ASYMPTOTIC RESULTS FOR THE STEFAN PROBLEM WITH KINETIC UNDERCOOLING

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Summary

We study the behaviour of the one-phase Stefan problem with kinetic undercooling; moving boundary problems governed by the same formulation also arise in the modelling of silicon oxidation and of solvent diffusion in glassy polymers. The one-phase model is carefully derived from a two-phase formulation in the limit of small thermal diffusivity in the solid. A linear kinetic undercooling law is assumed at the moving boundary and the one-phase model is then studied in a number of asymptotic regimes. In particular, results for small and large Stefan number are presented in one dimension and in a paradigm two-dimensional example.

1. Introduction

In the representation of solidification and melting processes by simple continuum models, the classical Stefan problem (described, for example, in Carslaw and Jaeger (**1**), Rubinstein (**2**), Elliot and Ockendon (**3**) and Crank (**4**)) has been generalized to include kinetic undercooling at the moving phase-change boundary (see, for example, Cahn *et al*. (**5**), Coriell and Parker (**6**), Chalmers (**7**), Coriell and Sekerka (**8**), Crowley (**9**)). This class of moving boundary problem involves non-equilibrium phase changes that are characterized by a dependence of the phase-change temperature on the velocity of the phase-change boundary. Another type of generalization that has also received much attention involves incorporating surface tension effects, usually through the Gibbs–Thomson condition (Mullins and Sekerka (**10**, **11**), Langer (**12**), Krukowski and Turski (**13**), Chadam and Ortoleva (**14**), Chadam *et al*. (**15**), Visintin (**16**), Luckhaus (**17**), Zhu *et al*. (**18**)). One of the motivations for the inclusion of either or both of these additional effects has been the 'ill-posed' behaviour of the classical Stefan problem in certain applications (see, for example, Ockendon (**19**, **20**), Fasano *et al*. (**21**), Lacey and Ockendon (**22**), Howison *et al*. (**23**), Fasano *et al*. (**24**)). Indeed, inclusion of kinetic undercooling has been shown to prevent finite-time blow up for supercooled (or superheated) problems (Xie (**25**)) and thus provide a possible regularizing effect. Several authors, notably Schaefer and Glicksman (**26**), Visintin (**27**), Dewynne *et al*. (**28**), Chen and Reitich (**29**), Umantsev and Davis (**30**), Doole (**31**) and Yi (**32**), have included both kinetic undercooling and surface tension effects. These authors have provided self-similar solutions, linear stability analysis and local existence and uniqueness proofs. Except in section 2.1, we shall concern ourselves with kinetic undercooling only.

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The layout of the paper is as follows. In section 2 we consider a multi-dimensional two-phase Stefan problem, where kinetic undercooling and surface tension are incorporated into the model at the moving phase boundary in the form of a linear kinetic condition. By taking the limit in which the conductivity in the solid phase becomes negligible we derive the appropriate conditions on the moving boundary for the one-phase problem. It should be stressed that versions of the one-phase problem, in which heat is not conserved, have been widely studied in the past, including many of the references noted above. Once heat conserving equations for the one-phase Stefan problem with kinetic undercooling have been derived, we show their equivalence to existing formulations of two other moving boundary problems, namely those describing the diffusion of solvents in glassy polymers and the oxidation of silicon. In section 3 we summarize some useful transformations and integral conservation statements and then proceed to examine the asymptotic behaviour of the solution for small and large time in section 4 and in the limits of small and large Stefan number in section 5. Finally, in section 6 we consider a two-dimensional problem which illustrates the extension of the results to higher dimensions. Further extensions are noted in the conclusions.

2. The one-phase model

2.1 *Derivation from the two-phase model*

We begin by considering the two-phase Stefan problem with, for completeness, both kinetic undercooling and surface tension effects. This problem has been considered in one space dimension by several authors, including Visintin (**27**) and Xie (**25**) (who show local existence and uniqueness of a solution), Charach and Zaltzman (**33**, **34**), Charach *et al*. (**35**) (who show that the classical Stefan problem is the long time attractor) and Guan and Wang (**36**) (who demonstrated global existence of solutions). Chen and Reitich (**29**) obtained local existence and uniqueness results for higher space dimensions. Regularity properties of solutions have been discussed by Friedman and Reitich (**37**) for surface tension and Götz and Zaltzman (**38**) for kinetic undercooling. Several numerical schemes for the one-dimensional case are discussed in Fabbri and Voller (**39**). The convergence of the two-phase Stefan problem to the one-phase problem has been considered by Stoth (**40**), with surface tension and kinetic undercooling effects neglected.

The governing equations for the two-phase multi-dimension problem may be written as

$$\frac{\partial}{\partial t}(\rho c_i u_i) = \nabla.(K_i \nabla u_i), \qquad \mathbf{x} \in D_i, \quad i = 1, 2, \quad D = D_1 \cup D_2,$$

where $i = 1$ denotes the liquid phase, $i = 2$ the solid phase, $u_i(\mathbf{x}, t)$, K_i and c_i denote the temperature, conductivity and specific heat and ρ is the density, which is taken to be the same in both phases. (We present the problem in terms of heat transfer; as already indicated, the same formulation also arises in problems of mass transfer, for which the one-phase limit discussed below is in fact more often relevant.)

The conditions on the moving phase boundary $S(\mathbf{x}, t) = 0$ are the Stefan condition

$$\left[K_i \frac{\partial u_i}{\partial n}\right]_{i=2}^{i=1} = -\rho v_n \left([c_i(u_i - u_m)]_{i=2}^{i=1} + L\right) \tag{1}$$

and temperature continuity together with kinetic undercooling and surface tension effects

$$u_1 = u_2 = u_m + \sigma\kappa + \beta v_n, \tag{2}$$

where n denotes the outward normal (that is, that from the liquid phase into the solid), v_n is the velocity of the phase boundary in that direction, $\partial/\partial n$ is the outward normal derivative, u_m is the equilibrium melting temperature, σ is the surface tension coefficient, κ the mean curvature and β the kinetic undercooling coefficient. Here, L is the latent heat per unit mass at the equilibrium temperature u_m (cf. Charach and Zaltzman (**33**, **34**) and Charach *et al*. (**35**), for example). The u_m terms in (1) could be eliminated by absorbing them into L, corresponding to a slightly different definition of the latent heat. In view of (2), (1) may be written as

$$\left[K_i \frac{\partial u_i}{\partial n}\right]_{i=2}^{i=1} = -\rho v_n \left([c_i]_{i=2}^{i=1}(u_1 - u_m) + L\right). \tag{3}$$

We assume appropriate initial conditions, and boundary conditions on the fixed boundary ∂D are given to complete the statement of the problem.

We introduce the dimensionless variables

$$\bar{\mathbf{x}} = \frac{\mathbf{x}}{\ell}, \qquad \bar{S} = \frac{S}{\ell}, \qquad \bar{t} = \frac{K_1}{\rho c_1 \ell^2} t, \qquad \bar{u}_1 = \frac{u_1 - u_m}{U}, \qquad \bar{u}_2 = \frac{u_2 - u_m}{U},$$

$$\bar{n} = \frac{n}{\ell}, \qquad \bar{\kappa} = \ell\kappa, \qquad \bar{v}_n = \frac{\rho c_1 \ell}{K_1} v_n,$$

where ℓ is a typical length scale and U is a representative temperature value. Further we define the dimensionless parameters

$$\lambda = \frac{L}{c_1 U}, \qquad \mu = \frac{\beta K_1}{\rho c_1 U \ell}, \qquad \nu = \frac{\sigma}{U\ell}, \qquad \delta = \frac{c_2}{c_1}, \qquad \theta = \frac{K_2}{K_1};$$

λ is commonly termed the Stefan number. For simplicity we have taken ρ, c_i and K_i $(i = 1, 2)$ to be constant. Dropping the overbars then gives the following dimensionless formulation:

$$\frac{\partial u_1}{\partial t} = \nabla^2 u_1, \qquad \mathbf{x} \in D_1, \tag{4}$$

$$\frac{\partial u_2}{\partial t} = \frac{\theta}{\delta} \nabla^2 u_2, \qquad \mathbf{x} \in D_2, \tag{5}$$

$$\text{on } S(\mathbf{x}, t) = 0 \qquad u_1 = u_2 = \nu\kappa + \mu v_n, \tag{6}$$

$$\frac{\partial u_1}{\partial n} - \theta \frac{\partial u_2}{\partial n} = -v_n\left((1 - \delta)u_1 + \lambda\right), \tag{7}$$

subject to suitably non-dimensionalized initial and fixed boundary conditions.

