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New approach to the morphological stability of the Stefan problem

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Abstract. Solutions of the Stefan problem are considered which differ from the common ‘undisturbed’ ones by quantities small enough to allow the linearization of the equations. Physical examples are given in the case of the melting or freezing mixture of two substances. Because of the peculiar form of the boundary condition, the linearized equations display a nonlinear character similar to the case of the usual Stefan problem. However, explicit solutions are given which deviate from the common ones because the shape of the interface is no longer plane.

Introduction

The so-called *Stefan problem* is a very old one. From the historical point of view, this name is related to the process of diffusion of heat in a medium accompanied by a change of state. More generally, this denomination has been given to every process of diffusion accompanied by a phase transition characterized by a certain type of boundary condition: namely that at the phase boundary (hereafter called *interface*), the derivative of the field under concern is related to the (unknown) velocity of the interface.

One of the reasons for interest in the Stefan problem is that one can obtain a solution through a very elegant procedure, although the general problem is a very difficult nonlinear one. In the case originally treated, a liquid (water) fills up a half space (i.e. a lake). At time $t = 0$, the external surface $x = 0$ of the lake is submitted to a temperature $T < T_{\text{melting}}$. At infinity (i.e. far from the surface) the temperature is held fixed, equal to $T_0 > T_{\text{melting}}$. Ice is then forming along an interface $x_0(t)$. Taking into account the latent heat produced, the thermal conductivity of water and of ice, and neglecting small density variations and convection, one has to calculate the velocity dx_0/dt of the interface.

The way Stefan solved the problem is well known: he showed that if the conditions

$$x_0 \frac{dx_0}{dt} = \text{constant} \quad (1)$$

$$T(x, t) = f\left(\frac{x}{x_0(t)}\right) \text{ in water and ice} \quad (2)$$

*) Décédé le 31.8.1978.

are imposed on the solution, then the problem is transformed into a much simpler one involving only ordinary linear differential equations. This procedure which transforms a nonlinear diffusion problem into a linear one by a set of Ansatz analogous to (1) and (2), we will call '*reducing*' in what follows.

The number of physical systems belonging to the class of Stefan problems which have been analysed is very large (see for instance the reviews of Parker [1] and Rubinstein [2]). They concern especially phase transitions of the first order and precipitation or solidification out of a liquid solution. There is however another type of Stefan problem which does not normally appear in the common literature: this is the problem of the destruction of superconductivity by a magnetic field ([3]–[7]). However, this problem clearly belongs to the same class of physical and mathematical problems (the destruction of Type-I superconductivity by a magnetic field is a first order phase transition).

To the same class of problems belong the cases where two quantities, obeying separately a diffusion equation, are coupled because of the thermodynamical relation which exists between them at the transition: for instance concentration of solute and temperature, magnetic field and temperature. The various geometries and arrangements lead also to numerous variants of the problem. Moreover, the questions that are posed in a Stefan problem are also very different ([1]–[2]).

The concepts of kinetical and morphological stability

We shall now take up the consideration of a special Stefan problem. In the following, we restrict ourselves to two cases: the isothermal growth of a solid out of a liquid solution filling the half space $x > 0$ and the inverse problem. We shall call the *unperturbed solution that solution of the problem obtained by the reducing procedure* (i.e. by imposing the condition (1) and (2)). The *stability* of this solution has been studied by a large number of authors. From a physical point of view, the most important work are perhaps the articles of Mullins and Sekerka ([8]–[9]), even though these authors consider the stability of plane interface moving with constant velocity.

In this paper, we shall use the technique of linear stability theory which is well known in hydrodynamics to study the time evolution of solutions which are in the 'neighbourhood' of the unperturbed solution. More precisely, we shall consider the time evolution of a solution of the form

$$c(\vec{x}, t) = c_0 \left(\frac{x}{x_0}(t) \right) + c_1(\vec{x}, t) \quad (3)$$

$$\vec{y}(x = x_0(t), y, z) = \vec{x}_0(t) + \vec{x}_1(y, z, t) \quad (4)$$

where $\vec{x}_0(t) = (x_0(t), y, z)$ and \vec{y} are the vector radius of a given point of the unperturbed and of the perturbed interface respectively: $c_0(x/x_0(t))$ and $c(\vec{x}, t)$ play the corresponding role for the concentration in the liquid phase (see Fig. 1).

