



Mathematical modeling phase transition in solids

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Abstract. We claim that the well-known Stefan condition on the moving inter-phase, accepted in mathematical physics, can not be imposed if energy sources are spatially distributed in the volume. A method based on Tikhonov and Samarskii ideas for numerical solution of the problem is developed. It treats the heat of fusion as an additional term in the expression for thermal capacity of the material. Mathematical modeling of energy relaxation of some processes useful in modern ion beam technologies is fulfilled. Necessity of taking into account effects completely outside the Stefan formulation is demonstrated.

Keywords: Heat transfer, phase transition, Stefan problem, finite difference method.

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1. Introduction

The Stefan problem concerns solid-liquid or liquid-vapor phase transitions when moving unknown beforehand surface S of phase transition is formed (see, e.g., [1]). In fact, a formulation of the Stefan problem was given for the first time by G. Lamé and B.P. Clapeyron in 1831 for a particular case of equal temperature of liquid and crystalline phases [2]. In 1889 J. Stefan published four papers devoted to the subject (in particular, to the description of soil freezing) in which the problem was formulated in a general form [3]. According to it, for the interphase the following condition

$$K_{sol} \frac{\partial T(x_S + 0, t)}{\partial x} - K_{liq} \frac{\partial T(x_S - 0, t)}{\partial x} = L \rho_{sol} V_S, \quad (1)$$

defining Stefan's problem, has been suggested. Here $V_S = d\xi_S/dt$ is the velocity of the boundary surface S , K_{sol} and K_{liq} are thermal conductivities of material for solid and liquid phases, L and ρ_{sol} are the melting heat and density, correspondingly and x_S is the spatial coordinates of boundary surface. Condition (1) has a clear physical meaning. Indeed, according to the Fourier law, heat flow j is proportional to the temperature gradient,

$$\mathbf{j} = -K \text{ grad } T.$$

Therefore, the left-hand side of (1) is the heat absorbed in the unit of area per the unit of time. The expression in the right-hand side is the heat connected with freezing or melting of material crossed per the unit of time by the the unit of area.

A complete mathematical formulation of the Stefan problem includes, besides (1), a condition of continuity on the surface S separating solid and liquid phases

$$T|_S = T^*, \quad (2)$$

where T^* denotes temperature of the phase transition, and the energy conservation law

$$\rho C \frac{\partial T}{\partial t} = -\text{div } \mathbf{j} + q(\mathbf{x}, t).$$

Here $q(\mathbf{x}, t)$ represents the power of external heat sources, C is the specific heat. In the original Stefan papers $q(\mathbf{x}, t) \equiv 0$, so that the whole heat transfer has been considered to be a consequence of the temperature gradient inside the medium.

If one also specifies initial and boundary conditions, the Stefan problem can be solved more often approximately, but sometimes exactly. Particular examples of suitable boundary conditions are considered below.

Relations (1) and (2) are usually used in numerical algorithms explicitly. Another approach was suggested by A.N. Tikhonov and A.A. Samarskii in 1953 [4]. According to it, conditions (1) and (2) are included themselves into the energy conservation equation to obtain generalized formulation of the Stefan problem in the form

$$(\rho C + L \delta(T - T^*)) \left(\frac{\partial T}{\partial t} + \mathbf{v} \text{ grad } T \right) = \text{div}(K \text{ grad } T) + q(\mathbf{x}, t), \quad (3)$$

where the term $L \delta(T - T^*) \partial T / \partial t$ describes the additional heat input expended on the phase transformation, $\mathbf{v} \text{ grad } T$ takes into account possible temperature change due to convection (hereafter we ignore it for simplicity). The main idea of this approach is quite clear, too. Namely, it is suggested to treat the heat of fusion L as an additional component of the thermal capacity ρC which gives contribution only at the point of phase transition.

Lately Samarskii and his followers have turned this idea into effective numerical algorithms (see, e.g. [5]). But even in those papers equation (3) is considered only as a corollary of the condition (1). For example, it was derived in [1] by substituting expression $L \delta(T - T^*) \partial T / \partial t$ instead of the term $L \delta(x - \xi_S(t)) V_S$, which is assumed to be included in the heat equation to account for the heat absorption on 2-dimensional interface S .

