

Approximate systems describing solid-liquid and liquid-vapour state changes (*)

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BY APPLYING the general balance equations of a system with an interface, two free-boundary problems are posed, which describe one-dimensional solid-liquid and liquid-vapour phase transitions.

Zastosowanie ogólnych równań zachowania do ciała z powierzchnią międzyfazową pozwoliło sformułować dwa zagadnienia dla ciała o powierzchni swobodnej, opisujące jednowymiarowe przejścia z fazy stałej do ciekłej i z fazy ciekłej do gazowej.

Применение общих уравнений сохранения к телу с межфазной поверхностью позволило сформулировать две задачи для тела со свободной поверхностью, описывая одномерный переход из твердой фазы в жидкую и из жидкой фазы в газовую.

1. Introduction

A GENERAL model has been proposed in previous papers [1, 2, 3] in order to describe the evolution of continuous systems with an interface during a state change. The structure of the obtained equations is too complex to carry out a satisfactory analysis of them. The reason for this complexity has to be found in the generality of the model which, in principle, is capable of describing a wide class of phenomena.

This last consideration suggests the possibility of obtaining a drastic simplification of the general equations when the ambit they refer to is specified. More precisely, it will be shown that a nondimensional analysis can put in evidence the different weight of the terms appearing in the equations, provided that the choice of reference variables is made starting from suitable physical criteria.

In this paper the aforesaid procedure will be adopted for studying the one-dimensional solid-liquid and liquid-vapour state changes.

In Sect. 2 the equations we proposed in [3] are written in the one-dimensional case for a system which is formed by an incompressible phase and a fluid one. The surface separating both phases is regarded as a discontinuity surface.

In the case of solid-liquid phase change we suppose that the liquid phase is also incompressible and, moreover, the densities of the two phases are almost equal. In these conditions the aforesaid system can be put in a simplified form which was already deduced in [4] by considerations that do not point out the approximations of the model leading to them. Such a system describes a free boundary problem for the temperature field which

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reduces to the classical Stefan one in the further hypothesis of equal densities in both phases.

A solution of the system (3.9) has been determined in [4] for the Cauchy problem on the whole real line. Here we exhibit the solution of an initial-boundary value problem relative to the system (3.9) which displays the interface motion as well as that of the free surface of the liquid phase. These results being available, we can evaluate the differences among the solutions of the system (3.9) and those of the Stefan problem. Moreover, they can be used to test the precision of numerical methods.

In the liquid-vapour transition, the vapour density is much smaller than the liquid density and, moreover, it cannot be constant owing to the compressibility of gas.

These considerations condition the mathematical formulation of the problem in a heavy way. We can prove that the thermodynamical state of the system is completely determined by the temperature field, as in the case of solid-liquid transition, but the temperature field satisfies a nonlinear parabolic equation in a domain whose boundaries are not known. In particular, the motion of the external surface is not determined by the motion of the interface (as in the solid-liquid case) but depends also on the values of the whole temperature field.

2. One-dimensional balance equations for a continuous system with an interface

A system \mathcal{B} is formed by two phases \mathcal{B}^- and \mathcal{B}^+ of the same substance, which are separated by a material interface \mathcal{S} . The evolution of \mathcal{B} is described by the balance laws of mass, linear momentum and energy in the form that was derived in [1, 2, 3].

From now on we restrict our attention to state changes verifying the following hypotheses:

- a) the phase \mathcal{B}^- is incompressible;
- b) the phase \mathcal{B}^+ is fluid;
- c) the interface \mathcal{S} has no material properties;
- d) the interface is plane and all the fields describing the evolution of \mathcal{B} depend on time t and on the coordinate x evaluated normally to the interface itself.

In the hypothesis a) the particles of \mathcal{B}^- can be supposed to be at rest, without loss of generality, and the pressure p is an unknown function of t only. Moreover, the balance equation of energy can be written in the following way:

$$(2.1) \quad \varrho^- c^- \vartheta_t = k^- \vartheta_{xx},$$

where ϑ is the temperature field and ϱ^- , c^- , k^- three arbitrary constants which represent density, specific heat and heat conductivity of \mathcal{B}^- , respectively.

In the phase \mathcal{B}^+ the balance equations are written as follows:

$$(2.2) \quad \begin{aligned} \varrho_t + (\varrho v)_x &= 0, \\ \varrho(v_t + v v_x) &= -p_x, \\ \varrho(\varepsilon_t + v \varepsilon_x) &= -p v_x + k^+ \vartheta_{xx}, \end{aligned}$$

where ϱ is the density of \mathcal{B}^+ , ε its internal energy, k^+ the heat conductivity.

In the hypotheses c), d) the conditions on the interface $\kappa = s(t)$ are expressed by the equations

$$(2.3) \quad \begin{aligned} -\rho^-\dot{s} &= \rho^+(v-\dot{s}) \equiv J, \\ \llbracket v \rrbracket J + \llbracket p \rrbracket &= 0, \\ \llbracket \frac{1}{2}(v-\dot{s})^2 + \varepsilon \rrbracket J + \llbracket p(v-\dot{s}) \rrbracket &= \llbracket k\vartheta_{\kappa} \rrbracket. \end{aligned}$$

In Eqs. (2.3) $\llbracket f \rrbracket$ denotes the jump of f across the interface.

