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Microscale theory of surface tension

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A phenomenological model of capillarity, which accounts for the structure of the liquid-vapor layer, is successively derived assuming that the entropy of a particle depends on the internal energy, the density, and the gradient of the density. Employing classical thermodynamic principles in combination with the balance of mass, momentum, and energy, a rheological expression for capillary stresses is obtained in terms of the free energy of a liquid-vapor system. It is demonstrated that this model admits potential solutions, provided that external forces are potential and the effects of viscous dissipation of energy and heat conductivity are neglected. Moreover, it is shown that a variational principle can be formulated for potential flows, which generalizes Luke's variational principle for free-boundary inviscid flow. This model can be applied to flows involving a topological change of the capillary interface, such as those associated with the spontaneous growth, coalescence and breakup of vaporous bubbles in a liquid. [S1063-651X(96)13011-7]

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I. INTRODUCTION

The classical theory of capillarity, originated by Gibbs [1], is based on the simplifying assumption that the interfacial layer between a liquid and its vapor has some predetermined thickness, and that the two adjoining phases are homogeneous up to their common dividing surface. This approach enables one to avoid the complex problem of the structure of the liquid-vapor layer, and to apply powerful methods of thermodynamics to the capillary interface, which is actually treated as a geometric surface of zero thickness [2,3]. It is conceivable that this is a good approximation of the capillary interface at a length scale much greater than the thickness of the interfacial layer. However, it is irrelevant in a number of significant flows in which the thickness of the interfacial layer becomes comparable to the characteristic length scale. For instance, the flows associated with the spontaneous growth of tiny vaporous bubbles in a liquid as pressure drops down, as well as their coalescence and breakup, cannot be adequately modeled without taking the structure of the liquid-vapor layer into account.

There are many papers devoted to the phase-field model of phase transitions, which incorporates the structure of the crystal-melt layer. The classical model of phase transitions in an incompressible medium at rest was proposed by Cahn and Hilliard [4,5], via allowing the free energy of a binary solution to depend both on the composition of the components and on its gradient. This conception is in agreement with the Landau-Ginzburg mean field theory [6]. The model is extended to time-dependent processes and applied to a number of solidification problems involving growth of solid particles from an initially homogeneous melt as temperature decreases [7–16]. The most important stage of completing the set of governing equations involves a mechanism of phase separation which is usually modeled by molecular diffusion described by Fick's law, with the chemical potential expressed in terms of the variational derivative of the free energy with respect to an order parameter, such as the composition of a binary medium.

An analogous approach is applied to a binary incompressible fluid [17,18]. In particular, a fourth-order diffusion equation derived in [10] is used to complete the model. Unfortunately, this model is likely incapable of giving the classical kinematical free-surface condition asymptotically as the thickness of the interfacial layer tends to zero. Indeed, in the limit the diffusion equation must be responsible for both the structure of the interfacial layer and the kinematical free-surface condition. In other words, the diffusion equation does not prevent phase transitions between two fluids, and hence Refs. [17,18] actually deal with miscible fluids.

In the present paper, a model of the capillarity of a compressible viscous liquid is derived using simple *a priori* axioms. The central postulate states that the entropy of a particle of a pure medium at equilibrium depends not only on its state, which can be described solely by density and internal energy, but also on the state of its local environment [4], which is here modeled by the gradient of the density. In other words, the density plays the role of an order parameter. This is in agreement with the molecular theory of surface tension, presented by Yang, Fleming, and Gibbs [19] for an isothermal equilibrium of a compressible one-component fluid (that is, in the above paper the local free energy of a system described by a classical Hamiltonian with a short-ranged interaction potential is demonstrated to be a function of temperature, density, and the squared gradient of the density; as a result, an expression for capillary stresses is obtained from the Euler-Lagrange equation reflecting the general statement of the condition for mechanical equilibrium of a liquid-vapor system). Then following the spirit of classical thermodynamics, an expression for the internal energy and entropy in terms of the free energy is immediately obtained from the maximum entropy principle, whereas the density is to satisfy a second-order equation involving the variational derivative of the free energy. An entropy production equation, derived from the balance of mass, momentum, and energy, is used to find an expression for capillary stresses, us-

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ing the axiom that entropy can be produced only due to viscous dissipation of energy and heat flux. Finally, the irreversible processes are modeled by classical Fourier and Stokes laws. Of course, for pure fluid no diffusion mechanism can be responsible for keeping the liquid-vapor layer extremely thin. Instead, this process is simply driven by the momentum equation with pressure and capillary stresses being related to the free energy. As a result, a consistent system of governing equations is successively obtained, which is shown to incorporate the classical equations of compressible fluid as a partucular case. Furthermore, it is demonstrated that an inviscid isothermal flow admits potential solutions satisfying a variational principle. This principle is an extension of Luke's variational principle for free-surface potential flows [20]. In the general case of viscous flow, a linearized model is used to describe localized density inhomogeneities.