The purpose of this paper is to show that the condition (3) supplies us with a more powerful description of phase transitions, that may be used even in the case when (1) and (2) are not applicable.

2. Heuristic arguments

As it was mention above, the possibility of solving the classical Stefan problem by making use of condition (3) has been demonstrated by Samarskii and his co-authors. Therefore, we only consider an example when (3) is applicable and (1), (2) are not. To this end let us study the following problem:

$$(\rho C + L \delta(T - T^*)) \frac{\partial T}{\partial t} = \text{div}(k \text{ grad } T) + q(t), \quad (4)$$

$$T(\mathbf{x}, 0) = T_0 < T^*,$$

where all parameters of (4) are suggested to be independent of \mathbf{x} . Due to the spatial uniformity, it is evident that the condition

$$\text{grad } T = 0$$

holds on the solutions of (1). In this case Eq. (4) is reduced to an ordinary differential one

$$(\rho C + L \delta(T - T^*)) \frac{dT}{dt} = q(t) \quad (5)$$

with the initial condition

$$T(0) = T_0.$$

Integrating both sides of (5) over t just near the phase transition temperature T^* , one obtains

$$\int_{T^*-0}^{T^*+0} (\rho C + L \delta(T - T^*)) dT = \int_t^{t+\delta t} q(t) dt, \quad (6)$$

where δt is a time necessary for the phase transition. It is evident from (6) that

$$\delta t \geq \frac{L}{Q}, \quad (7)$$

where Q is the maximum value of $q(t)$ in the interval $(t, t + \delta t)$. The inequality (7) means that the phase transition at a fixed spatial point lasts a finite, distinct from zero, time.

This simple example shows something completely different from the Stefan description of the phase transition. Let us examine it carefully.

1. First of all, instead of gradual warming (or cooling) up the pattern due to the influence of one of its boundaries, here we have an uniformly heated layer. Therefore, creation of 2-D surface $S(y, z)$ separating the solid and liquid phases in x is evidently impossible due to a total equivalence of all spatial points x .
2. One can also expect that finiteness of the phase transition time, δt , forces all points within a spatial layer of nonzero thickness to be at the same temperature T^* . This is expected even in the case when the power deposition $q(x, t)$, unlike in the example considered, is spatially irregular.

If we consider δ -function in (3) as a limit of a bounded function $D(T - T^*)$ localized in the vicinity of $T = T^*$, then the possibility to obtain

$$\frac{\partial T}{\partial t} \longrightarrow 0, \quad \text{grad } T \longrightarrow 0,$$

follows from the indefiniteness

$$D(T - T^*) \frac{\partial T}{\partial t} \longrightarrow \infty \cdot 0,$$

springing up in the left-hand side of (3). Clearly, that this indefiniteness can take a finite value and compensate in a space region with nonzero thickness the spatially distributed source $q(\mathbf{x}, t)$ which contributes to the right-hand side of (3). This, of course, is no more true if the external sources are absent and heat enters the pattern only through its boundary.

In a general case, one can expect existence of two jumps for spatial derivatives of temperature on the boundaries S of the volume V_{T^*} with $T = T^*$, instead of one for the classical Stefan problem, but the condition (1) is hardly met for any of them. Indeed, to prove the existence of two jumps — one from the side of the solid and another from the side of the melted phase — it is sufficient only to show that the spatial derivative on the surface S , taken externally, is not equal to zero. The coordinates of the boundary $\vec{\xi}(t)$ can be found as a solution of an equation

$$T(\mathbf{x}, t) - T^* = 0,$$

where $T(\mathbf{x}, t)$ is the solution of the heat equation (3) outside the volume V_{T^*} . Taking the total temporal derivative, one obtains

$$\frac{\partial T}{\partial t} + \text{grad } T \cdot \frac{d\vec{\xi}}{dt} = 0.$$

Thus $\text{grad } T = 0$ automatically implies $\partial T / \partial t = 0$. It is evident that such conditions are impossible if the external sources are not adjusted specially to stabilize the temperature in the infinitesimal layers adjacent to the volume V_{T^*} just before and just after the phase transition.