We shall linearize the equations of motion (i.e. the diffusion equation) around the unperturbed equation (i.e. we retain only terms linear in c_1 and \vec{x}_1). Because of the special form of the boundary conditions, the equations we shall obtain for $c_1(x, t)$ and $\vec{x}_1(x, z, t)$ are nevertheless nonlinear: they are analogous (but not similar) to the equations one gets for c in the case where the interface is supposed to be planar. What is important, however, is that a reducing procedure is possible

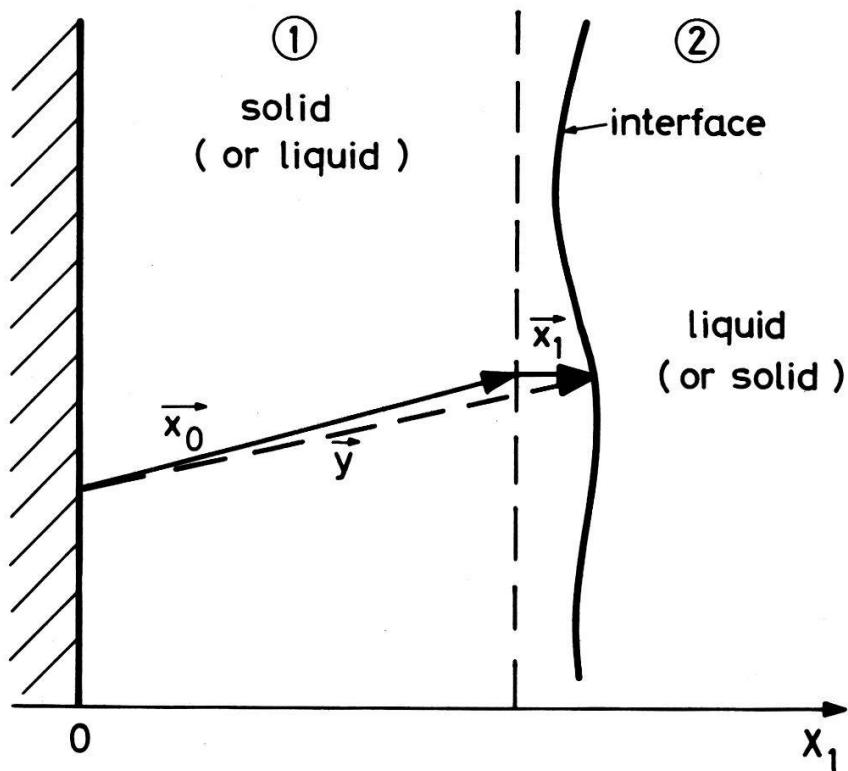


Figure 1

A solution occupies the half space $x > 0$. An interface divides this region into two domains. The liquid is characterized by a concentration $c(\vec{x}, t)$ (Phase 1 or 2) varying from place to place; the solid is supposed to be of uniform concentration c_s (Phase 2 or 1). The location of a point of the interface $\vec{y}(y, z, t)$ is the sum of a vector $\vec{x}_0(t) = (x_0(t), y, z)$, giving the position of the interface in the unperturbed state, and of a deviation $\vec{x}_1(y, z, t) = (x_1(y, z, t), 0, 0)$.

for these equations also. One can look for a special form of solution for c_1 and \vec{x}_1 so that the equation which the special solution satisfies is again a linear one. We shall distinguish two cases:

(a) *Kinetic deviation*

We speak of a *kinetic deviation* in the case where *the interface is still planar and parallel to the unperturbed one*. We can follow the evolution of the deviation $\vec{x}_1(y, z, t) = \vec{x}_1(t)$ which is necessarily accompanied of a deviation of the field $c_1(\vec{x}, t)$.

(b) *Morphological deviation*

We speak of a *morphological deviation* in all other cases, i.e. *when the deviation of the interface is not uniform*. In this case the deviation of the concentration field depends on y or z .

A reducing procedure will be shown to be possible in both cases. Moreover, we shall indicate how to generalize this procedure to higher order in perturbation theory in the case of a kinetic deviation. In all the cases we shall consider here, we shall discuss neither the existence nor the uniqueness of the solutions we shall find. In this sense, this paper does not discuss the stability of various formulations

of the Stefan problem, but rather it shows the existence of a new approach to the Stefan problem. Some examples are given, not because of their physical interest but as an illustration of the method which could be applied to other formulations of the Stefan problem, for instance when two fields such as the temperature and the concentration are coupled together.

We must emphasize an important point here for the cases we shall consider below. All effects related to the surface tension of the interface will be omitted. It is the price we must pay for generalizing the reducing procedure to the evolution of deviations. Convection effects are also omitted.