II. MODEL DERIVATION

Let us consider a viscous compressible liquid of density ρ. It is assumed that ρ varies continuously with respect to a position point $\mathbf{x}$ and time t, so the liquid forms an interfacial layer with its vapor. Let us denote velocity by $\mathbf{v}$, the pressure tensor (momentum flux) by P, the specific internal energy by e, and the heat flux by $\mathbf{q}$. In these variables the classical conservation laws of mass, momentum, and energy take the form

$$\frac{d\rho}{dt}+\rho\boldsymbol{\nabla}\cdot\mathbf{v}=0, \tag{1}$$

$$\rho\frac{d\mathbf{v}}{dt}+\boldsymbol{\nabla}\cdot P=\rho\mathbf{g}, \tag{2}$$

$$\rho\frac{de}{dt}+\boldsymbol{\nabla}\cdot\mathbf{q}+P:D=0, \tag{3}$$

where $\mathbf{g}$ is the gravity, D is the deformation rate tensor defined as the symmetric part of the tensor $\boldsymbol{\nabla}\mathbf{v}$, and

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

is the material time derivative. The centered dot denotes the inner product. As is required by the conservation law of angular momentum (momentum of momenta), the pressure tensor P must be symmetric. Note that $-P$ is the stress tensor.

Let us assume that the specific entropy s is a given function of specific internal energy e, density ρ, and immediate environment which is modeled by $\boldsymbol{\nabla}\rho$. Actually, due to the space isotropy, the entropy must be invariant with respect to the group of rotations, and therefore

$$s=s(e,\rho,\alpha), \tag{4}$$

where $\alpha=\frac{1}{2}|\boldsymbol{\nabla}\rho|^2$. In the absence of gravity, the maximum entropy principle has the following formulation: maximize

$$\int_{\mathcal{D}}\rho s(e,\rho,\alpha)d\mathcal{D}$$

under the constraints

$$\int_{\mathcal{D}}\rho e\, d\mathcal{D}=E, \quad \int_{\mathcal{D}}\rho\, d\mathcal{D}=M,$$

where $\mathcal{D}$ is a closed thermodynamic system of total energy E and mass M. Introducing Lagrange multipliers, the unconditional variational problem is to maximize the functional

$$\int_{\mathcal{D}}\rho s(e,\rho,\alpha)d\mathcal{D}-\frac{1}{\theta}\int_{\mathcal{D}}\rho e\, d\mathcal{D}+\frac{\zeta}{\theta}\int_{\mathcal{D}}\rho\, d\mathcal{D}.$$

Note that θ is the absolute temperature, and ζ is the chemical potential of the liquid-vapor system.

The Euler-Lagrange equations are specified to

$$\frac{\partial s(e,\rho,\alpha)}{\partial e}=\frac{1}{\theta}, \tag{5}$$

$$\frac{\delta\{\rho[e-\theta s(e,\rho,\alpha)]\}}{\delta\rho}=\zeta, \tag{6}$$

where

$$\frac{\delta F}{\delta\rho}=\frac{\partial F}{\partial\rho}-\boldsymbol{\nabla}\cdot\left(\frac{\partial F}{\partial\alpha}\boldsymbol{\nabla}\rho\right)$$

is the variational derivative. In addition, the density has to satisfy the boundary condition

$$\rho\frac{\partial s(e,\rho,\alpha)}{\partial\alpha}\frac{\partial\rho}{\partial n}=0 \quad \text{on} \quad \partial\mathcal{D}, \tag{7}$$

where $\mathbf{n}$ is a normal vector. Let us introduce the Legendre transform

$$f(\theta,\rho,\alpha)=\min_{e}[e-\theta s(e,\rho,\alpha)],$$

which coincides with the specific free energy. If the function $s(e,\rho,\alpha)$ is concave with respect to e, then Eq. (5) can be inverted with respect to e to give the equilibrium values of internal energy and entropy:

$$e=f(\theta,\rho,\alpha)-\theta\frac{\partial f(\theta,\rho,\alpha)}{\partial\theta}, \quad s=-\frac{\partial f(\theta,\rho,\alpha)}{\partial\theta}. \tag{8}$$

