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A similarity solution of a multiphase Stefan problem incorporating general non-linear heat conduction

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Abstract—A non-linear diffusion model of Fujita is adapted to obtain an analytic solution describing the temperature distribution and position of any number of phase boundaries as a material cools on an effectively semi-infinite base material. Each material is initially homogeneous and at a uniform temperature. The solution method may incorporate any materials with temperature-dependent thermal properties undergoing any number of phase changes. As an example, we incorporate transitions through five phases of iron with non-linear heat conduction, as the iron cools on a copper base.

1. INTRODUCTION

THERE is considerable interest in diffusion processes involving the movement of phase boundaries within materials. These processes occur in many areas of science and engineering such as the solidification of castings, melting or freezing of food products, thawing of permafrost, tarnishing of metal surfaces and the dissolution of bubbles or solid particles. Despite the multitude of investigations on such processes, relatively few explicit analytic models exist and many of their solutions assume that the heat or concentration diffusivity is constant within any phases present.

Fujita [1] derived linearization procedures for a class of one-dimensional non-linear diffusion equations with diffusivities of form:

$$\alpha(\beta-\Theta)^{-2}, \qquad (1)$$

where α (>0), β are constants and Θ is concentration. This class of equations and related adaptations have received detailed analysis [1–6] and have been applied to many diffusion processes, some of which were previously modelled using constant diffusivities [1 15]. In particular, an adaptation of (1) was applied to a class of single phase and two-phase Stefan problems by Hill and Hart [9] and Rogers [10, 11]. This paper considers a further class of Stefan free boundary problems.

An adaptation of the diffusivity form (1) is applied to the problem of describing the temperature distribution and position of any number of phase boundaries as a semi-infinite material solidifies on a semi-infinite base material. Both materials may change phase an arbitrary number of times with the number of phase changes in the solidifying material not necessarily being the same as the number in the base material. Each phase may have distinct thermal properties which may vary with temperature as in equation (1). Each phase change occurs isothermally and may be accompanied by the emission or absorption of heat. Each material is initially homogeneous and at a uniform temperature. The density of each material is assumed to be constant.

A closely related problem in linear heat conduction was considered by Weiner [16] in an investigation on the solidification of alloys and by Tien [17] in an investigation into the effect of latent heat release in the solid-state phase changes on the overall rate of the solidification of metals.

In the solution method any material with temperature dependent thermal properties may be incorporated. The thermal diffusivity function is replaced piecewise by segments of the form (1) by introducing, where appropriate, additional phase changes having zero latent heat of transformation.

2. FORMULATION OF THE PROBLEM

Following the notation of Weiner [16], a solidifying material, say material 1, occupying the region $x \geqslant 0$ abuts another material, say material 2, occupying the region $x \leqslant 0$. There is continuity of temperature and continuity of heat flux between the materials. Both materials are originally homogeneous and at uniform temperature, T_m for material 1 and T_{-n} ($<T_m$) for material 2. Each material may exist in a number of phases with each phase having distinct thermal properties which may vary with temperature.

At the commencement of solidification, for a time interval $0 < t < t_f$, the temperature T_0 at $x = 0$ will be within the temperature range for one phase of material 1 and for another phase of material 2. There are then say m phases in material 1 and n phases in material 2 (it is shown later that the temperature T_0 is constant). We denote the phase change temperatures as T_i;

NOMENCLATURE

a_i, b_i	thermal diffusivity parameters defined by equation (17)
$c_i(u_i)$	volumetric heat capacity for phase i
$D_i(u_i)$	thermal diffusivity for phase i
g_i	thermal density function defined by equation (44)
$K_i(u_i)$	thermal conductivity for phase i
L_i	volumetric latent heat of transformation from phase $i+\text{sgn}(i)$ to i
m	number of phases in the solidifying material
n	number of phases in the base material
t	time
T_m	initial temperature of the solidifying material
T_{-n}	initial temperature of the base material
T_i	phase transition temperature from phase $i+1$ to i
T_0	temperature at materials boundary $x=0$
$u_i(x,t)$	temperature distribution for phase i
v_i	arbitrary constant
x	length
$y_i(t)$	position of moving interface between phase $i+1$ and i
y_m	symbol for boundary at infinity
y_{-n}	symbol for boundary at negative infinity
y_0	symbol for boundary at $x = 0$.

Greek symbols

α_i, β_i	heat diffusivity parameters defined by equation (16)
δ_i	coefficient in the interface-position function defined by equation (31)
θ_i	Kirchhoff thermal density defined by equation (21)
Θ	concentration
Λ_i, λ_i	parameters defined by equations (35) and (36), respectively
μ_i	Kirchhoff thermal density distribution defined by equation (14)
τ	time parameter defined by equation (26)
ϕ_i	similarity variable defined by equation (44)
χ_i	Storm variable defined by equation (25).

Subscript

*	non-dimensional quantities.

Superscripts

*	non-dimensional quantities
	scales for non-dimensionalization.

$i = 1,\ldots,m-1$ for material 1 and T_j; $j = -1,\ldots,-n+1$ for material 2. Variables with a positive subscript will pertain to the solidifying material and a negative subscript will pertain to the base material.

Hence, for $0 < t < t_f$ and temperatures $T_{i-1} < u_i < T_i$; $i = 1,\ldots,m$ $[T_j < u_j < T_{j+1}$; $j = -1,\ldots,-n]$, material 1 [2] exists in m [n] phases with thermal conductivity $K_i(u_i)$; $i = -n,\ldots,-1, 1,\ldots,m$ and volumetric heat capacity $c_i(u_i)$; $i = -n,\ldots,-1,1,\ldots,m$.

At each interface $x = y_i(t)$; $i = -n+1,\ldots,-1, 1,\ldots,m-1$ separating phase i from phase $i+\text{sgn}(i)$, there is the Stefan condition:

$$K_i(u_i)\frac{\partial u_i}{\partial x} - K_{i+\text{sgn}(i)}(u_{i+\text{sgn}(i)})\frac{\partial u_{i+\text{sgn}(i)}}{\partial x} = L_i\frac{\mathrm{d}y_i}{\mathrm{d}t}, \quad (2)$$

where $\text{sgn}(z) = |z|z^{-1} = 1$ when $z > 0$ or -1 when $z < 0$, and L_i; $i = -n+1,\ldots,-1,1,\ldots,m-1$ are the volumetric latent heat of phase change from phase $i+\text{sgn}(i)$ to i. We choose L_i to be positive in sign when latent heat is emitted.