To the system (2.1), (2.2), (2.3) we have to add the request that each of its solutions satisfy the second principle of thermodynamics. Such a request leads to well-known restrictions of the constitutive equations relative to both phases. In the case we are considering, they reduce to the conditions $k^{\pm} \geq 0$ in the volume and to the other one

$$\vartheta \llbracket \eta \rrbracket J \geq \llbracket k\vartheta_{\kappa} \rrbracket$$

on the interface (η is the specific entropy). By eliminating $\llbracket k\vartheta_{\kappa} \rrbracket$ between the last equation and Eq. (2.3)₃, we reach the following relation on the interface:

$$\llbracket \frac{1}{2}(v-\dot{s})^2 + \Psi + \frac{p}{\rho} \rrbracket J \leq 0$$

($\Psi = \varepsilon - \eta\vartheta$ is the specific free energy).

Later on we shall assume that there is no energy dissipation on the interface; then the last relation will be satisfied as an equality and we must consider the equation

$$(2.4) \quad \llbracket \frac{1}{2}(v-\dot{s})^2 + \Psi + \frac{p}{\rho} \rrbracket = 0$$

besides Eqs. (2.1), (2.2) and (2.3).

3. Solid-liquid state change. A generalized Stefan problem

In this section we analyse the solid-liquid transition assuming that both phases are incompressible. We suppose that the solid phase is limited on the right by a fixed plane $\kappa = 0$ and on the left by the moving interface. Moreover, the liquid phase is situated between the interface and a free moving plane $\kappa = l(t)$ on the left; an external pressure p_e , which is of the order of the atmospheric pressure, is acting on this last plane. We also assume that the densities ρ^- and ρ^+ have about the same value so that the parameter $\alpha = (\rho^+ - \rho^-)/\rho^+$ is much less than the unity.

As a consequence of the incompressibility of \mathcal{B}^+ , the velocity field in this phase depends only on time. On the other hand, Eq. (2.3) permits to express such a function in terms of the velocity of the interface:

$$(3.1) \quad v = \alpha\dot{s}.$$

By introducing this last relation into Eqs. (2.2), (2.3), (2.4) and assuming the following constitutive equation

$$\varepsilon = \varepsilon(\vartheta) = c^+\vartheta + \varepsilon_0$$

for the internal energy of \mathcal{B}^+ , we obtain the following system:

$$\begin{array}{ll}
 \text{solid phase} & \text{liquid phase} \\
 p = p(t), & \alpha \rho^+ \dot{s} = -p_x, \\
 \vartheta_t = a^- \vartheta_{xx}, & \vartheta_t + \alpha \dot{s} \vartheta_x = a^+ \vartheta_{xx}, \\
 \text{interface} & \\
 \llbracket p \rrbracket = \alpha \rho^- \dot{s}^2, & \\
 \rho^- \llbracket \varepsilon \rrbracket \dot{s} + \frac{1}{2} \alpha^2 \rho^- \dot{s}^3 - \alpha p^+ \dot{s} = k^- \vartheta_x^- - k^+ \vartheta_x^+, & \\
 \llbracket \Psi \rrbracket + \frac{1}{2} \alpha^2 \dot{s}^2 - \alpha \frac{p^+}{\rho^-} = 0, &
 \end{array}
 \tag{3.2}$$

where $a^\pm = k^\pm / \rho^\pm c^\pm$ is the thermal diffusivity of \mathcal{B}^\pm .

We explicitly observe that the free boundary $l(t)$, which is moving with the particles of \mathcal{B}^+ , has the velocity

$$\dot{l}(t) = \alpha \dot{s}(t)$$

and therefore its motion is determined by that of the interface. In particular, from the last relation and the condition $\alpha \ll 1$, we derive that the linear dimensions of the whole system remain almost unchanged during the process.

An analysis of the magnitude order of different terms appearing in the equations we deduced in Sect. 2 leads to a drastic simplification of the problem we are faced with. To this end it is worthwhile to put the system (3.2) in a nondimensional form.

Let X be a length comparable with that of the system; as it is well known, the quantity $T = X^2/a^-$ denotes a time which is characteristic of conduction phenomena. This means that the interface velocity can be supposed to be comparable with the rate $U = X/T$. Finally let us assign the initial and boundary data of temperature and let Θ be the difference between their maximum and minimum.