It is worth stressing that $f(\theta,\rho,\alpha)$ must be a concave function of θ as a minimum of linear functions, and therefore the specific heat capacity is positive,

$$c\equiv\frac{\partial e}{\partial\theta}=-\theta\frac{\partial^2 f(\theta,\rho,\alpha)}{\partial\theta^2}>0.$$

Moreover, it is straightforward to check that Eq. (6) takes the form

$$\zeta=\frac{\delta[\rho f(\theta,\rho,\alpha)]}{\delta\rho}. \tag{9}$$

Note that the intensive thermodynamic variables θ and ζ are constant at equilibrium, whereas extensive variables, such as density, internal energy, entropy, and free energy, may or may not vary within $\mathcal{D}$.

In order to derive a consistent expression for P and $\mathbf{q}$, let us write

$$\rho\frac{de}{dt}=\rho\left[\frac{\partial e}{\partial\theta}\frac{d\theta}{dt}+\frac{\partial e}{\partial\rho}\frac{d\rho}{dt}+\frac{\partial e}{\partial\alpha}\boldsymbol{\nabla}\rho\cdot\frac{d}{dt}(\boldsymbol{\nabla}\rho)\right].$$

Using Eq. (1) and bearing in mind the identity

$$\frac{d}{dt}(\boldsymbol{\nabla}\rho)=\boldsymbol{\nabla}\left(\frac{d\rho}{dt}\right)-\boldsymbol{\nabla}\mathbf{v}\cdot\boldsymbol{\nabla}\rho,$$

one derives the following form of Eq. (3):

$$\rho\frac{\partial e}{\partial\theta}\frac{d\theta}{dt}+\boldsymbol{\nabla}\cdot\left(\mathbf{q}-\rho^2\boldsymbol{\nabla}\cdot\mathbf{v}\frac{\partial e}{\partial\alpha}\boldsymbol{\nabla}\rho\right)$$
$$+\left[P-\rho^2\frac{\delta e}{\delta\rho}G-\rho\frac{\partial e}{\partial\alpha}(\boldsymbol{\nabla}\rho\otimes\boldsymbol{\nabla}\rho-|\boldsymbol{\nabla}\rho|^2G)\right]:D=0\ .$$

The symbol $\otimes$ stands for the tensor product. Insofar as

$$\frac{\partial e}{\partial\theta}=\theta\frac{\partial s}{\partial\theta},$$

one obtains the entropy production equation

$$\rho\frac{ds}{dt}+\boldsymbol{\nabla}\cdot\left[\frac{1}{\theta}\left(\mathbf{q}-\rho^2\boldsymbol{\nabla}\cdot\mathbf{v}\frac{\partial f}{\partial\alpha}\boldsymbol{\nabla}\rho\right)\right]$$
$$+\frac{1}{\theta^2}\left(\mathbf{q}-\rho^2\boldsymbol{\nabla}\cdot\mathbf{v}\frac{\partial f}{\partial\alpha}\boldsymbol{\nabla}\rho\right)\cdot\boldsymbol{\nabla}\theta$$
$$+\frac{1}{\theta}\left[P-\rho^2\frac{\delta f}{\delta\rho}G-\rho\frac{\partial f}{\partial\alpha}(\boldsymbol{\nabla}\rho\otimes\boldsymbol{\nabla}\rho-|\boldsymbol{\nabla}\rho|^2G)\right]:D=0,$$

where $f=e-\theta s$ is the free energy. For an irreversible thermodynamic process, let us adopt the axiom that the entropy of a particle can be produced only due to viscous dissipation of energy and nonzero heat flux. This axiom immediately gives the expressions

$$P=\rho^2\frac{\delta f}{\delta\rho}G+\rho\frac{\partial f}{\partial\alpha}(\boldsymbol{\nabla}\rho\otimes\boldsymbol{\nabla}\rho-|\boldsymbol{\nabla}\rho|^2G)-\lambda\boldsymbol{\nabla}\cdot\mathbf{v}G-2\mu D, \tag{10}$$

$$\mathbf{q}=\rho^2\boldsymbol{\nabla}\cdot\mathbf{v}\frac{\partial f}{\partial\alpha}\boldsymbol{\nabla}\rho-\kappa\boldsymbol{\nabla}\theta\ . \tag{11}$$

Here, according to the Fourier and Stokes laws, λ and μ are, respectively, the dilatational and shear coefficients of viscosity, and κ is the coefficient of heat conductivity. All these coefficients are allowed to depend on temperature θ and density ρ. For simplicity, reciprocal coefficients are set to zero.