To obtain the one-phase formulation we consider the limit $\theta \to 0$. To leading order in the solid, away from the moving interface, we have

$$u_2 = U_2(\mathbf{x}), \tag{8}$$

$U_2(\mathbf{x})$ giving the initial temperature in the solid. However, there also exists an interior layer near the moving interface in which significant temperature change occurs in the solid. The scaling for this interior layer is

$$\mathbf{x} = \mathbf{x}_0(t) + \theta \hat{n} \mathbf{n},$$

where $S(\mathbf{x}_0, t) = 0$, so $\mathbf{x}_0$ lies on the moving boundary and $\mathbf{n}$ the unit outward normal to the moving boundary. At leading order within this layer in the solid we obtain from (5) that (provided $v_n > 0$)

$$\frac{\partial u_2}{\partial \hat{n}} = -\delta v_n (u_2 - U_2),$$

after matching with the outer solution (8). Using this last expression evaluated on the interface and noting that $\theta \partial/\partial n = \partial/\partial \hat{n}$, the Stefan condition (7) for the liquid becomes

$$\frac{\partial u_1}{\partial n} + v_n u_1 = v_n \left(\delta U_2 - \lambda\right),$$

where the first term on the right-hand side represents the sensible heat, and the second the latent heat, which is absorbed as melting proceeds. We shall be concerned with the particular case $U_2 \equiv 0$, which corresponds to the solid initially being at melting temperature, and the moving boundary condition then simplifies to

$$\frac{\partial u_1}{\partial n} + v_n u_1 = -\lambda v_n. \tag{9}$$

Henceforth we discuss the asymptotic properties of this one-phase model. Other uniform distributions U_2 correspond simply to a redefinition of λ. In dimensional terms, (9) reads

$$K_1 \frac{\partial u_1}{\partial n} + \rho c_1 v_n (u_1 - u_m) = -\rho L v_n.$$

We note that in the absence of kinetic undercooling and surface tension, if $U_2 \equiv 0$ then we have $u_2 \equiv 0$ and (9) holds exactly for the resulting one-phase problem. With ν or $\kappa \neq 0$, however, a truely one-phase problem is not possible, since we then have $u_2 \neq 0$ on the moving boundary which leads to temperature variations in the solid; a one-phase formulation can then be derived only by the type of asymptotic procedure just described.

The statement (9) of the Stefan condition for the one-phase problem conserves heat and should be contrasted with that adopted by, for example, Dewynne *et al.* (**28**), Gurtin (**41**), Charach and Zaltzman (**34**) and Yi (**32**), which neglects the $v_n u_1$ term and therefore does not do so. This is also remarked upon by Zhu *et al.* (**18**) for the case of surface tension, where it is also common (for example, Chadam and Ortoleva (**14**), Abergel *et al.* (**42**) and Doole (**31**)) to linearize the boundary condition (9), neglecting the second term. Since the boundary condition

$$\frac{\partial u_1}{\partial n} = -\lambda v_n \tag{10}$$

has been commonly used in place of (9), it is worth remarking upon some reasons which may have led to its erroneous use.

(a) If $\delta = 1$ (the case usually discussed), naively setting $\theta = 0$ in (7) yields (10). However, as we have shown, this procedure is not acceptable because the limit $\theta \to 0$ is singularly perturbed, (9) being the condition that correctly conserves heat at the interface.

(b) When kinetic undercooling and surface tension effects are both absent, equation (6) reduces to $u_1 = u_2 = 0$ and the conditions (9) and (10) are identical.

(c) In the large Stefan number limit ($\lambda \to \infty$) the rescalings $t = \lambda \hat{t}$, $v_n = \hat{v}_n/\lambda$ apply and (to leading order in $1/\lambda$), (9) reduces to

$$\frac{\partial u_1}{\partial n} = -\hat{v}_n,$$

again equivalent to (10). However, in this limit (4) also simplifies, to

$$\nabla^2 u_1 = 0,$$

giving the Hele-Shaw problem. It does not appear that (10) can be derived as an asymptotically self-consistent limit of (9) under circumstances for which the full heat equation (4) also arises in the leading-order balance.

2.2 *Formulation and applications*

The one-phase Stefan problem with kinetic undercooling that we shall be concerned with can now be stated in non-dimensional form in the one-dimensional case as follows:

$$\text{in } 0 < x < s(t) \qquad \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2}, \tag{11}$$

$$\text{on } x = s(t) \qquad u = \mu \dot{s}(t), \qquad \frac{\partial u}{\partial x} = -(u + \lambda)\dot{s}(t), \tag{12}$$

$$\text{on } x = 0 \qquad u = 1, \tag{13}$$

$$\text{at } t = 0 \qquad s = 0. \tag{14}$$

The suffix 1 on the temperature variable from the previous section has been dropped and we have chosen a Dirichlet condition on the fixed boundary $x = 0$. This gives the reference temperature $U = u_0 - u_m$ taking u_0 to be the dimensional temperature at $x = 0$. For convenience in what follows we take $\ell = \beta K_1/\rho L$, giving $\mu = \lambda$; through a suitable rescaling of the independent variables, this is equivalent to the choice $\ell = \beta K_1/\rho c_1 U$ which gives $\mu = 1$. The additional specification of $u_0 = u_m + L/c_1$ gives $\lambda = 1$, which corresponds to the scaling used by Dewynne *et al.* (**28**).

The system of equations (11) to (14) also arises in the penetration of solvents into glassy polymers (Astarita and Joshi (**43**), Astarita and Sarti (**44**), Astarita (**45**), Fasano and Ricci (**46**), Fasano *et al.* (**47**), Andreucci and Ricci (**48**), Cohen and Goodhart (**49**), Cohen and Erneux (**50**)) and the oxidation of silicon (King (**51**), Gröger and Strecker (**52**), King (**53**, **54**), Tayler and King (**55**)). For the sorption of solvents in glassy polymers, u represents the dimensionless concentration of the solvent in the swollen polymer region $0 < x < s(t)$, with $s(t)$ being the dimensionless position of the interface between the swollen polymer region containing the solvent and the glassy polymer region containing almost no solvent; equation (12) represents the swelling kinetics by a linear interface reaction. In the case of silicon oxidation, u represents the dimensionless concentration of the oxidant within the silicon dioxide, which occupies the region $0 < x < s(t)$, with $s(t)$ being the dimensionless position of the silicon/silicon dioxide boundary at which equation (12) represents a first-order reaction between oxidant and silicon. In the glassy polymer application a more general kinetic condition of the form

$$\dot{s}(t) = \psi\,(u(s(t), t)) \tag{15}$$

is often appropriate and commonly adopted in place (12), with $\psi(\xi) = k\xi^m$, where k and m are positive constants; this generalization has also been suggested in the case of silicon oxidation (Blanc (**56**) and Hu (**57**)). For other applications of nonlinear kinetic conditions see, for example, Kirkpatrick *et al.* (**58**) and Worster and Kerr (**59**). However, here we discuss the linear condition

only. The well-posedness and regularity of the solution to (11) to (14) for a more general kinetic condition of the type (15) has been shown by Fasano *et al.* (**47**); related results have also been obtained by Andreucci and Ricci (**48**) and Comparini and Ricci (**60**). Gröger and Strecker (**52**) independently showed existence and uniqueness for (11), (12) and (14) with a mixed condition on the fixed boundary. A suitable numerical scheme based on the application of the method of lines to one-dimensional parabolic free boundary problems (as described in Meyer (**61**) and Crank (**4**)) is discussed in Fasano *et al.* (**47**). We adopt this numerical scheme in order to illustrate and validate the asymptotic results derived in the following sections.

3. Transformations and conservation laws

In this section we collect together certain transformations and integral statements relevant to the system (11) to (14) and to certain generalizations. If $u(x, t)$ satisfies (11) to (14) (with $\mu = \lambda$ henceforth) then the function $v(x, t)$ defined by the transformation

$$v(x, t) = -\int_x^{s(t)} (u(x', t) + \lambda) dx' \tag{16}$$

satisfies the generalized one-phase Stefan problem or ablation problem (described in Crank (**4**)),

$$\text{in } 0 < x < s(t) \qquad \frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2}, \tag{17}$$

$$\text{on } x = s(t) \qquad v = 0, \qquad \frac{\partial v}{\partial x} = \lambda(\dot{s}(t) + 1), \tag{18}$$

$$\text{on } x = 0 \qquad \frac{\partial v}{\partial x} = 1 + \lambda, \tag{19}$$

$$\text{at } t = 0 \qquad s = 0. \tag{20}$$

Fasano *et al.* (**47**) used the transformation (16) to establish properties such as existence, uniqueness, regularity and continuous dependence on the initial data.

