a pressure-density diagram. The straight line \bar{p} is drawn such as to cut off equal areas (with a weighting factor $1/\rho^2$) above and below.

This derivation of Maxwell's rule is to be questioned as based on the assumption that the thermodynamic relations (2.3) are valid within the spinodal set ($\partial p/\partial \rho < 0$) which is clearly an unstable region. Remarks concerning the validity of Maxwell's rule were offered by Pippard in 1957 who noted that the arguments leading to its derivation are nonsense but the result is probably correct. Kahl in 1967 suggested that Maxwell's rule is not true unless the specific heats of the two bulk phases are equal. Davis and Scriven in 1983 pointed out that Maxwell tie-line constructions of coexisting phases are correct and that thermodynamic functions can be computed by integrating the equation of state over any desired density domain. On the other hand there is no experimental basis for the validity of the rule. For example, for water at 0°C, the steam tables give a value for $\rho_1/\rho_2 \approx 1/1500$ while Maxwell's rule with van der Waals equation of state predict $\rho_1/\rho_2 \approx 1/15$. A more elaborate discussion and detailed references on Maxwell's rule can be found in [1].

2.2 Van der Waals Variational Thermodynamics

If the interface in a liquid-vapor transition is assumed to be smooth and density gradients are introduced to round-off the discontinuity involved in the sharp interface, we are led to van der Waals approach to interfaces. The interface is assumed to be an inhomogeneous continuum extended from $-\infty$ to ∞ with a Helmholtz free energy of the form

$$F = \int_{-\infty}^{\infty} (f + \frac{1}{2} c \rho_x^2) dx , \quad (2.5)$$

where $f = f(\rho)$ is the usual homogeneous part of free energy per unit volume $c = c(\rho)$ is a thermodynamic influence parameter measuring the contribution of stabilizing density gradients to the total free energy.

At equilibrium, the functional F is assumed to be a minimum ($\delta F = 0$). Minimization of (2.5) subject to the constraint of conservation of mass

$$\int_{-\infty}^{\infty} (\rho - \rho_0) dx = 0 , \quad (2.6)$$

yields the differential equation

$$c \rho_{xx} + \frac{1}{2} c' \rho_x^2 = \mu - \bar{\mu} , \quad (2.7)$$

where $\mu \equiv f'$ is the usual homogeneous part of chemical potential per unit mass and the constant $\bar{\mu}$ is the Lagrange multiplier associated with the minimization problem (2.5) and (2.6). Physically, the quantity $\bar{\mu}$ represents the constant value of the chemical potential of inhomogeneous fluids at equilibrium.

For vapor-liquid transitions, the interfacial density ρ is determined as a solution of (2.7) subject to the boundary conditions

$$\rho \rightarrow \rho_1 \text{ as } x \rightarrow -\infty , \quad \rho \rightarrow \rho_2 \text{ as } x \rightarrow +\infty , \quad (2.8)$$

As shown in [2], this solution must satisfy the following conditions at infinity

$$\lim_{x \rightarrow +\infty} \rho_x = \lim_{x \rightarrow +\infty} \rho_{xx} = 0 . \quad (2.9)$$

It follows from (2.7) and (2.8) that

$$\mu(\rho_1) = \mu(\rho_2) = \bar{\mu} , \quad (2.10)$$

which establishes the equality of chemical potentials of the (bulk) vapor and liquid phases and confirm the macroscopic postulate (2.2) on a microscopic thermodynamic basis. On multiplying (2.7) by ρ_x , using the chain rule, and integrating with respect to x , we obtain

$$\frac{1}{2} c \rho_x^2 = (\mu - \bar{\mu}) d\rho + \text{const.} \quad (2.11)$$

Next, we recall the thermodynamic relations (2.3) and substitute them into (2.11). Then on using (2.10), (2.9) and (2.8) we conclude that

$$p(\rho_1) = p(\rho_2) = \bar{p} . \quad (2.12)$$

which establishes the equality of pressures of the (bulk) vapor and liquid phases and confirms the macroscopic postulate (2.1) on a microscopic basis. We see that the condition of mechanical equilibrium (2.12) is implied here by the condition of chemical equilibrium (2.10).