The governing equations for the temperature in each phase are:

$$c_i(u_i)\frac{\partial u_i}{\partial t} = \frac{\partial}{\partial x}\left[K_i(u_i)\frac{\partial u_i}{\partial x}\right], \quad |y_{i-\text{sgn}(i)}| < |x| < |y_i|,$$

$$i = -n,\ldots,-1,1,\ldots,m, \quad (3)$$

with continuity of temperature at each phase boundary,

$$u_i(y_{i-\text{sgn}(i)}, t) = T_{i-\text{sgn}(i)}, \quad u_i(y_i, t) = T_i,$$

$$i = -n,\ldots,-1,\ldots,m, \quad (4)$$

and continuity of flux between the materials,

$$K_1(u_1)\frac{\partial u_1}{\partial x} = K_{-1}(u_{-1})\frac{\partial u_{-1}}{\partial x} \quad \text{at } x = 0. \quad (5)$$

The initial conditions are:

$$\lim_{t\to 0} u_m = T_m, \quad x > 0, \quad \lim_{t\to 0} u_{-n} = T_{-n}, x < 0, \quad (6)$$

$$y_i(0) = 0, \quad i = -n+1,\ldots,-1,1,\ldots,m-1. \quad (7)$$

For conciseness, the symbols y_0, y_m and y_{-n} are used for the boundaries at $x = 0$, ∞ and $-\infty$, respectively, and the symbols $f(y_m)$ and $f(y_{-n})$ represent $\lim_{x\to\infty} f(x)$ and $\lim_{x\to-\infty} f(x)$, respectively.

We non-dimensionalize equations (2)–(7) as:

$$c_i^* \frac{\partial u_i^*}{\partial t_*} = \frac{\partial}{\partial x_*}\left[K_i^* \frac{\partial u_i^*}{\partial x_*}\right], |y_{i-\mathrm{sgn}(i)}^*| < |x_*| < |y_i^*|,$$

$$i = -n, \ldots, -1, 1, \ldots, m, \tag{8}$$

$$K_i^* \frac{\partial u_i^*}{\partial x_*} - K_{i+\mathrm{sgn}(i)}^* \frac{\partial u_{i+\mathrm{sgn}(i)}^*}{\partial x_*} = L_i^* \frac{\mathrm{d}y_i^*}{\mathrm{d}t_*} \quad \text{at } x_* = y_i^*$$

$$\text{for } i = -n+1, \ldots, -1, 1, \ldots, m-1, \tag{9}$$

$$u_i^*(y_{i-\mathrm{sgn}(i)}^*, t_*) = T_{i-\mathrm{sgn}(i)}^*, \quad u_i^*(y_i^*, t_*) = T_i^*,$$

$$i = -n, \ldots, -1, 1, \ldots, m, \tag{10}$$

$$K_1^* \frac{\partial u_1^*}{\partial x_*} = K_{-1}^* \frac{\partial u_{-1}^*}{\partial x_*} \quad \text{at } x_* = 0, \tag{11}$$

and initial conditions:

$$\lim_{t_* \to 0} u_m^* = 1, x_* > 0, \quad \lim_{t_* \to 0} u_{-n}^* = 0, x_* < 0, \tag{12}$$

$$y_i^*(0) = 0, \quad i = -n+1, \ldots, -1, 1, \ldots, m-1, \tag{13}$$

where $u_i^* = (u_i - T_{-n})/(T_m - T_{-n})$; $i = -n, \ldots, -1, 1, \ldots, m$ are scaled temperatures, $K_i^*(u_i^*) = K_i(u_i)/\bar{K}_0$; $i = -n, \ldots, -1, 1, \ldots, m$ are scaled thermal conductivities, $c_i^*(u_i^*) = c_i(u_i)/\bar{c}_0$; $i = -n, \ldots, -1, 1, \ldots, m$ are scaled volumetric heat capacities, $x_* = x[\bar{c}_0/(\bar{K}_0 t_s)]^{1/2}$ is scaled length, $t_* = t/t_s$ is scaled time, $y_i^*(t_*) = y_i(t)[\bar{c}_0/(\bar{K}_0 t_s)]^{1/2}$; $i = -n+1, \ldots, -1, 1, \ldots, m-1$ are scaled positions of the interfaces between phases, $L_i^* = \hat{L}_i^* \bar{L}_0/(\bar{c}_0(T_m - T_{-n}))$, $\hat{L}_i^* = L_i/\bar{L}_0$; $i = -n+1, \ldots, -1, 1, \ldots, m-1$ are scaled volumetric latent heats and $T_i^* = (T_i - T_{-n})/(T_m - T_{-n})$; $i = -n, \ldots, -1, 1, \ldots, m$ are scaled temperatures at boundaries and interfaces. $\bar{K}_0$, $\bar{c}_0$, $\bar{L}_0$ and t_s are scales for the thermal conductivity, volumetric heat capacity, volumetric latent heat and time, respectively.

Following the notation of Broadbridge, Tritscher and Avagliano [18], consider a transformation by Kirchhoff [19]:

$$\mu_i = \int_{v_i}^{u_i^*} K_i^*(\bar{u})\,\mathrm{d}\bar{u} = \int_{\omega_i}^{\Theta_i} D_i(\bar{\Theta})\,\mathrm{d}\bar{\Theta},$$

$$i = -n, \ldots, -1, 1, \ldots, m, \tag{14}$$

where $\Theta_i = \int_0^{u_i^*} c_i^*(\bar{u})\,\mathrm{d}\bar{u}$ is the heat density and $D_i = K_i^*/c_i^*$ is the heat diffusivity. v_i are arbitrary constants and $\omega_i = \int_0^{v_i} c_i^*(\bar{u})\,\mathrm{d}\bar{u}$.

Assume that in each phase the diffusivity is of the form:

$$D_i = \alpha_i(\beta_i - \Theta_i)^{-2}, \quad \alpha_i > 0. \tag{15}$$

The one-dimensional diffusion equation with this class of diffusivity was solved by Fujita [1] subject to concentration boundary conditions and by Knight [2, 3] with arbitrary initial conditions and a flux boundary condition. The Kirchhoff transformation then yields:

$$\mu_i = \alpha_i/(\beta_i - \Theta_i) - \alpha_i/(\beta_i - \omega_i), \tag{16}$$

in terms of which the thermal diffusivity is:

$$D_i = a_i^2(b_i - \mu_i)^2, \tag{17}$$

where $a_i = \alpha_i^{-1/2}$ and $b_i = -\alpha_i/(\beta_i - \omega_i)$.