Thus the full set of governing equations takes the form

$$\frac{\partial\rho}{\partial t}+\boldsymbol{\nabla}\cdot(\rho\mathbf{v})=0, \tag{12}$$

$$\rho\left(\frac{\partial\mathbf{v}}{\partial t}+\mathbf{v}\cdot\boldsymbol{\nabla}\mathbf{v}\right)=\rho\mathbf{g}-\boldsymbol{\nabla}p$$
$$+\boldsymbol{\nabla}\cdot(S+\lambda\boldsymbol{\nabla}\cdot\mathbf{v}G+2\mu D), \tag{13}$$

$$\rho\frac{\partial e}{\partial\theta}\left(\frac{\partial\theta}{\partial t}+\mathbf{v}\cdot\boldsymbol{\nabla}\theta\right)=\Phi+\boldsymbol{\nabla}\cdot(\kappa\boldsymbol{\nabla}\theta), \tag{14}$$

where

$$p=\rho^2\frac{\delta f}{\delta\rho},$$

$$S=\rho\frac{\partial f}{\partial\alpha}(|\boldsymbol{\nabla}\rho|^2G-\boldsymbol{\nabla}\rho\otimes\boldsymbol{\nabla}\rho),$$

$$\Phi=\lambda(\boldsymbol{\nabla}\cdot\mathbf{v})^2+2\mu D:D$$
$$+\rho\theta\left\{\rho\frac{\partial s}{\partial\rho}\boldsymbol{\nabla}\cdot\mathbf{v}+\frac{\partial s}{\partial\alpha}\boldsymbol{\nabla}\rho\cdot[D:\boldsymbol{\nabla}\rho+\boldsymbol{\nabla}(\rho\boldsymbol{\nabla}\cdot\mathbf{v})]\right\}\ .$$

Note that p plays the role of pressure, S is the tensor of capillary stresses, and Φ is the dissipation function. Of course, the internal energy $e(\theta,\rho,\alpha)$ and entropy $s(\theta,\rho,\alpha)$, where $\alpha=\frac{1}{2}|\boldsymbol{\nabla}\rho|^2$, are given by Eqs. (8) in terms of the free energy $f(\theta,\rho,\alpha)$.

III. EQUILIBRIUM OF A LIQUID-VAPOR SYSTEM

Let us analyze an equilibrium state of a liquid-vapor system in a horizontal layer of thickness L, assuming that density ρ varies in the direction of gravity only (flat interface). If $\mathbf{v}=\mathbf{0}$ and θ is constant, the force balance equation takes the form

$$\boldsymbol{\nabla}\cdot(pG-S)=\rho\mathbf{g}.$$

There exists an equilibrium with $\rho=\rho(x)$, where $\mathbf{x}=\mathbf{x}\cdot\mathbf{e}$ and $\mathbf{e}$ is the unit vector of the direction of $\mathbf{g}$ $(\mathbf{g}=g\mathbf{e})$. In this case,

$$S=\rho(x)\frac{\partial f(\theta,\rho(x),\frac{1}{2}\rho'(x)^2)}{\partial\alpha}|\rho'(x)|^2(G-\mathbf{e}\otimes\mathbf{e})\ ,$$

and the equilibrium equation reduces to $(0<x<L)$

$$\frac{\partial p}{\partial x}=\rho g,\quad p=\rho^2\left[\frac{\partial f}{\partial\rho}-\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial\alpha}\frac{\partial\rho}{\partial x}\right)\right]. \tag{15}$$

This is a third-order equation which requires three boundary conditions. In the view of Eq. (7), one can put

$$\rho'(0)=\rho'(L)=0,\qquad\int_0^L\rho(x)\mathrm{d}x=M.$$

Assuming that

$$\left|\rho\frac{\partial f}{\partial\alpha}\Big/\frac{\partial f}{\partial\rho}\right|\ll L^2\ ,$$

it is straightforward to demonstrate that, under some mild assumptions, $\rho(x)$ rapidly varies in a narrow interfacial layer, say $a<x<a+h$, where $h\ll L$. In this case, surface tension has the expression

$$\sigma(\theta)=\int_0^L \rho(x)\,\frac{\partial f\big(\theta,\rho(x),\tfrac{1}{2}\rho'(x)^2\big)}{\partial\alpha}|\rho'(x)|^2dx$$

$$\approx\int_a^{a+h}\rho(x)\,\frac{\partial f}{\partial\alpha}\big(\theta,\rho(x),\,\tfrac{1}{2}\rho'(x)^2\big)|\rho'(x)|^2dx.$$

