PHASE TRANSITION KINETICS AT THE INTERFACE OF TWO EXTENDED MASSES

E. G. Palagin

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The motion of a phase interface is examined in the case of two semi-infinite rods of the same material, one in the solid and the other in the liquid state. The variation of temperature at the phase interface is calculated.

A solution has been devised for determining the position of the phase interface for two semiinfinite rods of the same material, one being in a solid, the other in a liquid state of aggregation. At time t = 0 their ends are brought together at the point x = 0. The temperature of the solid rod is assumed to be everywhere lower than the melting point, while that of the liquid rod is higher, and it is assumed that there is no convection in the liquid.

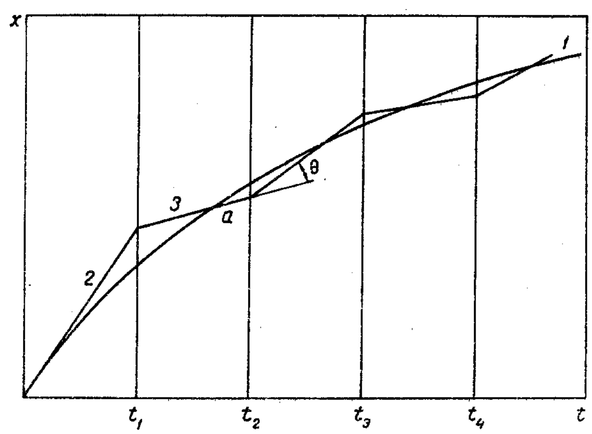

Illustration of the calculation scheme: 1) fusion curve x = y(t); 2) tangent x = k_1t; 3) broken line approximation.

The temperature at the boundary varies according to some unknown law, reflecting the kinetics of the crystallization process, and, as has been shown in a number of recent papers [1–3], this may have a very substantial influence on the end result.

For the case of an unchanging temperature front and constant temperature at time zero of the solid and liquid rods, the solution has been given by Schwarz [6, 7]. This method, however, does not permit calculation of the temperature field or the velocity of the boundary in the case of arbitrary initial conditions and a nonzero temperature front.

The problem of heat distribution may be written in the following form:

$$\frac{\partial u^{(j)}}{\partial t} = a_j^2 \frac{\partial^2 u^{(j)}}{\partial x^2} \qquad (j = 1,\ 2). \tag{1}$$

The boundary conditions are

$$\begin{aligned} u^{(1)}(x,\ 0) &= \varphi_0^{(1)}(x) < u_0 \quad \text{when } x < 0; \\ u^{(2)}(x,\ 0) &= \varphi_0^{(2)}(x) \geqslant u_0 \quad \text{when } x \geqslant 0; \end{aligned} \tag{2}$$

$$u^{(1)}(y,\ t) = u^{(2)}(y,\ t) = u_\Phi(t) \text{ when } t > 0; \tag{3}$$

$$\varkappa_1 \frac{\partial u^{(1)}}{\partial x}\bigg|_{x=y(t)} - \varkappa_2 \frac{\partial u^{(2)}}{\partial x}\bigg|_{x=y(t)} = \frac{dy}{dt}; \tag{4}$$

$$\frac{dy}{dt} = \varphi(T), \tag{5}$$

or, taking into account that $u_\Phi(t)$ = T − 273° C,

$$u_\Phi(t) = \psi\left(\frac{dy}{dt}\right). \tag{5*}$$

Condition (5) reflects the kinetics of the process and may be written in closed form as (see [4])

$$\varphi(T) = \frac{c}{\eta(T)} \exp\left[-\pi\alpha^2/pmKT \ln\frac{T_0}{T}\right]. \tag{6}$$

We divide the fusion curve y(t) into a number of sections by straight lines parallel to the x axis, and in each section we draw a straight line as an approximation of the curve (see figure). In the first section this will be the tangent (curve 2), and in the others it will be the broken line 3 oscillating about curve 1. It then follows from (5) that in section $t_n t_{n+1}$ the temperature at the crystallization front will be constant, though varying, of course, as we pass to the next section.

Therefore, to determine the temperature field in each medium at the n-th step we must solve the problem of heat distribution in a semi-infinite rod whose end moves according to a linear law y = k_nt and whose temperature is held constant.