Equations (8) transform to:

$$\frac{\partial \mu_i}{\partial t_*} = a_i^2(b_i - \mu_i)^2 \frac{\partial^2 \mu_i}{\partial x_*^2}, \quad |y_{i-\mathrm{sgn}(i)}^*| < |x_*| < |y_i^*|,$$

$$i = -n, \ldots, -1, 1, \ldots, m. \tag{18}$$

Choosing the lower limit of integration in the Kirchhoff integral variables as $v_i = T_{i-\mathrm{sgn}(i)}^*$ for $i = -n, \ldots, -2, 2, \ldots, m$ and $v_{-1} = v_1$ (with common value v_0 say), the equations (9)–(12) transform to:

$$\frac{\partial \mu_i}{\partial x_*} - \frac{\partial \mu_{i+\mathrm{sgn}(i)}}{\partial x_*} = L_i^* \frac{dy_i^*}{\mathrm{d}t_*} \quad \text{at } x_* = y_i^*,$$

$$i = -n+1, \ldots, -1, 1, \ldots, m-1, \tag{19}$$

$$\mu_i[u_i^*(y_{i-\mathrm{sgn}(i)}^*, t_*)] = \mu_i(T_{i-\mathrm{sgn}(i)}^*) = 0$$

$$i = -n, \ldots, -2, 2, \ldots, m, \tag{20}$$

$$\mu_i[u_i^*(y_i^*, t_*)] = \mu_i(T_i^*) = \theta_i,$$

$$i = -n, \ldots, -1, 1, \ldots, m, \tag{21}$$

$$\frac{\partial \mu_1}{\partial x_*} = \frac{\partial \mu_{-1}}{\partial x_*} \quad \text{at } x_* = 0, \tag{22}$$

$$\mu_1(u_1^*) = \mu_{-1}(u_{-1}^*) \quad \text{at } x_* = 0, \tag{23}$$

with initial conditions:

$$\lim_{t_* \to 0} \mu_m = \theta_m, \quad x_* > 0$$

and

$$\lim_{t_* \to 0} \mu_{-n} = \theta_{-n}, \quad x_* < 0. \tag{24}$$

3. SOLUTION

We first linearize equations (18) by using the linearization procedure derived by Knight [2], who modified a transformation of Storm [20],

$$\chi_i = \int_{y_{i-\mathrm{sgn}(i)}^*}^{x_*} a_i^{-1}(b_i - \mu_i)^{-1}\,\mathrm{d}x_*,$$

$$i = -n, \ldots, -1, 1, \ldots, m, \tag{25}$$

$$\tau = t_*. \tag{26}$$

In Appendix A, we derive the linear equations:

$$\frac{\partial \mu_i}{\partial \tau} = \frac{\partial^2 \mu_i}{\partial \chi_i^2} - a_i R_i(\tau) \frac{\partial \mu_i}{\partial \chi_i}$$

$$+ a_i^{-1}\{b_i - \mu_i[u_i^*(y_{i-\mathrm{sgn}(i)}^*, t_*)]\}^{-1} \frac{\mathrm{d}y_{i-\mathrm{sgn}(i)}^*}{\mathrm{d}t_*} \frac{\partial \mu_i}{\partial \chi_i}$$

$$0 < \mathrm{sgn}(-iD_i')\chi_i < \mathrm{sgn}(-iD_i')S_i(\tau)$$

$$\text{for } i = -n+1, \ldots, -1, 1, \ldots, m-1$$

$$0 < \mathrm{sgn}(-iD_i')\chi_i < \infty \quad \text{for } i = -n, m, \tag{27}$$

where $R_i(\tau)$ is the value of the flux at the phase boundary $x_* = y_{i-\mathrm{sgn}(i)}^*$:

$$R_i(\tau) = -\left.\frac{\partial \mu_i}{\partial x_*}\right|_{x_*=y^*_{i-\mathrm{sgn}(i)}} \quad i=-n,\ldots,-1,1,\ldots,m, \tag{28}$$

and $S_i(\tau)$ denotes the phase boundary $x_* = y_i^*$ in terms of the transformed coordinates:

$$S_i(\tau) = \int_{y^*_{i-\mathrm{sgn}(i)}}^{y_i^*} a_i^{-1}(b_i-\mu_i)^{-1}\mathrm{d}x_*,$$

$$i=-n+1,\ldots,-1,1,\ldots,m-1. \tag{29}$$

We note that the sign of χ_i is dependent upon whether the thermal diffusivity D_i is a decreasing or an increasing function of temperature (Broadbridge and Banks [21]).

In order to proceed further we need explicit functional forms for $R_i(\tau)$, $S_i(\tau)$, the thermal densities $\mu_i(u_i^*(0,t_*))$, $i=-1,1$ and y_i^*. These functional forms, in fact follow from the scaling invariance of the governing equations and boundary conditions.

The whole boundary value problem (13), (18)–(24) is invariant under the scaling group:

$$\mu_i^* = \mu_i \quad x_1^* = \exp(\varepsilon)x_* \quad t_1^* = \exp(2\varepsilon)t_*,$$

where ε is the real valued Lie group parameter (e.g. see Hill [22]). The invariants of the group are functions of μ_i and $x_* t_*^{-1/2}$. Therefore, we adopt self-similar solutions of the form:

$$\mu_i = h_i(\xi)$$

$$\text{with } \xi = x_* t_*^{-1/2}, \quad i=-n,\ldots,-1,1,\ldots,m. \tag{30}$$

From the form of the similarity solution, planes of constant temperature are located where $x_* t_*^{-1/2} = \xi$ (constant). This implies that the interfaces between phases move as:

$$y_i^*(t_*) = \delta_i t_*^{1/2}, \quad i=-n+1,\ldots,-1,1,\ldots,m-1. \tag{31}$$

where the δ_i are constants. As we shall demonstrate, the non-linear Stefan problem does have an exact solution in which the free boundaries satisfy equation (31). Since a well-posed Stefan problem leads to a unique position of the free boundaries, equation (31) is an inviolable law, rather than just a convenient assumption.

The invariance implies that the thermal densities $\mu_i(u_i^*(0,t_*))$, $i=-1,1$ are constant, which implies that the temperature T_0^* at $x_*=0$ is constant, just as in the related linear problem [16]. This property rests on the assumption of ideal uniform initial conditions and on ideal thermal contact between the two materials. If we choose T_0^* as the lower limit of integration in the Kirchhoff integral variables for the phases adjoining the boundary between the materials, the boundary equations at $x_*=0$ are simplified. The unknown temperature T_0^* then appears in the definition of the value of the Kirchhoff variable at the boundaries $x_* = y_i^*$; $i=-1,1$. The thermal boundary conditions at $x_*=0$ and $x_* = y_i^*$; $i=-1,1$ are then, respectively:

$$\mu_i[u_i^*(0,t_*)] = \mu_i(T_0^*) = 0$$

and

$$\mu_i[u_i^*(y_i^*,t_*)] = \mu_i(T_i^*) = \theta_i, \quad i=-1,1. \tag{32}$$

The flux $R_i(\tau)$ takes the explicit form:

$$R_i(\tau) = -\left.\frac{\partial \mu_i}{\partial x_*}\right|_{x_*=\delta_{i-\mathrm{sgn}(i)}t_*^{1/2}} = -\gamma_i \tau^{-1/2}, \tag{33}$$

where

$$\gamma_i = \left.\frac{\mathrm{d}\mu_i}{\mathrm{d}\xi}\right|_{\xi=\delta_{i-\mathrm{sgn}(i)}},$$

$$i=-n,\ldots,-1,1,\ldots,m \quad \text{and} \quad \delta_0 = 0,$$

and, as detailed in Appendix B, the phase boundaries $S_i(\tau)$ in terms of the new length coordinate may be expressed as:

$$S_i(\tau) = 2(\Lambda_i - \lambda_i)\tau^{1/2},$$

$$i=-n+1,\ldots,-1,1,\ldots,m-1, \tag{34}$$

where

$$\Lambda_i = a_i\gamma_{i+\mathrm{sgn}(i)} + [a_i L_i^* + a_i^{-1}(b_i-\theta_i)^{-1}]\delta_i/2, \tag{35}$$

and

$$\lambda_i = a_i\gamma_i + (2a_ib_i)^{-1}\delta_{i-\mathrm{sgn}(i)}. \tag{36}$$

Equations (27) may now take the canonical form:

$$\frac{\partial \mu_i}{\partial \tau} = \frac{\partial^2 \mu_i}{\partial \chi_i^2} + \lambda_i \tau^{-1/2}\frac{\partial \mu_i}{\partial \chi_i},$$

$$0 < \mathrm{sgn}(-iD_i')\chi_i < \mathrm{sgn}(iD_i')2(\Lambda_i-\lambda_i)\tau^{1/2}$$

for

$$i=-n+1,\ldots,-1,1,\ldots,m-1,$$

and

$$0 < \mathrm{sgn}(-iD_i')\chi_i < \infty \quad \text{for } i=-n,m. \tag{37}$$

We now have the parameters δ_i, γ_i, and T_0^* to be determined rather than the arbitrary functions $y_i^*, \mu_i(u_i^*(0,t_*))$; $i=-1,1$, $R_i(\tau)$ and $S_i(\tau)$. The boundary conditions remain linear. Equations (19)–(22), (24) and (32) transform to:

$$\left.\left[a_i^{-1}(b_i-\mu_i)^{-1}\frac{\partial \mu_i}{\partial \chi_i}\right]\right|_{\chi_i=2(\Lambda_i-\lambda_i)\tau^{1/2}} - \left.\left\{a^{-1}_{i+\mathrm{sgn}(i)}(b_{i+\mathrm{sgn}(i)}-\mu_{i+\mathrm{sgn}(i)})^{-1}\frac{\partial \mu_{i+\mathrm{sgn}(i)}}{\partial \chi_{i+\mathrm{sgn}(i)}}\right\}\right|_{\chi_{i+\mathrm{sgn}(i)}=0}$$

$$= L_i^*\delta_i(4\tau)^{-1/2}$$

$$\text{for } i=-n+1,\ldots,-1,1,\ldots,m-1, \tag{38}$$

$$\mu_i = 0 \quad \text{at } \chi_i = 0 \quad i=-n,\ldots,-1,1,\ldots,m, \tag{39}$$

$$\mu_i = \theta_i \quad \text{at } \chi_i = 2(\Lambda_i-\lambda_i)\tau^{1/2}$$

$$\text{for } i=-n+1,\ldots,-1,1,\ldots,m-1, \tag{40}$$

$$\mu_i \to \theta_i \quad \text{as}\, \chi_i \to \operatorname{sgn}(-iD_i')\infty, \quad i = -n, m, \tag{41}$$

$$\left[a_1^{-1}(b_1-\mu_1)^{-1}\frac{\partial \mu_1}{\partial \chi_1}\right]\Bigg|_{\chi_i=0} = \left[a_{-1}^{-1}(b_{-1}-\mu_{-1})^{-1}\frac{\partial \mu_{-1}}{\partial \chi_{-1}}\right]\Bigg|_{\chi_{-1}=0}, \tag{42}$$

and initial conditions:

$$\lim_{\tau \to 0} \mu_m = \theta_m \quad \operatorname{sgn}(-iD_m')\chi_m > 0$$

and

$$\lim_{\tau \to 0} \mu_{-n} = \theta_{-n} \quad \operatorname{sgn}(-iD_{-n}')\chi_{-n} < 0. \tag{43}$$

The boundary value problem (37)–(43) is invariant under the scaling group:

$$\mu_i^* = \mu_i \quad \chi_i^* = \exp(\varepsilon)\chi_i, \quad \tau_1 = \exp(2\varepsilon)\tau.$$

The invariants are functions of μ_i and $\chi_i\tau^{-1/2}$. Assuming similarity solutions:

$$g_i(\phi_i) = \mu_i/\theta_i \quad \text{with}\, \phi_i = \chi_i(4\tau)^{-1/2}+\lambda_i,$$
$$i = -n,\ldots,-1,1,\ldots,m, \tag{44}$$

equations (37), (39)–(41) and (43) reduce to:

$$g_i''(\phi_i)+2\phi_i g_i'(\phi_i) = 0,$$
$$\operatorname{sgn}(-iD_i')\lambda_i < \operatorname{sgn}(-iD_i')\phi_i < \operatorname{sgn}(-iD_i')\Lambda_i$$
$$\text{for}\, i = -n+1,\ldots,-1,1,\ldots,m-1$$
$$\text{and}\, \operatorname{sgn}(-iD_i')\lambda_i < \operatorname{sgn}(-iD_i')\phi_i < \infty$$
$$\text{for}\, i = -n, m, \tag{45}$$

$$g_i(\phi_i) = 0 \quad \text{at}\, \phi_i = \lambda_i, \quad i = -n,\ldots,-1,1,\ldots,m, \tag{46}$$

$$g_i(\phi_i) = 1 \quad \text{at}\, \phi_i = \Lambda_i,$$
$$i = -n+1,\ldots,-1,1,\ldots,m-1 \tag{47}$$

and

$$g_i(\phi_i) \to 1 \quad \text{as}\, \phi_i \to \operatorname{sgn}(-iD_i')\infty, \quad i = -n, m. \tag{48}$$

The flux may be expressed as:

$$-\frac{\partial \mu_i}{\partial x_*} = -a_i^{-1}[b_i-\theta_i g_i(\phi_i)]^{-1}\theta_i g_i'(\phi_i)(4\tau)^{-1/2}. \tag{49}$$

Then, comparing (33) and (49), we deduce:

$$a_i^{-1}[b_i-\theta_i g_i(\phi_i)]^{-1}\theta_i g_i'(\phi_i) = 2\gamma_i \quad \text{at}\, \phi_i = \lambda_i,$$
$$i = -n,\ldots,-1,1,\ldots,m, \tag{50}$$

and from the continuity of flux between the materials, equation (42), we have:

$$\gamma_1 = \gamma_{-1}. \tag{51}$$

The Stefan condition boundary equations (38) take the form:

$$a_i^{-1}[b_i-\theta_i g_i]^{-1}\theta_i g_i' = 2\gamma_{i+\operatorname{sgn}(i)}+L_i^*\delta_i \quad at\, \phi_i = \Lambda_i,$$
$$i = -n+1,\ldots,-1,1,\ldots,m-1. \tag{52}$$

Equations (45)–(48) yield analytic solutions:

$$g_i(\phi_i) = \frac{\operatorname{erf}\phi_i - \operatorname{erf}\lambda_i}{\operatorname{sgn}(-iD_i')-\operatorname{erf}\lambda_i},$$
$$\operatorname{sgn}(-iD_i')\lambda_i < \operatorname{sgn}(-iD_i')\phi_i < \infty \quad \text{for}\, i = -n, m \tag{53}$$

and

$$g_i(\phi_i) = \frac{\operatorname{erf}\phi_i - \operatorname{erf}\lambda_i}{\operatorname{erf}\Lambda_i-\operatorname{erf}\lambda_i},$$
$$\operatorname{sgn}(-iD_i')\lambda_i < \operatorname{sgn}(-iD_i')\phi_i < \operatorname{sgn}(-iD_i')\Lambda_i,$$
$$\text{for}\, i = -n+1,\ldots,-1,1,\ldots,m-1. \tag{54}$$

Here, $\operatorname{erf}(z) = 2\pi^{-1/2}\int_0^z \exp(-w^2)\,dw$ is the error function.