Obviously, the condition of chemical equilibrium (2.10), together with the thermodynamic relation

$$dp = \rho d\mu , \quad (2.13)$$

which is a direct consequence of (2.3), gives

$$\int_{\rho_1}^{\rho_2} \frac{p'}{\rho} d\rho = 0 . \quad (2.14)$$

Integration by parts yields

$$\left[\frac{p}{\rho} \right]_{\rho_1}^{\rho_2} + \int_{\rho_1}^{\rho_2} \frac{p}{\rho^2} d\rho = 0 , \quad (2.15)$$

which in conjunction with the condition of mechanical equilibrium (2.12) implies Maxwell's rule

$$\int_{\rho_1}^{\rho_2} (p - \bar{p}) \frac{1}{\rho^2} d\rho = 0 . \quad (2.16)$$

It thus follows that Maxwell's rule cannot be escaped within the thermodynamic structure of van der Waals theory of fluid interfaces.

Finally, it can be shown within the framework of van der Waals theory (by taking properly the derivative with respect to area of the total free energy [3] that the appropriate thermodynamic expression for the surface tension is

$$\sigma = \int_{-\infty}^{\infty} c \rho_x^2 dx . \quad (2.17)$$

In passing, it is noted that the second variation $\delta^2 F$ has not been computed by van der Waals himself. Stability questions within this theory can be conveniently addressed by considering the sign of the second variation.

This problem has not been addressed clearly in the literature even though some attempts are outlined in [3]. One of the difficulties involved is the fact that one deals with infinite domains and the usual theory of classical calculus of variations needs some modification. A conclusive discussion of the second variation is given in [4]. The second variation (of the modified functional to include the constraint) is computed as

$$J(\rho; h) = \int_{-\infty}^{\infty} \{ c(\rho(x)) h_x^2 + Q(x) h^2 \} dx, \quad (2.18)$$

where

$$Q(x) \equiv f''(\rho(x)) + \frac{1}{2} c''(\rho_x) \rho_x^2 - [c(\rho(x))]_{xx}, \quad (2.19)$$

and $h \equiv \delta\rho$ is such that

$$\int_{-\infty}^{\infty} h(x) dx = 0. \quad (2.20)$$

The classical necessary conditions for a minimizer reduce to the following

$$\begin{aligned} \text{Legendre:} & \quad c(\rho) \geq 0, \\ \text{Weirstrass:} & \quad \frac{1}{2} c(\rho) [r - \rho_x]^2 \geq 0 \text{ for } r \in \mathbb{R}, \\ \text{Jacobi:} & \quad c(\rho) > 0 \text{ and } J[\rho; h] \geq 0 \forall h. \end{aligned} \quad (2.21)$$

If it is assumed that $c > 0$ only the positivity of $J[\rho; h]$ is to be considered. The classical sufficient conditions for bounded domains require strict positivity of J since then it is implied that J is coercive (due to Poincaré's inequality). For infinite domains such inequality is not available and the only applicable sufficient condition is coercivity. This condition which is overlooked in [3], is established in [4] and leads to the proof of the following.

Theorem 1. Only the monotone solutions of (2.7) are minimizers.

As we shall see this needs not be the case in the mechanical theory where a condition of stability is not postulated.

3. MECHANICS OF FLUID INTERFACES

As discussed in [1], in the mechanical theory of fluid interfaces, the interfacial layer is viewed as a continuum which obeys the conservation laws of mass and momentum. At equilibrium, the conservation of mass is satisfied identically, while the momentum equation simply reads

$$\text{div } \underline{T} = 0, \quad (3.1)$$

where \underline{T} is the interfacial stress. The constitutive equation for the stress \underline{T} should reflect the effect of surface tension which, in some sense, provides an approximate measure of the long-range interatomic forces. It is essentially this surface tension which under certain conditions leads to the formation of fluid microstructures. We adopt a gradient-approximation to represent the constitutive equation for \underline{T} as follows

$$\underline{T} = -p(\rho) \underline{1} + \underline{T}^E, \quad (3.2)$$

where the first part of the right-hand side is the appropriate stress in the absence of transitions and \underline{T}^E is the surface tension dependent extra stress component. This is, in general, of the form

$$\underline{T}^E = \underline{T}^E(\rho, \nabla\rho, \nabla^2\rho) , \quad (3.3)$$