3. Numerical simulation of phase transitions

To verify the conclusions which we have just come to, let us study numerically the dynamics of phase transition induced by a short powerful ion beam in solids. At present this technology is really used for modification of surface layers to create new materials with unique physical and chemical properties (see, e.g. [6]). The process is underlain by the equation for heat transfer which we discussed in the previous sections:

$$\rho(T)c(T)\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k(T)\frac{\partial T}{\partial x} \right) + q. \quad (8)$$

The initial and boundary conditions could be taken in the form:

$$T(x, 0) = T_0, \quad \frac{\partial T(0, t)}{\partial x} = \frac{\partial T(l_0, t)}{\partial x} = 0.$$

Let us consider, for definiteness, an iron pattern, which thermal properties are described in popular reference books, and choose dimensionless (DL for brevity) variables

$$T := T/T_0, \quad x := x/l_0, \quad t := t/\tau$$

as follows:

$$T_0 = 293 \text{ K}, \quad l_0 = 10^{-5} \text{ m (the pattern thickness),}$$

$$\tau = 3 \cdot 10^{-7} \text{ s (duration of ion beam pulse from an accelerator).}$$

For DL power deposition q we take a simple model with analytical representation

$$q(x, t) = Q q_1(x)q_2(t),$$

where

$$q_i(z) = \frac{1}{1 + \exp \mu_i(z - z_i)}.$$

Q describe the total DL energy brought into the pattern (here $Q = 59.44$, $x_1 = 0.07$, $t_1 = 1$, $\mu_i = 100$). For simplicity, we neglect in (8) a small difference between physical parameters for the solid and liquid phases.

Now, using of the general idea due to Tikhonov and Samarskii [4], we assume an expression:

$$\rho(T)c(T) = 1 + \lambda \delta(T - T^*, \Delta)$$

for DL specific heat, where λ denotes the DL heat of fusion and $\delta(T - T^*, \Delta)$ is an approximate δ -function, smoothed with the help of the Gaussian distribution of width Δ (see Figure 1)¹.

¹There were other methods of smoothing in original papers by Samarskii et al. They used regularization on the space grid.

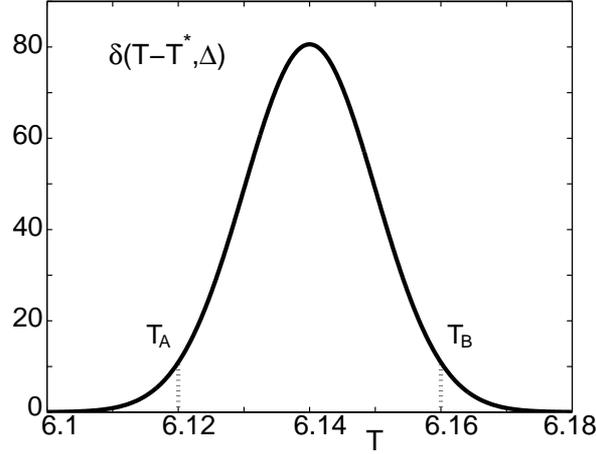


Figure 1: Approximate δ -function with maximum at T^* and smearing equals Δ (for $\Delta = 0.03$).

Now Eq. (8) can be solved numerically on the space-time grid x and t with steps h_x and h_t , within intervals $x \in (0, 1)$, $t \in (0, t_{max})$:

$$\begin{aligned} x_j &= h_x \cdot j, \quad j = 0, \dots, n_x, \quad h_x = 1/n_x, \\ t_k &= h_t \cdot k, \quad k = 0, \dots, n_t, \quad h_t = t_{max}/n_t, \end{aligned}$$

where n_x and n_t are numbers of partitions.