However, as in the classical Stefan problem of a two-phase system, the coefficients in the solution are determined by solving transcendental equations. The flux boundary equations (50) and (52) yield:

$$\frac{\theta_i \exp(-\lambda_i^2)}{a_i b_i \pi^{1/2}[\operatorname{sgn}(-iD_i')-\operatorname{erf}\lambda_i]} = \gamma_i, \quad i = -n, m, \tag{55}$$

$$\frac{\theta_i \exp(-\lambda_i^2)}{a_i b_i \pi^{1/2}[\operatorname{erf}\Lambda_i-\operatorname{erf}\lambda_i]} = \gamma_i,$$
$$i = -n+1,\ldots,-1,1,\ldots,m-1, \tag{56}$$

and

$$\frac{\theta_i \exp(-\Lambda_i^2)}{a_i(b_i-\theta_i)\pi^{1/2}[\operatorname{erf}\Lambda_i-\operatorname{erf}\lambda_i]} = \gamma_{i+\operatorname{sgn}(i)}+L_i^*\delta_i/2$$
$$\text{for}\, i = -n+1,\ldots,-1,1,\ldots,m-1. \tag{57}$$

Now, γ_i and δ_i may be eliminated from equations (55)–(57). This choice leads to a system of equations which have a direct solution procedure. Eliminating δ_i from (35), (36) and solving for γ_i gives:

$$\begin{aligned}\gamma_i = {} & [a_{i-\operatorname{sgn}(i)}(b_{i-\operatorname{sgn}(i)}-\theta_{i-\operatorname{sgn}(i)})(\Lambda_{i-\operatorname{sgn}(i)} \\ & -\lambda_i a_i b_i a_{i-\operatorname{sgn}(i)}L_{i-\operatorname{sgn}(i)}^*)-\lambda_i a_i b_i]/ \\ & [a_{i-\operatorname{sgn}(i)}^2(b_{i-\operatorname{sgn}(i)}-\theta_{i-\operatorname{sgn}(i)}) \\ & \times(1-a_i^2 b_i L_{i-\operatorname{sgn}(i)}^*)-a_i^2 b_i] \\ & \text{for}\, i = -n,\ldots,-2,2,\ldots,m,\end{aligned} \tag{58}$$

and

$$\gamma_i = \frac{\lambda_i}{a_i} \quad \text{for}\, i = -1, 1. \tag{59}$$

Then substituting (58) into (36) and solving for δ_i yields:

$$\begin{aligned}\delta_i = {} & 2a_{i+\operatorname{sgn}(i)}b_{i+\operatorname{sgn}(i)}\lambda_{i+\operatorname{sgn}(i)}-2a_{i+\operatorname{sgn}(i)}^2 b_{i+\operatorname{sgn}(i)} \\ & \times[(\Lambda_i-a_{i+\operatorname{sgn}(i)}b_{i+\operatorname{sgn}(i)}a_i L_i^*\lambda_{i+\operatorname{sgn}(i)}) \\ & \times a_i(b_i-\theta_i)-a_{i+\operatorname{sgn}(i)}b_{i+\operatorname{sgn}(i)}\lambda_{i+\operatorname{sgn}(i)}]/ \\ & [a_i^2(b_i-\theta_i)(1-a_{i+\operatorname{sgn}(i)}^2 b_{i+\operatorname{sgn}(i)}L_i^*) \\ & -a_{i+\operatorname{sgn}(i)}^2 b_{i+\operatorname{sgn}(i)}] \\ & \text{for}\, i = -n+1,\ldots,-1,1,\ldots,m-1.\end{aligned} \tag{60}$$

Finally, equations (58)–(60) are substituted into (55)–(57) and the resultants algebraically rearranged to form the system of equations:

$$0 = \theta_i - a_i b_i \pi^{1/2} \exp(\lambda_i^2)[\operatorname{sgn}(-iD_i') - \operatorname{erf}\lambda_i] \times [a_{i-\operatorname{sgn}(i)}(b_{i-\operatorname{sgn}(i)} - \theta_{i-\operatorname{sgn}(i)})(\Lambda_{i-\operatorname{sgn}(i)} - \lambda_i a_i b_i a_{i-\operatorname{sgn}(i)} L^*_{i-\operatorname{sgn}(i)}) - \lambda_i a_i b_i] / [a^2_{i-\operatorname{sgn}(i)}(b_{i-\operatorname{sgn}(i)} - \theta_{i-\operatorname{sgn}(i)})(1 - a_i^2 b_i L^*_{i-\operatorname{sgn}(i)}) - a_i^2 b_i] \quad \text{for } i = -n, m, \tag{61}$$

$$\lambda_{i+\operatorname{sgn}(i)} = a_i(b_i - \theta_i)(1 - a^2_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)} L_i^*)\Lambda_i / (a_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)}) - \theta_i [a_i^2(b_i - \theta_i) \times (1 - a^2_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)} L_i^*) - a^2_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)}] / [a_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)} a_i (b_i - \theta_i)\pi^{1/2} \exp \Lambda_i^2 (\operatorname{erf}\Lambda_i - \operatorname{erf}\lambda_i)] \quad \text{for } i = -n+1, \ldots, -1, 1, \ldots, m-1, \tag{62}$$

$$\operatorname{erf}\Lambda_i = \operatorname{erf}\lambda_i + \theta_i [a^2_{i-\operatorname{sgn}(i)}(b_{i-\operatorname{sgn}(i)} - \theta_{i-\operatorname{sgn}(i)}) \times (1 - a_i^2 b_i L^*_{i-\operatorname{sgn}(i)}) - a_i^2 b_i] / \{a_i b_i \pi^{1/2} \exp \lambda_i^2 [a_{i-\operatorname{sgn}(i)}(\Lambda_{i-\operatorname{sgn}(i)} - \lambda_i a_i b_i a_{i-\operatorname{sgn}(i)} L^*_{i-\operatorname{sgn}(i)}) \times (b_{i-\operatorname{sgn}(i)} - \theta_{i-\operatorname{sgn}(i)}) - \lambda_i a_i b_i]\} \quad \text{for } i = -n+1, \ldots, -2, 2, \ldots, m-1 \text{ and} \tag{63}$$

$$\operatorname{erf}\Lambda_i = \operatorname{erf}\lambda_i + \theta_i / (b_i \pi^{1/2} \lambda_i \exp \lambda_i^2) \text{ for } i = -1, 1. \tag{64}$$

From (51) and (59):

$$\frac{\lambda_1}{a_1} = \frac{\lambda_{-1}}{a_{-1}}. \tag{65}$$

Equations (61)–(65) form a closed system of $2m+2n-1$ equations for the determination of the $2m+2n-1$ constants Λ_k; $k = -n+1, \ldots, -1, 1, \ldots, m-1$, λ_l; $l = -n, \ldots, -1, 1, \ldots, m$ and T_0^*, the temperature at $x_* = 0$. T_0^* defines the constants θ_i, a_i, b_i; $i = -1, 1$ from equations (32).