which by assuming to be polynomial of second degree and order reduces to

$$\underline{T}^E = [\alpha(\rho)\Delta\rho + \beta(\rho)|\nabla\rho|^2]\underline{1} + \gamma(\rho)\nabla^2\rho + \delta(\rho)\nabla\rho \otimes \nabla\rho , \quad (3.4)$$

where the various coefficients are functions of ρ and the symbol \otimes denotes dyadic so that $(\nabla\rho \otimes \nabla\rho)_{ij} \equiv \rho_{,i} \rho_{,j}$. Thus, the system of equations which is to be solved for defining the structure of the interface is

$$\left. \begin{aligned} \underline{T} &= (-p + \alpha\Delta\rho + \beta|\nabla\rho|^2)\underline{1} + \gamma\nabla^2\rho + \delta\nabla\rho \otimes \nabla\rho , \\ \operatorname{div}\underline{T} &= 0. \end{aligned} \right\} \quad (3.5)$$

Upon substitution of (3.5)₁ into (3.5)₂ we obtain the following over-determined system of non-linear differential equations for the density

$$\nabla(-p + a\Delta\rho + \tilde{b}|\nabla\rho|^2) = (c\nabla\rho)\nabla\rho , \quad (3.6)$$

where

$$\left. \begin{aligned} a &\equiv \Delta + \frac{1}{2} \frac{c'}{c} |\nabla|^2 , \quad \tilde{b} \equiv b + \frac{1}{2} (c - a \frac{c'}{c}) , \\ a &\equiv \alpha + \gamma , \quad b \equiv \beta + \delta , \quad c \equiv \gamma' - \delta , \end{aligned} \right\} \quad (3.7)$$

with a prime denoting derivative with respect to ρ . As is pointed out in [1] one can establish the following

Theorem 2. If $\tilde{b} \neq 0$, then the solutions of (3.6) are of either, of the forms

$$\left. \begin{aligned} \rho &= \rho(x) , \\ \rho &= \rho(r) ; \quad r = \sqrt{x^2 + y^2} , \\ \rho &= \rho(R) ; \quad R = \sqrt{x^2 + y^2 + z^2} , \end{aligned} \right\} \quad (3.8)$$

i.e., they are either parallel planes, or concentric cylinders, or concentric spheres.

Remark: The theorem does not hold when $\tilde{b} \equiv 0$. In that case more general shapes for three-dimensional interfaces are possible. Moreover, for radially symmetric cases the condition $\tilde{b} \equiv 0$ allows the derivation of results for three-dimensional interfaces similar to those established for one-dimensional ones as discussed below.

For planar interfaces the density $\rho = \rho(x, y, z)$ and the stress $\underline{T} = \underline{T}(x, y, z)$ are functions of one coordinate only, say x . It follows that the only nonvanishing components of stress are

$$T_{xx} = -p + a\rho_{xx} + b\rho_x^2 , \quad T_{yy} = T_{zz} = -p + \alpha\rho_{xx} + \beta\rho_x^2 , \quad (3.9)$$

with the coefficients a and b defined in (3.7). Accordingly, the only non-trivially satisfied component of the equilibrium equations (3.1) i.e.,

$$-\frac{\partial T_{xx}}{\partial x} = 0 , \quad (3.10)$$

gives

$$a\rho_{xx} + b\rho_x^2 = p - \bar{p}, \quad (3.11)$$

where \bar{p} is a constant.

Equation (3.11) governs the structure of one-dimensional interfaces. It is noted that formally (3.11) is similar to (2.7) but there are deep differences in the interpretation. For vapor-liquid transitions the interfacial density ρ is determined as a solution of (3.11) subject to the boundary conditions

$$\rho \rightarrow \rho_1 \text{ as } x \rightarrow -\infty, \quad \rho \rightarrow \rho_2 \text{ as } x \rightarrow +\infty. \quad (3.11^*)$$