Denoting the moving boundary by $t = \omega(x)$ (so that $\omega(s(t)) = t$), the following variant of the Duvaut transformation (Crank (**4**)):

$$w(x, t) = \int_{\omega(x)}^{t} u(x, t') dt' = -\int_x^{s(t)} \big(v(x', t) - \lambda\big)\, dx', \tag{21}$$

yields the system

$$\text{in } 0 < x < s(t) \qquad \frac{\partial w}{\partial t} = \frac{\partial^2 w}{\partial x^2} - \lambda, \tag{22}$$

$$\text{on } x = s(t) \qquad w = 0, \qquad \frac{\partial w}{\partial x} = -\lambda, \tag{23}$$

$$\text{on } x = 0 \qquad w = t, \tag{24}$$

$$\text{at } t = 0 \qquad s = 0. \tag{25}$$

The equations (11), (12) and (14) imply the integral relation

$$\int_0^{s(t)} (u(x,t)+\lambda)dx + \int_0^t \frac{\partial u}{\partial x}(0,t')dt' = 0, \tag{26}$$

which is more useful when a Neumann condition holds on $x = 0$ in place of (13), an expression of this type being used by Cohen and Erneux (**50**). Equation (26) is a global conservation expression; earlier one-phase models for the Stefan problem with kinetic undercooling typically violate this condition (see sections 1 and 2); imposing (10) instead of (9), one has in place of (26)

$$\frac{d}{dt}\int_0^{s(t)} (u(x,t)+\lambda)dx + \frac{\partial u}{\partial x}(0,t) = \lambda\left(\frac{ds}{dt}\right)^2.$$

The term on the right-hand side amounts to heat or mass generation at the moving boundary and leads to the possibility of self-sustaining travelling waves ($s(t) = Vt$ for constant V), which have been extensively investigated in the literature; that such solutions are not usually physically appropriate in the contexts in which they have been proposed is clear from their failure to conserve heat or mass.

An integral result for the first moment (Fasano *et al.* (**47**)) follows from (11) to (14), namely

$$\int_0^{s(t)} x(u(x,t)+\lambda)dx + \lambda s - t = 0\,; \tag{27}$$

this can aid the analysis of the small and large time behaviour, for example. Conservation laws of the type (26) to (27) are also useful in analysing the Cauchy problem, for example, when (11) holds for $-s_-(t) < x < s_+(t)$ with

$$\begin{aligned}
&\text{on } x = s_+(t) && u = \lambda\dot{s}_+, && \frac{\partial u}{\partial x} = -(u+\lambda)\dot{s}_+,\\
&\text{on } x = -s_-(t) && u = \lambda\dot{s}_-, && \frac{\partial u}{\partial x} = (u+\lambda)\dot{s}_-,\\
&\text{at } t = 0 && u = U(x), &&
\end{aligned}$$

from which it follows that

$$\frac{d}{dt}\left(\int_{-s_-}^{s_+}(u(x,t)+\lambda)dx\right) = \frac{d}{dt}\left(\int_{-s_-}^{s_+} x(u(x,t)+\lambda)dx + \lambda(s_+ - s_-)\right) = 0. \tag{28}$$

As $t \to \infty$ we have that $u \to 0$ and the final positions of the moving boundaries, $S_+ \equiv s_+(\infty)$, $S_- \equiv s_-(\infty)$, can be thus given explicitly in terms of the initial conditions, without solving the problem for all t, via

$$\lambda\,(S_+ + S_-) = \int_{-s_-(0)}^{s_+(0)} (U(x)+\lambda)\,dx,$$

$$\lambda\,(S_+ - S_-)\left(\frac{1}{2}\,(S_+ + S_-) + 1\right) = \int_{-s_-(0)}^{s_+(0)} x\,(U(x)+\lambda)\,dx + \lambda\,(s_+(0) - s_-(0))\,.$$

Applying the first part of (28) to the multidimensional problem, with

$$\text{at } t = \omega(\mathbf{x}) \qquad u = \lambda v_n, \qquad \frac{\partial u}{\partial n} = -(u+\lambda)v_n,$$

we obtain

$$\frac{\partial w}{\partial t} = \nabla^2 w - \lambda\left(1 - \nabla.\left(\frac{\nabla\omega}{|\nabla\omega|}\right)\right), \tag{29}$$

$$\text{at } t = \omega(\mathbf{x}) \qquad w = 0, \qquad \frac{\partial w}{\partial n} = -\lambda, \tag{30}$$

the term in ω (which involves the mean curvature of the moving boundary as it passes through a point $\mathbf{x}$) introducing a dependence on the past history that is not present in the one-dimensional case (22). However, in the radially symmetric N-dimensional case with $r = |\mathbf{x}|$, we recover a purely local equation, namely

$$\frac{\partial w}{\partial t} = \frac{1}{r^{N-1}}\frac{\partial}{\partial r}\left(r^{n-1}\frac{\partial w}{\partial r}\right) - \lambda\left(1 - \frac{N-1}{r}\right).$$

For the Cauchy problem, with fluid domain $\Omega(t)$, the conserved quantities (28) generalize to

$$\frac{d}{dt}\int_{\Omega(t)}\left(\mathcal{F}(\mathbf{x})(u(\mathbf{x},t)+\lambda) + \frac{\lambda\nabla\mathcal{F}.\nabla\omega}{|\nabla\omega|}\right)dV = 0$$

for any $\mathcal{F}(\mathbf{x})$ such that

$$\nabla^2\mathcal{F} = 0 \qquad \text{for } \mathbf{x} \in \Omega(t).$$

4. Asymptotic behaviour for small and large times

In this section we assume that $\lambda = O(1)$ and present results for the behaviour of (11) to (14) for small and large time, some of which have been noted by previous authors (see Cohen and Erneux (**50**), Charach and Zaltzman (**34**) and Charach *et al.* (**35**)). We also compare these results with numerical simulations.

For small time, the asymptotic results,

$$s(t) = \frac{t}{\lambda} - \frac{t^2}{2\lambda^2}\left(1 + \frac{1}{\lambda}\right) + O(t^3), \tag{31}$$

$$u(x,t) = 1 - \left(1 + \frac{1}{\lambda}\right)x + O(t^2), \qquad \text{for } x = O(t),\ 0 < x/t < 1/\lambda, \tag{32}$$

are readily deduced, while the large time behaviour is given by

$$s(t) \;=\; 2\alpha\sqrt{t} - 1 + O(1/\sqrt{t}), \tag{33}$$

$$u(x,t) \;=\; 1 - \frac{\operatorname{erf}\left(x/2\sqrt{t}\right)}{\operatorname{erf}(\alpha)} + O\left(1/t\right) \qquad \text{as } t \to \infty, \tag{34}$$

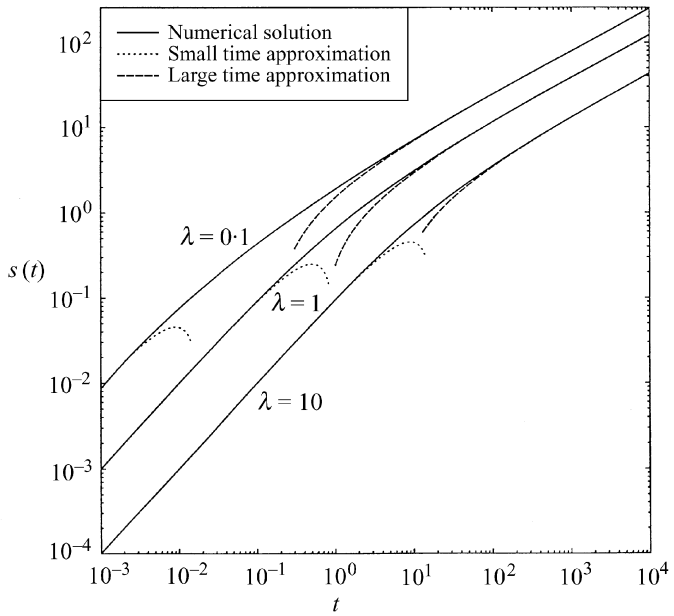

Fig. 1 Illustration of the evolution of the moving boundary $s(t)$ determined by the numerical solution of (11) to (14) for the selected values $\lambda = 0{\cdot}1$, 1 and 10. We show the two term expansions of the small and large time approximations (31) and (33)

where the leading-order behaviour is the well-known Neumann solution to the classical Stefan problem in which $\mu = 0$ in (11) to (14), α being given by the unique positive root of the transcendental equation (see Carslaw and Jaeger (**1**)),

$$\sqrt{\pi}\alpha e^{\alpha^2}\operatorname{erf}(\alpha) = \frac{1}{\lambda}. \tag{35}$$

As an aside, we note that (as with the model of Dewynne *et al.* (**28**)) (11), (12), (14) has an exact solution in the form

$$u = f_1(\eta) + \frac{1}{\sqrt{t}} f_2(\eta), \qquad s(t) = 2\alpha\sqrt{t}, \qquad \eta = x/\sqrt{t}.$$

However, this solution is not applicable to the initial-boundary-value problem that we consider here.