By introducing the dimensionless variables and fields

$$\begin{array}{llll}
 x = \frac{x}{X}, & t = \frac{t}{T}, & p = \frac{p}{P}, & \theta = \frac{\vartheta - \vartheta_M}{\Theta}, & v = \frac{v}{U}, \\
 \dot{s} = \frac{\dot{s}}{V}, & \varepsilon = \frac{\varepsilon}{c^- \Theta}, & \psi = \frac{\Psi}{c^- \Theta}, & &
 \end{array}
 \tag{3.3}$$

where ϑ_M is the melting temperature at ordinary pressure, we obtain the following dimensionless system:

$$\begin{array}{ll}
 \text{solid phase} & \text{liquid phase} \\
 p = p(t), & p_x = -\alpha A \rho \dot{s}, \\
 \theta_t = \theta_{xx}, & \theta_t + \alpha \dot{s} \theta_x = a \theta_{xx}, \\
 \text{interface} & \\
 \llbracket p \rrbracket = \alpha A \dot{s}^2, &
 \end{array}
 \tag{3.4}$$

$$(3.4) \quad \llbracket c \rrbracket \dot{s} + \frac{1}{2} \alpha B \dot{s}^3 - \alpha \frac{B}{A} p^+ \dot{s} = \theta_x^- - k \theta_x^+,$$

[cont.]

$$\llbracket \psi \rrbracket + \frac{1}{2} \alpha^2 B \dot{s}^2 - \alpha \frac{B}{A} p^+ = 0,$$

where we introduced the dimensionless quantities

$$(3.5) \quad \rho = \frac{\varrho^+}{\varrho^-}, \quad c = \frac{c^+}{c^-}, \quad k = \frac{k^+}{k^-}, \quad a = \frac{a^+}{a^-},$$

$$A = \frac{\varrho^- V^2}{P}, \quad B = \frac{V^2}{c^- \Theta}.$$

Tables 1 and 2 contain numerical values of physical quantities we are considering and show that the numbers A , B and B/A are quite negligible with respect to α .

Table 1.

		ϱ g/cm ³	$c/10^6$ erg/g ^o K	$k/10^6$ erg/cm · s ^o K	ϑ_M °K	$A/10$ erg/g
Iron	-	7.36	6.91	2.91	1808	2.72
	+	6.90	8.66	2.33		
Copper	-	8.62	4.81	30.93	1356	2.13
	+	8.36	5.44	30.93		
Aluminium	-	2.55	11.39	24.19	930	3.93
	+	2.38	10.47	24.19		
Water	-	0.91	19.26	0.221	273	3.35
	+	1.00	41.86	0.055		

Table 2.

	α	k	a	λ	A	B	B/A
Iron	-0.067	0.80	0.68	2.18	2.4×10^{-12}	2.6×10^{-16}	1.1×10^{-4}
Copper	-0.031	1.00	0.91	3.27	4.7×10^{-10}	8.5×10^{-14}	1.8×10^{-4}
Aluminium	-0.071	1.00	1.17	3.72	1.7×10^{-10}	6.6×10^{-14}	3.8×10^{-4}
Water	0.087	0.25	0.11	6.37	1.4×10^{-14}	3.0×10^{-17}	2.1×10^{-3}

The numerical results contained in Tables 1 and 2 permit us to neglect the terms having as factors A , B or B/A so that the system (3.4) reduces to the following set of equations:

$$(3.6) \quad \begin{array}{ll} \text{solid phase} & \text{liquid phase} \\ p = p(t), & p = p(t), \\ \theta_t = \theta_{xx}, & \theta_t + \alpha \dot{s} \theta_x = a \theta_{xx} \end{array}$$

(3.6) interface
 [cont.]
$$\begin{aligned} \llbracket p \rrbracket &= 0, \\ \llbracket \epsilon \rrbracket \dot{s} &= \theta_x^- - k\theta_x^+, \\ \llbracket \psi \rrbracket &= 0. \end{aligned}$$

The pressure field is therefore continuous and uniform throughout both phases and coincides with the external pressure p_e .

Moreover, the condition $\llbracket \psi \rrbracket = 0$ supplies the temperature on the interface; in fact, by recalling the definition of the free energy, it can be put in the form

(3.7)
$$\llbracket \epsilon \rrbracket - \frac{\vartheta \llbracket \eta \rrbracket}{c^- \Theta} = 0.$$

On the other hand, the specific internal energy and entropy of an incompressible fluid are functions of temperature alone. Then the relation (3.7) represents an equation in the unknown ϑ whatever the external pressure is. Consequently, its solution is given by the melting temperature ϑ_M at atmospheric pressure. If we recall the definition of latent heat $\Lambda = \vartheta \llbracket \eta \rrbracket$ and put $\lambda = \Lambda/c^-$, we can write Eq. (3.7) in the form

(3.8)
$$\llbracket \epsilon \rrbracket = \lambda.$$

Concluding, the whole set of equation (3.6) leads to the following system:

(3.9)
$$\begin{array}{ll} \text{solid phase} & \text{liquid phase} \\ \theta_t = \theta_{xx}, & \theta_t + \alpha \dot{s} \theta_x = a \theta_{xx}, \\ \text{interface} & \\ \theta = 0, & \\ \lambda \dot{s} = \theta_x^- - k\theta_x^+, & \end{array}$$

which represents a Stefan problem when we add to it the initial and boundary data of θ as well as the initial positions of the interface s_0 and free boundary l_0 .

4. An exact solution of the system (3.9)

CARSLAW and JAEGER determined a solution of the system (3.9), equipped with initial data on the whole real line R , by employing the similitude method (see [4], p. 290). Similarly, CHAMBRE ([5]) found an exact solution on R for the state change of a viscous fluid taking into account the influence of convective phenomena.