The following difference scheme with weights γ was implemented (see [7] for details):

$$e_j^k \frac{T_j^{k+1} - T_j^k}{h_t} = k_0 \left[\gamma \frac{T_{j+1}^{k+1} - 2T_j^{k+1} + T_{j-1}^{k+1}}{h_x^2} + (1 - \gamma) \frac{T_{j+1}^k - 2T_j^k + T_{j-1}^k}{h_x^2} \right] + q_j^{k+\frac{1}{2}}, \quad (9)$$

where

$$T_j^k = T(x_j, t_k), \quad e_j^k = \rho(T_j^k)c(T_j^k), \quad q_j^{k+\frac{1}{2}} = q(x_j, t_k + \frac{h_t}{2}),$$

and the upper index numerates different moments of time (time “levels”), the lower one specifies a set of spatial co-ordinates. The scheme is absolutely convergent at $\gamma = 0.5$ and possesses the second-order accuracy for both variables.

From initial condition $T(x, 0) = T_0$, values T_j^0 ($j = 0, \dots, n_x$) on a zero time level are known. The boundary conditions

$$\frac{T_1^k - T_{-1}^k}{2h_x} = \frac{T_{n_x+1}^k - T_{n_x-1}^k}{2h_x} = 0, \quad k = 1, \dots, n_t$$

allow one to introduce symmetric points $x_{-1} = -h_x$ and $x_{n_x+1} = 1 + h_x$ with appropriate values $T_{-1}^k = T_1^k$ and $T_{n_x+1}^k = T_{n_x-1}^k$ respectively. So, we can use the

Eq. (9) in points x_0 and x_{n_x} . Using initial and boundary conditions, we obtain a system of n_x linear algebraical equations with the same number of variables. Thus, under the accepted approximation, we reduced the partial differential equation (8) to system (9) of linear algebraic equations. The matrix of this system is tridiagonal and after its solution¹ we obtain value T_j^1 ($j = 0, \dots, n_x$) at the first time level. Repeating this process, values T_j^k on every time level k are computed.

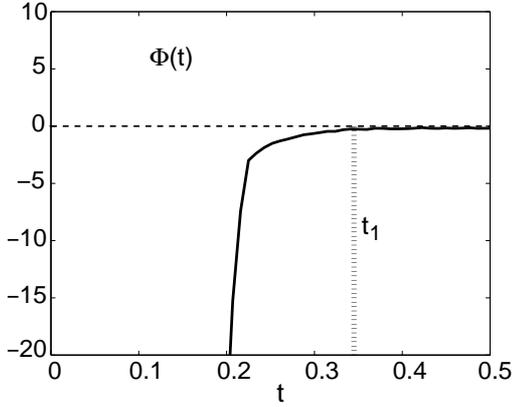


Figure 2: Time dependence of function $\phi(t)$.

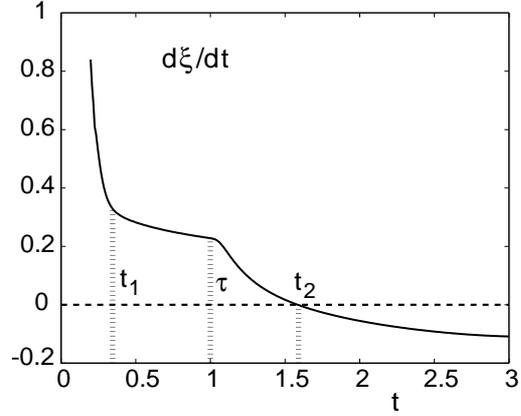


Figure 3: Velocity of the boundary surface.

The result of straightforward verification of the Stefan condition (1) is shown in Figure 2, where the function

$$\phi(t) = k \left(\left. \frac{\partial T}{\partial x} \right|_{T_A} - \left. \frac{\partial T}{\partial x} \right|_{T_B} \right) - \lambda \frac{d\xi}{dt} \quad (10)$$

is depicted.

The left and right points, in which the spatial derivatives of temperature were taken in (10), are shown in Figure 1. They define a spatial layer which nearly the whole fusion energy is absorbed within. From Figure 2 one can see that condition (1) is satisfied indeed, but only after a characteristic relaxation time t_1 has elapsed. The physical meaning of t_1 is clear from Figure 3. Namely, it corresponds to the transition from a rapid to slow motion of the exterior interphase surface. In the case when boundary motion is rapid, the heat necessary for fusion is brought into the melting layer directly from the external source $q(x, t)$. The slow motion corresponds to the ordinary Stefan mode when the process is controlled mainly by the heat entered into the layer through its boundary.