Figure 1 shows the growth of the free boundary $s(t)$ for selected values of λ, where $s(t)$ has been determined by the numerical solution of (11) to (14) using the method of lines given in Fasano *et al.* (**47**). For comparison, the small time two term expansion (31) and the large time two term expansion (33) are also shown for each λ. A feature worth noting is the shortening of the 'intermediate time' behaviour as λ increases, the small and large time approximations together providing good approximations over greater sections of the time range.

The expression (35) for α can be evaluated asymptotically for small and large λ giving

$$\alpha = \frac{1}{\sqrt{2\lambda}} - \frac{1}{6\sqrt{2}\lambda^{3/2}} + O(1/\lambda^{5/2}) \qquad \text{as } \lambda \to \infty, \tag{36}$$

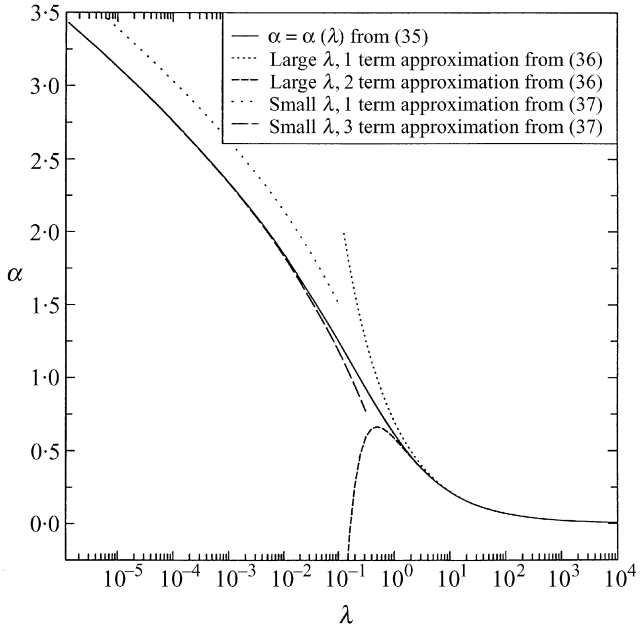

Fig. 2 A plot of α determined from the transcendental equation (35) for varying λ. The approximations (36) and (37) are also shown

and

$$\alpha \sim \ln^{1/2}(1/\lambda)\left(1 - \frac{\ln\ln(1/\lambda)}{4\ln(1/\lambda)} - \frac{\ln(\sqrt{\pi})}{2\ln(1/\lambda)}\right) \qquad \text{as } \lambda \to 0\,. \tag{37}$$

These results will be needed in section 5. Figure 2 shows the dependence of α on λ, determined by (35), together with asymptotic expansions (36) and (37). It is worth remarking that the leading-order behaviour, $\alpha \sim \ln^{1/2}(1/\lambda)$, does not even begin to be a good approximation until $\ln(1/\lambda) = O(10^2)$, whereas the three term expansion (37) shows good agreement up to $\lambda \approx 10^{-2}$. Figure 2 provides an indication that the small and large Stefan number analyses can successfully describe the behaviour over large ranges of λ, and we now consider these limits.

5. The limits of small and large Stefan number

In the limit of large Stefan number ($\lambda \to \infty$), we rescale $t = \lambda\tau$ and expand in inverse powers of λ to give the following expansions, the leading-order problem being quasi-steady:

$$s(\tau) = (2\tau+1)^{1/2} - 1 - \frac{1}{3\lambda}\left(\frac{\tau-1}{(2\tau+1)^{1/2}} + \frac{1}{(2\tau+1)}\right) + O(1/\lambda^2), \tag{38}$$

$$u(x,\tau) = 1 - \frac{x}{(2\tau+1)^{1/2}} - \frac{x}{6\lambda}\left(\frac{2}{(2\tau+1)^{1/2}} - \frac{x^2}{(2\tau+1)^{3/2}} + \frac{4}{(2\tau+1)^2}\right) + O(1/\lambda^2)\,. \tag{39}$$

The leading-order terms have previously been obtained by Grinberg and Chekmareva (**62**) as well as Deal and Grove (**63**) in the context of silicon oxidation and Cohen and Erneux (**50**) for solvent

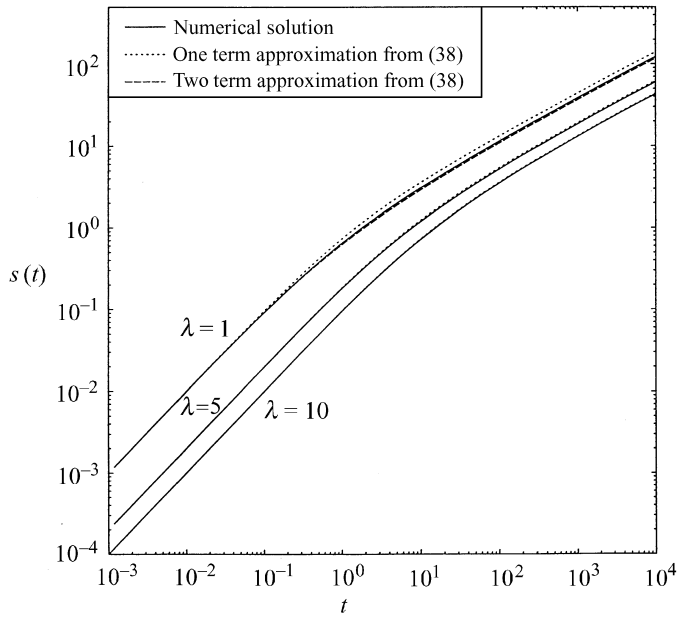

Fig. 3 Illustration of the large λ one and two term asymptotics from (38) for the values $\lambda = 1, 5, 10$

penetration in polymers. Figure 3 illustrates the one and two term expansion for the moving boundary position from (38) for selected values of λ and is compared to the full numerical solution, showing good agreement even down to $\lambda = 1$. We note that this limit is of practical relevance for both silicon oxidation and polymer sorption.

The limit of small Stefan number ($\lambda \to 0$), seems to have received little attention but exhibits more interesting behaviour. There are two relevant timescales in this limit, namely $t = O(\lambda^2)$ and $t = O(\ln(1/\lambda))$, the former being suggested by the breakdown of the expansion (31) with the latter being implicit in the large time result (33) and the expansion (37).

Introducing the scalings

$$t = \lambda^2 \hat{t}, \qquad x = \lambda \hat{x}, \qquad s = \lambda \hat{s},$$

and posing

$$u \sim \hat{u}_0(\hat{x}, \hat{t}), \qquad \hat{s} \sim \hat{s}_0(\hat{t}) \qquad \text{as } \lambda \to 0,$$

at leading order we obtain the 'zero Stefan number' problem:

$$\text{in } 0 < \hat{x} < \hat{s}_0(\hat{t}) \qquad \frac{\partial \hat{u}_0}{\partial \hat{t}} = \frac{\partial^2 \hat{u}_0}{\partial \hat{x}^2}, \tag{40}$$

$$\text{on } \hat{x} = 0 \qquad \hat{u}_0 = 1, \tag{41}$$

$$\text{on } \hat{x} = \hat{s}_0(\hat{t}) \qquad \hat{u}_0 = \hat{s}_0', \qquad \frac{\partial \hat{u}_0}{\partial \hat{x}} = -\hat{u}_0 \hat{s}_0', \tag{42}$$

$$\text{at } \hat{t} = 0 \qquad \hat{s}_0 = 0, \tag{43}$$

where $'$ denotes $d/d\hat{t}$. It should be emphasized that the incorporation of kinetic undercooling leads

to a moving boundary being present even in the zero Stefan number problem. The analogous transformation to (16), namely

$$\hat{v}(\hat{x},\hat{t}) = -\int_{\hat{x}}^{\hat{s}_0} \hat{u}_0(\xi,\hat{t})d\xi,$$

gives

$$\text{in } 0 < \hat{x} < \hat{s}_0(\hat{t}),\ \hat{t} > 0 \qquad \frac{\partial \hat{v}}{\partial \hat{t}} = \frac{\partial^2 \hat{v}}{\partial \hat{x}^2}\ ; \tag{44}$$

$$\text{on } \hat{x} = 0 \qquad \frac{\partial \hat{v}}{\partial \hat{x}} = 1\ ; \tag{45}$$

$$\text{on } \hat{x} = \hat{s}_0(\hat{t}) \qquad \hat{v} = 0, \quad \frac{\partial \hat{v}}{\partial \hat{x}} = \hat{s}_0', \tag{46}$$

$$\text{at } \hat{t} = 0 \qquad \hat{s}_0 = 0, \tag{47}$$

which is the classical Stefan problem with a Neumann condition on the fixed boundary; integrating again leads to a formulation equivalent to (22) to (25), except that the λ term is absent from (22). This correspondence between the zero latent heat Stefan problem with kinetic undercooling and the classical Stefan problem does not appear to generalize to higher dimensions, so the former does in fact represent a novel moving boundary problem.