In this section we exhibit an exact solution of the system (3.9) in a semi-bounded domain; this solution puts the motion of the interface $s(t)$ and free boundary $l(t)$ in evidence.

More precisely, we suppose that the solid phase occupies the region $0 < x \leq \infty$ at temperature $\theta_I \leq 0$. At the instant $t = 0$ the temperature becomes $\theta_B > 0$ at the extremum $x = 0$ so that the system begins to melt. The evolution of the system is described by the following equations and data:

$$\begin{aligned}
 \theta_t + \alpha \dot{s} \theta_x &= a \theta_{xx}, & (x, t) \in (\alpha s(t), s(t)) \times [0, \infty), \\
 \theta_t &= \theta_{xx}, & (x, t) \in (s(t), \infty) \times [0, \infty), \\
 \theta &= 0, & x = s(t), \quad t \geq 0, \\
 \lambda \dot{s} &= \theta_x^- - k \theta_x^+, & x = s(t), \quad t \geq 0, \\
 \theta &= \theta_I, & x \geq 0, \quad t = 0, \\
 \theta &= \theta_B, & x = \alpha s(t), \quad t \geq 0, \\
 s(0) &= 0.
 \end{aligned}
 \tag{4.1}$$

Let us try a solution of Eqs. (4.1) in the form

$$\begin{aligned}
 \theta(x, t) &= \begin{cases} f\left(\frac{x}{2\sqrt{at}}\right), & (x, t) \in (\alpha s(t), s(t)) \times [0, \infty), \\ g\left(\frac{x}{2\sqrt{t}}\right), & (x, t) \in (s(t), \infty) \times [0, \infty), \end{cases} \\
 s(t) &= 2\varphi \sqrt{at}, \quad t \in [0, \infty).
 \end{aligned}
 \tag{4.2}$$

When we put $z = x/2\sqrt{at}$ and recall Eqs. (4.1), we obtain the following boundary problem for the function $f(z)$:

$$\begin{aligned}
 f'' + 2(z - \alpha\varphi)f' &= 0, \\
 f(\alpha\varphi) &= \theta_B, \quad f(\varphi) = 0,
 \end{aligned}
 \tag{4.3}$$

whose solution is given by

$$f(z) = \theta_B \left[1 - \frac{F(z) - F(\alpha\varphi)}{F(\varphi) - F(\alpha\varphi)} \right],
 \tag{4.4}$$

where

$$F(z) = \frac{2}{\pi} \int_0^z e^{-\zeta^2 + 2\alpha\varphi\zeta} d\zeta.
 \tag{4.5}$$

Similarly, we obtain the following problem for the function $g(z)$ ($z = x/2\sqrt{t}$):

$$\begin{aligned}
 g'' + 2zg' &= 0, \\
 g(\sqrt{a\varphi}) &= 0, \quad \lim_{z \rightarrow \infty} g(z) = \theta_I
 \end{aligned}
 \tag{4.6}$$

that admits the solution

$$g(z) = \theta_I \left[1 - \frac{\operatorname{erfc} z}{\operatorname{erfc} \sqrt{a\varphi}} \right],
 \tag{4.7}$$

where erfc is the complementary error function. In conclusion, the temperature field is given by

$$\theta(x, t) = \begin{cases} \theta_B \left[1 - \frac{F\left(\frac{x}{2\sqrt{at}}\right) - F(\alpha\varphi)}{F(\varphi) - F(\alpha\varphi)} \right], & (x, t) \in (\alpha s(t), s(t)) \times [0, \infty), \\ \theta_I \left[1 - \frac{\operatorname{erfc} \frac{x}{2\sqrt{t}}}{\operatorname{erfc} \sqrt{a\varphi}} \right], & (x, t) \in (s(t), \infty) \times [0, \infty). \end{cases}
 \tag{4.8}$$

By introducing Eqs. (4.2) and (4.8) in the Stefan condition (4.1)₄, we obtain the following equation which permits us the determination of φ :

$$(4.9) \quad \varphi e^{(1-2\alpha)\varphi^2} [F(\varphi) - F(\alpha\varphi)] \frac{\operatorname{erfc} \sqrt{a\varphi}}{\frac{\theta_I \sqrt{a}}{\theta_B \kappa} e^{(1-2\alpha-a)\varphi^2} [F(\varphi) - F(\alpha\varphi)] + \operatorname{erfc} \sqrt{a\varphi}} = \frac{k\theta_B}{\sqrt{\pi\lambda a}}.$$

In particular, if $\theta_I = 0$ (i.e., the system is initially at the melting temperature), we have $\theta(x, t) = 0$ identically in the solid phase and the problem reduces to a single phase. Then the equation determining the parameter φ assumes a simpler form:

$$(4.10) \quad \varphi e^{(1-2\alpha)\varphi^2} [F(\varphi) - F(\alpha\varphi)] = \frac{k\theta_B}{\sqrt{\pi\lambda a}}.$$

It is interesting to compare this deduced formula with those supplying the well-known Neumann solution of the Stefan problem ([4], pp. 283–286) to which they reduce when $\alpha = 0$.