Advance of the phase boundary of a binary solution

We consider a binary solution filling the half space $x > 0$ (Fig. 1). The concentration of the solute is supposed to be both weak and supersaturated so that

- (1°) linear equations apply for the solute concentration $\tilde{c}(\vec{x}, t)$.
- (2°) for $0 < x < x_0(t)$, the solution is in the solid state with a constant concentration c_s and the phase boundary $x_0(t)$ is moving forward.
- (3°) for $x_0(t) < x < \infty$, the solution takes the form of a supersaturated liquid in which the solute concentration satisfies a diffusion equation

$$D \Delta \tilde{c} = \frac{\partial \tilde{c}}{\partial t} \quad (5)$$

together with the boundary conditions

$$\tilde{c}(x_0(t), t) = c_l < c_s \quad (6)$$

$$\tilde{c}(\infty, t) = c_\infty > c_l \quad (7)$$

Δ is the Laplace operator, c_l is the equilibrium concentration of a saturated solution at the given temperature T (recall that the process is supposed to be isothermal). D is a diffusion constant.

- (4°) across the interface, the conservation of the solute demands that the following relations holds

$$D \frac{\partial \tilde{c}}{\partial x} = (c_s - c_l) \frac{dx_0}{dt} \quad (8)$$

If the interface is not planar, (8) takes the form

$$D(\vec{n} \cdot \vec{\nabla})\tilde{c} \Big|_{x=x_b} = (c_s - c_l)\vec{n} \cdot \vec{V} \quad (9)$$

\vec{V} and \vec{n} are respectively the velocity of the interface and the unit vector orthogonal to it at the point x_b located on the interface.

Equations (5)–(8) constitute together a classical example of the Stefan problem. Equations (8) and (9) simply express the conservation of solute during the process of solidification.

The well-known procedure for obtaining an exact solution of this particular case of the Stefan problem is to look for a solution of the form

$$\begin{aligned}\tilde{c}_0(\vec{x}, t) &= c_0(\xi) \\ \xi &= \alpha \frac{x}{x_0}(t)\end{aligned}\tag{10}$$

As can be directly checked by introducing (10) into (5)–(8), $x_0(t)$ must satisfy

$$x_0 \frac{dx_0}{dt} = 2D\alpha^2\tag{11}$$

or, by an arbitrary choice of the integration constant,

$$x_0^2(t) = 4D\alpha^2 t\tag{12}$$

$$c_0'' + 2\xi c_0' = 0\tag{13}$$

where the prime denotes derivation with respect to ξ . Using the boundary conditions (6)–(8), one finally obtains

$$c_0(\xi) = \frac{1}{1 - \operatorname{erf} \alpha} \{c_e - c_\infty \operatorname{erf} \alpha + (c_\infty - c_l) \operatorname{erf} \xi\}\tag{14}$$

and

$$\alpha \sqrt{\pi} (1 - \operatorname{erf} \alpha) \exp \alpha^2 = \frac{c_\infty - c_l}{c_s - c_l}\tag{15}$$

$\operatorname{erf} z$ is the so-called error function

$$\operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2) dt\tag{16}$$

Evolution of a displaced boundary

We consider here an interface whose shape deviates from the planar shape; we shall retain here only deviations whose amplitude are sufficiently small so that they satisfy equations which are linear in this amplitude as well as in the corresponding correction to the concentration of the liquid phase.

Let us define \vec{x}_0 as the radius vector of a given point of the unperturbed interface and \vec{n}_0 as the unit vector normal to the interface. As a consequence,

$$\begin{cases} \vec{x}_0 = (x_0(t), y, z) \\ \vec{n}_0 = (1, 0, 0) \\ \frac{dx_0}{dt} = \frac{d\vec{x}_0}{dt} \cdot \vec{n}_0 \end{cases}\tag{17}$$

Similarly, we define the corresponding quantities for the perturbed interface, i.e. for the interface which deviates from the location just calculated (e.g. (12)):

$$\begin{cases} \vec{y} = \vec{x}_0 + \vec{x}_1 \\ \vec{n} = \vec{n}_0 + \vec{n}_1 \\ v = \frac{d\vec{y}}{dt} \cdot \vec{n} = \frac{dx_0}{dt} + v_1 \end{cases} \quad (18)$$

The symbols with indices 0 and 1 refer to the unperturbed quantities and to the deviations respectively. Notice that the component of the velocity of the boundary in the direction of \vec{n} is the only one which can be given a precise meaning. Notice also that in the linear approximation, \vec{n} being a unit vector,

$$\vec{n}_0 \cdot \vec{n}_1 = 0 \quad (19)$$

We need a one-to-one correspondance between the points of the unperturbed and perturbed boundary so that to each \vec{x}_0 there exists only one \vec{y} . As a consequence, we choose \vec{x}_1 in the following way:

$$\vec{x}_1 = \tilde{A}(\vec{x}_0, t) \vec{n}_0 \quad (20)$$

so that, using (18) and (19), we get

$$v_1 = \frac{d}{dt} \tilde{A}(\vec{x}_0, t) \quad (21)$$

(recall that we keep only terms linear in \tilde{A}).