The system (40) to (43) cannot be solved analytically, but we have as $\hat{t} \to 0$

$$\hat{s}_0(\hat{t}) \quad = \quad \hat{t} - \frac{\hat{t}^2}{2} + O(\hat{t}^3), \tag{48}$$

$$u_0(x,\hat{t}) \quad = \quad 1 - \hat{x} + O(\hat{t}^2) \qquad \text{for } \hat{x} = O(\hat{t}),\ \ 0 < \hat{x}/\hat{t} < 1, \tag{49}$$

and as $\hat{t} \to +\infty$ we have a singular perturbation problem with two regions, whereby

$$\hat{u}_0 \sim \operatorname{erfc}\left(\hat{x}/2\hat{t}^{1/2}\right) \qquad \text{for } \hat{x} = O(\hat{t}^{1/2}), \tag{50}$$

and

$$\hat{u}_0 \sim \hat{s}_0' \exp\left(-\hat{s}_0'\hat{z}\right) \qquad \text{for } \hat{z} = O(1/\hat{s}_0'), \tag{51}$$

where $\hat{z} = \hat{x} - \hat{s}_0(\hat{t})$. Matching these two expressions yields

$$\hat{s}_0 \sim \sqrt{2\hat{t}\ln\hat{t}}\left(1 - \frac{\ln\ln\hat{t}}{\ln\hat{t}} + \frac{\ln(2/\sqrt{\pi})}{\ln\hat{t}}\right) \qquad \text{as } \hat{t} \to +\infty, \tag{52}$$

a result which is of interest in its own right, giving the large time behaviour of the zero Stefan number version of the problem. For the second timescale, $t = O(\ln(1/\lambda))$, we introduce the scalings

$$t = \ln(1/\lambda)\,\bar{t}, \qquad x = \ln^{1/2}(1/\lambda)\,\bar{x}, \qquad s = \ln(1/\lambda)\,\bar{s},$$

and obtain the boundary-layer solution (cf. (50))

$$u \sim \operatorname{erfc}\left(\bar{x}/2\bar{t}^{1/2}\right) \qquad \text{for } \bar{x} = O(1)\ . \tag{53}$$

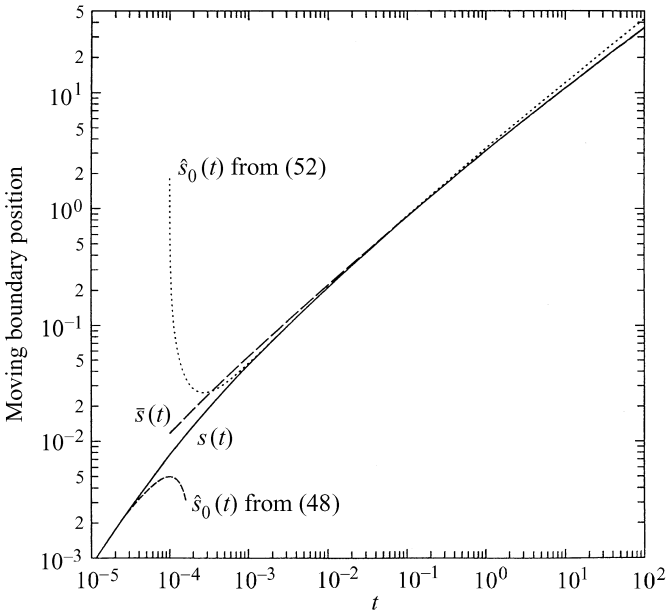

Fig. 4 An illustration of the asymptotic results obtained for small λ. Shown for the case $\lambda = 0{\cdot}01$ are the numerical solution for the moving boundary position, the asymptotic approximation (52) together with the approximation (54). Also shown is the two term small time expansion (48)

The interior layer (cf. (51)) has the scalings

$$x = \ln(1/\lambda)\,\bar{s}(\bar{t};\lambda) + \bar{z}, \qquad u \sim \lambda\,\bar{u}_0(\bar{z},\bar{t})$$

and, after imposing the moving boundary conditions, we obtain

$$\bar{u}_0 = \left(\bar{s}_0' + 1\right)\exp\left(-\bar{s}_0'\bar{z}\right) - 1,$$

with $'$ now denoting $d/d\bar{t}$. Matching with (53) then yields

$$\bar{s} \sim 2\bar{t}^{1/2}\left(1 - \frac{\ln\ln(1/\lambda)}{4\ln(1/\lambda)} - \frac{\ln(\sqrt{\pi}(\bar{t}^{-1/2}+1))}{2\ln(1/\lambda)}\right), \tag{54}$$

with $\bar{s}_0 = 2\bar{t}^{1/2}$, which matches with (52) as $\bar{t} \to 0^+$ and reproduces the required large time behaviour (see (33) and (37)).

To illustrate the emergence of these two timescales for small λ, the asymptotic approximations (48), (52) and (54) are shown for $\lambda = 0{\cdot}01$, together with the numerical solution for $s(t)$, in Fig. 4, the agreement being good in the relevant regimes.

6. Mask edge problems

6.1 *Formulation*

This section is concerned with possibly the simplest class of genuinely two-dimensional problem, whereby the moving boundary encroaches under a mask edge, and thus illustrates multi-dimensional

behaviour. The results given here generalize those of King (**53**, **54**) (which involve the large Stefan number limit $\lambda \to \infty$, albeit with additional effects from volume creation during the surface reaction which we do not consider here) and Wallman *et al.* (**64**) (which concerns the corresponding Stefan problems without kinetic undercooling). The problem we study is

$$\left.\begin{array}{ll} \text{in } 0 < y < f(x,t), -\infty < x < +\infty & \dfrac{\partial u}{\partial t} = \dfrac{\partial^2 u}{\partial x^2} + \dfrac{\partial^2 u}{\partial y^2}, \\ \text{on } y = 0,\ x < 0 & u = 1, \\ \text{on } y = 0,\ x > 0 & \dfrac{\partial u}{\partial y} = 0, \\ \text{on } y = f(x,t) & \dfrac{\partial u}{\partial n} + v_n u = -u = -\lambda v_n, \end{array}\right\} \tag{55}$$

where

$$v_n = \frac{\partial f}{\partial t} \Big/ \left(1 + \left(\frac{\partial f}{\partial x}\right)^2\right)^{1/2}, \qquad \frac{\partial u}{\partial n} = \left(\frac{\partial u}{\partial y} - \frac{\partial f}{\partial x}\frac{\partial u}{\partial x}\right) \Big/ \left(1 + \left(\frac{\partial f}{\partial x}\right)^2\right)^{1/2}.$$

The surface $y = 0$ is covered by an insulating mask for $x > 0$, while the surface temperature is held fixed for $x < 0$. As described in Appendix A, this problem is not in general uniquely specified. However, there are two solutions that are of most interest when the initial data takes the form $f(x, 0) = 0$. We start by deriving the small time behaviour of the solution which arises on taking the limit $\epsilon \to 0+$ when there is a uniform initial layer $f(x, 0) = \epsilon^2$, with $0 < \epsilon \ll 1$ and $u(x, y, 0) = 0$. This layer provides a 'crack' along which diffusion can take place and the moving boundary initially propagates extremely rapidly under the mask ($y = 0, x > 0$). We then discuss the small time behaviour when there is no such crack.