As pointed out in [2] the following holds

Theorem 3. There exists exactly one set of characteristic transition numbers $(\bar{p}, \rho_1, \rho_2)$ for which equation (3.11) is solvable with boundary conditions (3.11^{*}). These numbers are determined from the area condition

$$\int_{\rho_2}^{\rho_1} (p - \bar{p})E(\rho) d\rho = 0, \quad E(\rho) \equiv \frac{1}{a} \exp\left(2 \int \frac{b}{a} d\rho\right), \quad (3.12)$$

and the pressure conditions

$$p(\rho_1) = p(\rho_2) = \bar{p}. \quad (3.13)$$

Then the solution $\rho(x)$ is unique (up to choice of x_0), and monotone increasing with an explicit representation

$$x = x_0 + \int_{\rho(x_0)}^{\rho(x)} \frac{d\rho}{\sqrt{2F(\rho)/G(\rho)}}; \quad F(\rho) \equiv \int_{\rho_1}^{\rho} (p - \bar{p})E(\rho) d\rho, \quad G(\rho) \equiv aE(\rho). \quad (3.14)$$

Remark: As shown in [2], (3.11) possesses two more types of non-trivial bounded solutions. These are reversals which are symmetric with respect to a single point where a maximum or minimum is attained and oscillations which are symmetric with respect to at least two points and therefore periodic. The graph for reversals and oscillations is still represented by means of transition elements (3.14), the area condition (3.12) still holds but the pressure condition (3.13) is replaced respectively by $p(\rho_1) = \bar{p}$, $p(\rho_2) < \bar{p}$ and $p(\rho_2) < \bar{p} < p(\rho_1)$. For more details one can consult [2] and the review article [5].

As a result of the area condition (3.12)₁ of previous theorem we see that according to the mechanical theory, Maxwell's line is relocated in conformity with the weighting factor $E(\rho)$ as given by (3.12)₂ rather than $1/\rho^2$ as given by (2.16). It is thus shown that Maxwell's statement is not a universal law but rather a relation of constitutive nature (depending on the form of interfacial stress). On comparing (3.12)₂ and (2.16) we conclude the following [1]

Theorem 4. A sufficient condition for the validity of Maxwell's rule within the structure of the mechanical theory of interfaces is

$$\frac{2b}{\rho^2} = \left(\frac{a}{\rho^2}\right)'. \quad (3.15)$$

In concluding the development of the mechanical theory of interfaces we note that a purely mechanical definition of surface tension is possible in terms of the surface stress as follows

$$\sigma = \int_{-\infty}^{\infty} (T_{zz} - T_{xx}) dx . \quad (3.16)$$

On noting (3.12) and (3.9) we conclude that

$$\sigma = \int_{-\infty}^{\infty} c \rho^2 dx , \quad (3.17)$$

i.e., with the definition

$$c = \gamma' - \delta , \quad (3.18)$$

the mechanical and thermodynamic expressions for the surface tension are identical.

Next we note that some recent molecular theories [3] have proposed certain statistical models for the interface which, among other things, imply in our notation the relations

$$\gamma = 2\alpha , \quad \delta = 2\beta . \quad (3.19)$$

Then the formula for the surface tension coefficient becomes

$$c = \frac{2}{3} (a' - b) . \quad (3.20)$$

In these statistical models, the molecular coefficients a and b can be written explicitly in terms of the "third moment of force" $u(\rho)$ when typical approximations for the pair correlation function are adopted. Three such models were discussed in [3]. For the first it turns out that

$$a = \frac{1}{16} \rho^2 u' + \frac{1}{2} \rho u , \quad b = \frac{1}{16} \rho^2 u'' + \frac{1}{4} \rho u' - \frac{1}{4} u . \quad (3.21)$$

Then, in view of (3.20), the surface tension coefficient $c(\rho)$ can be expressed in terms of a single molecular function $u(\rho)$ by

$$c = \frac{1}{2} u + \frac{1}{4} \rho u' . \quad (3.22)$$

By direct substitution we see that (3.21) is compatible with (3.15) only when the function $u(\rho)$ has the special form

$$u = C_1 \rho + C_2 , \quad (3.23)$$

where C_1 and C_2 are constants of integration. It follows that the surface tension coefficient $c(\rho)$ is also a linear function of density, namely

$$c = \frac{3}{4} C_1 \rho + \frac{1}{2} C_2 , \quad (3.24)$$

and the molecular coefficients a and b have the special form

$$a = \frac{9}{16} C_1 \rho^2 + \frac{1}{2} C_2 \rho , \quad b = -\frac{1}{4} C_2 . \quad (3.25)$$

In view of (3.19) and (3.7)_{3,4} explicit formulae can also be written for the interfacial stress \underline{T} as given by (3.5)₁ and (3.9). Analogous restrictions can be found for the other two molecular models listed in [3]. These restrictions were not noted in [3] mainly because Maxwell's rule was unconditionally assumed to hold at the outset and the consistency condition (3.15) was not utilized.