Let us give another expression for surface tension in terms of the excess quantities. Note that Eq. (9) can be written as

$$\zeta=f+\rho\,\frac{\delta f}{\delta\rho}-\frac{\partial f}{\partial\alpha}|\boldsymbol{\nabla}\rho|^2,$$

or, equivalently,

$$\rho\,\frac{\partial f}{\partial\alpha}|\boldsymbol{\nabla}\rho|^2=\rho(f-\zeta)+p.$$

Let us put $g=0$, which implies that p is constant. Since ζ is also constant at equilibrium, one derives the following expression for surface tension:

$$\sigma=\int_0^L\{\rho(x)[f(x)-\zeta]+p\}dx$$

$$\approx\int_a^{a+h}\{\rho(x)[f(x)-\zeta]+p\}dx.$$

In other words, the surface tension is equal to the excess Gibbs potential. It is straightforward to demonstrate that, as $h/L\to 0$, this approximate expression transforms to the classical definition of surface tension as the excess free energy. This is true even in the general case of $g\neq 0$, because pressure is finite due to Eq. (15). In this case, the surface tension is positive if the excess free energy in the interfacial layer is large enough [18].

IV. POTENTIAL FLOW OF AN INVISCID ISOTHERMAL FLUID

It is straightforward to check that

$$\frac{1}{\rho}(\boldsymbol{\nabla}p-\boldsymbol{\nabla}\cdot S)=\boldsymbol{\nabla}\zeta-\frac{\partial f}{\partial\theta}\boldsymbol{\nabla}\theta, \tag{16}$$

where ζ is given by Eq. (9). Indeed, since $S\cdot\boldsymbol{\nabla}\rho=\mathbf{0}$,

$$\begin{aligned}\frac{1}{\rho}(\boldsymbol{\nabla}p-\boldsymbol{\nabla}\cdot S)&=\boldsymbol{\nabla}\left(\frac{p}{\rho}\right)+\frac{p}{\rho^2}\boldsymbol{\nabla}\rho-\boldsymbol{\nabla}\cdot\left(\frac{S}{\rho}\right)\\&=\boldsymbol{\nabla}\left(\rho\,\frac{\delta f}{\delta\rho}\right)+\frac{\delta f}{\delta\rho}\boldsymbol{\nabla}\rho\\&\quad-\boldsymbol{\nabla}\cdot\left[\frac{\partial f}{\partial\alpha}(|\boldsymbol{\nabla}\rho|^2G-\boldsymbol{\nabla}\rho\otimes\boldsymbol{\nabla}\rho)\right]\\&=\boldsymbol{\nabla}\left(\rho\,\frac{\delta f}{\delta\rho}-\frac{\partial f}{\partial\alpha}|\boldsymbol{\nabla}\rho|^2\right)+\frac{\partial f}{\partial\rho}\boldsymbol{\nabla}\rho+\frac{\partial f}{\partial\alpha}\boldsymbol{\nabla}\alpha\\&=\boldsymbol{\nabla}\left(f+\rho\,\frac{\delta f}{\delta\rho}-\frac{\partial f}{\partial\alpha}|\boldsymbol{\nabla}\rho|^2\right)-\frac{\partial f}{\partial\theta}\boldsymbol{\nabla}\theta\\&=\boldsymbol{\nabla}\zeta-\frac{\partial f}{\partial\theta}\boldsymbol{\nabla}\theta\,,\end{aligned}$$

because $\boldsymbol{\nabla}\rho\cdot\boldsymbol{\nabla}\boldsymbol{\nabla}\rho=\boldsymbol{\nabla}\alpha$. In particular, an isothermal reversible flow of capillary fluid, with the effects of viscosity and heat conductivity neglected, is governed by the following system of equations:

$$\frac{\partial\rho}{\partial t}+\boldsymbol{\nabla}\cdot(\rho\mathbf{v})=0, \tag{17}$$

$$\frac{\partial\mathbf{v}}{\partial t}+\mathbf{v}\cdot\boldsymbol{\nabla}\cdot\mathbf{v}=\mathbf{g}-\boldsymbol{\nabla}\left[\frac{\delta(\rho f)}{\delta\rho}\right], \tag{18}$$