The concentration in the liquid phase also is modified in the presence of a perturbation of the boundary

$$\tilde{c}(\vec{x}, t) = c_0(\xi) + \tilde{c}_1(\vec{x}, t) \quad (22)$$

On the boundary, we obtain in the linear approximation

$$\tilde{c}(\vec{x}, t) + c_0(\alpha) + \tilde{c}_1(\vec{x}_0, t) + \tilde{A}(\vec{x}_0, t) \cdot \frac{\partial c_0(\xi)}{\partial \xi} \Big|_{\xi=\alpha} = c_e \quad (23)$$

so that $c_1(x, t)$ satisfies the diffusion equation

$$D \Delta \tilde{c}_1 = \frac{\partial \tilde{c}_1}{\partial t} \quad (24)$$

Using (6), (7), (9) and (22) we write the boundary conditions for \tilde{c}_1 as

$$\tilde{c}_1(\infty, t) = 0 \quad (25)$$

$$\tilde{c}_1(\vec{x}_0, t) = -2 \frac{\tilde{A}}{x_0} (c_s - c_l) \alpha^2 \quad (26)$$

$$\frac{d\tilde{A}}{dt} = -\frac{2\tilde{A}}{x_0} \alpha^2 \frac{dx_0}{dt} + \frac{D}{c_s - c_l} \frac{\partial c_1}{\partial x} \Big|_{x=x_0} \quad (27)$$

Because of the form of the boundary conditions, this is a nonlinear problem. However, we can transform it into a linear one by an 'Ansatz' similar to the reducing procedure used to solve the unperturbed Stefan problem.

We write indeed

$$\tilde{A}(\tilde{x}_0, t) = a(x_0)h(\eta, \zeta) \quad (28)$$

$$\tilde{c}_1(x, y, z, t) = c_1(\xi, \eta, \zeta, x_0) = (c_s - c_l) \frac{a(x_0)}{x_0} g(\xi, \eta, \zeta) \quad (29)$$

where

$$\eta = \frac{y}{x_0}, \quad \zeta = \frac{z}{x_0}$$

and so we define 3 new functions a , h and g to be determined. Introducing (28) and (29) into (24) to (27), we get

$$g_{\xi\xi} + g_{\eta\eta} + g_{\zeta\zeta} + 2(\xi g_\xi + \eta g_\eta + \zeta g_\zeta) + 2\left(1 - \frac{x_0}{a} \cdot \frac{da}{dx_0}\right)g = 0 \quad (30)$$

$$g(\alpha, \eta, \zeta) = -2\alpha^2 h(\eta, \zeta) \quad (31)$$

$$g_\xi(\alpha, \eta, \zeta) = 2\alpha\left(2\alpha^2 + \frac{x_0}{a} \frac{da}{dx_0}\right)h - \eta h_\eta - \zeta h_\zeta \quad (32)$$

$$g(\infty, \eta, \zeta) = 0 \quad (33)$$

where

$$g_\xi = \frac{\partial g}{\partial \xi}, \quad g_\eta = \frac{\partial g}{\partial \eta}, \quad \text{etc.}$$

Now the problem becomes linear if we demand

$$\frac{x_0}{a} \frac{da}{dx_0} = -k = \text{constant} \quad (34)$$

The value of k is very important, because it determines the evolution of the system. Given h , we shall see what can be said about g and k .

One-dimensional case (kinematical deviation)

As a first example, we shall consider the problem of a planar perturbation; i.e. we write

$$h(\eta, \zeta) = h_0 = \text{constant} \quad (35)$$

On the other hand, we shall take g as being independent of both η and ζ , so that the problem is a pure one-dimensional one.

From the physical point of view, we analyse now a situation where the interface does not occupy the position given by equation (12). As a consequence, the concentration depends only on ξ and x_0 . Equations (30)–(33) now become

$$m'' + 2\xi m' + 2(1+k)m = 0 \quad (36)$$

$$m(\alpha) = -2\alpha^2 \quad (37)$$

$$m'(\alpha) = 2\alpha^2(2\alpha^2 - k) \quad (38)$$

$$m(\infty) = 0 \quad (39)$$

where

$$m(\xi) = g(\xi)/h_0 \quad (40)$$

The general solution of (36) can be written

$$m(\xi) = Am_1(\xi) + Bm_2(\xi) \quad (41)$$

where A and B are constants to be determined by the boundary conditions and m_1 and m_2 can be expressed with the help of the confluent hypergeometric function [9] $M(\alpha, \beta, z)$. Indeed