The equations are in a form amenable to a simple bisection numerical scheme with only two variables to iterate. T_0^* is chosen as one of the variables to iterate as the constants θ_l, a_l, b_l; $l = -1, 1$ are defined when T_0^* is specified. This choice also enables the diffusivity parameters a_l, b_l; $l = -1, 1$ of phases $l = -1, 1$ to be adjusted to closer match the diffusivity of these phases. In practice, as the temperature T_0^* becomes more accurately determined, diffusivity data may be rejected if it falls outside of the temperatures encountered in these phases. The other variable to iterate is either λ_1 or λ_{-1} as this specification determines the remaining constants Λ_i; $i = -n+1, \ldots, -1, 1, \ldots, m-1$ and λ_k; $k = -n, \ldots, -1, 2, \ldots, m$ or λ_k; $k = -n, \ldots, -2, 1, \ldots, m$. There is a coupled recurrence relation between these constants by equations (62)–(64).

The solution is achieved as follows. Consider the case of λ_1 being chosen as the other variable to iterate. For each iteration of T_0^* and each iteration of λ_1, the constants Λ_i; $i = 1, \ldots, m-1$ and λ_k; $k = 2, \ldots, m$ are determined from equations (62)–(64). These values are checked for consistency using equation (61). When a consistent value of λ_1 is obtained, then, from equations (65) and (62)–(64) the remaining constants Λ_j; $j = -1, \ldots, -n+1$ and λ_l; $l = -1, \ldots, -n$ are determined. Finally, the overall consistency is checked using equation (61).

The case of λ_{-1} as the other variable to iterate is similar to the above. For numerical efficiency λ_1 is chosen if $m < n$ and λ_{-1} is chosen if $n < m$.

To complete the parametric solution, from equations (44):

$$\mu_i = \theta_i g_i(\phi_i), \quad i = -n, \ldots, -1, 1, \ldots, m, \tag{66}$$

where the g_i are defined by equations (53)–(54). The μ_i defined by equation (14) are inverted when the thermal conductivities are given. The Storm transformations equations (25) and (26) are inverted to obtain:

$$x_* = 2a_i\{b_i(\phi_i - \lambda_i) + \theta_i[\phi_i \operatorname{erf}\lambda_i - \phi_i \operatorname{erf}\phi_i + \pi^{-1/2}\exp(-\lambda_i^2) - \pi^{-1/2}\exp(-\phi_i^2)] / [\operatorname{sgn}(-iD_i') - \operatorname{erf}\lambda_i\} t_*^{1/2} + y^*_{i-\operatorname{sgn}(i)}, \quad \operatorname{sgn}(-iD_i')\lambda_i < \operatorname{sgn}(-iD_i')\phi_i < \infty \text{ for } i = -n, m, \tag{67}$$

$$x_* = 2a_i\{b_i(\phi_i - \lambda_i) + \theta_i[\phi_i \operatorname{erf}\lambda_i - \phi_i \operatorname{erf}\phi_i + \pi^{-1/2}\exp(-\lambda_i^2) - \pi^{-1/2}\exp(-\phi_i^2)] / [\operatorname{erf}\Lambda_i - \operatorname{erf}\lambda_i]\} t_*^{1/2} + y^*_{i-\operatorname{sgn}(i)}, \quad \operatorname{sgn}(-iD_i')\lambda_i < \operatorname{sgn}(-iD_i')\phi_i < \operatorname{sgn}(-iD_i')\Lambda_i \text{ for } i = -n+1, \ldots, -1, 1, \ldots, m-1, \tag{68}$$

where, from (31) and (60):

$$y_i^* = 2a_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)} \{\lambda_{i+\operatorname{sgn}(i)} - a_{i+\operatorname{sgn}(i)} \times [(\Lambda_i - a_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)} a_i L_i^* \lambda_{i+\operatorname{sgn}(i)}) \times a_i(b_i - \theta_i) - a_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)} \lambda_{i+\operatorname{sgn}(i)}] / [a_i^2(b_i - \theta_i)(1 - a^2_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)} L_i^*) - a^2_{i+\operatorname{sgn}(i)} b_{i+\operatorname{sgn}(i)}]\} t_*^{1/2} \quad \text{for } i = -n+1, \ldots, -1, 1, \ldots, m-1 \tag{69}$$

are the positions of the phase boundaries and $y_0^* = 0$.

4. TWO EXAMPLES

For illustration purposes, the freezing of pure iron on a pure copper base and the converse problem of the freezing of pure copper on a pure iron base are considered. The problem of iron solidifying on copper was chosen as iron changes through various phases during cooling and the thermal properties vary highly near the magnetic transition. We chose copper as the base material so a large temperature range is obtained in the solidifying iron. Also, copper is often used as the primary heat extraction medium during continuous

Table 1. Phase transition and heats of transformation for pure iron and pure copper

Phase transition	Temperature (K)	Volumetric latent heat (J cm^{-3})
Liquid iron to δ iron	1810	2040
δ iron to γ iron	1673	83
γ iron to non-magnetic α iron	1183	124
Non-magnetic α iron to magnetic α iron	1043	235
Liquid copper to solid copper	1356	1630

casting. As we shall see from the solution, the steel–copper interface remains below the melting point of copper, even when there is no intermediate layer of mould-flux. We use an initial temperature of the liquid iron as 1830 K, which is typical for a casting process, and the initial temperature of the copper base is 300 K.

The problem of copper solidifying on iron was chosen to demonstrate a heat conduction problem in which the base material undergoes phase changes, with absorption of latent heat during its heating. We use the same initial conditions for the liquid and solid as in the previous problem.