We will determine the velocity k from condition (4), which for the (n + 1)-th step will have the form

$$\varkappa_1 \frac{\partial u^{(1)}}{\partial x}\bigg|_{x=k_n t_n} - \varkappa_2 \frac{\partial u^{(2)}}{\partial x}\bigg|_{x=k_n t_n} = k_{n+1}. \tag{4a}$$

We introduce the new variables

$$\begin{aligned} \bar{u}^{(1)}(x,\ t) &= u^{(1)}(x,\ t) - u_\Phi, \\ \bar{u}^{(2)}(x,\ t) &= u^{(2)}(x,\ t) - u_\Phi. \end{aligned}$$

Equation (1) and conditions (2)–(5) may be written, respectively, in the form

$$\frac{\partial \bar{u}^{(j)}}{\partial t} = a_j^2 \frac{\partial^2 \bar{u}^{(j)}}{\partial x^2} \quad (j = 1,\ 2), \tag{1'}$$

$$\bar{u}^{(1)}(x,\ 0) = \varphi_0^{(1)}(x) - u_\phi = \bar{\varphi}_0^{(1)}(x),$$
$$\bar{u}^{(2)}(x,\ 0) = \varphi_0^{(2)}(x) - u_\phi = \bar{\varphi}_0^{(2)}(x), \tag{2'}$$

$$\bar{u}^{(1)}(y(t),\ t) = \bar{u}^{(2)}(y(t),\ t) = 0, \tag{3'}$$

$$\varkappa_1 \frac{\partial \bar{u}^{(1)}(y(t),\ t)}{\partial x} - \varkappa_2 \frac{\partial \bar{u}^{(2)}(y(t),\ t)}{\partial x} = \frac{dy}{dt}, \tag{4'*}$$

$$\frac{dy}{dt} = \varphi^*(0) = k, \tag{5'}$$

$$\psi^*(k) = 0. \tag{6'}$$

Later we will use Green's method, the application of which to equations of parabolic type was proved in [8, 9].

We introduce the operators

$$L(\bar{u}) \equiv a_j^2 \frac{\partial^2 \bar{u}}{\partial x^2} - \frac{\partial \bar{u}}{\partial t} = 0,$$
$$M(v) \equiv a_j^2 \frac{\partial^2 v}{\partial x^2} + \frac{\partial v}{\partial t} = 0.$$

Then

$$\iint_D [vL(\bar{u}) - \bar{u}M(v)]\, dxdt =$$
$$= \int_C \bar{u}v dx + a_j^2 \left(v\frac{\partial \bar{u}}{\partial x} - \bar{u}\frac{\partial v}{\partial x}\right) dt, \tag{7}$$

where D is the region bounded by the characteristics (t = const) and by the curves representing the equations of motion of the ends of the section; C is the boundary of this region.

If we assume that

$$\bar{u} = \bar{u}(x,\ t)$$

and

$$v \equiv G_0^{*(j)}(x,\ t,\ \xi,\ \tau) = \frac{1}{2\sqrt{\pi a_j^2 (t-\tau)}} \exp\left[-\frac{(x-\xi)^2}{4a_j^2(t-\tau)}\right],$$

then, taking into account that one end of the section is removed to infinity, while at the other end we have condition (6'), the basic integral formula may be written in the form [5]

$$\bar{u}^{(j)}(x,\ t) = (-1)^j \int_0^{(-1)^j \cdot \infty} G_0^{*(j)}(x,\ t,\ \xi,\ 0)\, \bar{\varphi}_0^{(j)}(\xi)\, d\xi +$$
$$+ (-1)^{j+1} a_j^2 \int_0^t G_0^{*(j)} \Big|_{\xi=k\tau} \frac{\partial \bar{u}^{(j)}}{\partial \xi}\Big|_{\xi=k\tau} d\tau,$$

or, in the case of the liquid rod,

$$\bar{u}^{(2)}(x,\ t) = \int_0^\infty G_0^{*(2)}(x,\ t,\ \xi,\ 0)\, \bar{\varphi}_0^{(2)}(\xi)\, d\xi -$$
$$- a_2^2 \int_0^t G_0^{*(2)}\Big|_{\xi=k\tau} \frac{\partial \bar{u}^{(2)}}{\partial \xi}\Big|_{\xi=k\tau} d\tau. \tag{8}$$