6.2 *'Reaction-controlled' behaviour*

Our analysis here is a direct generalization of that of King (**53**, **54**). We write

$$x = \epsilon^2 \hat{x}, \qquad y = \epsilon^2 \hat{y}, \qquad f = \epsilon^2 \hat{f}, \qquad t = \epsilon^2 \hat{t},$$

and for $\hat{x} = O(1), \hat{t} = O(1)$ we have

$$u \sim 1, \qquad \hat{f} \sim \hat{f}_0(\hat{x}, \hat{t})$$

with

$$\frac{\partial \hat{f}_0}{\partial \hat{t}} = \frac{1}{\lambda}\left(1 + \left(\frac{\partial \hat{f}_0}{\partial \hat{x}}\right)^2\right)^{1/2}, \tag{56}$$

$$\text{at } \hat{t} = 0 \qquad \hat{f}_0 = 1,$$

so that

$$\hat{f}_0 = 1 + \frac{\hat{t}}{\lambda}. \tag{57}$$

The more important region is that beneath the mask, with $\hat{X} \equiv \epsilon\hat{x} = O(1)$, $\hat{X} > 0$, in which

$$u \sim u_0(\hat{X}, \hat{t}), \qquad \frac{\partial u}{\partial \hat{y}} \sim \epsilon^2 \left(\frac{\partial u_0}{\partial \hat{t}} - \frac{\partial^2 u_0}{\partial \hat{X}^2} \right) \hat{y}$$

and, writing $\hat{f} \sim F_0(\hat{X}, \hat{t})$, the moving boundary conditions yield

$$\lambda \frac{\partial F_0}{\partial \hat{t}} = \frac{\partial}{\partial \hat{X}} \left(F_0 \frac{\partial u_0}{\partial \hat{X}} \right) - \frac{\partial}{\partial \hat{t}} \left(F_0 u_0 \right), \qquad \lambda \frac{\partial F_0}{\partial \hat{t}} = u_0, \tag{58}$$

so that matching with (57) to give the required condition at $X = 0$ yields the novel nonlinear evolution equation (which is placed in a slightly broader context in Appendix B)

$$\frac{\partial}{\partial \hat{t}} \left(F_0 \left(1 + \frac{\partial F_0}{\partial \hat{t}} \right) \right) = \frac{\partial}{\partial \hat{X}} \left(F_0 \frac{\partial^2 F_0}{\partial \hat{X} \partial \hat{t}} \right), \tag{59}$$

subject to

$$\left.\begin{array}{ll} \text{at } \hat{t} = 0 & F_0 = 1, \quad \dfrac{\partial F_0}{\partial \hat{t}} = 0, \\ \text{on } \hat{X} = 0 & F_0 = 1 + \dfrac{\hat{t}}{\lambda}, \\ \text{as } \hat{X} \to +\infty & F_0 \to 1. \end{array}\right\} \tag{60}$$

The behaviour of (59), (60) as $\hat{t} \to +\infty$ is given at leading order for $\hat{X} = O(\hat{t}^{1/2})$ by the (compactly supported) similarity solution

$$F_0 = \hat{t} g(\hat{X}/\hat{t}^{1/2});$$

moreover, when $\epsilon = 0$ one of the possible solutions to (55) (the zero contact angle solution described in Appendix A) has the small time behaviour,

$$f \sim t\, g(x/t^{1/2}) \qquad \text{as } t \to 0+. \tag{61}$$

In both cases, $g(\eta)$ is given by the free boundary problem,

$$\left.\begin{array}{ll} & g\left(1 + g - \dfrac{\eta}{2} g'\right) - \frac{1}{2}\eta \left(g \left(1 + g - \dfrac{\eta}{2} g' \right) \right)' = \frac{1}{2} \left(g \left(g' - \eta g'' \right) \right)', \\ \text{on } \eta = 0 & g = 1/\lambda, \\ \text{at } \eta = \eta_0 & g = g' = 0, \quad g'' = 1, \end{array}\right\} \tag{62}$$

where $'$ denotes $d/d\eta$ and η_0 must be determined as part of the solution. It is straightforward to solve (62) numerically, for example, by transforming to a fixed domain using the scalings

$$\eta = \eta_0(1 - \xi), \qquad g = \eta_0^2 h,$$

the problem for $h = h(\xi)$ then being solved as an initial-value problem with $h(0) = h'(0) = 0, h''(0) = 1$ ($'$ now being $d/d\xi$) with η_0 being prescribed and the condition $h(1) = 1/\lambda\eta_0^2$ being used to determine λ for that value of η_0. This is more straightforward than the alternative method of

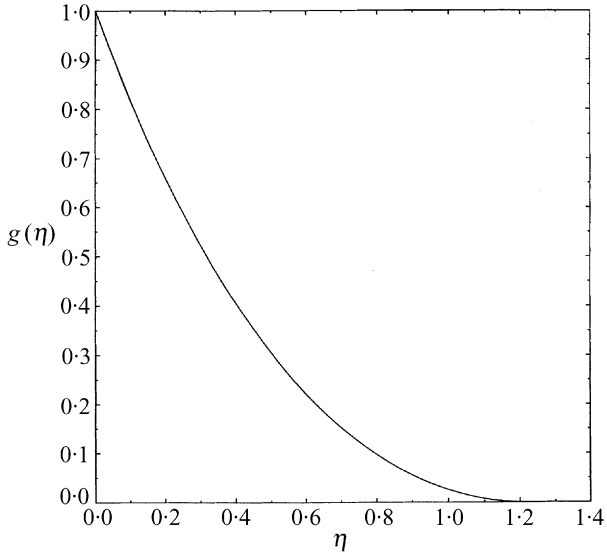

Fig. 5 The solution $g(\eta)$ to (62) in the case $\lambda = 1$; we obtain numerically that $\eta_0 \approx 1{\cdot}2217$

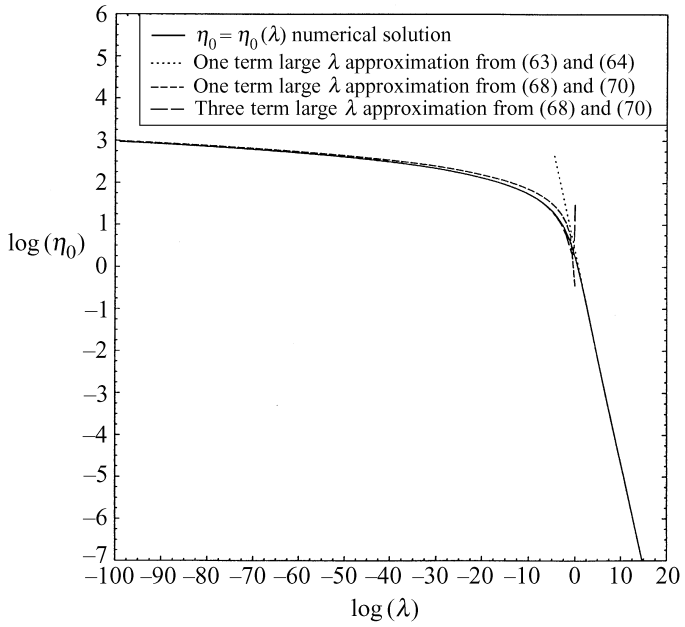

Fig. 6 A numerical plot of the position of the free boundary η_0 in (62) with the Stefan number λ. Also shown for comparison are the leading-order large λ approximation $\eta_0 = (2/\lambda)^{1/2}$ and the three term small λ approximation from (68) and (70) using $A_0 = 6{\cdot}6$

prescribing λ and then solving a boundary-value problem in order to determine η_0. Figure 5 shows $g(\eta)$ in the case $\lambda = 1$ (with η_0 determined iteratively) and Fig. 6 shows dependence of η_0 on λ.

As $\lambda \to \infty$, the scalings

$$g = \frac{\hat{g}}{\lambda}, \qquad \eta = \frac{\hat{\eta}}{\lambda^{1/2}}, \qquad \eta_0 = \frac{\hat{\eta}_0}{\lambda^{1/2}} \tag{63}$$

reproduce the solution of King (**53**, **54**),

$$\hat{g} \sim \tfrac{1}{2}\left(\sqrt{2} - \hat{\eta}\right)^2 \quad \text{for } \hat{\eta} < \sqrt{2}, \qquad \hat{\eta}_0 \sim \sqrt{2} \qquad \text{as } \lambda \to \infty. \tag{64}$$

The leading-order behaviour, $\eta_0 \sim (2/\lambda)^{1/2}$, is shown in Fig. 6 for comparison with the full numerical solution.