Next we consider the question of general compatibility of the mechanical and the variational theory of van der Waals. It can be shown [1] by manipulating on the differential forms of the governing equations of the mechanical and variational theories (differentiate (3.11) with respect to x , multiply by $1/\rho$ and use a definition such as (2.13)) that the two approaches yield equivalent results when certain molecular conditions are satisfied. These conditions are summarized in the following

Theorem 5. Necessary and sufficient conditions for the compatibility of the mechanical and van der Waals variational theory are the molecular relations

$$\alpha + \gamma = \rho c, \quad \beta + \delta = \frac{1}{2} (\rho c' - c), \quad c = \gamma' - \delta. \quad (3.26)$$

On noting that the most general form of a quadratic null interfacial stress $\hat{\underline{T}}$ (i.e., $\text{div} \hat{\underline{T}} = 0$) is given by the expression

$$\hat{\underline{T}} = -(\gamma \Delta \rho + \gamma' |\nabla \rho|^2) \underline{1} + \gamma \nabla \rho^2 + \gamma' \nabla \rho \otimes \nabla \rho, \quad (3.27)$$

we also establish the following

Theorem 6. Up to a null interfacial stress, necessary and sufficient conditions for the compatibility of the mechanical and van der Waals variational theory are the molecular conditions

$$\alpha = \rho c, \quad \beta = \frac{1}{2} (\rho c)', \quad \gamma = 0, \quad \delta = -c. \quad (3.28)$$

4. CONTINUUM THERMODYNAMICS OF FLUID INTERFACES

In this section we provide an alternative thermodynamic framework to consider fluid interfaces. This framework is based on a generalized approach to continuum thermodynamics as indicated, among others, by an earlier proposal of the author for media with microstructure [6]. This approach allows to study not only equilibrium but also dynamic interfaces as opposed to the variational approach of van der Waals which is suited for equilibrium situations only.

Motivated by [6] we assume the following forms of balance laws

$$\left. \begin{aligned} \dot{\rho} + \text{div}(\rho \underline{v}) &= 0, \\ \text{div} \underline{T} &= \rho \dot{\underline{v}}, \\ \rho \dot{\epsilon} &= \underline{T} \cdot \nabla \underline{v} - \text{div} \underline{q} + \rho r + \hat{\epsilon}, \\ \rho \dot{\eta} + \text{div} \frac{\underline{q}}{\theta} - \frac{\rho r}{\theta} &\geq 0. \end{aligned} \right\} \quad (4.1)$$

where ρ is the density of the interfacial material, \underline{v} the velocity, \underline{T} the stress tensor, ϵ its internal energy, \underline{q} the heat flux, r the external heat supply, η the entropy and θ the absolute temperature. The only statement

that is different than classical continuum thermodynamics is the energy equation (4.1)₃ which includes the extra term $\hat{\varepsilon}$. This term is introduced to model the effects of surface tension and long-range forces.

On defining a free energy per unit mass by

$$\psi \equiv \varepsilon - \theta\eta, \quad (4.2)$$

the equation of mass balance (4.1)₁, momentum balance (4.1)₂, energy balance (4.1)₃, and entropy inequality (4.1)₃ yield the following inequality which needs to be satisfied identically

$$\rho(\dot{\psi} + \eta\dot{\theta}) - \underline{T} \cdot \nabla \underline{v} + \theta^{-1} \underline{q} \cdot \nabla \theta - \hat{\varepsilon} \leq 0. \quad (4.3)$$

To proceed further we need constitutive equations for $\{\underline{T}, \varepsilon, \eta, \underline{q}\}$. In conformity with the analysis of previous sections we assume that these are of the form

$$\{\underline{T}, \varepsilon, \eta, \underline{q}\} \xrightarrow{\text{facts}} \{\rho, \theta, \nabla \rho, \nabla^2 \rho, \nabla \theta, \nabla \underline{v}\}. \quad (4.4)$$

We note immediately that if we omit the extra energy term $\hat{\varepsilon}$ and set $\hat{\varepsilon} \equiv 0$, then (4.3) and (4.4) imply

$$\psi_{\nabla \rho} = \psi_{\nabla^2 \rho} = 0, \quad (4.5)$$

which drops the dependence of the free energy on the density gradients, thus requiring an unrealistic zero surface tension coefficient.