In order to solve the boundary value problem, we must eliminate the term $\partial \bar{u}^{(2)}/\partial\xi$. For this purpose we first replace v in (7) by the function v_1,

$$v_1 \equiv G_1^{*(2)}(x,\ t,\ \xi,\ \tau) = \frac{1}{2\sqrt{\pi a_2^2(t-\tau)}} \exp\left[-\frac{(x_1-\xi)^2}{4a_2^2(t-\tau)}\right],$$

where x_1 is the abscissa of some point external to the region D under examination. Then, taking into account our boundary conditions for the liquid rod, we may write (7) in the form

$$f(x,\ t)\left[\int_0^\infty G_1^{*(2)}(x,\ t,\ \xi,\ 0)\, \bar{\varphi}_0^{(2)}(\xi)\, d\xi - \right.$$
$$\left. - a_2^2 \int_0^t G_1^{*(2)}\Big|_{\xi=k\tau} \frac{\partial \bar{u}^{(2)}}{\partial \xi} d\tau\right] = 0, \tag{9}$$

where $f(x, t)$ is an arbitrary multiplier whose form is not yet known. We subtract (9) from (8) and require that

$$G^{(2)}|_{\xi=k\tau} = G_0^{*(2)}|_{\xi=k\tau} - f(x,\ t)\, G_1^{*(2)}|_{\xi=k\tau} = 0.$$

Then

$$\bar{u}^{(2)}(x,\ t) = \int_0^\infty G^{(2)}(x,\ t,\ \xi,\ 0)\, \bar{\varphi}_0^{(2)}(\xi)\, d\xi. \tag{10}$$

Thus

$$G^{(2)} = \frac{1}{2\sqrt{\pi a_2^2(t-\tau)}} \left\{\exp\left[-\frac{(x-\xi)^2}{4a_2^2(t-\tau)}\right] - \right.$$
$$\left. - f(x,\ t) \exp\left[-\frac{(x_1-\xi)^2}{4a_2^2(t-\tau)}\right]\right\}. \tag{11}$$

From the condition $G^{(2)}|_{\xi=k\tau} = 0$ it follows that

$$\exp\left[-\frac{(x-\xi)^2}{4a_2^2(t-\tau)}\right] = f(x,\ t) \exp\left[-\frac{(x_1-\xi)^2}{4a_2^2(t-\tau)}\right],$$

from which, taking logarithms and after some transformations we obtain

$$\xi = \frac{2a_2^2(t-\tau)\ln f(x,\ t)}{x - x_1} + \frac{x + x_1}{2}. \tag{12}$$

*We note that in the case of the rod melting through, condition (4') is written somewhat differently:

$$\varkappa_2^* \frac{\partial u^{(2)}}{\partial x}\Big|_{x=y(t)} - \varkappa_1^* \frac{\partial u^{(1)}}{\partial x}\Big|_{x=y(t)} = \frac{dy}{dt},$$

where $\varkappa_1^* = \lambda_1/L\rho_2$, $\varkappa_2^* = \lambda_2/L\rho_2$.

Equation (12) is the equation of a straight line in the coordinates ξ and τ. Comparing it with the equation $\xi = k\tau$ of this line, we can make them coincide by choice of $f(x, t)$ and x_1. From this it follows that at the end of a semi-infinite section moving according to the law $\xi = k\tau$, the function $G^{(2)}(x, t, \xi, \tau) = 0$.

Thus, we obtain

$$f(x, t) = \exp\left[\frac{kt - x}{a_2^2}k\right]. \tag{13}$$

As x_1 we choose the point with symmetrical x relative to the same line $\xi = k\tau$, i.e., $x_1 = 2kt - x$. Hence we have the required equality $G^{(2)}|_{\xi=k\tau} = 0$. Then (11) is transformed to

$$G^{(2)} = \frac{1}{2\sqrt{\pi a_2^2 (t-\tau)}}\left\{\exp\left[-\frac{(x-\xi)^2}{4a_2^2(t-\tau)}\right] - \right.$$
$$\left. - \exp\left[-\frac{(2kt - x - \xi)^2}{4a_2^2(t-\tau)} + \frac{k^2t - kx}{a_2^2}\right]\right\}. \tag{14}$$

Expression (14) satisfies $L(u) = 0$ with respect to the variables x, t and $M(v)$ with respect to ξ, τ; it may readily be seen that it is the Green's function of our problem.

