HAL
open science

Linear Growth of a Liquid Droplet Divided from its Vapour by a " SOAP BUBBLE"- like Fluid Interface

Francesco Dell'Isola

To cite this version:

Francesco Dell'Isola. Linear Growth of a Liquid Droplet Divided from its Vapour by a " SOAP BUBBLE"- like Fluid Interface. International Journal of Engineering Science, 1989, pp.15. hal-00498047

HAL Id: hal-00498047

https://hal.science/hal-00498047v1

Submitted on 6 Jul 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

LINEAR GROWTH OF A LIQUID DROPLET DIVIDED FROM ITS VAPOUR BY A "SOAP BUBBLE"-LIKE FLUID INTERFACE

FRANCESCO DELL'ISOLA

Dipartimento di Matematica e sue Applicazioni, Università di Napoli, Via Mezzocannone 8, I-80134 Napoli, Italy

(Communicated by E. Ş. SUHUBI)

Abstract—The theory proposed in [1, 3] is particularized to describe the spherically symmetric growth, in the neighbourhood of an equilibrium state far from the critical temperature, of a liquid incompressible droplet surrounded by its vapour when the interface between the phases behaves as a fluid membrane which resembles a soap bubble. A free moving boundary problem for an integro-differential equation of parabolic type is deduced in which the second-order time derivative of the radius $R(t)$ of the droplet appears, together with a volume source term which depends on the history of R.

1. INTRODUCTION

The aim of this paper is to deduce from the general theory expounded in [1, 3] a one-dimensional free-moving-boundary-problem modelling the spherically symmetric growth of a liquid droplet surrounded by its vapour when:

(i) the vapour behaves as a perfect gas;
(ii) the liquid is incompressible;
(iii) the interface between liquid and vapour behaves as a "soap bubble"-like fluid nonmaterial membrane, i.e. it carries thermomechanical quantities (as surface linear momentum and internal energy), and surface specific inner energy ε_σ is given by the relation:

$$\varepsilon_\sigma = \Gamma(\vartheta)/\rho_\sigma + C_\sigma(\vartheta_\sigma)\vartheta_\sigma + D_\sigma$$

which has the same structure of specific inner energy of the bidimensional material continuous system usually used to model soap bubbles. A justification of this definition is given in [20] from both a physical and mathematical point of view (see also the Appendix);
(iv) the growth takes place in the neighbourhood of an equilibrium state in which both phases are present and whose temperature is far from the critical one. This means that the evolution equations of the system can be linearized.

In Section 2 the results obtained in [1] are summarized.

In Section 3 hypotheses (i), (ii), (iii) are translated in a mathematical language, while in Section 4 the hypotheses of spherical symmetry and nonmateriality are exploited in order to particularize the results quoted in [2].

In Section 5 we recognize that in the previous sections a free-moving-boundary-problem (FMBP) for speed, temperature and density fields has been formulated, and choose a set of initial and boundary conditions for it, suggested by a particular physical situation.

In Section 6 our main result is stated: when linearized, quoted FMBP can be solved if and only if a given FMBP for the temperature field alone is solved.

In Sections 7–10 quoted result is proved.

We remark that together with some technical hypotheses we formulate one which has a particular physical meaning: surface constitutive equations must yield boundary conditions which Serrin proved assure uniqueness of compressible fluid motion (see [12]). In [3] the necessity of such an hypothesis was underlined in the general case: we give here one which is suitable for considered particular case.

ES 27-9-D

In Section 11 a limitation of the general theory arising even when dealing with our particular case is discussed: when phase transition takes place with a speed greater than that of the sound in the vapour, the model proposed in [3] has to be implemented.

2. EVOLUTION EQUATIONS FOR CONTINUOUS SYSTEMS WITH AN INTERFACE

In [1] balance equations and constitutive relations are proposed for a physical system, constituted by a pure substance, in which:

(a) phase transition is taking place;
(b) the phases are shared by an interface $\mathcal{S}$ carrying thermomechanical properties.

In the regions occupied by bulk materials the quoted balance equations read:

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \rho \dot{\mathbf{x}} = 0$$

$$\rho \ddot{\mathbf{x}} = \operatorname{div} \mathbf{T} + \rho \mathbf{b}$$

$$\rho \dot{\varepsilon} = \mathbf{T} : \operatorname{grad} \dot{\mathbf{x}} - \operatorname{div} \mathbf{h} + \rho r \tag{2.1}$$

where ρ, ε, r and $\mathbf{b}$ are, respectively, mass density, specific energy, energy supply and external body force. Moreover $\mathbf{T}$ is the Cauchy stress tensor, $\mathbf{h}$ the heat flux vector, $\dot{\mathbf{x}}$ the volume velocity field, : denotes the operation of saturation between tensors, while the symbols grad and div denote the usual differential operators.

On the interface $\mathcal{S}$ sharing the phases we have:

$$\frac{\delta_n}{\delta t} \rho_\sigma - 2Hc_n\rho_\sigma + (\rho_\sigma v^\alpha)_{|\alpha} + [\![\dot{\rho}(\dot{x}_n - c_n)]\!] = 0$$

$$\rho_\sigma \frac{\delta_n}{\delta t} v^i + \rho_\sigma v^i_{,\alpha} v^\alpha - T^{i\alpha}_{\sigma|\alpha} + [\![\rho(\dot{\mathbf{x}} - \mathbf{v})(\dot{x}_n - c_n) - \mathbf{T} \cdot \mathbf{n}]\!] = 0$$

$$\rho_\sigma \frac{\delta_n}{\delta t} \varepsilon_\sigma + \rho_\sigma \varepsilon_{\sigma,\alpha} v^\alpha - T^{i\alpha}_\sigma v^i_{,\alpha} + h^\alpha_{\sigma|\alpha}$$

$$+ \left[\!\!\left[\rho\left(\frac{1}{2}(\dot{\mathbf{x}} - \mathbf{v})^2 + (\varepsilon - \varepsilon_\sigma)\right)(\dot{x}_n - v_n) - (\dot{\mathbf{x}} - \mathbf{v}) \cdot \mathbf{T} \cdot \mathbf{n} + \mathbf{h} \cdot \mathbf{n} \right]\!\!\right] = 0 \tag{2.2}$$

where ρ_σ, ε_σ, $\rho_\sigma \mathbf{v}$, are respectively the surface mass density, the specific energy, the surface density of linear momentum; c_n the speed of the interface along its normal $\mathbf{n}$, H the mean curvature of the interface, $\mathbf{v} \equiv v^i \mathbf{e}_i \equiv v^\alpha \mathbf{a}_\alpha + v_n \mathbf{n}$, with $\mathbf{e}_i$ an arbitrary set of orthonormal vectors of $\mathbb{R}^3$ and $\mathbf{a}_\alpha$ the basis vectors associated to the surface coordinate $\mathcal{U}^\alpha$, $(\alpha = 1, 2,\ i = 1, 2, 3)$; $\dot{x}_n \equiv \dot{\mathbf{x}} \cdot \mathbf{n}$, $\mathbf{T}_\sigma$ is the surface stress tensor (as it maps vectors tangent to $\mathcal{S}$ in $\mathbb{R}^3$ we have defined $\mathbf{T}_\alpha(\mathbf{a}_\alpha) \equiv T^{i\alpha}_\sigma \mathbf{e}_i$), $\mathbf{h}_\sigma$ the surface heat flux vector. Moreover the symbols:

$$\frac{\delta_n}{\delta t}, \quad (\cdots)_{|\alpha}, \quad (\cdots)_{,\alpha}$$

denote respectively the Thomas operator (defined for instance in [1]), the covariant derivative along $\mathbf{a}_\alpha$ and the derivative with respect to the variable $\mathcal{U}^\alpha$, while the summation over the repeated indices is intended.