$$m_1(\xi) = M\left(\frac{1+k}{2}, \frac{1}{2}; -\xi^2\right) \quad (42)$$

$$m_2(\xi) = M\left(1+\frac{k}{2}, \frac{3}{2}; -\xi^2\right) \quad (43)$$

We look for a solution k independent of α . As a consequence, the boundary conditions (37)–(39) can be satisfied only for

$$\varepsilon = 1 + k > 0 \quad (44)$$

In fact, $m_1(\xi)$ and $m_2(\xi)$ vanish for $\xi^2 \rightarrow \infty$ for all values of k satisfying (44) and only for those values. We see that if (44) is realized, there always exists one and only one solution (41) satisfying (36)–(39). Now (34) and (44) imply

$$\frac{a}{x_0} = \left(\frac{t_0}{t}\right)^{\varepsilon/2} \quad (45)$$

where t_0 is some quantity having the dimension of time. Equation (45) shows that the relative deviation of the interface a/x_0 decreases with time, although the rate of decreasing can be as slow as one wishes.

Localized morphological deviation of the interface

We consider a deformation of the interface of the form

$$h_{mn}(\eta, \zeta) = \chi_m(\eta)\chi_n(\zeta) \quad (46)$$

where m, n are fixed nonnegative integers and

$$\chi_l(y) = \left(\frac{d}{dy}\right)^l e^{-y^2} \quad (47)$$

satisfies the differential equation

$$\frac{d^2}{dy^2} \chi_l + 2y \frac{d}{dy} \chi_l + 2(1+l)\chi_l = 0 \quad (48)$$

Notice that we could define a basis for a localized deformation with the help of h_{mn} . With this choice for $h(\eta, \zeta)$, $g(\xi, \eta, \zeta)$ satisfies the equations

$$g_{\xi\xi} + g_{\eta\eta} + g_{\zeta\zeta} + 2(\xi g_\xi + \eta g_\eta + \zeta g_\zeta) + 2(1+k)g = 0 \quad (49)$$

$$g(\infty, \eta, \zeta) = 0 \quad (50)$$

$$g(\alpha, \eta, \zeta) = -2\alpha^2 h_{mn} \quad (51)$$

$$g_\xi(\alpha, \eta, \zeta) = \alpha^2 \{h_{m+2,n} + h_{m,n+2} + 2(2+m+n+2\alpha^2-k)h_{mn}\} \quad (52)$$

It is easy to see that the function

$$g(\xi, \eta, \zeta) = u_{nm}(\xi)h_{nm}(\eta, \zeta) + u_{n+2,m}(\xi) \cdot h_{n+2,m}(\eta, \zeta) + u_{n,m+2}(\xi)h_{n,m+2}(\eta, \zeta) \quad (53)$$

where $u_{\alpha'\beta'}$ satisfies

$$\frac{d^2 u_{\alpha'\beta'}}{d\xi^2} + 2\xi \frac{d}{d\xi} u_{\alpha'\beta'} + 2(k - \alpha' - \beta' - 1)u_{\alpha'\beta'} = 0 \quad (54)$$

$$u_{\alpha'\beta'}(\infty) = 0 \quad \text{for } (\alpha', \beta') = (n, m), (n+2, m) \text{ and } (n, m+2)$$

is a solution to equations (49)–(52). (Notice that we have not specified the boundary conditions that $u_{\alpha'\beta'}$ must obey on the plane $\xi = \alpha$, because they are not important here.)

Equation (54) is automatically verified if

$$k > m + n + 3 \quad (55)$$

because the set of equation (54) is quite analogous to equations (36)–(39). Such a perturbation decreases as (notice that $\epsilon > 0$)

$$\frac{a}{x_0} \sim \left(\frac{1}{x_0}\right)^{k+1} \sim t^{-(m+n+4+\epsilon)/2} \quad (56)$$

For a gaussian deformation $h_{00}(\eta, \zeta) e^{-(\eta^2+\zeta^2)}$ we get a rate equal to

$$\frac{a}{x_0} \sim t^{-2-\epsilon/2} \quad (57)$$

As a consequence, we can retain two major features of these solutions:

- (1°) As the domain of the liquid phase is not bounded, the equations of motion together with a boundary condition do not furnish a discrete spectrum for the eigenvalue but rather a continuous one.
- (2°) For a given solution, there is a unique k because this quantity governs the motion of the interface. As a consequence, we cannot superpose solutions corresponding to different values of k . This is a consequence of the nonlinearity of the problem.