The phase transition temperatures and the heats of transformation of iron and of copper are shown in Table 1. The phase transition temperatures are taken from ref. [23] and the volumetric latent heats are calculated using molar latent heats from ref. [24], and densities (interpolated or extrapolated as required) from refs. [25, 26]. The thermal diffusivity of the phases of iron and of copper are shown in Fig. 1. The highly varying diffusivity within the magnetic α and non-magnetic α phases of iron are not of a form which the diffusivity relation (17) can accommodate directly. However, a very close approximation to these forms of diffusivity may be obtained by fitting piecewise segments of the relation (17). This is achieved by introducing, where appropriate, additional fictitious phase changes having zero latent heat of transformation. For example, the diffusivity of the magnetic α phase is approximated piecewise using five segments of relation (17) by introducing four additional fictitious phase changes. A close fit, within the 4% error of measurement, is obtained by choosing these phase changes at temperatures of 500, 700, 900 and 1000 K (see Fig. 1). A similar procedure is used for the non-magnetic α and γ phases where the diffusivity of each of these phases is approximated piecewise using two segments of relation (17). The diffusivity of the solid copper and the liquid copper are approximated piecewise using five and two segments of relation (17), respectively (see Fig. 1). We have shown segments of (17) fitted piecewise over the temperature range 300–1900 K: however, during calculation we reject any segments that fall outside of the actual temperatures encountered in the materials.

The thermal conductivity of the phases of iron and of copper are shown in Fig. 2. For calculation purposes, the integration of the thermal conductivity is achieved numerically using the trapezoidal rule and linear interpolation where required.

The temperature distribution within each phase vs length divided by square root of time, for the solidification of iron on copper, is shown in Fig. 3. The temperature at the fixed magnetic-α–copper boundary remains at 785 K, which is well below the melting point of copper. The coefficients from equations (31) describing the position of the phase fronts are, non-magnetic α to magnetic α, 0.96 mm s$^{-1/2}$; γ to non-magnetic α, 1.41 mm s$^{-1/2}$; δ to γ, 3.39 mm s$^{-1/2}$ and liquid to δ, 4.25 mm s$^{-1/2}$.

The temperature distribution vs length divided by square root of time, for the solidification of copper on

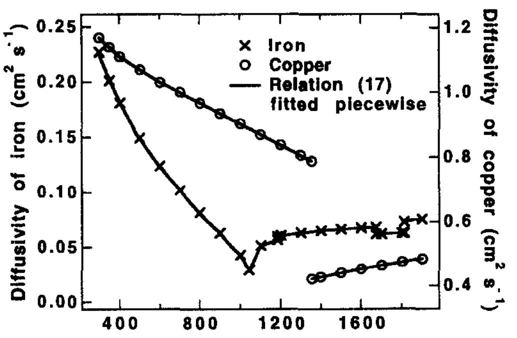

FIG. 1. Recommended thermal diffusivity of iron and copper versus temperature [27].

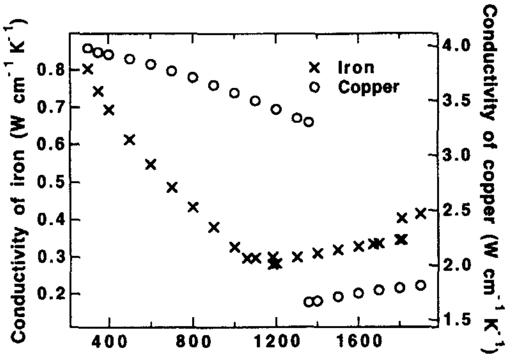

FIG. 2. Recommended thermal conductivity of iron and copper versus temperature [23].

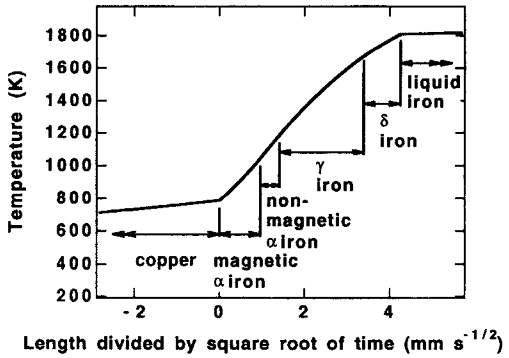

FIG. 3. Temperature distribution for the solidification of iron on a copper base. The initial temperatures were 1830 K for the iron and 300 K for the copper.

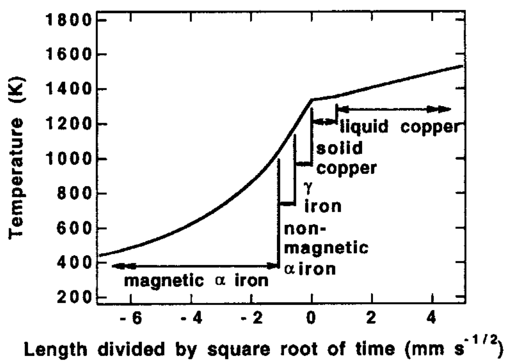

FIG. 4. Temperature distribution for the solidification of copper on an iron base. The initial temperatures were 1830 K for the copper and 300 K for the iron.

iron, is shown in Fig. 4. The temperature at the copper–iron boundary is 1336 K. The coefficients from equations (31) describing the position of the phase fronts are, non-magnetic α to magnetic α, -1.10 mm s$^{-1/2}$; γ to non-magnetic α, -0.56 mm s$^{-1/2}$; and liquid to solid copper, 0.83 mm s$^{-1/2}$.

5. CONCLUSION

Equations (53)–(54) and (61)–(69) are an exact parametric solution describing the temperature distribution and position of any phase boundaries as a semi-infinite material solidifies on a semi-infinite base material. The solution method may incorporate any material with temperature dependent thermal properties. Hence, compared to a linear model, our nonlinear model offers a faithful representation of the thermal properties of real materials. The solution may be used to test the ability of numerical schemes to cope with non-linear thermal properties before such schemes are applied to three-dimensional problems involving complicated geometries.

The solution may be reformulated to include changes in density between phases by the same procedure as in the linear formulation [28] and, by a suitable change in terminology, the solution technique may be applied to concentration diffusion problems of this type.

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APPENDIX A

We establish the linear equations (27) from the non-linear equations (18), via the Storm transformation (25)–(26). From (18):

$$\frac{\partial \mu_i}{\partial t_*} = a_i^2(b_i-\mu_i)^2\frac{\partial^2\mu_i}{\partial x_*^2}. \tag{A1}$$