Finally the symbol $[\![g]\!]$ denotes the quantity $g^+ - g^-$ where $g^\pm$ are the limits of g on the surface respectively from the region where the unit normal $\mathbf{n}$ to the surface $\mathcal{S}$ is pointing and from the other one.

3. CONSTITUTIVE EQUATIONS FOR BULK PHASES AND INTERFACE: LINEAR MATERIALS AND THE "SOAP BUBBLE" APPROXIMATION

Constitutive equations for bulk materials and the interface have to be added to (2.1), (2.2) in order to specify the properties of the considered materials. We will deal with "linear" materials, i.e. with materials whose constitutive equations show a "linear" behaviour. This linear behaviour occurs for instance when the considered process takes place in the "neighbourhood" of an equilibrium state (see Section 8).

Let us begin with constitutive equations for the interface $\mathcal{S}$.

We assume that the interface $\mathcal{S}$ does not show resistivity to heat flux (this circumstance often experimentaly occurs, see for instance [13]) so that on $\mathcal{S}$ the temperature field ϑ does not suffer any kind of jump. More precisely this means:

$$[\![\vartheta]\!] = 0 \qquad \vartheta^+ = \vartheta^- = \vartheta_\sigma \tag{3.1}$$

Moreover we assume that $\mathcal{S}$ is as a "soap bubble"-like film, i.e. that $\mathcal{S}$ behaves as a fluid membrane and its inner specific energy has a structure which parallels that of soap bubble films. In formulas this means:

$$\mathbf{T}_\sigma = \gamma \mathbf{I}_\sigma \tag{3.2}$$

$$\varepsilon_\sigma = \Gamma(\vartheta_\sigma)/\rho_\sigma + C(\vartheta_\sigma)\vartheta_\sigma + D_\sigma \tag{3.3}$$

$\gamma(\vartheta_\sigma, \rho_\sigma)$ being the surface tension and $\mathbf{I}_\sigma$ the identity matrix on $\mathcal{S}$.

In what follows we assume:

$$C(\vartheta_\sigma) = C_\sigma \quad \text{independent of } \vartheta_\sigma \tag{3.4}$$

Moreover as we will restrict ourselves (Section 8) to the description of motions near an equilibrium state, we will assume negligible surface adsorption of mass on the interface. In [11] there are described some experimental instances where these hypotheses are justified. Therefore

$$[\![J]\!] = [\![\rho(\dot{x} - c_n)]\!] = 0 \tag{3.5}$$

However (3.5) does not mean that $\mathcal{S}$ is material.

With regard to the remaining surface constitutive equations, which have to be specified, we assume, according to [3], that:

$$\left(\frac{1}{2}(\dot{\mathbf{x}} - \mathbf{v})^2 + g\right)^+ + \left(\frac{1}{2}(\dot{\mathbf{x}} - \mathbf{v})^2 + g\right)^- - 2g_\sigma = \alpha_1 [\![J]\!] \tag{3.6}$$

$$\left[\!\!\left[\frac{1}{2}(\dot{\mathbf{x}} - \mathbf{v})^2 + g\right]\!\!\right] = \alpha_2(J^+ + J^-) \tag{3.7}$$

$$\cdot(v_n - c_n) = \alpha_3\{2H\gamma - [\![\hat{p}]\!]\} \tag{3.8}$$

where $\hat{p}$ is defined as $\mathbf{n}\cdot\mathbf{T}\cdot\mathbf{n}$ on both sides of $\mathcal{S}$, the specific Gibbs volume and surface potentials $\gamma \equiv \psi + \hat{p}/\rho$ and $g_\sigma \equiv \psi_\sigma - \gamma/\rho_\sigma$ are defined in terms of the volume and surface specific free energies and finally α_i are suitable negative quantities.

Next we discuss constitutive equations for bulk phases.

We will assume that the liquid phase is incompressible while the vapour behaves as a perfect gas so that:†

$$\rho_l = \text{constant} \qquad \mathbf{T}_l = -p_l \mathbf{I} \tag{3.9}$$

$$\mathbf{T}_v = -p_v \mathbf{I} \qquad p_v = R_v \rho_v \vartheta \tag{3.10}$$

Equation (3.10) implies, together with entropy principle (see for instance [2]), that the specific volume internal energy in the vapour phase ε_v depends only on the temperature ϑ.

† In what follows when misunderstanding is possible we will use the index l and v to distinguish between the liquid phase and the vapour one. Moreover we will assume that the normal $\mathbf{n}$ is pointing towards the vapour phase so that if g denotes a volume quantity to be evaluated on $\mathcal{S}$ the following equalities hold: $g^+ = g_v$ and $g^- = g_l$.

Moreover it is experimentally verified that Regnault's law for vaporization heat holds. This law states the linear dependence of vaporization latent heat on temperature. In formulas it reads:

$$L(\vartheta) = L_0 + \Lambda_R(\vartheta - \vartheta_0) \tag{3.11}$$

where L_0 is vaporization latent heat at the temperature ϑ_0, and Λ_R is called Regnault's constant. While in general both L_0 and Λ_R depend on the pressure, we will assume that they are constant.

Quoted considerations imply that if we assume that:

$$\varepsilon_v = c_v(\vartheta - \vartheta_0), \tag{3.12}$$

because of (3.11), we will have:

$$\varepsilon_l = c_l(\vartheta - \vartheta_0) - L_0, \tag{3.13}$$

where $c_v - c_l = \Lambda_R$. We underline that both the specific heats c_l and c_v together with the coefficient R_v and the latent heat L_0 experimentally are verified to be greater than zero. Finally we will assume the Fourier law for the heat conduction:

$$\begin{aligned} \mathbf{h} &= -K_l \nabla\vartheta \quad \text{in the liquid phase} \\ \mathbf{h} &= -K_v \nabla\vartheta \quad \text{in the vapour phase} \end{aligned} \tag{3.14}$$

where $K_v > 0$ and $K_l > 0$.

4. SPHERICALLY SYMMETRIC SYSTEMS IN THE ABSENCE OF EXTERNAL BODY FORCES

We limit ourselves to deal with the spherically symmetric evolution of the system S of a liquid droplet in the presence of its pure vapour.

More precisely, we will assume that:

(a) The fields describing S depend only on the distance r from the centre of the spherical volume initially occupied by the considered droplet.

(b) All the vector fields have nonzero components only along the radial direction. In particular on the interface this means that

$$\dot{\mathbf{x}}_\tau^+ = \dot{\mathbf{x}}_\tau^- = \mathbf{v}_\tau = \mathbf{0}\dagger. \tag{4.1}$$

Assumptions (a) and (b) imply that:

(i) The shape of the interface remains always spherical so that its evolution will be completely known if the function $R(t)$ giving its radius is known. This circumstance implies that any surface quantity f_σ depends on the variable t alone and that moreover we have

$$\frac{\delta_n}{\delta t} f_\sigma = \frac{\mathrm{d}}{\mathrm{d}t} f_\sigma \tag{4.2}$$

(ii) We will denote the surviving radial component, depending on the radial coordinate r alone, with the same letter used for the corresponding vector field. For instance if $\mathbf{h}$ is the heat flux vector field, because of our assumptions, its only nonvanishing component is the radial one which depends only on the variable r and will be denoted by the letter h.