Having thus explicitly clarified the important role of the extra energy term, we proceed by assuming it to be of the following form

Model 1: $\hat{\varepsilon} = \text{div} \underline{h}. \quad (4.6)$

In this case the appropriate constitutive equations are of the form

$$\{\psi, \eta, \underline{T}, \underline{q}, \underline{h}\} \xrightarrow{\text{facts}} \{\rho, \theta, \nabla \rho, \nabla^2 \rho, \nabla \theta, \nabla \underline{v}\}. \quad (4.7)$$

It then turns that (4.3) and (4.7) are compatible only when

$$\begin{aligned} \psi &= \psi(\rho, \theta, \nabla \rho), \quad \eta = -\psi_{\theta}, \\ \underline{h}_{\nabla^2 \rho} \cdot \nabla^3 \rho &= 0, \\ \underline{h}_{\nabla \theta} \cdot \nabla^2 \theta &= 0, \\ \underline{h} &= \rho \dot{\rho} \psi_{\nabla \rho} + \underline{h}^R(\rho, \theta, \nabla \rho, \nabla^2 \rho, \nabla \theta), \end{aligned} \quad (4.8)$$

$$\{\underline{T} + [\rho^2 \psi_{\rho} - \rho \text{div}(\rho \psi_{\nabla \rho})] \underline{1} + \rho \psi_{\nabla \rho} \otimes \nabla \rho\} \cdot \nabla \underline{v} + \text{div} \underline{h}^R - \theta^{-1} \underline{q} \cdot \nabla \theta \geq 0.$$

While it is possible to seek explicit solutions of (4.8)_{3,4} by utilizing results from the theory of null Lagrangeans and invariants, we consider for simplicity special solutions such that

$$\underline{h}_{\nabla^2 \rho} = \underline{h}_{\nabla \theta} = 0 \rightarrow \underline{h}_{\nabla^2 \rho}^R = \underline{h}_{\nabla \theta}^R = 0. \quad (4.9)$$

Then evaluation of (4.8)₆ at equilibrium ($\nabla \underline{v} = \nabla \theta = 0$) yields

$$\underline{h}_\rho^R = h_{\nabla\rho}^R = 0 \rightarrow \underline{h}^R = \underline{h}^R(\theta) , \quad (4.10)$$

which in conjunction with invariance considerations reduces (4.8)₅ to the simple form

$$\underline{h} = \rho \dot{\rho} \psi_{\nabla\rho} , \quad (4.11)$$

and (4.8)₆ to a residual dissipation inequality of the form

$$\{\underline{T} + [\rho^2 \psi_\rho - \rho \operatorname{div}(\rho \psi_{\nabla\rho})] \underline{1} + \rho \psi_{\nabla\rho} \otimes \nabla\rho\} \cdot \nabla \underline{v} - \theta^{-1} \underline{q} \cdot \nabla \theta \geq 0 . \quad (4.12)$$

Instead of listing the implications of (4.12) in the general case, we confine attention for simplicity to non-viscous isothermal interfaces, i.e.,

$$\nabla \underline{v} = \nabla \theta = 0 , \quad (4.13)$$

Then (4.12) implies

$$\underline{T} = [-\rho^2 \psi_\rho + \rho \operatorname{div}(\rho \psi_{\nabla\rho})] \underline{1} - \rho \psi_{\nabla\rho} \otimes \nabla\rho , \quad (4.14)$$

which under the classical assumption that the free energy density is a quadratic form

$$\psi = \frac{c}{2\rho} |\nabla\rho|^2 , \quad (4.15)$$

with $c = c(\rho)$ denoting the surface tension, becomes

$$\underline{T} = [-p(\rho) + \rho c \Delta\rho + \frac{1}{2}(\rho c)' |\nabla\rho|^2] \underline{1} - c \nabla\rho \otimes \nabla\rho . \quad (4.16)$$