In Fig. 1 the function appearing on the first side of Eq. (4.10) is represented for different values of α ; it is possible to conclude that the advancing of the interface is accelerated

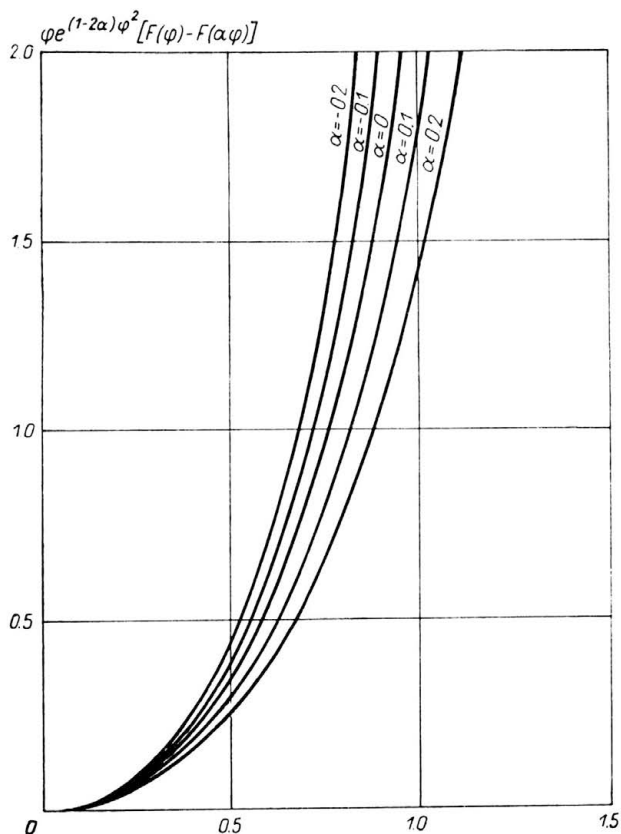


FIG. 1.

or delayed with respect to the Stefan case (equal densities) according to $\alpha > 0$ (liquid denser than the solid) or $\alpha < 0$ (solid denser than the liquid). The solutions of Eq. (4.10) are represented in Table 3.

Table 3.

	$\alpha = 0$	$\alpha \neq 0$
Iron	0.480	0.463
Copper	0.390	0.384
Aluminium	0.328	0.316
Water	0.417	0.439

5. One-dimensional liquid-vapour state change

The liquid-vapour state change is a very complex phenomenon which is produced by the combination of conduction and convection. Inside the liquid, vapour bubbles form that can unite with each other and give rise to larger bubbles. These reach the free surface where they release the contained vapour.

However, when the external temperature is only a few degrees different from that of evaporation, the phenomenon takes place with simpler modalities.

Let us consider, in a rigid container with a freely moving piston, a liquid mass subjected to a pressure less than the critical one. Moreover, let us suppose the liquid at rest and at the saturation temperature. If the temperature of the piston is increased by some degrees, a vaporization process begins across the liquid surface near the piston (see [6], p. 491) and a vapour phase is formed which has a density less than the liquid one; consequently the total volume occupied by the system increases proportionally to the quantity of matter supporting a phase change.

In these conditions on phase transition we can apply the methodology proposed in Sects. 3 and 4 for studying the solid-liquid state change in order to obtain a reasonable description of the problem we are concerned with.

With respect to the case of solid-liquid state change, we now have two fundamental differences: i) the vapour phase is not incompressible but, on the contrary, its density depends on the pressure and temperature; ii) the densities of the two phases are so different from each other that the vapour density can be quite neglected with respect to the liquid one. In other words, the two cases differ for the state equations describing the system and for the approximations that we can introduce.

We can presume that the interface between the two phases remains flat throughout the process and that the fields describing the system evolution depend only on the coordinate along the axis orthogonal to the interface. Moreover, the liquid can be supposed to be incompressible with respect to temperature and pressure variations provided that the pressure is not in the neighbourhood of the critical one.

Therefore the conditions a), ..., d) of Sect. 2 are satisfied and then the system we are considering is described by Eqs. (2.1), ..., (2.4).

From the jump condition (2.3) we obtain

$$(5.1) \quad v = \frac{\rho^+ - \rho^-}{\rho^+} \dot{s}.$$

On the other hand, the vapour density is always negligible with respect to the liquid one in a liquid-vapour transition (for instance, at atmospheric pressure and temperature of 100 °C, the water density is 0.958 g/cm whereas the vapour density is 0.596×10^{-3} g/cm³). Therefore Eq. (5.1) can be put in the approximate form

$$(5.2) \quad v = -\frac{\rho^-}{\rho^+} \dot{s}.$$

This last equality permits us to eliminate v from the other jump conditions. With simple calculations we derive the following equations:

$$(5.3) \quad \begin{aligned} \llbracket p \rrbracket &= -\rho^- \left(\frac{\rho^-}{\rho^+} \right) \dot{s}^2, \\ \frac{1}{2} \rho^- \left(\frac{\rho^-}{\rho^+} \right)^2 \dot{s}^3 + \rho^- \left(\llbracket \varepsilon \rrbracket + \frac{p^+}{\rho^+} \right) \dot{s} &= k^- \vartheta_*^- - k^+ \vartheta_*^+, \\ \frac{1}{2} \left(\frac{\rho^-}{\rho^+} \right)^2 \dot{s}^2 + \llbracket \psi \rrbracket + \frac{p^+}{\rho^+} &= 0. \end{aligned}$$

As in the case of the melting of a solid body, we can obtain a simpler model describing the evaporation by a dimensionless analysis of the system (2.1), (2.2), (2.3), (2.4). In fact this analysis will lead us to further suitable approximations.