where $f=f(\rho,\,\tfrac{1}{2}\,|\boldsymbol{\nabla}\rho|^2)$. For potential external force, $\mathbf{g}=-\boldsymbol{\nabla}\Pi$, the velocity field can be potential as well,

$$\mathbf{v}=-\boldsymbol{\nabla}\varphi. \tag{19}$$

Since φ is determined by $\mathbf{v}$ apart from an arbitrary function of time, one obtains the problem

$$\frac{\partial\rho}{\partial t}=\boldsymbol{\nabla}\cdot(\rho\boldsymbol{\nabla}\varphi), \tag{20}$$

$$\frac{\partial\varphi}{\partial t}=\tfrac{1}{2}|\boldsymbol{\nabla}\varphi|^2+\frac{\delta(\rho f)}{\delta\rho}+\Pi(\mathbf{x},t), \tag{21}$$

which has to be solved in a region $\mathcal{D}$ with the following boundary conditions:

$$\frac{\partial\rho}{\partial n}=0,\quad\frac{\partial\varphi}{\partial n}=0\quad\text{on }\partial\mathcal{D}. \tag{22}$$

The first condition stems from Eq. (7), but the second one reflects the impermeability of the rigid boundary of the flow domain. This is a self-contained system of equations which is capable of mimicking the effect of capillarity. Numerical solution of Eqs. (20)–(22) will be the subject of a separate paper.

Variational principle

Let us demonstrate that the above equations do admit a variational principle which transforms to that derived in [20]. Following [21], let us write the classical Lagrange principle with the contraint given by the continuity equation (17),

$$L(\rho,\mathbf{v},\varphi)=\int_0^T\int_{\mathcal{D}}\Big\{\rho\left(\tfrac{1}{2}|\mathbf{v}|^2-f-\Pi\right)-\varphi\left[\frac{\partial\rho}{\partial t}+\boldsymbol{\nabla}\cdot(\rho\mathbf{v})\right]\Big\}d\mathcal{D}\,dt,$$

where φ is here the Lagrange multiplier. The variation of the above functional with respect to $\mathbf{v}$ and ρ immediately gives Eqs. (19) and (21). Upon inserting these expressions into L, one finds

$$L=\int_0^T\int_{\mathcal{D}}\left(p-\rho\frac{\partial f}{\partial\alpha}|\boldsymbol{\nabla}\rho|^2\right)d\mathcal{D}\,dt.$$

In the case of vanishing thickness of the capillary layer, the liquid phase will occupy the region $\mathcal{D}^*(t)\subset\mathcal{D}$ with the free liquid-vapor boundary $\mathcal{S}(t)$, and the functional reduces to

$$L=\int_0^T\left[\int_{\mathcal{D}^*(t)}p\,d\mathcal{D}-\int_{\mathcal{S}(t)}\sigma\,d\mathcal{S}\right]dt.$$

This is the main result obtained in [20] and discussed in detail in [21].

V. LINEARIZED MODEL

Let us consider a steady-state solution $\rho=\rho_0$, $\mathbf{v}=\mathbf{0}$, and $\theta=\theta_0$, which corresponds to equilibrium of a homogeneous fluid occupying the whole space at $\mathbf{g}=\mathbf{0}$. Linearizing Eqs. (12)–(14) at this state gives

$$\frac{\partial\rho'}{\partial t}+\rho_0\boldsymbol{\nabla}\cdot\mathbf{v}=0, \tag{23}$$

$$\rho_0\frac{\partial\mathbf{v}}{\partial t}=\left(\rho^2\frac{\partial s}{\partial\rho}\right)_0\boldsymbol{\nabla}\theta'-\left[\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial f}{\partial\rho}\right)\right]_0\boldsymbol{\nabla}\rho'+\left(\rho^2\frac{\partial f}{\partial\alpha}\right)_0\boldsymbol{\nabla}(\Delta\rho')+(\lambda_0+\mu_0)\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\mathbf{v})+\mu_0\Delta\mathbf{v}, \tag{24}$$

$$\left(\rho\frac{\partial e}{\partial\theta}\right)_0\frac{\partial\theta'}{\partial t}=\kappa_0\Delta\theta'+\left(\rho^2\theta\frac{\partial s}{\partial\rho}\right)_0\boldsymbol{\nabla}\cdot\mathbf{v}, \tag{25}$$