The inverse problem: dissolution of a solid into the liquid solution

We shall now consider a rather artificial problem which is nearly the opposite of the problem discussed above: we shall impose that the strip $0 < x < x_0(t)$ is liquid; the concentration \tilde{c} of the liquid varies with x and satisfies the diffusion equation (5) with the boundary conditions

$$\tilde{c}(x_0(t), t) = c_l < c_s \quad (58)$$

$$\tilde{c}(0, t) = c_0 < c_l \quad (59)$$

The condition (9) remains unchanged. Notice the condition (59) which implies that the solid phase existing for $x > x_0(t)$ will become liquid and therefore that

dx_0/dt will be >0 . The interesting feature of this system is that the domain of definition of the liquid is now bounded. However, the condition (59) is rather artificial because it is difficult to maintain a constant concentration at one point ($x = 0$). Notice that there are other Stefan problems where such a situation is quite natural: for instance the isothermal destruction of superconductivity by a magnetic field imposed or a sample at $x = 0$ (see [3]). The magnetic field does not penetrate the still superconducting domain $x > x_0(t)$ and therefore the normal domain is characterized by a diffusion equation for the field and is bounded ($0 < x < x_0(t)$). An analysis similar to the analysis made here can be found in [7]. We consider now two different solutions to this problem.

A. Planar boundary, unperturbed problem

The solution of this problem is very similar to the previous one; if we consider the velocity dx_0/dt of the interface, it takes the same form as above (equation (11)). The only difference lies in the distribution of the concentration, given by

$$c_0(\xi) = c_0 + \frac{c_l - c_0}{\operatorname{erf} \alpha} \operatorname{erf} \xi \quad (60)$$

and in the definition of α

$$\sqrt{\pi \alpha} \operatorname{erf} \alpha \exp \alpha^2 = \frac{c_l - c_0}{c_s - c_l} \quad (61)$$

B. Kinetical deviation

In this case, recall that the problem is still one-dimensional. Using the same procedure that we applied above, we obtain for the function $m(\xi)$ defined by (40):

$$m'' + 2\xi m' + 2(1 + k)m = 0 \quad (62)$$

$$m(\alpha) = -2\alpha^2 \quad (63)$$

$$m'(\alpha) = 2\alpha(2\alpha^2 - k) \quad (64)$$

$$m(0) = 0 \quad (65)$$

Compared with equations (36)–(39), the only change concerns condition (39) which is replaced by (65). Now this modification is important because the domain of definition of ξ is now bounded.

In the limit $\xi \rightarrow 0$, $M(\alpha, \beta, -\xi^2) \rightarrow 1$ so that, using (43), we conclude that

$$m(\xi) = K\xi M\left(1 + \frac{k}{2}, \frac{3}{2}, -\frac{\xi^2}{\alpha^2}\right) \quad (66)$$

K being a constant one can eliminate between (63) and (64), with the result

$$\alpha m'(\alpha) = (k - 2\alpha^2)m(\alpha) \quad (67)$$

The properties of the confluent hypergeometric function are such that (67) is

fulfilled if and only if

$$k = -\frac{da}{dx_0} \cdot \frac{x_0}{a} = 1 \quad (68)$$

so that the amplitude of the relative deviation decreases as

$$\frac{a}{x_0} \sim x_0^{-2} \sim t^{-1} \quad (69)$$

The boundary can then be said to be stable with respect to the type of perturbation considered here.

More general solution in the case of a planar boundary

As we saw above, it is possible to reduce the Stefan problem if one allows small deviations to the unperturbed problem. The procedure used for the reduction of the equations is a generalization of the one used in the unperturbed case. A question now arises: is it possible to apply this procedure to higher orders in the perturbation?

We shall show this can be done in principle in the simplest case of a planar boundary (one-dimensional case). We begin with the original one-dimensional problem (the liquid occupies the domain $x < y_0$).

$$D \frac{\partial^2 \tilde{c}}{\partial x^2} = \frac{\partial \tilde{c}}{\partial t} \quad (70)$$

$$\tilde{c}(0, t) = c_0 \quad (71)$$

$$\tilde{c}(y_0, t) = c_l \quad (72)$$

$$D \frac{\partial \tilde{c}}{\partial x} \Big|_{x=y_0} = (c_s - c_l) \frac{dy_0}{dt} \quad (c_s > c_l) \quad (73)$$

A. $c_0 < c_l$

In this case, as seen above, one expects dy_0/dt to be >0 . We make the following change of variables:

$$w = \frac{x}{\beta \sqrt{t}} \quad (74)$$

$$\varepsilon = \frac{y_0(t)}{\beta \sqrt{t}} - 1 \quad (75)$$

β is a constant such that if we allow the system to evolve in its unperturbed state, the interface occupies the position

$$x = x_0 = \beta \sqrt{t} \quad (76)$$

at time t . On the other hand, if the system is perturbed with respect to this

evolution, the interface satisfies the equation

$$x = y_0(t) \quad (77)$$

during its motion; $y_0(t)$ is unknown. We see that ε can now be interpreted as the relative deviation of the position of the interface at time t . We assume that (74) and (75) define a valid change of variables and that it possesses an inverse, so that one can write