† In [9] surface balance equations (2.2) were fully justified when the following equality was verified on the interface:

$$\mathbf{x}_\tau^+ = \dot{\mathbf{x}}_\tau^- = \mathbf{v}_\tau$$

Because of (b) in the case of spherical symmetry this assumption can be verified even by nonviscous fluids, with which we are dealing (see Section 3).

Using (i) and (ii) we can now prove:

LEMMA 4.1: If assumptions (a) and (b) are verified, no singular mass production takes place in $r=0$ and the volume constitutive equations listed in Section 3 are assumed, then equations (2.1) become:

In the liquid phase, i.e. $\forall r \in [0, R(t))$

$$\dot{x}_l(r) = 0$$

$$p_l(r, t) = p_l(t)$$

$$c_l\rho_l/K_l \frac{\partial \vartheta}{\partial t} = \frac{1}{r}\frac{\partial^2(r\vartheta)}{\partial r^2} \tag{4.3}$$

In the vapour phase, i.e. $\forall r > R(t)$

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial r}\dot{x} + \rho\frac{1}{r^2}\frac{\partial(r^2\dot{x})}{\partial r} = 0\dagger$$

$$\rho\left(\frac{\partial \dot{x}}{\partial t} + \dot{x}\frac{\partial \dot{x}}{\partial r}\right) = R_v\vartheta\frac{\partial \rho}{\partial r} + R_v\rho\frac{\partial \vartheta}{\partial r}\ddagger$$

$$\rho c_v\left(\frac{\partial \vartheta}{\partial t} + \frac{\partial \vartheta}{\partial r}\dot{x}\right) = -p\frac{1}{r^2}\frac{\partial(r^2\dot{x})}{\partial r} + K_v\frac{1}{r}\frac{\partial^2(r\vartheta)}{\partial r^2} \tag{4.4}$$

PROOF: We first of all remark that in order to obtain equation $(4.4)_1$ we just used the expression of the divergence operator in the spherical system of coordinates, while, in order to obtain the remaining equations (4.4), we projected the equations $(2.1)_{1,2}$ along the versor e_r and used the expression in spherical coordinates of divergence, material derivation and gradient operators. On the other hand equation $(4.3)_1$ is easily obtained when we recall that because of the assumed incompressibility of liquid phase equation (2.1) becomes; $(r^2\dot{x})_{,r} = 0$§, so that we have $\dot{x} = \mathscr{k}(t)/r^2$ which is compatible with our assumption about the absence of singular mass production only if $\mathscr{k}(t) = 0$. Equations $(4.3)_{2,3}$ are an obvious consequence of equation $(2.1)_{1,2}$ when equation $(4.3)_1$ is taken into account. ■

With regard to the surface constitutive and balance equations, (i) and (ii) allow us to prove:

LEMMA 4.2: If $\alpha_3 \neq 0$, (a) and (b) are verified, and surface constitutive equations listed in Section 3 are assumed then equations (2.2), (3.5), and (3.6)–(3.8) respectively become:

$$\rho_\sigma = \frac{M}{4\pi R^2} \equiv \frac{c_m}{R^2}\,\|$$

$$\rho_\sigma\frac{\mathrm{d}v}{\mathrm{d}t} + \frac{(v-\dot{R})}{\alpha_3} + \rho^-\dot{R}^2\frac{\rho^+ - \rho^-}{\rho^+} = 0$$

$$c_\sigma\rho_\sigma\frac{\mathrm{d}\vartheta_\sigma}{\mathrm{d}t} - \frac{2\gamma v}{R} - \frac{2\dot{R}\vartheta_\sigma}{R}\frac{\mathrm{d}\Gamma}{\mathrm{d}\vartheta_\sigma} + \frac{2\Gamma\dot{R}}{R} - \rho^-\dot{R}\left[\!\left[\frac{1}{2}(\dot{\mathbf{x}} - \mathbf{v})^2 + \varepsilon\right]\!\right] + [\![p(\dot{x} - v)]\!] + [\![h]\!] = 0 \tag{4.5}$$

where

$$c_\sigma \equiv \left(\rho_\sigma C_\sigma - \vartheta_\sigma\frac{\mathrm{d}\Gamma}{\mathrm{d}\vartheta_\sigma}\right)\frac{1}{\rho_\sigma}$$

$$\dot{x}^+ = \dot{R}\frac{\rho^+ - \rho^-}{\rho^+} \tag{4.6}$$

$$\alpha_3\{-2\gamma/R - [\![\hat{p}]\!]\} = (v - \dot{R}) \tag{4.7}$$

$$[\![g]\!] = -2\alpha_2\rho^-\dot{R} - \left[\!\left[\frac{1}{2}(\dot{x} - v)^2\right]\!\right] \tag{4.8}$$

$$2g_\sigma = \left(g + \frac{1}{2}(\dot{x} - v)^2\right)^- + \left(g + \frac{1}{2}v^2\right)^+ \tag{4.9}$$

† See [8].
‡ See [8].
§ The commas denote differentiation with respect to the variables which follow them.
‖ M is the total mass of the surface of the droplet which remains constant because of (3.5).

PROOF: We begin remarking that (4.6) is an obvious consequence of $(3.2)_2$ when we recall $(4.3)_1$ and that $c_n = \dot{R}$. Moreover (3.5) implies that $(2.2)_1$ becomes:

$$\frac{\mathrm{d}\rho_\sigma}{\mathrm{d}t} + \frac{2\dot{R}}{R}\rho_\sigma = 0.$$

This last differential equation has a solution $(4.5)_1$. Equations (4.7)–(4.9) are obtained using (4.6) and (3.5) in (3.6)–(3.8). Equation $(4.5)_2$ is obtained from $(2.2)_2$ using (a) and (b) and substituting in the resulting formula both $(4.5)_1$ and (4.7). Finally equation $(4.5)_3$ is obtained when we recall that because of $(4.5)_1$ and (3.3) we have:

$$\rho_\sigma \frac{\mathrm{d}\varepsilon_\sigma}{\mathrm{d}t} = \rho_\sigma c_\sigma \frac{\mathrm{d}\vartheta_\sigma}{\mathrm{d}t} + \Gamma\frac{2\dot{R}}{R} - \frac{2\dot{R}\vartheta_\sigma}{R}\frac{\mathrm{d}\Gamma}{\mathrm{d}\vartheta_\sigma} \qquad \blacksquare$$

We conclude this section remarking that the assumption $\alpha_3 \neq 0$ has a physical justification. It is equivalent to state that $v - \dot{R}$ can eventually be different from zero, which is, on the other hand, equivalent to state that an interchange of mass between the phases can take place. For more details about this subject see [1].†

5. THE SYSTEM OF EQUATIONS (4.3)–(4.9) AS A FREE-MOVING-BOUNDARY-PROBLEM (FMBP). A SET OF INITIAL AND BOUNDARY CONDITIONS

From a mathematical point of view the system of equations (4.3)–(4.9) represents a FMBP. In fact (4.3)–(4.9) are the evolution equations (EE) for the set of fields (SF) univocally determining the state of considered system S. More precisely if $T \in \mathbb{R} \cup \{\infty\}$ is the length of the time interval in which two different phases are present in S, we have that SF is made up by:

(1) the real valued function $R(t) > 0$ defined in $[0, T]$;
(2) the real valued function v defined on the subset of $R^+ \times R^+$:

$$\bigcup_{t\in[0,\,T]} \{R(t), t\};$$

(3) the real valued functions ϑ, $\dot{x}$, ρ whose domains $D^+_{b_i}$ are defined as follows, $i = 1, 2, 3$‡

$$D^+_{b_i} \equiv \{(r, t) \in R^+ \times R^+ : R(t) \leq r \leq b_i\};$$

(4) the real valued function ϑ whose domain D^- is

$$D^- \equiv \{(r, t) \in R^+ \times R^+ : 0 \leq r \leq R(t)\};$$

(5) the real valued function $p_l(t)$ defined in $[0, T]$.