where ρ' and θ' are the perturbed quantities, and subscript zero indicates the variables taken at the equilibrium state. This problem can be reduced to variables (ρ',η',θ'), where $\eta'=\boldsymbol{\nabla}\cdot\mathbf{v}$, namely

$$\frac{\partial\rho'}{\partial t}+\rho_0\eta'=0\ , \tag{26}$$

$$\rho_0\frac{\partial\eta'}{\partial t}=\left(\rho^2\frac{\partial s}{\partial\rho}\right)_0\Delta\theta'-\left[\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial f}{\partial\rho}\right)\right]_0\Delta\rho'+\left(\rho^2\frac{\partial f}{\partial\alpha}\right)_0\Delta^2\rho'+(\lambda_0+2\mu_0)\Delta\eta', \tag{27}$$

$$\left(\rho\frac{\partial e}{\partial\theta}\right)_0\frac{\partial\theta'}{\partial t}=\kappa_0\Delta\theta'+\left(\rho^2\theta\frac{\partial s}{\partial\rho}\right)_0\eta'. \tag{28}$$

Let us analyze the disturbances into normal modes, and look for solutions of the form

$$(\rho',\eta',\theta')=(R,H,\Theta)\mathrm{e}^{\mathbf{ik}\cdot\mathbf{x}-\omega t},$$

where R, H, and Θ are constant, $\mathbf{k}$ is a wave vector, and ω is the complex frequency. As a result, the dispersion equation is obtained as

$$(\omega-\chi_0|\mathbf{k}|^2)[\omega^2-2\nu_0|\mathbf{k}|^2\omega+(\beta_0+\gamma_0|\mathbf{k}|^2)|\mathbf{k}|^2]+\delta_0|\mathbf{k}|^2\omega=0,$$

where

$$\chi_0=\left(\rho\frac{\partial e}{\partial\theta}\right)_0^{-1}\kappa_0,\qquad \nu_0=\frac{\lambda_0+2\mu_0}{2\rho_0},$$

$$\beta_0=\left[\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial f}{\partial\rho}\right)\right]_0,\qquad \gamma_0=\left(\rho^2\frac{\partial f}{\partial\alpha}\right)_0,$$

$$\delta_0=\left(\frac{\partial e}{\partial\theta}\right)_0^{-1}\left[\rho^2\theta\left(\frac{\partial s}{\partial\rho}\right)^2\right]_0.$$

It is straightforward to check that all the roots of this polynomial have positive real parts if $|\mathbf{k}|\neq 0$ and

$$2\nu_0+\chi_0>0,\qquad \chi_0(\beta_0+\gamma_0|\mathbf{k}|^2)>0,$$

$$(2\nu_0+\chi_0)(2\nu_0\chi_0+\delta_0)+2\nu_0(\beta_0+\gamma_0|\mathbf{k}|^2)>0.$$

It is clear that the only non-trivial condition of stability is

$$\beta_0+\gamma_0|\mathbf{k}|^2>0,$$

because all the physical properties are positive except for β_0.

In particular, the stability condition is not valid if $\beta_0<0$. Adopting the principle of the exchange of stability (i.e., a stationary pattern of motions prevails at the onset of instability), the critical wave vector is found at $\omega=0$ as $|\mathbf{k}|=\sqrt{-\beta_0/\gamma_0}$. It is straightforward to check that the secondary solution is $\rho'=Re^{\mathbf{ik}\cdot\mathbf{x}}$, $\eta'=0$, and $\theta'=0$. Therefore, $1/|\mathbf{k}|$ can be identified with the characteristic size of critical nuclei. This situation occurs for the van der Waals gas [22] below its critical state. Indeed, in variables rendered dimensionless by their critical values, the specific free energy can be expressed as

$$f=\frac{8\theta}{3}\ln\frac{\rho}{3-\rho}-3\rho+c\,\theta(1-\ln\theta)+\frac{\varepsilon^2}{2}\theta|\boldsymbol{\nabla}\rho|^2,$$

where the parameter ε is assumed to be small. In particular,

$$p=\frac{8\theta\rho}{3-\rho}-3\rho^2-\varepsilon^2\rho^2\boldsymbol{\nabla}\cdot(\theta\boldsymbol{\nabla}\rho),$$

$$s=c\ln\theta-\tfrac{8}{3}\ln\frac{\rho}{3-\rho}-\frac{\varepsilon^2}{2}|\boldsymbol{\nabla}\rho|^2,$$

$$e = c\theta - 3\rho.$$

In this case, the entropy as a function of extensive thermodynamic variables has the form

$$s = c\ln\frac{e+3\rho}{c} - \tfrac{8}{3}\ln\frac{\rho}{3-\rho} - \frac{\varepsilon^2}{2}|\boldsymbol{\nabla}\rho|^2.$$