$$t = t(\varepsilon) \quad (78)$$

If one introduces (74) and (75) into equations (70) to (73)

$$\frac{\partial^2 c}{\partial w^2} + \frac{\gamma^2}{2} w \frac{\partial c}{\partial w} = \gamma^2 \vartheta \frac{\partial c}{\partial \varepsilon} \quad (79)$$

with the boundary conditions

$$c(0, \varepsilon) = c_0 \quad (80)$$

$$c((1 + \varepsilon), \varepsilon) = c_l \quad (81)$$

$$\frac{\partial c}{\partial w}((1 + \varepsilon), \varepsilon) = (c_s - c_l) \left[\frac{1 + \varepsilon}{2} + \vartheta \right] \gamma^2 \quad (82)$$

and with the definitions

$$c(w, \varepsilon) = c(x(w, \varepsilon), t(\varepsilon)) \quad (83)$$

$$\vartheta(\varepsilon) = t(\varepsilon) \left(\frac{dt}{d\varepsilon} \right)^{-1} \quad (84)$$

$$\beta^2 = D\gamma^2 \quad (85)$$

The value of γ^2 is calculated by letting $\varepsilon = 0$, $\vartheta = 0$ in the equations (79)–(82). We find

$$\frac{\gamma^2}{2} \exp \frac{\gamma^2}{4} \int_0^1 dv \exp -\frac{(v\gamma)^2}{4} = \frac{c_l - c_0}{c_s - c_l} \quad (86)$$

(Notice that w differs from ξ by a constant factor.) Now, we could in principle solve the (nonlinear) equations (79)–(82). However, a perturbation scheme is now in principle directly accessible if we develop c and ϑ in powers of ε , with the hope that such a development is meaningful. We must take care that ϑ vanishes with ε , so that we could write

$$c(w, \varepsilon) = c_0(w) + \varepsilon c_1(w) + \frac{\varepsilon^2}{2!} c_2(w) + \dots \quad (87)$$

$$\vartheta(\varepsilon) = \varepsilon \vartheta_1 + \frac{\varepsilon^2}{2!} \vartheta_2 + \frac{\varepsilon^3}{3!} \vartheta_3 + \dots \quad (88)$$

Retaining terms up to the first power of ε only is exactly equivalent to the analysis made above: this is a consequence of the choice of the variable ε . If we go one higher order in the power of ε , we determine $c_2(w)$ with the help of $c_1(w)$ and so on (the convergence of this procedure has to be checked). At the same time, we

get the corresponding values of $\vartheta_1, \vartheta_2 \dots$ and therefore determine $\vartheta(\varepsilon)$, which is equivalent to the determination of $y_0(t)$. Instead of doing this, we shall solve (79)–(82) by an approximation scheme valid in the case where $c_l - c_0/c_s - c_l$, and therefore γ^2 , are very small. (61) tells us that

$$\lim \gamma^2 = 2 \frac{c_l - c_0}{c_s - c_l} \quad \left(\frac{c_l - c_0}{c_s - c_l} \rightarrow 0 \right) \quad (88)$$

First, we divide c by $c_s - c_l$ and call $n(w, \varepsilon)$ the resulting function:

$$n(w, \varepsilon) = \frac{c(w, \varepsilon)}{c_s - c_l} \quad (89)$$

Now we develop n as a power series of γ^2

$$n = n_0 + \gamma^2 n_1 + 0(\gamma^4) \quad (90)$$

$$\vartheta = \vartheta_0 + 0(\gamma^2) \quad (91)$$

The boundary conditions (80)–(82) now become

$$n(0, \varepsilon) = \frac{c_0}{c_s - c_l} \quad (92)$$

$$n(1 + \varepsilon, \varepsilon) = \frac{c_l}{c_s - c_l} = \frac{c_0}{c_s - c_l} + \frac{\gamma^2}{2} + 0(\gamma^4) \quad (93)$$

$$\frac{\partial n}{\partial w}(1 + \varepsilon, \varepsilon) = \gamma^2 \left[\frac{1 + \varepsilon}{2} + \vartheta_0 \right] + 0(\gamma^4) \quad (94)$$

Because of (79), n_0 now satisfies

$$\frac{\partial^2 n_0}{\partial w^2} = 0 \begin{cases} n_0(0, \varepsilon) = \frac{c_l}{c_s - c_l} \\ n_0(1 + \varepsilon, \varepsilon) = \frac{c_0}{c_s - c_l} \end{cases} \quad (95)$$

$$\frac{\partial^2 n_1}{\partial w^2} + \frac{w}{2} \frac{\partial n_0}{\partial w} = \vartheta_0 \frac{\partial n_0}{\partial \varepsilon} \begin{cases} n_1(0, \varepsilon) = 0 \\ n_1(1 + \varepsilon, \varepsilon) = \frac{1}{2} \\ \frac{\partial n_1}{\partial w}(1 + \varepsilon, \varepsilon) = \frac{1 + \varepsilon}{2} + \vartheta_0(\varepsilon) \end{cases} \quad (96)$$