In choosing the reference values, the notable difference between the densities of the two phases is determinant. From this it follows: 1) a corresponding remarkable variation of the linear dimensions of the volume occupied by a given matter quantity when its phase changes; 2) a noticeable difference between the vapour particle velocities and the interface velocity.

These remarks impose the choice of comparison terms for the length, density and velocity according to the phase. In particular, we refer the densities to their values $\bar{\rho}^-$ and $\bar{\rho}^+$ at atmospheric pressure and vaporization temperature. Owing to the incompressibility hypotheses, the density will have the same value $\bar{\rho}^-$ on the whole liquid region.

Let us introduce the dimensionless rate $\alpha = \bar{\rho}^+/\bar{\rho}^- \ll 1$ (for the water, $\alpha = 0.622 \times 10^{-3}$); the rate of the linear dimensions of the regions occupied by a given mass of matter in the liquid phase to that in the vapour phase is about α . Therefore we fix the two values X^- and X^+ to which we refer the spatial variable in such a way that X^- coincides with the initial dimension of the liquid phase and $X^+ = X^-/\alpha$.

When we adopt the quantity $T = X^{-2}/a$ as reference time, we obtain two velocities $U^- = X^-/T$ and $U^+ = X^+/T$; we refer the vapour velocity to the latter and the interface velocity to the former. The following dimensionless variables are then obtained:

$$t = \frac{t}{T}, \quad x = \begin{cases} \frac{x}{X^-}, & 0 \leq x \leq s(t), \\ \frac{s(t)}{X^-} + \frac{x-s(t)}{X^+}, & s(t) \leq x \leq l(t), \end{cases}$$

$$\rho = \frac{\rho^+}{\bar{\rho}^+}, \quad \dot{s} = \frac{\dot{s}}{V^-}, \quad v = \frac{v}{V^+}.$$

The remaining dimensionless fields are defined by the positions

$$\theta = \frac{\vartheta - \vartheta_v}{\Theta}, \quad p = \frac{p}{\bar{\rho}^+ c^- \Theta}, \quad \epsilon = \frac{\epsilon}{c^- \Theta}, \quad \psi = \frac{\Psi}{c^- \Theta},$$

where ϑ_v is the vaporization temperature at atmospheric pressure, Θ a characteristic temperature value and c^- the liquid specific heat.

The choice of the reference pressure is justified by the consideration that the constant $\bar{\rho}^+ c^- \Theta$ is of the same order as the atmospheric pressure P (for water when we put $\Theta = 40^\circ\text{C}$, we have $P/\bar{\rho}^+ c^- \Theta \simeq 1.1$).

Simple calculations allow us to write the following system:

	liquid phase		vapour phase
	$p = p(t),$		$\rho_t + (\rho v)_x = 0,$
	$\theta_t = \theta_{xx},$		$p_x = -A\rho(v_t + vv_x),$
			$\rho(\epsilon_t + v\epsilon_x) = -pv_x + \alpha k\theta_{xx},$
(5.4)			interface
			$v = -\frac{\dot{s}}{\rho^+},$
			$[[p]] = -A \frac{\dot{s}^2}{\rho^+},$
			$\frac{1}{2} A \frac{\dot{s}^3}{\rho^{+2}} + \left([[\epsilon]] + \frac{p^+}{\rho^+} \right) \dot{s} = \theta_x^- - \alpha k\theta_x^+,$
			$\frac{1}{2} A \frac{\dot{s}^2}{\rho^{+2}} + [[\psi]] + \frac{p^+}{\rho^+} = 0,$

where we have introduced the nondimensional quantity

$$A = \frac{V^{+2}}{c^- \Theta}.$$

The number A is of the order of the rate among kinetic energy and heat per unit volume. In the hypotheses of this paper, A can be supposed to be negligible (for instance, for water, when we put $X^+ = 10^2$ cm, $\Theta = 40^\circ\text{C}$, we have $A = 6.10 \times 10^{-13}$). In such an approximation, the pressure field is constant throughout the vapour region and continuous across the interface; therefore it has a constant value on the whole system.