It thus follows that this particular thermodynamic model restricts the mechanical theory summarized in (3.5)₁ by imposing the conditions

$$\alpha = \rho c , \quad \beta = \frac{1}{2}(\rho c)' , \quad \gamma = 0 , \quad \delta = -c , \quad (4.17)$$

which are precisely the conditions of Theorem 6 implied by van der Waals theory up to a null stress. We thus conclude that Model 1 implies both the vanishing of one of the four coefficients in the expression for the interfacial stress and also Maxwell's rule, i.e.,

$$\gamma = 0 , \quad \text{MR holds} . \quad (4.18)$$

Next we note that restriction (4.18)₁ can be removed but (4.18)₂ remains valid by including into the form of $\hat{\varepsilon}$ the work done by null stresses. We thus assume

$$\underline{\text{Model 2:}} \quad \hat{\varepsilon} = \hat{T} \cdot \nabla \underline{v} + \operatorname{div} \underline{h} , \quad (4.19)$$

with \underline{h} being as before and \hat{T} being a null stress, i.e.,

$$\operatorname{div} \hat{T} = 0 , \quad (4.20)$$

such that the momentum balance remains unchanged. On restricting attention as before to a quadratic free energy density function ψ and therefore to a quadratic null stress \hat{T} , it follows that

$$\hat{T} = -(\gamma \Delta\rho + \gamma' |\nabla\rho|^2) \underline{1} + \gamma \nabla^2 \rho + \gamma' \nabla\rho \otimes \nabla\rho . \quad (4.21)$$

Then, the expression for the total stress becomes

$$\underline{T} = [-p(\rho) + \alpha \Delta\rho + \beta |\nabla\rho|^2] \underline{1} + \gamma \nabla^2\rho + \delta \nabla\rho \otimes \nabla\rho, \quad (4.22)$$

where the molecular coefficients are given by the expressions

$$\alpha + \gamma = \rho c, \quad \beta + \delta = \frac{1}{2}(\rho c' - c), \quad c = \gamma' - \delta, \quad (4.23)$$

which are precisely the conditions of Theorem 5. We thus conclude that Model 2 gives the same equilibrium results as the variational van der Waals theory and implies again Maxwell's rule, i.e.,

$$\gamma \neq 0, \quad \text{MR holds.} \quad (4.24)$$

A thermodynamic structure compatible with the mechanical theory which neither imposes a restriction to the form of interfacial stress nor implies Maxwell's rule is possible if we further generalize the constitutive representation for the extra energy $\hat{\epsilon}$ and allow it to be delivered by a form not necessarily of a divergence type. We thus assume

$$\text{Model 3:} \quad \hat{\epsilon} = \hat{T} \cdot \nabla \underline{y} + a \hat{\rho} + \underline{b} \cdot \nabla \hat{\rho}, \quad (4.25)$$

where a is a scalar and \underline{b} a vector function of the variables $(\rho, \nabla\rho, \nabla^2\rho)$. It turns out that (4.25) allows the mechanical theory to survive without imposing any restriction, i.e.,

$$\gamma \neq 0, \quad \text{MR needs not be valid.} \quad (4.26)$$

A brief discussion of the continuum thermodynamics for fluid interfaces was also given in [7]. A rather detailed discussion of Model 1 is presently being studied in [8] and an elaborate discussion of all three models will be presented in a forthcoming article [9].

5. EXTENSIONS

In this concluding section we wish to point out that the analysis given in the previous sections can be utilized for other problems in phase transformations. A detailed discussion of such possibilities is presented in [5]. It is shown there how the concept of "excited" and "normal" states can lead to constitutive equations of the gradient type for other phase transformation phenomena such as spinodal decomposition, localization of dislocations into slip bands and localization of strain into shear bands and necks.

It will suffice to indicate here that for certain problems the concept of "excited" and "normal" states allows one to identify a stress-like quantity \underline{T} which relates to an appropriate internal variable α by an equation of the form

$$\underline{T} = (-\hat{p}(\alpha) + \hat{\alpha}(\alpha) \Delta\alpha + \hat{\beta}(\alpha) |\nabla\alpha|^2) \underline{1} + \hat{\gamma} \nabla^2\alpha + \hat{\delta} \nabla\alpha \otimes \nabla\alpha, \quad (5.1)$$

which together with an equilibrium-like relation for \underline{T} leads to differential equations for α of the form that we already studied in this paper. Solutions of these equations yield phase transformations governed by modulations in the variable α .

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