(95) and (96) uniquely determine $\vartheta_0(\varepsilon)$:

$$t(\varepsilon) \frac{d\varepsilon}{dt} = \vartheta_0(\varepsilon) = \frac{1}{2} \left[\frac{1}{1 + \varepsilon} - (1 + \varepsilon) \right] \quad (97)$$

so that we finally obtain

$$y_0(t) = \beta \sqrt{t} \left(1 + \frac{\tau_0}{t} \right)^{1/2} \quad (98)$$

τ_0 is an integration constant. We see that the relative deviation of the unperturbed position of the boundary tends to vanish as time increases.

B. $c_0 > c_l$ (*metastable case from the point of view of thermodynamics*)

As one expects dx_0/dt to be <0 , we make the following change of variables

$$w = \frac{x}{\beta\sqrt{-t}} \quad (99)$$

$$\varepsilon = \frac{y_0(t)}{\beta\sqrt{-t}} - 1 \quad (100)$$

In the unperturbed state, the interface reaches the surface $x = 0$ at time $t = 0$, so that all times considered here are negative.

This second case is very similar to the previous one. In fact, we obtain the same equations for the concentration c with the only exception that $\gamma^2 = \beta^2/D$ has to be replaced everywhere by $-\gamma^2$, which therefore satisfies

$$\frac{\gamma^2}{2} \exp - \frac{\gamma^2}{4} \int_0^1 dv \exp \frac{(v\gamma)^2}{4} = \frac{c_0 - c_l}{c_s - c_l} \quad (101)$$

We then obtain

$$\frac{\partial^2 c}{\partial w^2} - \gamma^2 \frac{\partial c}{\partial w} w = -\gamma^2 \vartheta \frac{\partial c}{\partial \varepsilon} \quad (102)$$

with the boundary conditions

$$c(0, \varepsilon) = c_0 \quad (103)$$

$$c(1 + \varepsilon, \varepsilon) = c_l \quad (104)$$

$$\frac{\partial c}{\partial w}(1 + \varepsilon, \varepsilon) = -(c_s - c_l)\gamma^2 \left(\frac{1 + \varepsilon}{2} + \vartheta \right) \quad (105)$$

If we now develop $n = c/c_s - c_l$ and ϑ as a power series in γ^2 , we obtain for ϑ_0 exactly the same relation with ε as previously, namely

$$\vartheta_0 = \frac{1}{2} \left[\frac{1}{1 + \varepsilon} - (1 + \varepsilon) \right] \quad (106)$$

which now leads to

$$y_0(t) = \beta\sqrt{-t} \left(1 + \frac{\tau_0}{t} \right)^{1/2} \quad (107)$$

As t increases from $-\infty$ to -0 , $y_0(t)/\beta\sqrt{-t}$ increases and ultimately becomes singular at a time which depends on τ_0 , which can be ≥ 0 . *In that case, the unperturbed solution is therefore unstable against a deviation of the planar interface* (or kinematically unstable); the solution is most probably also morphologically unstable. Notice that the surface tension we omitted does not play any role in the case of the kinematical instability. One can therefore conclude that in the case studied here, *thermodynamical metastability implies instability*.

Conclusion

In this paper, we have discussed the use of the linear stability theory in the Stefan problem. Instead of establishing existence theorems, we have merely looked for solutions differing from the well known 'unperturbed' ones by quantities small enough to allow the linearization of the equations of motion with respect to these amplitudes. However, the linearized equations are still nonlinear because of the peculiar form of the boundary condition. As a consequence, we had to find an Ansatz permitting us to transform the equations into truly linear ones.

In the case of the simple systems studied here, the results obtained are not especially interesting from the physical point of view. However, the method used here can be extended to more interesting situations where, for instance, there is a coupling between temperature and another field, such as the concentration. In the examples treated here, we have remarked that the *transition out of a metastable state implies instability from the point of view of the dynamics of the transition*.

In fact, this instability seems to be connected with the sign of the gradient of the considered field in the neighbourhood of the interface (here the concentration). This relation has already been presented in previous articles [5], [8].

On the other hand, the approach introduced here allows us to describe the time evolution of a morphological or kinematical deviation of the interface. The domain of validity of this approach is however restricted to Stefan problems where the surface tension can be neglected. The extension of this approach to systems characterized by a surface tension is not trivial.

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