Equations (4.3)–(4.9) are a FMBP for SF because both $D^+_{b_i}$ and D^- depend on the unknown function $R(t)$ (see Fig. 1). The particular physical situation in which S finds itself will specify the initial and boundary conditions to be added to EE in order to uniquely determine SF.

We will limit ourselves to the following situation:

The vapour surrounding the droplet extends up to distances much greater than radius $R(t)$ of the droplet. This means that we can choose $b_{2,3} = \infty$. Moreover the vapour is surrounded by an ambient which can be regarded as a heat source with fixed temperature Θ_e so that a fixed distance b_1 (eventually finite) from the centre of the droplet the vapour has a temperature equal to Θ_e.

Initial and boundary conditions (IBC) characterizing this situation are: $\vartheta(b_1, t) = \Theta_e$; $\vartheta(r, 0) = \vartheta_0(r)$; $\rho(r, 0) = \rho_0(r)$; $\dot{x}(r, 0) = \dot{x}_0(r)$; $v(0) = v_0$; $\rho_\sigma(0) = \rho_{\sigma 0}$; $R(0) = R_0$; $\dot{R}(0) = \dot{R}_0$

† In [1] the quantity α_3 is called $1/\alpha_3$ instead. It is simply seen that this is just a notational change which is not affecting the reasonings there developed. On the other hand the choice we have done now makes more clear the quoted physical justification.

‡ We assume that $b_i \in R^+ \cup \langle\infty\rangle$. Physical meaning of the quantities b_i will be cleared up at the end of the section.

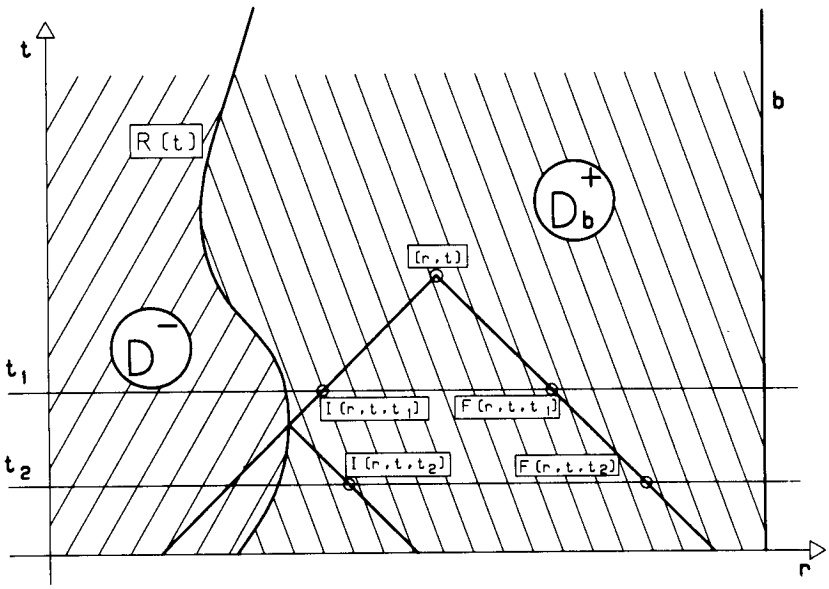

Fig. 1

and

$$\sup_{D_{b_1}^{\ddagger} \cup D^-} \vartheta(r, t) < \infty;$$

where $\vartheta_0, \dot{x}_0, \rho_0$ are given functions defined in $[0, b_i]$ respectively and $v_0, \rho_{\sigma 0}, R_0, \dot{R}_0$ are suitable constants.†

6. STATEMENT OF THE MAIN RESULT

In the following sections we linearize EE in the neighbourhood of the equilibrium state in which the temperature field has the constant Θ and the pressure field in the vapour has the constant‡ value P_e, obtaining a linear system of evolution equations (LEE) for SF. The FMBP of Section 5 type for LEE can be reduced to FMBP for the temperature field only§.

This result is made possible by the statement of the following Theorem 6.1.

It states that LEE is equivalent to a system of equations SEE in one of which (SEE ϑ) the function ϑ only appears (together with $R(t)$ and other known quantities). SEE ϑ is an integro-differential equation as the separation of LEE is obtained representing the solution of the linear hyperbolic system of equations appearing in them by means of the method of characteristic curves.

THEOREM 6.1: Let us assume that:

(i) liquid phase is incompressible, its vapour is a perfect gas and hypotheses listed in Sections 3 and 4 hold;

(ii) if **A** is the matrix

$$\mathbf{A}(\vartheta, p_l, p_v, \rho_\sigma, R) \equiv \begin{pmatrix} -2c_{1\sigma}\alpha_3/R & 1 & -1 \\ g_{v,\vartheta} - g_{l,\vartheta} & g_{v,p} & -g_{l,p} \\ g_{v,\vartheta} + g_{l,\vartheta} - 2g_{\sigma,\vartheta} & g_{v,p} & g_{l,p} \end{pmatrix}$$

where g_l and g_v are Gibbs potentials in liquid and vapour phase, $c_{1\sigma}$ is defined in

† These data are not independent. In fact constitutive equations (4.6)–(4.9) have to be taken into account.
‡ We have assumed that no body forces are present.
§ It seems possible that an iterative method similar to that used in [6] could be sufficient to solve this last FMBP.

equation (8.1) and $\mathbf{A}_0$ is $\mathbf{A}$ evaluated at the considered equilibrium condition then we assume that $\det \mathbf{A}_0 \neq 0$;

(iii) the field ϑ is such that $\vartheta_{,i}$ and $\vartheta_{,rr}$ are continuous and the fields ρ and $\dot{x}$ belong to C^1;

(iv) $R \in C^2([0, T])$, $\sup_{t\in[0,T]} |\dot{R}| < a$; where $a^2 \equiv R_v\Theta$.

Then the linearized system LEE associated with the EE in the neighbourhood of an equilibrium state characterized by the quantities Θ and P_e can be solved under initial and boundary conditions IBC if and only if the following FMBP can be solved.

Find a couple $(\vartheta_r, R(t))$ which satisfy:

$$c_l\rho_l\vartheta_{r,t} - K_l\vartheta_{r,rr} = 0 \quad \text{in } D^- \tag{6.1}$$

$$c_v\rho_v(\mathscr{E})\vartheta_{r,t} = K_g\vartheta_{r,rr} + c_v\Theta\Phi_{,t} + \tilde{k}\int_0^t \vartheta_{r,rr}\Big|_{I_\tau}^{F_\tau} \mathrm{d}\tau \quad \text{in } D_{b_1}^+ \tag{6.2}$$

$$\lambda_1\ddot{R} + \lambda_2\dot{R} + \lambda_3 v' + R^{-1}[\![K\vartheta_{r,r}]\!] + \vartheta' R^{-1}[\![K]\!] = 0 \tag{6.3}$$

$$\left.\begin{array}{c}\vartheta_r(0, t) = 0;\ \vartheta_r(R(t), t) = R(t)\vartheta'(t);\ \vartheta_r(r, 0) = r\vartheta_0(r)\\ \vartheta_r(b_1, t) = b_1\Theta_e;\ R(0) = R_0;\ \dot{R}(0) = \dot{R}_0\end{array}\right\} \tag{6.4}$$

where $\tilde{k} \equiv -c_v a^2\rho_v(\mathscr{E})$, $\rho_v(\mathscr{E})$ is the equilibrium vapour density†, while F_τ, I_τ, Φ are suitable functionals (which are defined during the proof) depending on r, t, the function $R(t)$ and in the case of Φ on IBC. Moreover λ_i are suitable constants, v' an integral functional depending on the function $R(t)$‡ and ϑ' a linear function of the variables R, $\dot{R}$, v'§.