¹Recursive relations for determining the solution of algebraic problem (9) comprise the well-known sweep method, called also forward-backward or Thomas algorithm [1].

It is also seen from Figure 3 that transition to the Stefan mode takes place earlier than the external source to be totally turned off:

$$t_1 < \tau.$$

Time t_2 shown in Figure 3 denotes a moment when the thickness of the melted material begins to diminish due to heat escape into a more cooler solid phase.

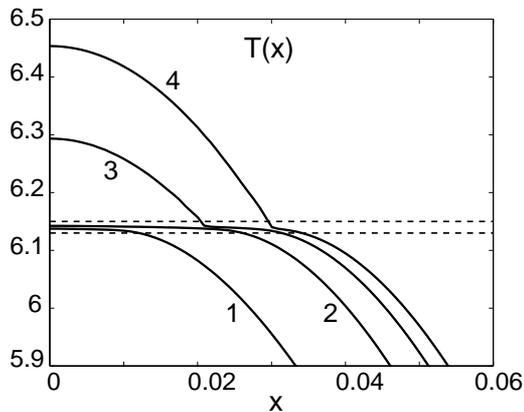


Figure 4: Spatial temperature distribution for: 1 – $t = 0, 162$; 2 – $t = 0, 186$; 3 – $t = 0, 204$; 4 – $t = 0, 216$ ($\Delta = 0.01$)

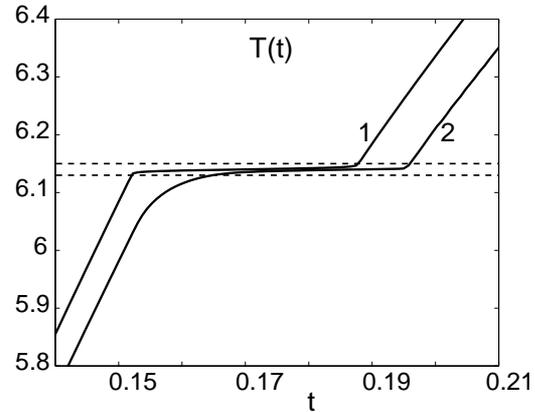


Figure 5: Evolution of temperature for: 1 – $x = 0$; 2 – $x = 0.04$ ($\Delta = 0.01$)

Figure 4 and 5 also confirm the conclusions which we have come to in the previous section. Formation of the “tableland” (whose height corresponds to the fusion temperature) for spatial temperature distribution is distinctly seen in Figure 4. The narrow strip restricted by two dashed lines in Figure 4 and 5 exhibits the width of the smoothed δ -function. We believe that existence of two breaks for the spatial derivative is masked in Figure 4 with this δ -function smearing. Figure 5 demonstrates a temperature evolution for two divorced spatial points. One can make sure that the above mentioned time interval corresponding to the same temperature at the different spatial points really exists. It is evident that such a behavior of temperature has nothing to do with the traditional description in the framework of (1) and (2).

4. Conclusion

To the best of our knowledge, the peculiarities of phase transition dynamics, we discussed in this paper, have never been considered explicitly in mathematical physics. This fact may be explained partially by the necessity to use very powerful spatially distributed external sources of heat, in order the above mentioned effects to be

urgent. Such sources were hardly available for industrial applications not long ago. However, the examples which given above are likely evidences of the fact that such sources, “interfering” in the thermal conductive processes, are integral parts of all most recent ion beam technologies. The numerical investigations, which have been undertaken, show that the δ -function approach to phase transitions is a suitable instrument to tackle these problems, though the authors of this idea have never used it in such a context.

Here we have shown that it is more expedient to turn over this order and take its last element as the basis for solving both the classical Stefan problem and a more general one including spatially distributed sources. In other words, both of these solutions could be considered as an idealized limiting case $\Delta \rightarrow 0$ of a natural physical point of view that none of phase transitions take place at the exactly defined value of fusion temperature.

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