Then Eqs. (5.4) assume the approximate form:

$$\begin{array}{ll}
 \text{liquid phase} & \text{vapour phase} \\
 \theta_t = \theta_{xx}, & \rho_t + (\rho v)_x = 0, \\
 & \rho(\epsilon_t + v\epsilon_x) = -pv_x + \alpha k\theta_{xx}, \\
 (5.5) & \text{interface} \\
 & v = -\frac{\dot{s}}{\rho^+}, \\
 & \left([\epsilon] + \frac{p^+}{\rho^+} \right) \dot{s} = \theta_x^- - \alpha k\theta_x^+, \\
 & [\psi] + \frac{p^+}{\rho^+} = 0,
 \end{array}$$

6. The one-phase problem for a perfect gas

We have to specify the constitutive equations of both phases if we want to go on analyzing the system (5.5). As we already observed in Sect. 5, when the pressure is sufficiently less than the critical one, the liquid can be considered as incompressible. The internal energy and entropy depend on temperature alone and they are expressed by the following dimensionless equations:

$$(6.1) \quad \epsilon = (\theta^* + \theta) - \epsilon_0, \quad \eta = \ln(\theta^* + \theta) - \eta_0,$$

where $\theta^* = \vartheta_v/\Theta$ and ϵ_0, η_0 are constants.

In the same hypothesis on the external pressure, the vapour is described with close approximation by the constitutive equations of perfect gases that we can write in the form

$$(6.2) \quad \epsilon = c(\theta^* + \theta), \quad \eta = c \ln(\theta^* + \theta) - \frac{R}{mc^-} \ln \rho,$$

where R is the universal constant of gases, $c = c^+/c^-$ is the rate of specific heats at constant volume, m the molecular mass. The additive constants have been omitted in Eqs. (6.2) since it is always possible to assume that they vanish in one of the two phases.

We need the constitutive equation for the pressure in order to complete the description of the vapour:

$$(6.3) \quad p = \frac{R}{mc^-} \rho(\theta^* + \theta).$$

By recalling the definition of free energy $\psi = \epsilon - (\theta^* + \theta)\eta$, the condition (5.5)₆ assumes the form

$$\frac{R}{mc^-} \ln \left(\frac{mc^-}{R} \right) p + \left(\frac{mc^+ - mc^- + R}{mc^-} \right) [1 - \ln(\theta^* + \theta)] - \eta_0 + \frac{\epsilon_0}{\theta^* + \theta} = 0.$$

This last equation can be put in explicit form by solving it with respect to p :

$$(6.4) \quad p = C(\theta^* + \theta)^{-\gamma} e^{-\frac{mc^- \epsilon_0}{R(\theta^* + \theta)}}$$

where $\gamma = -(mc^+ - mc^- - R)/R$ and $C = R \exp\{\gamma + (mc^- \eta_0/R)\}/mc^-$. The inverse function of Eq. (6.4) defines the vaporization curve which associates the vaporization temperature with each external pressure value. The density is then given by Eq. (6.3) and we can conclude that all the fields assume constant values on the interface.

If we define the dimensionless latent heat $\lambda = (\theta^* + \theta)[\eta]$, from Eq. (5.5)₆ we deduce

$$(6.5) \quad \lambda = [\epsilon] + \frac{p^+}{\rho^+}$$

and Eq. (5.5)₅ assumes the form

$$(6.6) \quad \lambda \dot{s} = \theta_x^- - \alpha k \theta_x^+,$$

λ being a constant depending on the external pressure.

By introducing into Eq. (6.5) the constitutive equations, we obtain the following expression of

$$(6.7) \quad \lambda = \lambda(\theta) = \left(\frac{mc^+ - mc^- + R}{mc^-} \right) (\theta^* + \theta) + \epsilon_0.$$

This relation shows that far from the critical point the latent heat is a linear function of temperature on the interface. Figures 2 and 3 show respectively the vaporization curve (6.4) and the behaviour of the latent heat on temperature variation. The characteristic

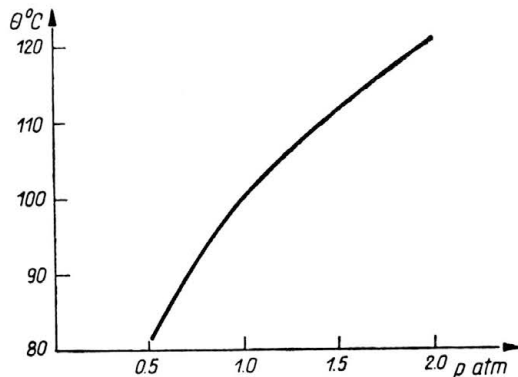


FIG. 2.

values relative to the vapour-water case have been assigned to the parameters; moreover, the constants ϵ_0 and η_0 have been fixed by imposing that the vaporization curve contains the point $\vartheta = \vartheta_v = 100^\circ\text{C}$, $p = P = 1 \text{ atm}$ and that the latent heat assumes the experimental value $2.26 \times 10^{10} \text{ erg/g}$ at 100°C .