We prove this theorem in the next sections.

7. LINEARIZATION OF VOLUME IN THE NIEGHBOURHOOD OF AN EQUILIBRIUM STATE

We first study the equilibrium state to be considered.

In [20] the equilibrium conditions implied by EE are used to prove Gibbs' phase rule. In the considered instance it is stated as follows:

GIBBS' PHASE RULE: If constitutive equations of bulk phases and their interface are those listed in Section 3, the equilibrium temperature Θ and vapour pressure P_e belong to suitable intervals characteristic of the material, then there exists a unique (uniform field of) pressure in the liquid phase and a unique radius R of the droplet for which the equilibrium conditions are verified. (See Appendix for more details.)

We therefore get some equilibrium functions of the equilibrium parameters

$$\mathscr{E} = (\Theta, P_e):$$

$R(\mathscr{E})$ i.e. the equilibrium droplet radius;
$\rho_v(\mathscr{E})$ as determined by constitutive equations of the vapour;
$p_l(\mathscr{E})$ which is determined when $\gamma(\mathscr{E})$ is given;
$p_v(\mathscr{E}) \equiv P_e$ for notations consistency;
$\rho_\sigma(\mathscr{E})$ the equilibrium surface mass density

Secondly we consider the linearized form of EE in the neighbourhood of the equilibrium state characterized by $\mathscr{E}$.

In order to obtain volume LEE we express all SF as the sum of their equilibrium part plus their "disturbance from equilibrium" part and neglect all terms in EE where the products of two of these disturbance (or of their derivatives) occur||. If we denote each disturbance with

† $\mathscr{E}$ represents the set of parameters characterizing the equilibrium states.
‡ See equation (9.1).
§ See equation (9.3).
|| This linearizing procedure is suggested in [8], p. 436.

the same letter denoting the original field but primed, we finally obtain:

In the vapour phase

$$\forall r \in [R(t), \infty]$$

$$\rho'_{,t} + \rho_v(\mathscr{E})1/r^2(r^2\dot{x}')_{,r} = 0 \tag{7.1}$$

$$\rho_v(\mathscr{E})\dot{x}'_{,t} + R_v\Theta\rho'_{,r} + R_v\rho_v(\mathscr{E})\vartheta'_{,r} = 0 \tag{7.2}$$

$$\forall r \in [R(t), b_1]$$

$$c_v\rho_v(\mathscr{E})\vartheta'_{,t} + p_v(\mathscr{E})1/r^2(r^2\dot{x}')_{,r} = K_v 1/r(r\vartheta')_{,rr} \tag{7.3}$$

In the liquid phase, i.e. $\forall r \in [0, R(t)]$

$$c_l\rho_l\vartheta'_{,t} - K_l 1/r(r\vartheta')_{,rr} = 0 \tag{7.4}$$

Finally we recognize the hyperbolic nature of the system of equations (7.1), (7.2) and introduce a new set of unknown functions replacing ϑ', ρ' and $\dot{x}'$.

If hypothesis (iii) holds, and regarding the term $p_v(\mathscr{E})1/r^2(r^2\dot{x}')_{,r}$ as a source term we see that equation (7.3) is of parabolic type, for which suitable existence and uniqueness theorems are proved in [14].

If we substitute in it (7.1) equation (7.3) becomes:

$$c_v\rho_v(\mathscr{E})\vartheta'_{,t} = K_v 1/r(r\vartheta')_{,rr} + R_v\Theta\rho'_{,t} - 0 \tag{7.5}$$

Using the results quoted in [8] the following is easily shown.

LEMMA 7.1: If we define $\vartheta_r \equiv r\vartheta'$, $\rho_r \equiv r\rho'$, $v_r \equiv r\dot{x}$ the volume linearized system LEE obtained by EE near the equilibrium state characterized by $\mathscr{E}$ is equivalent to the following one

In the vapour phase

$$\rho_{r,t} + \rho_v(\mathscr{E})v_{r,r} + \rho_v(\mathscr{E})v_r/r = 0 \tag{7.6}$$

$$\rho_v(\mathscr{E})v_{r,t} + R_v\Theta(\rho_{r,r} - \rho_r/r) + \rho_v(\mathscr{E})R_v(\vartheta_{r,r} - \vartheta_r/r) = 0 \tag{7.7}$$

$$c_v\rho_v(\mathscr{E})\vartheta_{r,t} = K_v\vartheta_{r,rr} + R_v\Theta\rho_{r,t} \tag{7.8}$$

In the liquid phase

$$c_l\rho_l\vartheta_{r,t} - K_l\vartheta_{r,rr} = 0 \tag{7.9}$$

Moreover the system of equations (7.6) and (7.7) is hyperbolic (regarding the term $\rho_v(\mathscr{E})R_v(\vartheta_{r,r} - \vartheta_r/r)$ as a source). Its characteristic curves are, in the plane of coordinates r and t, the straight lines whose slopes are $\pm 1/\sqrt{R_v\Theta}$.

We conclude this section remarking that the last of IBCs implies the following condition for ϑ_r:

$$\vartheta_r(0, t) = 0 \tag{7.10}$$

8. LINEARIZATION OF SURFACE CONSTITUTIVE AND EVOLUTION EQUATIONS IN THE NEIGHBOURHOOD OF AN EQUILIBRIUM STATE

We use the same procedure as in Section 7, expressing all considered quantities as the sum of their "equilibrium" parts plus "disturbance from equilibrium" parts. More precisely we use the notations shown in Table 1.

Table 1

$v = 0 + v'$; $R = R(\mathscr{E}) + R'$; $p_v = p_v(\mathscr{E}) + p'_v$; $p_l = p_l(\mathscr{E}) + p'_l$;
$\vartheta = \Theta + \vartheta'$; $\dot{R} = 0 + \dot{R}'$; $\rho_\sigma = \rho_\sigma(\mathscr{E}) + \rho'_\sigma$; $\rho_v = \rho(\mathscr{E}) + \rho'_v$;
$g_v = g_v(\Theta, p_v(\mathscr{E}) + g'_v$; $g_l = g_l(\Theta, p_l(\mathscr{E})) + g'_l$, where
$g'_v \equiv g_{v,\vartheta}(\mathscr{E})\vartheta' + g_{v,p}(\mathscr{E})p'_v$, $g'_l \equiv g_{1,\vartheta}(\mathscr{E})\vartheta' + g_{1,p}(\mathscr{E})p'_l$;
$g_\sigma = g_\sigma(\mathscr{E}) + g_{\sigma,\rho_\sigma}(\mathscr{E})\rho'_\sigma + g_{\sigma,\vartheta}\vartheta'$.