For $\lambda \to 0$ the rescaling $g = \hat{g}/\lambda$ holds in the outer region $\eta = O(1)$, in which $\hat{g} \sim \hat{g}_0(\eta)$ with $\hat{g}_0$ (the 'zero Stefan number' solution) satisfying

$$\left.\begin{array}{ll} & \hat{g}_0\left(\hat{g}_0 - \frac{1}{2}\eta\hat{g}_0'\right) - \frac{1}{2}\eta\left(\hat{g}_0\left(\hat{g}_0 - \frac{1}{2}\eta\hat{g}_0'\right)\right)' = \frac{1}{2}\left(\hat{g}_0\left(\hat{g}_0' - \eta\hat{g}_0''\right)\right)', \\ \text{on } \eta = 0 & \hat{g}_0 = 1, \\ \text{as } \eta \to +\infty & \hat{g}_0 \to 0, \end{array}\right\} \tag{65}$$

that is, $\hat{g}_0$ is not compactly supported. The far-field behaviour of (65) can be shown by the WKBJ method to be

$$\hat{g}_0 \sim A_0 \eta^{-7/2} e^{-\eta^2/4} \qquad \text{as } \eta \to +\infty \tag{66}$$

for some constant A_0 which must be determined as part of the solution, a numerical estimate being $A_0 \approx 6{\cdot}6$. The scalings in an interior layer at the moving boundary are then

$$\eta = \ln^{1/2}(1/\lambda) S(\lambda) + \frac{z}{\ln^{1/2}(1/\lambda)}, \qquad g \sim \frac{G_0}{\ln(1/\lambda)} \tag{67}$$

where, taking

$$S(\lambda) = 2\left(1 - \frac{3}{8}\frac{\ln\ln(1/\lambda)}{\ln(1/\lambda)} + \frac{2\ln A_0 - 7\ln 2}{4\ln(1/\lambda)}\right), \tag{68}$$

gives from (66) the matching condition

$$G_0 \sim e^{-z} \qquad \text{as } z \to -\infty. \tag{69}$$

From (67) it follows that $G_0(z)$ satisfies

$$\frac{d}{dz}\left(G_0\left(1 - \frac{dG_0}{dz}\right)\right) = \frac{d}{dz}\left(G_0 \frac{d^2 G_0}{dz^2}\right),$$

which represents a travelling wave balance in (59), so that (69) and the moving boundary conditions yield

$$G_0 = e^{-z} - 1 + z \ \text{ for } z < 0, \qquad \eta_0 \sim S(\lambda)\ln^{1/2}(1/\lambda). \tag{70}$$

For the purposes of comparison with the numerical solution, the one and three term expansions for η_0 given by (70) and (68) are also shown in Fig. 6, using the value $A_0 = 6{\cdot}6$.

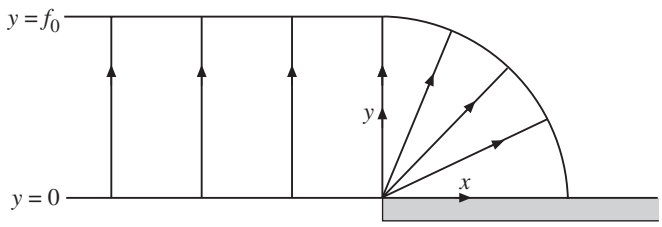

Fig. 7 A schematic illustration of the moving boundary $y = f_0(x, t)$ together with the characteristic projections of equation (71)

6.3 *Small time behaviour—no initial 'crack'*

The other type of solution of most relevance here arises when no diffusion is possible along the interface $y = 0, x > 0$ and the moving boundary meets the mask at angle $\pi/2$ (see Appendix A for further discussion of such matters and a generalization of the solution below). In this case the small time behaviour is of the form

$$u \sim 1, \qquad f \sim t\Phi(x/t),$$

where $f_0 = t\Phi(x/t)$ satisfies (cf. (56))

$$\frac{\partial f_0}{\partial t} = \frac{1}{\lambda}\left(1 + \left(\frac{\partial f_0}{\partial x}\right)^2\right)^{1/2}, \tag{71}$$

$$\text{at } t = 0 \qquad f_0 = 0, \tag{72}$$

and we now obtain (using for example, that $\Phi(\eta)$ satisfies a Clairaut equation),

$$\Phi(\eta) = \begin{cases} \dfrac{1}{\lambda} & \text{if } \eta < 0, \\ \dfrac{1}{\lambda}\left(1 - \lambda^2\eta^2\right)_+^{1/2} & \text{if } \eta > 0. \end{cases}$$

The moving boundary, together with the characteristic projections of (71), are indicated in Fig. 7.

6.4 *Other limits*

For large time and provided $\lambda > 0$ then, whatever the behaviour at the contact point, we recover the similarity solution discussed in Wallman *et al.* (**64**)

$$u \sim C(x/t^{1/2}, y/t^{1/2}) \qquad \text{as } t \to +\infty,$$

where $C = 0$ holds on the moving boundary (that is, the kinetic undercooling term is negligible for large time). That this applies in all cases relates to the uniqueness of the mask edge problem in the absence of kinetic undercooling. For large Stefan number, $\lambda \to \infty$, the rescalings $t = \lambda\hat{t}$, $v_n = \hat{v}_n/\lambda$ produce at leading order a quasi-steady problem of Hele-Shaw type (cf. King (**53**)). Finally, for $\lambda \to 0$, the main timescale $t = O(\ln(1/\lambda))$ (cf. section 5) reproduces the characteristic picture of Fig. 7, but for different reasons; the analysis closely follows that of the zero kinetic undercooling case (Wallman *et al.* (**64**)) and details are omitted here. It is thus noteworthy that,

when λ is small, the small time behaviour and later evolution of the moving boundary are of the same type (that is, as indicated both by Fig. 7 and by Wallman *et al.* (**64**, Fig. 2), though over the timescale $t = O(\lambda^2)$ (cf. the analysis of the one-dimensional case in section 5) it temporarily departs from this behaviour, being described to leading order by the zero Stefan number solution. The zero Stefan number case has large time (as well as small time) behaviour of the type shown in Fig. 7, but with the interface moving as $t^{1/2} \ln^{1/2} t$ rather than as $t^{1/2}$ (cf. section 5).

7. Discussion

There are certain generalizations of the problem (11) to (14) which are worth briefly remarking upon. The first is that the Dirichlet condition on the fixed boundary may be replaced by the more general mixed boundary condition

$$\text{on} \quad x = 0 \qquad \frac{\partial u}{\partial x} = H\,(u - 1) \tag{73}$$

for constant H, this being of particular relevance in silicon oxidation. In this case, the transformation (16) then yields the system (17) to (20) with, in place of (19), the following non-standard condition, which is sometimes described as being of fourth type, on the fixed boundary:

$$\text{on} \quad x = 0 \qquad H\frac{\partial v}{\partial x} = \frac{\partial v}{\partial t} + H(1 + \lambda), \tag{74}$$

for which Ughi (**65**) has shown solution existence and uniqueness. Another generalization involves the replacement of the condition (13) on the moving boundary by the more general statement (15), this being particularly relevant in the glassy polymer application. In this case, the transformation (16) reduces (11) to (14) with (15) to the Stefan-like problem (17) to (20) with the second condition in (18) replaced by the nonlinear free boundary condition

$$\dot{s} = \psi\left(\frac{\partial v}{\partial x}(s(t), t), t\right). \tag{75}$$

Well-posedness and regularity of the solution for this more general system are analysed in Fasano *et al.* (**47**).

In this paper we have analysed what is in some respects a relatively minor generalization of the classical Stefan problem, but one which can exhibit significantly different behaviour; in particular, we note the possibilities of non-analytic moving boundaries (notably propagating corners and discontinuities in curvature, as indicated by Fig. 9; such solutions tend to become smoother as time increases) and of non-uniqueness (cf. Appendix A). We have emphasized (9) as the correct formulation of the moving boundary condition; the condition (10) leads to very different behaviour in many of the limits we have described and as noted earlier, particularly in terms of the occurrence (or otherwise) of travelling waves as possible descriptions of the large time behaviour.

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APPENDIX A

Non-uniqueness in the mask edge problem

In section 6 we have outlined the behaviour of two distinct solutions to the mask edge problem (55). The solution of section 6.2 can be regarded as the zero contact angle solution and that of section 6.3 as having contact angle $\pi/2$. Our purpose here is to show that these are in fact the extremes of a family of solutions which is parametrized by the angle at which the moving boundary makes contact with the mask.