At the n-th section for each of the rods we have

$$\bar{u}_n^{(j)}(x, t) = (-1)^j \int_0^{(-1)^j\cdot\infty} G_{n-1}^{(j)} \bar{\varphi}_{n-1}^{(j)}(\xi)\, d\xi,$$

where

$$\bar{\varphi}_n^{(j)}(x) \equiv \bar{u}_n^{(j)}(x, t_n), \tag{A}$$

$$y_n = \sum_{i=1}^{n} k_i t_i, \quad y_0 = t_0 = 0. \tag{B}$$

Carrying out the appropriate transformations and taking into account (14) and the remarks made above, we obtain the temperature distribution in the rods at each section in the form

$$\bar{u}_n^{(j)}(x, t) = \frac{(-1)^j}{2\sqrt{\pi a_j^2 t}} \cdot \int_0^{(-1)^j\cdot\infty} \left\{\exp\left[-\frac{(x-\xi)^2}{4a_j^2 t}\right] - \right.$$
$$\left. - \exp\left[-\frac{(2k_n t - x - \xi)^2}{4a_j^2 t} + \frac{k_n^2 t - k_n x}{a_j^2}\right]\right\} \times$$
$$\times \left[\varphi_{n-1}^{(j)}(\xi) - u_{n\Phi}\right] d\xi + u_{n\Phi} \tag{15}$$

and the values of the derivatives when $x = k_n t$ are

$$\left.\frac{\partial u_n^{(j)}}{\partial x}\right|_{x=k_n t} = \frac{(-1)^j}{2\sqrt{\pi}\, a_j^3 t^{3/2}} \int_0^{(-1)^j\cdot\infty} \xi \exp\left[-\frac{(k_n t - \xi)^2}{4a_j^2 t}\right] \times$$
$$\times \left|\varphi_{n-1}^{(j)}(\xi) - u_{n\Phi}\right| d\xi. \tag{16}$$

Substituting (16) into (4) with values $t = t_n$ (t_n is the limiting value of time for the given step), we determine the velocity k_{n+1} at the $(n + 1)$-th step.

Time at each step is reckoned from zero, while the coordinate origin is located at the boundary of the two media. This is done purely for convenience of calculation, and of course, the essence of the method and the final result are not affected. The thickness of the solidified layer may easily be found from (B).

At the first step we obtain the velocity value from (5) by substituting a value of the temperature front equal to $u_{1\Phi} = \varphi^{(1)}(0)$.

Thus the problem is completely solved by the method described.

Estimate of convergence. By replacing a section of the true curve by the tangent to it, we depart somewhat from the true curve during time Δt. In calculating the value of the derivative at the new point we introduce some error due to the difference between the computed and the true ordinates. To this error is added the fresh error from substituting a straight line, and so on. It is therefore appropriate to consider the matter of convergence of the process.

It may be shown that the larger the slope of the line $\mathrm{tg}\,\Theta = k$ (see fig.), i.e., the further it is above the true curve, the smaller the slope of the approximation line at the following step, which will thus draw closer to our curve. A negative error is even possible. In this case the point of intersection $x = k_{n-1}t$ and $t = t_{n-1}$ (the point a in the figure) will be below the curve $x = y(t)$, which will entail an increase of the slope of the next straight line section at the next stage, and therefore draw it closer to the fusion curve. These circumstances follow from (4a) if, as k increases, the quantity $\partial u^{(1)}/\partial x|_{x=k_n t}$ decreases, i.e., $\partial/\partial k[\partial u^{(1)}/\partial x|_{x=k_n t}] < 0$, while $\partial u^{(2)}/\partial x|_{x=k_n t}$ increases, i.e., $\partial/\partial k[\partial u^{(2)}/\partial x|_{x=k_n t}] > 0$. To prove this we differentiate (16) with respect to k, after again writing (5*) in the form