We begin linearizing constitutive equations $(3.10)_{1,2}$, and (3.5):

$$\gamma = \gamma_0(\Theta) + c_{1\sigma}(\Theta)\vartheta' + c_{2\sigma}(\Theta)\rho'_\sigma \tag{8.1}$$

$$p'_v = R_v\Theta\rho'_v + R_v\rho(\mathscr{E})\vartheta' \tag{8.2}$$

$$\dot{x}_v(R(t), t) = \dot{R}'(1 - \rho_l/\rho_v(\mathscr{E})) \tag{8.3}$$

In the second place we quote the linearized form of equations (3.6)–(3.8):

$$\mathbf{A}_0\mathbf{x} = \mathbf{b} \tag{8.4}$$

where the matrix $\mathbf{A}_0$ was defined in hypothesis (ii) of Theorem 6.1 and the vectors $\mathbf{x}$ and $\mathbf{b}$ are given by:

$$\mathbf{x} \equiv \begin{pmatrix} \vartheta' \\ p'_v \\ p'_l \end{pmatrix} \qquad \mathbf{b} \equiv \begin{pmatrix} v' - \dot{R}' + 2\alpha_3 c_{2\sigma}(\Theta)\rho'_\sigma/R(\mathscr{E}) \\ -2\alpha_2\rho_l\dot{R}' \\ R'4c_m g_{\sigma\rho}/R^3(\mathscr{E}) \end{pmatrix}$$

Finally we quote the linearized form of surface mass, linear momentum and energy balance equations:

$$\rho_\sigma = c_m/R^2(\mathscr{E}) - 2c_m/R^3(\mathscr{E})R' \equiv c_m/R^2(\mathscr{E}) + \rho'_\sigma \tag{8.5}$$

$$\alpha v'_{,t} + v' = \dot{R}' \tag{8.6}$$

$$\frac{c_\sigma c_m}{R^2(\Theta)}\frac{\mathrm{d}\vartheta'}{\mathrm{d}t} - \frac{2\gamma_0}{R(\Theta)}v' - \rho_l\mathscr{L}(\Theta)\dot{R}' + [\![K\vartheta'_{,r}]\!] = 0 \tag{8.7}$$

where $\alpha = \alpha_3 c_m/R^2(\mathscr{E})$ and

$$\mathscr{L}(\Theta) \equiv L(\Theta) + \frac{2}{\rho_l}\left\{\frac{\Gamma'(\Theta)}{R(\mathscr{E})} + \frac{\Gamma(\Theta)}{R(\mathscr{E})}\right\}.$$

We remark that in order to obtain previous equations we used the fact that among equilibrium quantities appearing in Table 1 the relations listed in [20] hold.

9. SOME REMARKS ABOUT EQUATIONS (8.1)–(8.7). A NEW FORM OF EQUATION (8.7)

Equation (8.6) allows us to express explicitly v' in terms of the function $R'(\tau)$ $(\rho \leq t)$. In fact (8.6) is equivalent to:

$$v'(t) = \left(\int_0^t \dot{R}'(\tau)\mathrm{e}^{\tau/\alpha}\,\mathrm{d}\tau\right)\mathrm{e}^{-t/\alpha}/\alpha + v'_0 \tag{9.1}$$

where $\rho_\sigma(0)v'_0$ is the initial surface linear momentum. Equation (9.1) allows us to observe that the constant α plays the role of a characteristic time: if $t - \tau \gg \alpha$ then $\dot{R}(\tau)$ has a negligible influence on $v'(t)$.

Concerning equation (8.4) and the related hypothesis (iii) of Theorem 6.1, i.e. that:

$$\det \mathbf{A}_0 \equiv \Delta \neq 0 \tag{9.2}$$

we remark that in [7] and [20] no such request on constitutive equations was necessary in order to assume that equilibrium states are correctly characterized by the proposed theory.

On the other hand in [3] the necessity was fully justified to introduce further conditions in order to have assured well-posedness of the dynamical problem represented by EE. We claim that when considering the system S and LEE these conditions reduce to (9.2).

In order to obtain explicitly the dependence of ϑ' on the function $R(t)$ we have to solve the linear system (8.4). We have:

$$\vartheta' = \Delta^{-1}(a_{1\vartheta}R' + a_{2\vartheta}\dot{R}' + a_{3\vartheta}v') \tag{9.3}$$

where†

$$a_{1\vartheta} = (g_{v,p} - g_{l,p})4c_m g_{\sigma,p}/R^3(\mathscr{E}) + 8\alpha_3 c_m c_{2\sigma} g_{v,p} g_{l,p}/R^4(\mathscr{E})$$

$$a_{2\vartheta} = -2g_{v,p}g_{l,p} + 2\alpha_2\rho_l(g_{v,p} + g_{l,p}); \qquad \alpha_{3\vartheta} = 2g_{v,p}g_{l,p}$$

We finally substitute equations (8.6) and (9.3) into (8.7) obtaining:

$$\lambda_1\ddot{R} + \lambda_2\dot{R} + \lambda_3 v' + R^{-1}[\![K\vartheta_{r,r}]\!] + \vartheta' R^{-1}[\![K]\!] = 0 \tag{9.4}$$

where

$$\lambda_1 = c_\sigma c_m a_{2\vartheta}\Delta^{-1}R^{-2}(\mathscr{E}); \qquad \lambda_2 = -\rho_l\mathscr{L}(\Theta) + c_\sigma c_m a_{1\vartheta}\Delta^{-1}R^{-2}(\mathscr{E}) + c_\sigma a_{3\vartheta}\Delta^{-1}\alpha_3^{-1};$$

$$\lambda_3 = -2\gamma_0 R^{-2}(\mathscr{E}) - c_\sigma a_{2\vartheta}\Delta^{-1}\alpha_2^{-1}$$

Equation (9.4) is the searched free moving boundary condition as in it the only unknown functions appearing are $\vartheta_r(R(t), t)$ and $R(t)$.

We remark that when surface effects and curvature radii can be neglected we have $\lambda_1 = \lambda_3 = 0$ and $\lambda_2 = -\rho_l L(\Theta)$ so that (9.4) reduces to the free moving boundary condition quoted in [9] and [10]. We finally remark that in (9.4) the second order time derivative of $R(t)$ appears. This circumstance is due to the accounted dependence of phase transition temperature on the "speed" of the interface‡.

10. A SEPARATED SYSTEM OF EVOLUTION EQUATIONS (SEE) EQUIVALENT TO LEE

We begin recalling and introducing some notations (see Fig. 1):

$$D_\infty^+ \equiv \{(\xi, \tau) \in R^+ \times R^+ : R(\tau) \leq \xi\};$$

If $a^2 = R_v\Theta$, $a > 0$ then (see Fig. 2)

$$D(r, t) \equiv \{(\xi, \tau) \in R^+ \times R^+ : 0 \leq \tau \leq t,\ r + a(\tau - t) \leq \xi \leq r - a(\tau - t)\};$$

Once fixed the curve $R(t)$ we define the application:

$$P_R : R^+ \times R^+ \to R^+ \times R^+$$

as follows (see Fig. 2). $P_R(r, t)$ is the intersection [unique because of assumption (iv) of Theorem 6.1] of the characteristic line stemming from the point (r, t) whose angular coefficient is a with the curve $R(t)$.

$$D^*(r, t) \equiv (D_\infty^+ \cap D(r, t)) - D(P_R(r, t))$$

We can now define the functionals $I_\tau(R, r, t)$, $F_\tau(R, r, t)$ as follows:

$$D^*(r, t) \equiv \bigcup_{\tau\in[0, t]} \{\tau\} \times [I_\tau, F_\tau]$$

We finally define the functional $\Phi(R, r, t)$: once the curve $R(t)$§ is fixed it is well known (see [8]) that there exist a unique couple $u_1(r, t)$ and $u_2(r, t)$ solution of the homogenized system (7.6)–(7.7)‖ and satisfying the initial and boundary conditions:

$$u_1(r, 0) = r\rho_0(r) \qquad u_2(r, t) = r\dot{x}_0(r) \quad \forall r \in [R(t), \infty]$$

$$\left.\begin{aligned} u_1(R(t), t) &= R(t)\rho_v'(t) \\ u_2(R(t), t) &= R(t)\dot{R}'(1 - \rho_l/\rho_v(\mathscr{E})) \end{aligned}\right\} \quad \forall t \in [0, T] \tag{10.1}$$

where ρ_v' is obtained solving (8.4) and substituting so found p_v' into (8.2).