First, we transform the left hand side of (A1):

$$\begin{aligned}\frac{\partial \mu_i}{\partial t_*} &= \frac{\partial \mu_i}{\partial \tau} + \frac{\partial \mu_i}{\partial \chi_i}\left[\int_{y^*_{i-\mathrm{sgn}(i)}}^{x_*} a_i a_i^{-2}(b_i-\mu_i)^{-2}\frac{\partial \mu_i}{\partial t_*}\,\mathrm{d}x_*\right] \\ &\quad - \frac{\partial \mu_i}{\partial \chi_i}\left(a_i^{-1}\{b_i-\mu_i[u_i^*(y^*_{i-\mathrm{sgn}(i)},t_*)]\}^{-1}\frac{\mathrm{d}y^*_{i-\mathrm{sgn}(i)}}{\mathrm{d}t_*}\right) \\ &= \frac{\partial \mu_i}{\partial \tau} + \frac{\partial \mu_i}{\partial \chi_i}\left(a_i\int_{y^*_{i-\mathrm{sgn}(i)}}^{x_*}\frac{\partial^2\mu_i}{\partial x_*^2}\,\mathrm{d}x_*\right) \\ &\quad - \frac{\partial \mu_i}{\partial \chi_i}\left(a_i^{-1}\{b_i-\mu_i[u_i^*(y^*_{i-\mathrm{sgn}(i)},t_*)]\}^{-1}\frac{\mathrm{d}y^*_{i-\mathrm{sgn}(i)}}{\mathrm{d}t_*}\right) \quad \text{from (A1)} \\ &= \frac{\partial \mu_i}{\partial \tau} + \frac{\partial \mu_i}{\partial \chi_i}\left(a_i\frac{\partial \mu_i}{\partial x_*} - a_i\left.\frac{\partial \mu_i}{\partial x_*}\right|_{x_*=y^*_{i-\mathrm{sgn}(i)}}\right) \\ &\quad - \frac{\partial \mu_i}{\partial \chi_i}\left(a_i^{-1}\{b_i-\mu_i[u_i^*(y^*_{i-\mathrm{sgn}(i)},t_*)]\}^{-1}\frac{\mathrm{d}y^*_{i-\mathrm{sgn}(i)}}{\mathrm{d}t_*}\right) \\ &= \frac{\partial \mu_i}{\partial \tau} + (b_i-\mu_i)^{-1}\left(\frac{\partial \mu_i}{\partial \chi_i}\right)^2 \\ &\quad + a_iR_i(\tau)\frac{\partial \mu_i}{\partial \chi_i} - a_i^{-1}\{b_i-\mu_i[u_i^*(y^*_{i-\mathrm{sgn}(i)},t_*)]\}^{-1} \\ &\quad \times \frac{\mathrm{d}y^*_{i-\mathrm{sgn}(i)}}{\mathrm{d}t_*}\frac{\partial \mu_i}{\partial \chi_i}, \end{aligned} \tag{A2}$$

where $R_i(\tau)$ is defined by (28). Now the right-hand side of (A1) is:

$$\begin{aligned} a_i^2(b_i-\mu_i)^2\frac{\partial^2\mu_i}{\partial x_*^2} &= a_i^2(b_i-\mu_i)^2\left[a_i^{-1}(b_i-\mu_i)^{-1}\right. \\ &\quad \left.\times\frac{\partial^2\mu_i}{\partial \chi_i^2}\frac{\partial \chi_i}{\partial x_*} + a_i^{-2}(b_i-\mu_i)^{-3}\left(\frac{\partial \mu_i}{\partial \chi_i}\right)^2\right] \\ &= \frac{\partial^2\mu_i}{\partial \chi_i^2} + (b_i-\mu_i)^{-1}\left(\frac{\partial \mu_i}{\partial \chi_i}\right)^2. \end{aligned} \tag{A3}$$

Substituting (A2) and (A3) into (A1) gives the desired result:

$$\begin{aligned}\frac{\partial \mu_i}{\partial \tau} &= \frac{\partial^2\mu_i}{\partial \chi_i^2} - a_iR_i(\tau)\frac{\partial \mu_i}{\partial \chi_i} \\ &\quad + a_i^{-1}\{b_i-\mu_i[u_i^*(y^*_{i-\mathrm{sgn}(i)},t_*)]\}^{-1}\frac{\mathrm{d}y^*_{i-\mathrm{sgn}(i)}}{\mathrm{d}t_*}\frac{\partial \mu_i}{\partial \chi_i}. \end{aligned} \tag{A4}$$

APPENDIX B

We derive the explicit form of the phase boundary $S_i(\tau)$. From equations (29) and (31):

$$S_i(\tau) = \int_{\delta_{i-\mathrm{sgn}(i)}t_*^{1/2}}^{\delta_i t_*^{1/2}} a_i^{-1}(b_i-\mu_i)^{-1}\,\mathrm{d}x_*. \tag{B1}$$

Then:

$$\begin{aligned}\frac{\mathrm{d}S_i}{\mathrm{d}t_*} &= \int_{\delta_{i-\mathrm{sgn}(i)}t_*^{1/2}}^{\delta_i t_*^{1/2}} a_ia_i^{-2}(b_i-\mu_i)^{-2}\frac{\partial \mu_i}{\partial t_*}\,\mathrm{d}x_* \\ &\quad + a_i^{-1}\{b_i-\mu_i[u_i^*(\delta_i t_*^{1/2},t_*)]\}^{-1}\delta_i t_*^{-1/2}/2 \\ &\quad - a_i^{-1}\{b_i-\mu_i[u_i^*(\delta_{i-\mathrm{sgn}(i)}t_*^{1/2},t_*)]\}^{-1}\delta_{i-\mathrm{sgn}(i)}t_*^{-1/2}/2 \\ &= a_i\int_{\delta_{i-\mathrm{sgn}(i)}t_*^{1/2}}^{\delta_i t_*^{1/2}}\frac{\partial^2\mu_i}{\partial x_*^2}\,\mathrm{d}x_* + a_i^{-1}(b_i-\theta_i)^{-1}\delta_i t_*^{-1/2}/2 \\ &\quad - a_i^{-1}b_i^{-1}\delta_{i-\mathrm{sgn}(i)}t_*^{-1/2}/2 \\ &\text{from (20), (21), (32) and (A1)} \\ &= a_i\left[\left.\frac{\partial \mu_i}{\partial x_*}\right|_{x_*=\delta_i t_*^{1/2}} - \left.\frac{\partial \mu_i}{\partial x_*}\right|_{x_*=\delta_{i-\mathrm{sgn}(i)}t_*^{1/2}}\right] \\ &\quad + a_i^{-1}(b_i-\theta_i)^{-1}\delta_i t_*^{-1/2}/2 \\ &\quad - a_i^{-1}b_i^{-1}\delta_{i-\mathrm{sgn}(i)}t_*^{-1/2}/2 \\ &= [a_i(L_i^*\delta_i + 2\gamma_{i+\mathrm{sgn}(i)} - 2\gamma_i) + a_i^{-1}(b_i-\theta_i)^{-1}\delta_i \\ &\quad - a_i^{-1}b_i^{-1}\delta_{i-\mathrm{sgn}(i)}]t_*^{-1/2}/2 \text{ by (19) and (33).} \end{aligned} \tag{B2}$$

Integrating (B2) and noting that $S_i \to 0$ as $t_* \to 0$ then,

$$S_i(\tau) = 2(\Lambda_i - \lambda_i)\tau^{1/2}, \tag{B3}$$

where

$$\Lambda_i = a_i\gamma_{i+\mathrm{sgn}(i)} + [a_iL_i^* + a_i^{-1}(b_i-\theta_i)^{-1}]\delta_i/2 \tag{B4}$$

and

$$\lambda_i = a_i\gamma_i + (2a_ib_i)^{-1}\delta_{i-\mathrm{sgn}(i)}, \tag{B5}$$

which completes the derivation.