$$u_{n\Phi} = \psi(k_n).$$

Then

$$\frac{\partial}{\partial k_n}\left[\left.\frac{\partial u_n^{(1)}}{\partial x}\right|_{x=k_n t}\right] = -\frac{1}{2\sqrt{\pi}\, a_1^3 t^{3/2}} \int_{-\infty}^{0} \xi\, \frac{k_n t - \xi}{2a_1^2} \times$$
$$\times \exp\left[-\frac{(k_n t - \xi)^2}{4a_1^2 t}\right] \left|\varphi_{n-1}^{(1)}(\xi) - u_{n\Phi}\right| d\xi +$$
$$+ \frac{1}{2\sqrt{\pi}\, a_1^3 t^{3/2}} \times \int_{-\infty}^{0} \xi \exp\left[-\frac{(k_n t - \xi)^2}{4a_1^2 t}\right] \psi'_{k_n}(k_n)\, d\xi =$$
$$= \frac{1}{4\sqrt{\pi}\, a_1^5 t^{3/2}} \times \int_0^{\infty} \xi (k_n t + \xi) \times$$
$$\times \exp\left[-\frac{(k_n t + \xi)^2}{4a_1^2 t}\right] \left[\varphi_{n-1}^{(1)}(-\xi) + \psi(k_n)\right| d\xi -$$
$$- \frac{\psi'_{k_n}(k_n)}{2\sqrt{\pi}\, a_1^3 t^{3/2}} \int_0^{\infty} \xi \exp\left[-\frac{(k_n t + \xi)^2}{4a_1^2 t}\right] d\xi.$$

Both terms are negative:

$$\left|\left|\varphi_{n-1}^{(1)}(\xi) - u_{n\Phi}\right| < 0\right|.$$

Therefore,

$$\frac{\partial}{\partial k_n}\left[\frac{\partial u_n^{(2)}}{\partial x}\bigg|_{x=k_nt}\right]=$$

$$=-\frac{1}{2\sqrt{\pi}\,a_2^3t^{3/2}}\int_0^{\infty}\xi\,\frac{k_nt-\xi}{2a_2^2}\exp\left[-\frac{(k_nt-\xi)^2}{4a_2^2t}\right]\times$$

$$\times\left[\varphi_{n-1}^{(2)}(\xi)+\right.$$

$$\left.+\psi(k_n)\right]d\xi+\frac{\psi'_{k_n}(k_n)}{2\sqrt{\pi}\,a_2^3t^{3/2}}\int_0^{\infty}\xi\exp\left[-\frac{(k_nt-\xi)^2}{4a_2^2t}\right]d\xi$$

or, making the substitution

$$(k_nt-\xi)/2a_2\sqrt{t}=z,$$

we obtain

$$\frac{\partial}{\partial k_n}\left[\frac{\partial u_n^{(2)}}{\partial x}\bigg|_{x=k_nt}\right]=\frac{1}{\sqrt{\pi}\,a_2^3}\int_{-k_n\sqrt{t}/2a_2}^{\infty}(k_n\sqrt{t}+$$

$$+2a_2z)\,z\exp[-z^2]\left[\varphi_{n-1}^{(2)}(k_nt+2a_2\sqrt{t}z)+\psi(k_n)\right]dz+$$

$$+\frac{\psi'_{k_n}(k_n)}{\sqrt{\pi t}\,a_2^2}\int_{-k_n\sqrt{t}/2a_2}^{\infty}(k_n\sqrt{t}+2a_2z)\exp[-z^2]\,dz,$$

from which it is easily seen that

$$\frac{\partial}{\partial k_n}\left[\frac{\partial u_n^{(2)}}{\partial x}\bigg|_{x=k_nt}\right]>0,$$

which was to be proved.

Since the choice of step size with respect to time is arbitrary, the calculation may be carried out with any required degree of accuracy.

NOTATION

$u^{(j)}(x, t)$) temperature of rod (in $j = 1, 2$, 1 refers to the solid phase and 2 to the liquid; u_0) fusion temperature, °C; $y(t)$) phase interface; λ_j, ρ_j, c_j, L) thermal conductivity, density, specific heat, and heat of fusion of the medium, respectively; $a_j^2 = \lambda_j/c_j\rho_j$; $\varkappa_j = \lambda_j/L\rho_1$; c) a constant of the given substance; $\mu(t)$) a factor taking account of the mobility of molecules of the liquid from which the crystalline part is formed; α) specific linear energy at the crystal-melt interface; k) Boltzmann constant; m) number of molecules forming unit surface of the crystal face; T_0) phase equilibrium temperature, °K; T) temperature at the boundary, °K.

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Hydrometeorological Institute, Leningrad