† In the following expressions all quantities are evaluated in the equilibrium condition characterized by $\mathscr{E}$.

‡ This dependence implicitly appeared already in [6] where a planar symmetric system is considered, in which both surface phenomena and compressibility of the phases are negligible.

§ The curve $R(t)$, because of (iv) of Theorem 6.1, is *not* characteristic so that the mixed data problem for the hyperbolic system (7.6)–(7.7) in D_∞^+ is well-posed (see [8] and [19]).

‖ Where u_1 plays the role of ρ_r and u_2 that of v_r.

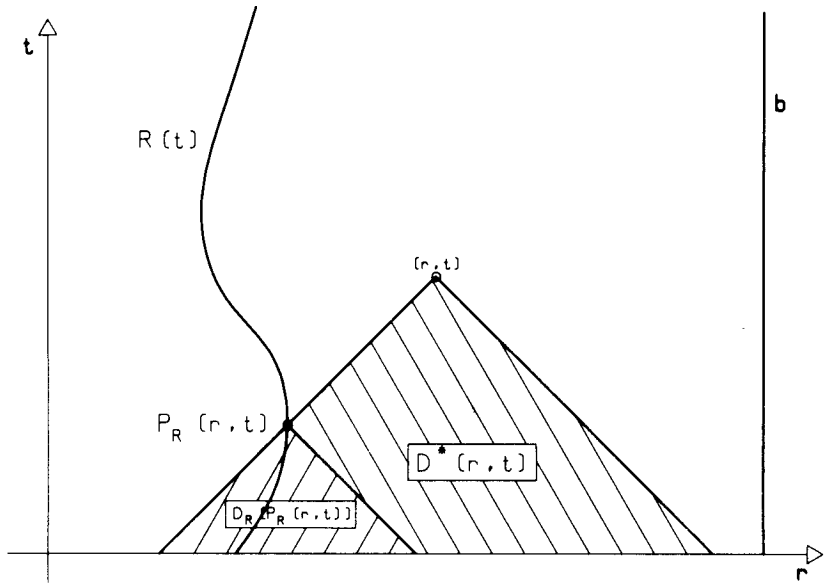

Fig. 2

We define

$$\Phi(R, r, t, \mathrm{IBC}) \equiv u_1(r, t)$$

We now consider the couple of functions ρ_r and v_r which are the unique (see [8]) solution in the domain D_∞^+ of the system (7.6)–(7.7) satisfying the conditions (10.1), when $R(t)$ is fixed and verifies (iv) of Theorem 6.1.

The function ρ_v can be easily represented in terms of ϑ_r and Φ.

THEOREM 10.1: If assumption (iv) of Theorem 6.1 is verified then the function ρ_r whose time derivative appears in equation (7.8) can be represented as:

$$\rho_r(r, t) = \Phi(R, r, t, \mathrm{IBC}) + R_v \rho(\mathscr{E}) \iint_{D^*(r,t)} \vartheta_{r,rr} \, \mathrm{d}\xi \, \mathrm{d}\tau \tag{10.2}$$

PROOF: It is a simple application of the methods developed in [8] for the solution of linear hyperbolic system with the method of characteristic curves. We remark here only that because of linearity of the considered system we know that ρ_r can be represented by the sum of Φ plus a solution Ψ of the nonhomogeneous system verifying vanishing initial and boundary conditions. On the other hand the function

$$\iint_{D(r,t)} R_v \rho(\mathscr{E}) \vartheta_{r,rr} \, \mathrm{d}\xi \, \mathrm{d}\tau$$

actually vanishes when $t = 0$ and verifies the nonhomogeneous system (to see this it is necessary to find the form of the system (7.6)–(7.7) in the "characteristic" system of coordinates). It is now simple algebra to see that:

$$\Psi = R_v \rho(\mathscr{E}) \iint_{D^*(r,t)} \vartheta_{r,rr} \, \mathrm{d}\xi \, \mathrm{d}\tau. \qquad \blacksquare$$

We finally calculate $\rho_{r,t}$ using the results of the previous theorem. In this way we have separated LEE. In fact substituting the so found expression for $\rho_{r,i}$ in (7.8) we obtain an equation (SEE ϑ) in which the only unknown functions are ϑ and $R(t)$. SEE ϑ and (9.4) represent the FMBP quoted in Theorem 6.1).

THEOREM 10.2:

$$\frac{\partial}{\partial t}\iint_{D^*(r,t)} \vartheta_{r,rr}\,\mathrm{d}\xi\,\mathrm{d}\tau = -a\int_0^t \vartheta_{r,rr}\Big|_{I_\tau}^{F_\tau}\mathrm{d}\tau.$$

PROOF: Let us apply Fubini's Theorem:

$$\frac{\partial}{\partial t}\int_0^t \mathrm{d}\tau\int_{I_\tau}^{F_\tau}\vartheta_{r,rr}\,\mathrm{d}\xi \equiv \frac{\partial}{\partial t}\int_0^t G(r,t,\tau)\,\mathrm{d}\tau.$$

We remark that just defined G is such that (see Fig. 1) $G\langle r, t, t\rangle = 0$, so that this last derivative is equal to:

$$-a\int_0^t \vartheta_{r,rr}\Big|_{I_\tau}^{F_\tau}\mathrm{d}\tau,$$

where we have used that both $F_{\tau,t}$ and $I_{\tau,t}$ are equal to $-a$. ■

In this way we have completely proved Theorem 6.1.

11. CONSIDERATIONS ABOUT REASONABLENESS OF THE GENERAL FMBP FORMULATED IN [3]

Theorem 6.1 assures that when the speed of the liquid–vapour interface is less than the sound speed in the vapour the application of the general theory developed in [3] to considered case yield a one-dimensional FMBP† which actually reduces, when surface phenomena can be neglected, to already known FMBPs. On the other hand even in classical continuum theory when shock waves have a speed greater than that of the sound a reformulation of the theory is needed (see [19]).

We conclude that a reformulation of quoted general theory will be necessary to describe phase transition phenomena in which the interface normal speed is greater than the speed of the sound in one of the phases.

Acknowledgements—I am greatly indebted to Professor A. Romano who introduced me to a very interesting research field and spent a lot of time in discussing this work, making valuable suggestions. It is only due to his friendly but stern encouragement and to his intelligent guidance that I have been motivated to try my best and for this, I thank him. This work was partially supported by GNFM (Gruppo Nazionale per la Fisica Matematica) of Italian CNR.