It is interesting to observe that the condition (5.5)₆ can be put in the form

$$(6.8) \quad g^+(\theta, p) - \psi^-(\theta) = 0$$

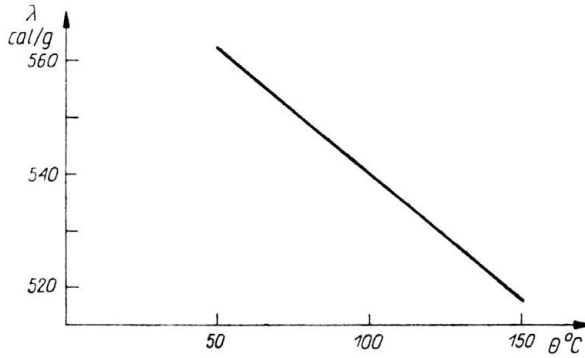


FIG. 3.

by introducing the Gibbs potential of the vapour

$$g^+(\theta, p) = \psi(\theta, \rho(\theta, p)) + \frac{p}{\rho(\theta, p)}.$$

By recalling the thermodynamic relations

$$\frac{\partial g^+}{\partial \theta} = -\eta^+, \quad \frac{\partial g^+}{\partial p} = \rho^+, \quad \frac{\partial \psi^-}{\partial \theta} = -\eta^-,$$

we can obtain, from Eq. (6.8), the following differential equation between the variables θ and p along the vaporization curve:

$$(6.9) \quad \frac{dp}{d\theta} = \frac{\rho^+ \lambda(\theta)}{\theta^* + \theta}.$$

The formula (6.9) is the well-known Clapeyron equation.

If the initial and boundary temperature data in the liquid phase coincide with the vaporization temperature at a given pressure, the field assumes this constant value on the whole liquid phase. Consequently, the field equations must be solved in one phase alone. From now on we limit ourselves to this case, for which we show that it is possible to determine the density and velocity fields when the temperature is given.

Equations (5.5)_{2,3} imply the following:

$$(6.10) \quad (\rho\epsilon)_t + [(\rho\epsilon + p)v - \alpha k \theta_x]_x = 0$$

in which, owing to Eqs. (6.2)₁ and (6.3), we can put $\rho\epsilon = mc^+p/R = \text{constant}$. Therefore, Eq. (6.10) can be integrated with respect to the variable x ; the time function we derive is determined by Eq. (5.5)₄ and then we obtain the following relation:

$$(6.11) \quad v = \frac{\alpha k R}{(mc^+ + R)p} \theta_x + \left[\frac{\lambda R}{(mc^+ + R)p} - \frac{1}{\rho^+} \right] \dot{s}.$$

Finally, by employing Eqs. (6.3), (6.11) and (5.5)₃, we have

$$(6.12) \quad \theta_t + \left[\frac{\alpha k R}{(mc^+ + R)p} \theta_x + \left(\frac{\lambda R}{(mc^+ + R)p} - \frac{1}{\rho^+} \right) \dot{s} \right] \theta_x = \alpha \frac{k R}{(mc^+ + R)p} (\theta^* + \theta) \theta_{xx}.$$

This equation has to be integrated in the domain $\Omega = \{(x, t) : t > 0, s(t) < x < l(t)\}$ whose boundaries are in turn unknowns; moreover, the solution must assume the vaporization value $\bar{\theta}$ on the interface and satisfy the (Stefan) condition (6.6) that now we may put in the form

$$\lambda(\bar{\theta})\dot{s} = -\alpha k \theta_x.$$

It is evident that these conditions are not sufficient for determining univocally the solution: the initial datum $\theta_0(x) \geq \bar{\theta}$ and the boundary condition $\theta_1(t) > \bar{\theta}$ on $l(t)$ must be added to them. Moreover, a further condition is necessary in order to determine the function $l(t)$ which describes the free surface motion. The global balance of mass supplies this other condition:

$$s(t) + \int_{s(t)}^{l(t)} \rho(x, t) dx = M,$$

where ρ is expressed by Eq. (6.3) and M is a constant that represents the nondimensional mass per unit surface.

Concluding, the domain Ω occupied by the vapour and the temperature field $\theta(x, t)$ is the solution of the following problem:

$$\begin{aligned} \theta_t + \left[\frac{\alpha k R}{(mc^+ + R)p} \theta_x + \left(\frac{\lambda R}{(mc^+ + R)p} - \frac{1}{\rho^+} \right) \dot{s} \right] \theta_x &= \alpha \frac{k R}{(mc^+ + R)p} (\theta^* + \theta) \theta_{xx}, \quad \theta(x, t) \in \Omega, \\ \theta(s(t), t) &= \bar{\theta}, \quad \theta(l(t), t) = \theta_1(t) > \bar{\theta}, \quad t > 0, \\ \theta(x, 0) &= \theta_0(x) \geq \bar{\theta}, \quad s(t) \leq x \leq l(t), \\ \lambda(\bar{\theta})\dot{s} &= -\alpha k \theta_x(s(t), t), \quad t > 0, \\ s(t) + \frac{pmc^-}{R} \int_{s(t)}^{l(t)} \frac{dx}{\theta^* + \theta(x, t)} &= M, \quad t > 0, \\ s(0) &= s_0, \quad l(0) = l_0. \end{aligned} \tag{6.13}$$

The problem (6.13) defines a free boundary problem relative to a parabolic equation which is more complex than the corresponding one describing the liquid-solid Stefan problem. In fact, in our case, the equation is nonlinear; moreover, the evolution of the free surface $l(t)$ depends on the interface motion and the whole vapour temperature field.

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