The critical wave vector is determined by the condition

$$|\mathbf{k}|^2 = \frac{6}{\varepsilon^2\rho_0\theta_0}\left[1 - \frac{4\theta_0}{\rho_0(3-\rho_0)^2}\right],$$

the right-hand side of which is positive provided that

$$\theta_0 < \frac{\rho_0(3-\rho_0)^2}{4}.$$

For example, if $\rho_0 = 1$, that corresponds to the critical state, then $\theta_0 < 1$. This model is capable of describing equilibrium density profiles and localized density inhomogeneities (critical nuclei). As is expected, the size of critical nuclei has the order of ε. Also note that capillary forces do not arise in the linearized model.

It is worth emphasizing that the surface tension of the van der Waals gas is proportional to ε and hence vanishes as $\varepsilon \to 0$ [23]. The same fact is revealed in [10] for a solidification problem. In order to avoid this shortcoming, one has to assume that the free energy in the interfacial layer is large enough [11,17,18].

VI. CONCLUSION

A model of capillarity of a one-component compressible fluid is derived from the balance of mass, momentum, and energy, completed with thermodynamic relations. The order parameter of the fluid is its density, which varies continuously in the liquid-vapor layer, and the fluid entropy depends additionally on the gradient of density. Naturally, no diffusion mechanism of phase separation is adopted for a one-component fluid. Instead, the phase separation is driven by the momentum equation, with pressure being the variational derivative of free energy times density squared. The derived model transforms to the classical model of motion of a compressible viscous gas provided that any dependence of thermodynamic variables on $\alpha = \frac{1}{2}|\boldsymbol{\nabla}\rho|^2$ is suppressed, and contains the classical variational principle for potential inviscid isothermal flow.

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[1] J. W. Gibbs, *Collected Works* (Yale University Press, New Haven, CT, 1948), Vol. 1.
[2] S. Ono and S. Kondo, *Molecular Theory of Surface Tension in Liquids* (Springer-Verlag, Berlin, 1960).
[3] L. G. Napolitano, Acta Astronaut. **5**, 655 (1978).
[4] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).
[5] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **31**, 688 (1959).
[6] L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Addison-Wesley, Reading, MA, 1958).
[7] W. W. Mullins and R. F. Sekerka, J. Appl. Phys. **34**, 323 (1963).
[8] W. W. Mullins and R. F. Sekerka, J. Appl. Phys. **35**, 445 (1964).
[9] S. M. Allen and J. W. Cahn, Acta Metall. **27**, 1085 (1979).
[10] G. Caginalp, Arch. Rat. Mech. Anal. **92**, 206 (1986).
[11] G. Caginalp, Phys. Rev. A **39**, 5887 (1989).
[12] S. Angenent and M. E. Gurtin, Arch. Rat. Mech. Anal. **108**, 323 (1989).
[13] H. W. Alt and I. Pawlov, Adv. Math. Sci. Appl. **1**, 319 (1992).
[14] J. Sprekels and S. Zheng, J. Math. Anal. Appl. **176**, 200 (1993).
[15] C. Sagui and R. C. Desai, Phys. Rev. E **52**, 2822 (1995).
[16] G. Caginalp and J. Jones, Ann. Phys. **237**, 66 (1995).
[17] V. N. Starovoitov, J. Appl. Mech. Tech. Phys. **35**, 891 (1994).
[18] L. K. Antanovskii, Phys. Fluids **7**, 747 (1995).
[19] A. J. M. Yang, P. D. Fleming III, and J. H. Gibbs, J. Chem. Phys. **64**, 3732 (1976).
[20] J. C. Luke, J. Fluid Mech. **27**, 395 (1967).
[21] R. L. Seliger and G. B. Whitham, Proc. R. Soc. London Ser. A **305**, 1 (1968).
[22] Y. B. Rumer and M. S. Ryvkin, *Thermodynamics, Statistical Physics, and Kinetics* (Mir, Moscow, 1980).
[23] L. M. Truskinovskii, Dok. Akad. Nauk SSSR **269** (3), 587 (1983) [Sov. Phys. Dokl. **28**, 248 (1983)].