REFERENCES

[1] F. DELL'ISOLA and A. ROMANO, On the derivation of thermomechanical balance equations for continuous systems with a nonmaterial interface. *Int. J. Engng Sci.* **25,** 1459–1468 (1987).
[2] A. ROMANO, Thermodynamics of a continuum with an interface and Gibbs' rule. *Ric. Mat. Napoli* **XXXI** (1982).
[3] F. DELL'ISOLA and A. ROMANO, A phenomenological approach to phase transition in classical field theory. *Int. J. Engng Sci.* **25,** 1469–1475 (1987).
[4] PERRUCCA, *Fisica Generale,* Vol. I UTET (1963).
[5] J. N. MURREL and E. A. BOUCHER, *Properties of Liquids and Solutions.* Wiley, New York (1982).
[6] A. CAPUANO and F. DELL'ISOLA, Deduction of a generalized Stefan Problem and its solution by means of an iterative method. *Arch. Mech. (AMS) Warsaw* No. 3 (1987).
[7] A. ROMANO, Properties of the Gibbs' potential and the equilibrium of a liquid droplet with its vapour. *Ren. Sem. Math. Univ. Padova* **69** (1983).
[8] R. COURANT and D. HILBERT, *Methods of Mathematical Physics,* Vol. II. Interscience, New York (1962).
[9] A. FRIEDMAN, FMBP for parabolic equations: evaporation or condensation of a liquid drop. *J. Math. Mech.* **9,** No. 1 (1960).
[10] I. I. COLODNER, Free moving boundary problems for the heat equation with applications to problems of change of phase. *Commun. Pure appl. Math.* **9,** 1–31 (1956).
[11] A. W. ADAMSON, *Physical Chemistry of Surfaces.* Wiley, New York (1982).
[12] J. SERRIN, On the uniqueness of compressible fluid motion. *Arch. Rat. Mech. Anal.* **4,** 271–288 (1959).

† Quoted FMBP has reasonable chances to be well-posed.

[13] B. GEBHART, *Heat Transfer*, McGraw–Hill, New York (1961).
[14] M. GEVREY, Sur les équations aux dérivées partielles du type parabolique. *J. Math.* (6 Séries), Tome IX, Fasc. IV (1913).
[15] K. LEWIS and M. RANDALL, *Thermodynamics*. McGraw–Hill, New York (1970).
[16] E. FERMI, *Termodinamica*. Boringhieri (1977).
[17] S. ONO and S. KONDO, Molecular theory of surface tension in liquids. *Hanbuch. Phys.* **10** (1960).
[18] *The Scientific Papers of J. W. Gibbs*, Dover, New York (1961).
[19] R. COURANT and K. O. FRIEDRICS, *Supersonic Flow and Shock Waves. Applied Mathematical Sciences*, Vol. 21. Springer, New York (1976).
[20] F. DELL'ISOLA, Equilibrium of a one component liquid droplet with its vapour: constitutive equations of soap bubble-like nonmaterial interfaces and effect of curvature on surface tension. In preparation.
[21] R. C. TOLMAN, The effect of droplet size on surface tension, *J. Chem. Phys.* **17,** No. 3 (1949).

(*Received* 9 *February* 1988; *revision received* 4 *November* 1988; *received for publication* 21 *February* 1989)

APPENDIX

Constitutive Equations of "Soap Bubble"-Like Nonmaterial Interfaces and Effect of Curvature on Equilibrium Surface Tension

In this Appendix we justify the assumptions made in the previous sections quoting some results found in [20]. The aim of that paper is:

(i) To find a set of surface constitutive equations for bidimensional nonmaterial continua such that:
  (a) classical equilibrium relations and rules hold;
  (b) the considered nonmaterial interface looks like, in a sense to make rigorous, a "soap bubble" (SB). In this way we justify the success of classical theories stemming from the ideas of J. W. Gibbs which deal with both material and nonmaterial interfaces using the same techniques.
(ii) To specialize further on quoted surface constitutive equations in order to obtain the equilibrium dependence of surface tension $g^*(r)$ on the radius r of the droplet is that found by Tolman [21]:

$$g^*(r) = \gamma_0/(1 + 2\delta r^{-1}) \tag{A1}$$

In fact, as it is possible to prove this for material bidimensional continua, we assume that:

$$\varepsilon_\sigma = r(\vartheta) + \Gamma(\vartheta)\rho_\sigma^{-1} \tag{A2}$$

This implies (entropy principle) that:

$$\psi_\sigma = R(\vartheta) + \vartheta F(\rho_\sigma) - \lambda(\vartheta)\rho_\sigma^{-1} \tag{A3}$$

where $R(\vartheta)$ is given in terms of $r(\vartheta)$, F can be arbitrarily chosen and

$$\lambda = \vartheta \int \vartheta^{-2}\Gamma(\vartheta)\,\mathrm{d}\vartheta$$

Now we prove that:

THEOREM A1: If $N_1(\vartheta)$ $N_2(\vartheta)$ and $\rho_\sigma^*(\vartheta)$ are equilibrium (planar interfaces) surface tension, surface energy and surface mass density, if F is linear and liquid phase is incompressible and the vapour a perfect gas then Tolman formula holds together with Gibbs' phase rule. Moreover in general we have

$$\lambda = f(\rho_\sigma^*(\vartheta))\{\rho_\sigma^*(\vartheta)\}^2 + N_1(\vartheta) \tag{A4}$$

where $f(\rho_\sigma) = \partial F/\partial\rho_\sigma$.

When $F = 0$ and $R = 0$ because of (A4) formula (A3) reduces to classical relation between free energy and surface tension. The results in Theorem A1 are important when dealing with nonequilibrium evolutions of the system under consideration, as done in previous sections. In fact nonmaterial interfaces which more naturally can be considered, at least as a starting point, are exactly SB-like. Moreover $g^*(r)$ gives us important information about constitutive equations of this interface:

LEMMA: Let us consider SB-like interfaces. If the equilibrium surface tension $N_1(\vartheta)$ and inner energy $N_2(\vartheta)$, (for planar interfaces) are given as functions of temperature, and F is one-to-one then $g^*(r)$ is determined.

Now it is known that the Tolman formula is not in general experimentally verified, see [4], even if no sufficiently accurate experimental $g^*(r)$ is found in literature. Quoted lemma gives us two possibilities:

(1) Either the set of g^* which can be obtained in the class of SE-interfaces has as unique member Tolman expression (A1), so that in order to take into account experimental evidence we have to abandon the SB assumption;
(2) or quoted set does not reduce to (A1), because of the variation of F in the set of C^1 one-to-one functions. In this case it is possible, without skipping SB assumption, to describe a more general dependence of γ on r.

More details about this problem are found in [20].

We conclude remarking that while proving Theorem 1 and the Lemma we get for free a very important result: the equilibrium surface mass density ρ_σ^* as an experimentally measurable function of temperature

Planar interfaces

$$\rho_\sigma^* = (\rho_l - \rho_v)(N_2 - N_1 + \vartheta N_1')(\rho_l\varepsilon_l - \rho_v\varepsilon_v)^{-1}$$

Droplets
(in equilibrium with a vapour whose density is ρ_v and such that $\rho_{ve}(\vartheta)$ is its equilibrium density for planar interfaces, $K = \text{const.}$)

$$\rho_\sigma(\vartheta, \rho_v) = \rho_\sigma^*(\vartheta) + K \ln(\rho_v / \rho_{ve}(\vartheta))$$

Its importance relies into both applications and conceptual aspects: ρ_σ appears in evolution equations which are found in the previous sections; the theories developed in literature make some *a priori* assumptions concerning the structure of the interface which should be self-consistent.

For more details see [20].