Defining the contact point to be $(x, y) = (q(t), 0)$, the dominant local behaviour of (55) close to that point satisfies

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = 0,$$

$$\text{on } y = 0,\ x < q(t) \qquad \frac{\partial u}{\partial y} = 0,$$

$$\text{on } y = f(x,t) \qquad \frac{\partial u}{\partial n} = 0, \qquad \frac{\partial f}{\partial t} = \frac{u}{\lambda}\left(1 + \left(\frac{\partial f}{\partial x}\right)^2\right)^{1/2},$$

so that

$$u(x, y, t) \sim u_q(t), \qquad \frac{\partial f}{\partial t} \sim \frac{u_q(t)}{\lambda}\left(1 + \left(\frac{\partial f}{\partial x}\right)^2\right)^{1/2}, \tag{A1}$$

where $u_q(t) = u(q(t), 0, t)$. The time-dependent eikonal equation (A1), which gives the local behaviour, implies that it is possible to impose a contact angle ϕ, whereby

$$\text{at } y = 0,\ x = q(t) \qquad \frac{\partial f}{\partial x} = -\tan\phi,$$

for $0 \leqslant \phi \leqslant \pi/2$; an angle $\phi > \pi/2$ cannot be imposed since the characteristics are required to propagate away from the fixed boundary $y = 0$. The situation is best clarified by a schematic of the small time behaviour for fixed angle $\phi \in (0, \pi/2)$, as given in Fig. 8; this should be compared with Fig. 7. The behaviour for small ϕ can be analysed by studying solutions to (59) with non-zero contact angle. The contact angle ϕ is permitted to be time-dependent and could be specified in a variety of ways, for example by prescribing it as a function of $\dot{q}(t)$; some such prescription (with $0 \leqslant \phi \leqslant \pi/2$; see (ii) below, however) is required in order for the problem to be completely specified. It follows from (A1) that the relationship $u_q = \lambda \dot{q} \sin\phi$ holds between $\phi, \dot{q}$ and u_q. For the initial data $f(x, 0) = 0$ and prescribed $\phi \in (0, \pi/2)$, the small time solution of section 6.3 generalizes to

$$\Phi(\eta) = \begin{cases} \dfrac{1}{\lambda} & \text{if } \eta < 0, \\ \dfrac{1}{\lambda}\left(1 - \lambda^2\eta^2\right)^{1/2} & \text{if } 0 < \eta < \frac{1}{\lambda}\sin\phi, \\ \dfrac{1}{\lambda}\sec\phi\,(1 - \lambda\sin\phi\,\eta)_+ & \text{if } \eta > \frac{1}{\lambda}\sin\phi, \end{cases}$$

with $q(t) \sim t/\lambda \sin\phi$ as $t \to 0$.

Further to the comments above, the two extreme cases of the family of solutions can be characterized as follows.

(i) *Zero contact angle*, $\phi = 0$. We have $u_q = 0$ and for positive Stefan number the local behaviour can be deduced from (59) as

$$f \sim \tfrac{1}{2}(q - x)^2, \qquad u \sim \lambda\dot{q}(q - x) \qquad \text{as } x \to q^-.$$

The equivalent zero Stefan number problem has unbounded q (cf. (66)).

(ii) *No characteristics propagate away from the mask* $y = 0, x > 0$ (implying that the contact angle is

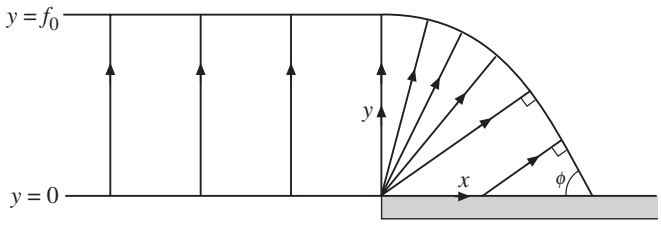

Fig. 8 Schematic of the moving boundary and characteristic projections for small time when $f(x, 0) = 0$ and $0 < \phi < \pi/2$

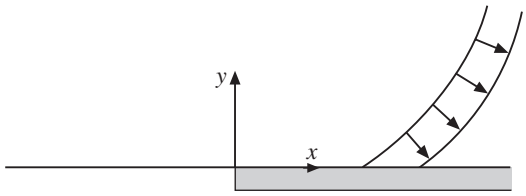

Fig. 9 Schematic of a configuration with contact angle greater than $\pi/2$, showing characteristic projections and moving boundary positions

greater than or equal to $\pi/2$). Figure 7 is of this type (while Fig. 8 is not) but, for suitable initial conditions, configurations in which the contact angle is greater than $\pi/2$ are also possible; the contact angle cannot then be prescribed, however, but is determined as part of the solution. This is implicit in the direction of the characteristics of (A1); see the schematic in Fig. 9.

The above analysis has the important implication that many multi-dimensional Stefan problems with kinetic undercooling are not uniquely specified unless the contact angle is prescribed; the corresponding problems without kinetic undercooling have a unique solution which typically provides the large time outer solution to the finite kinetic undercooling case, whatever the contact angle (as already noted, this applies in particular to (55)). The analysis of section 6.2 shows how the (uniquely specified) zero contact angle solution is selected by taking the limit $\epsilon \to 0$; by contrast, in cases in which

$$\text{on } y = 0,\ x > 0 \qquad\qquad \frac{\partial u}{\partial y} = 0$$

represents a symmetry condition, rather than a physical boundary, the scenario outlined above in (ii) applies (when the initial conditions imply a configuration such as that in Fig. 9, the moving boundary will then contain a corner). The extreme cases (i) and (ii) are therefore those which are expected to arise most frequently in applications. We note that such issues of non-uniqueness remain applicable in the Hele-Shaw limit ($\lambda \to \infty$).

APPENDIX B

An evolution equation for 'slender' Stefan problems

In Evans *et al.* (**66**, Appendix), the evolution equation

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial x}\left(f\frac{\partial p}{\partial x}\right), \tag{B1}$$

where p is the pressure, was noted as the analogue for Hele-Shaw and porous media (Darcy) flows of Reynolds equation from lubrication theory. Here we briefly consider its generalization to Stefan problems, which can be

read off from (58) as (after a rescaling)

$$\frac{\partial}{\partial t}\left(f\left(1+\frac{u}{\lambda}\right)\right)=\frac{\partial}{\partial x}\left(f\frac{\partial u}{\partial x}\right), \tag{B2}$$

from which we recover (B1) in the limit $\lambda \to \infty$, as is to be expected. We note the following points about (B2).

(i) Travelling wave solutions, $f = f(x - qt)$, $u = u(x - qt)$, satisfy

$$A - qf(1 + u/\lambda) = f\frac{du}{dz}$$

for constants q and A. When $A = 0$ we simply have

$$u = -1 + Be^{-qz/\lambda}$$

for constant B, whatever the relationship between u and f.

(ii) To obtain a closed system, u must be specified as a function of f and to achieve this the temperature boundary condition on the moving boundary must be specified (the derivation of equation (B2) involves (9) but not (6)). Incorporating surface energy (parameter ν_1) and kinetic undercooling (parameter ν_2) implies

$$u = -\nu_1\frac{\partial^2 f}{\partial x^2}+\nu_2\frac{\partial f}{\partial t}$$

so that

$$\frac{\partial}{\partial t}\left(f\left(1-\frac{\nu_1}{\lambda}\frac{\partial^2 f}{\partial x^2}+\frac{\nu_2}{\lambda}\frac{\partial f}{\partial t}\right)\right)=\frac{\partial}{\partial x}\left(f\left(-\nu_1\frac{\partial^3 f}{\partial x^3}+\nu_2\frac{\partial^2 f}{\partial x\partial t}\right)\right). \tag{B3}$$

Somewhat remarkably, equation (B3) admits the important similarity reductions, $f = (\pm t)\, g(x/(\pm t)^{1/2})$, (cf. (61)). Such formulations are relevant to, for instance, the 'necking-off' of a region of a given phase.

(iii) In the zero Stefan number limit $\lambda \to 0$ equation (B3), with appropriate rescalings, takes the bilinear form

$$\frac{\partial}{\partial t}\left(f\left(\frac{\partial f}{\partial t}-\mu\frac{\partial^2 f}{\partial x^2}\right)\right)=\frac{\partial}{\partial x}\left(f\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial t}-\mu\frac{\partial^2 f}{\partial x^2}\right)\right)$$

for some constant μ.